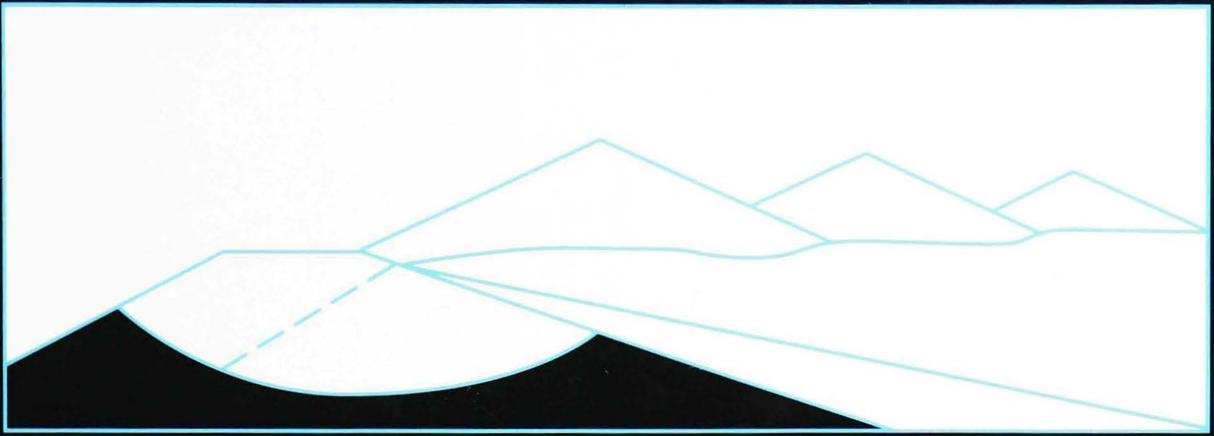
Colorado Geological Survey
Special Publication 38

Proceedings: Summitville Forum '95



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Fort Collins, Colorado
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January 17–20, 1995

Errata: Revised Page 14, Plumlee and others, Summitville Forum '95 Proceedings.

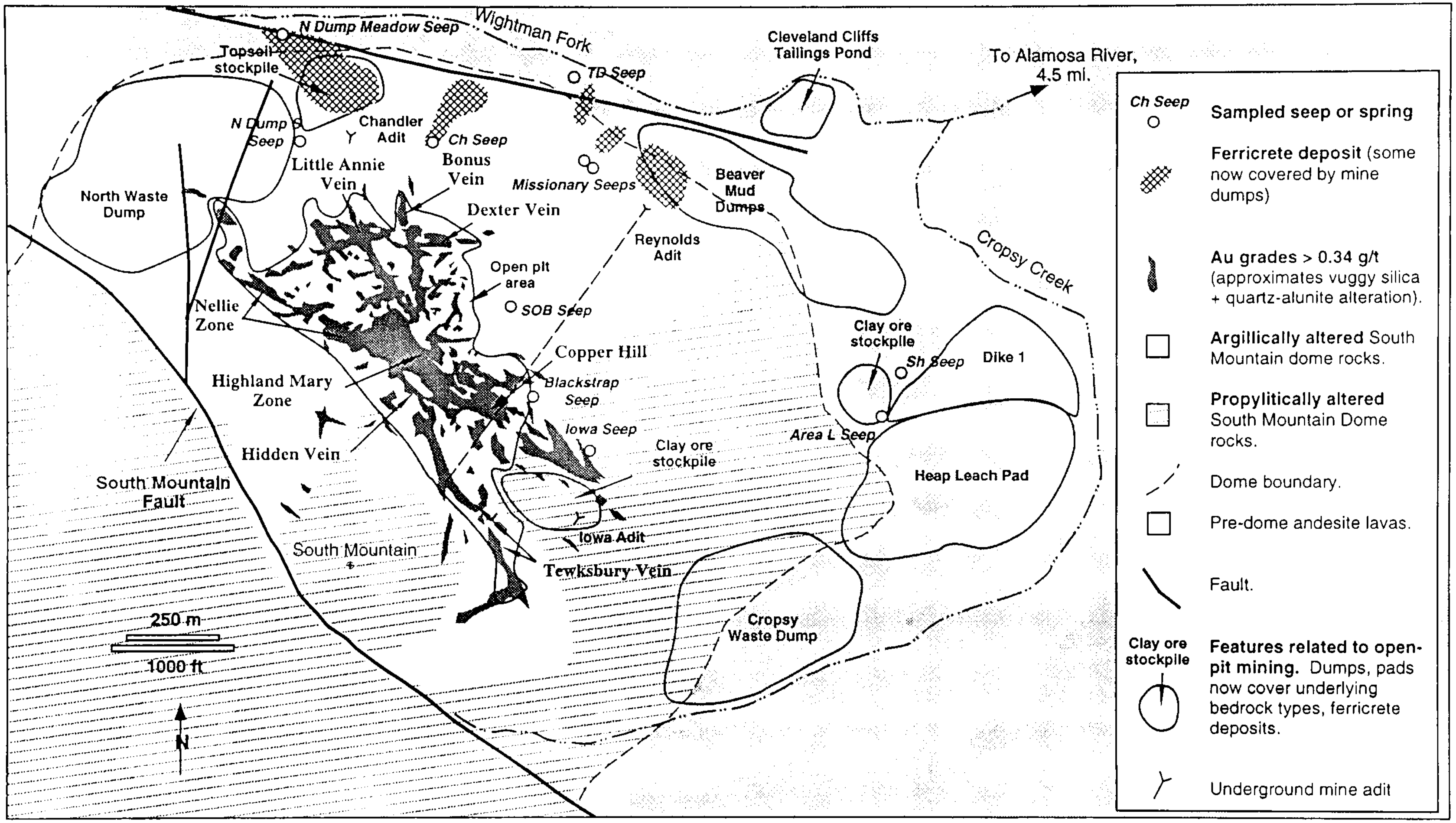


Figure 1. Generalized map of the Summitville mine site showing geologic features (major alteration and ore zones, ferricrete deposits) in relation to past and recent mine features. Also shown are the locations of active seeps sampled for chemical analysis (see Plumlee et al., this volume). The distribution of argillic and propylitic alteration was taken from a surficial geologic map prepared by Mike Perkins and Bill Nieman for the Anaconda Company in the early 1980's. The distribution of acid sulfate alteration (vuggy silica and quartz alunite zones) is approximated by gold grades greater than 0.34 grams per ton (after Gray and Coolbaugh, 1994 in press). The location of ferricrete deposits is approximate based on distributions observed in aerial photographs taken of the site in 1968 and 1980 by Intra-Search, Inc; many of the deposits are now covered by material from the recent open pit mining operations.

Errata

Proceedings: Summitville Forum '95

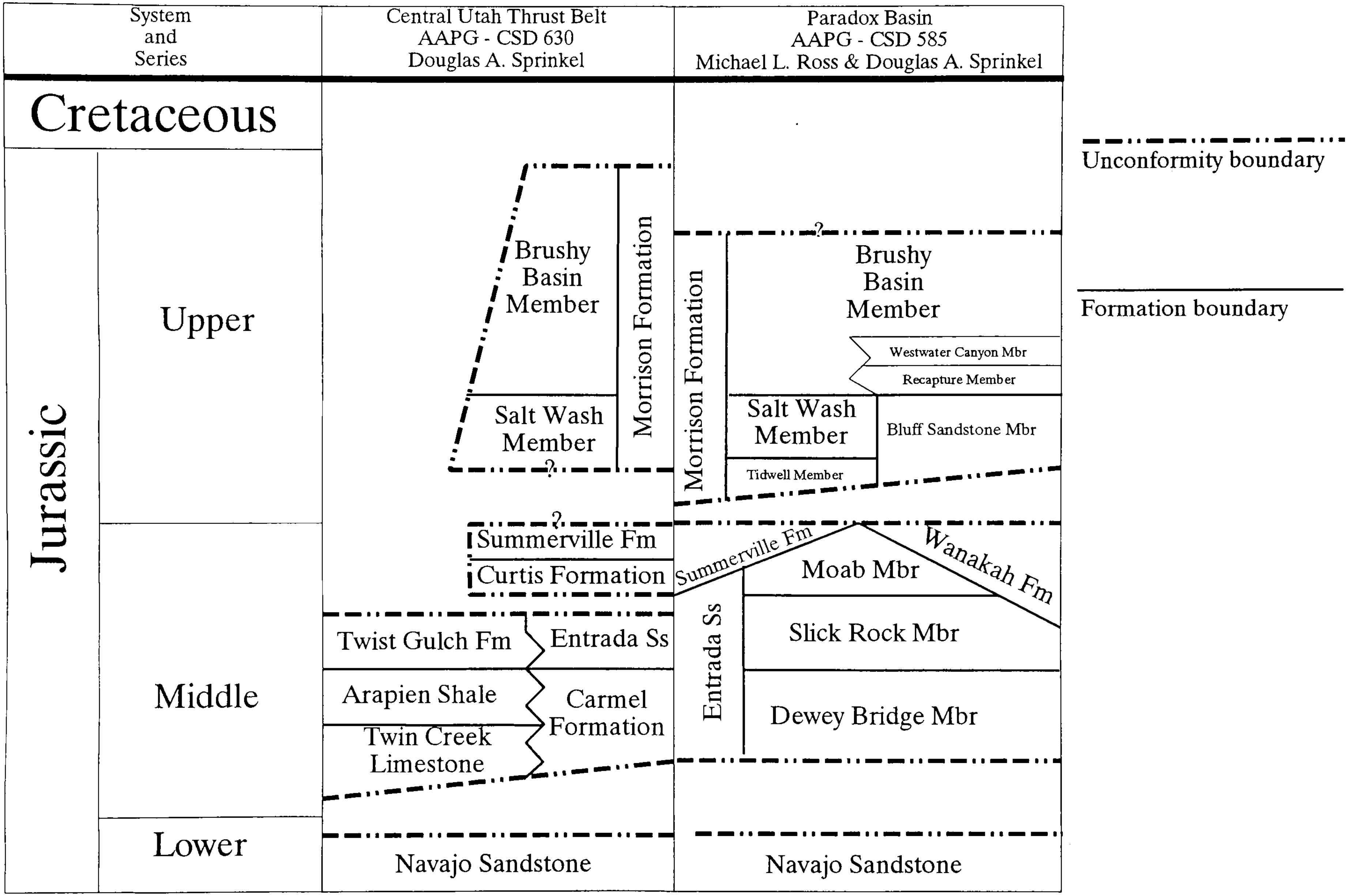
Page 165, Table 3. Corrected values in AR34.5 Max. column are underlined.

ble 3. Summary statistics for selected constituents for selected sites on the Alamosa River

oncentrations in micrograms per liter except pH in standard units. Min., minimum concentration; Max., maximum concentration; Med., median concentration; TAl, total-coverable aluminum; DAl, dissolved aluminum; TCu, total-recoverable copper; DCu, dissolved copper; TFe, total-recoverable iron; DFe, dissolved iron; TMn, total-recoverable nganese; DMn, dissolved manganese; TZn, total-recoverable zinc; DZn, dissolved zinc]

	AR49.5			**AR45.5**			**AR45.4**			**AR34.5**		
	Min.	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**
TAl	<10	520	165	1,100	5,400	1,850	2,600	5,100	2,900	1,800	16,000	2,200
DAl	<10	40	<10	<10	4,800	65	120	3,900	750	<10	1,800	50
TCu	<1	2	<1	4	24	8.5	105	2,800	832	100	1,500	450
DCu	<1	2	<1	<1	26	2.5	39	2,600	732	14	1,100	250
TFe	40	330	195	1,700	22,000	5,200	4,600	12,000	6,800	3,200	77,000	4,900
DFe	5	44	19.5	250	4,800	1,085	1,600	5,300	2,300	30	2,700	1,300
TMn	<10	40	30	90	530	180	470	890	730	390	1,400	570
DMn	2	17	8	54	530	170	450	850	720	360	950	570
TZn	<10	40	<10	<10	90	30	120	500	230	90	1,300	220
DZn	<3	6	<3	4	87	24	130	500	210	70	290	200
pH	6.4	7.6	6.9	3.5	6.8	6.0	4.7	5.4	4.9	4.6	7.0	6.05

SHEET 2 - ERRATA



Errata- This figure illustrates the changes made to the Central Utah Thrust Belt and Paradox Basin stratigraphic columns. In the Central Utah Thrust Belt, the Morrison Formation is restricted to the Upper Jurassic. In the Paradox Basin, the stratigraphic block from the base of the Entrada Sandstone to the top of the Morrison Formation should be shifted down as shown above. Other changes include subdividing the Entrada Sandstone into three members and repositioning the members of the Morrison Formation.

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Proceedings: Summitville Forum '95

A forum held in conjunction with:
Tailings and Mine Waste '95
Colorado State University
Geotechnical Engineering Program
Department of Civil Engineering
Fort Collins, Colorado, USA

Editors:
Harry H. Posey[1], James A. Pendleton[1] and Dirk Van Zyl[2]

STATE OF COLORADO
1876

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DEDICATION

This publication is fondly dedicated to the memory of Walt Ficklin, who died unexpectedly on October 11, 1993, at the age of 56.

Walt was a highly respected analytical chemist and environmental geochemist with the U.S. Geological Survey. He was best known for his development of techniques for determination of arsenic speciation in environmental samples, and for his work on mine-drainage geochemistry. Walt's gentle wit, giving nature, and expertise in his job made him a joy to work with. His extensive knowledge of wildflowers and geography made field work with him a true multi-disciplinary learning experience. He enjoyed gardening, making apple cider, and pitching a mean game of softball.

The many people whose lives were enriched by knowing Walt will miss him greatly.

PREFACE

PROCEEDINGS: SUMMITVILLE FORUM '95

The San Luis Valley is the second most important crop producing region in Colorado, and is an important way station to recreation in the San Juans and the Rio Grande Basin. The Alamosa River, which flows east from the Continental Divide into the southern San Luis Valley, is the principle source of water for crops and livestock near Capulin and La Jara and the valley south of Monte Vista. The most significant cash crops irrigated from the Alamosa are alfalfa, barley and wheat. Potatoes are an important cash crop in the Valley, but only a few potato fields are irrigated by the Alamosa. Cattle and sheep feed on Alamosa irrigated alfalfa and water from the river as well. Irrigation ponds, which are filled with Alamosa River water often are stocked with fish for private use. Thus, the Alamosa River is a very important component of the local economy and provides livelihood for a significant component of the agricultural community.

When Galactic Resources, Ltd. announced the pending abandonment of the Summitville mine due to bankruptcy, it sounded a serious alarm in the citizens downstream. In the wake of the announcement there came an almost immediate response from the San Luis Valley residents, particularly the agricultural sector. Their concerns helped focus attention immediately on the potential downstream effects.

Several entities within the valley—the Alamosa-La Jara Water Conservancy and Conejos County—already had suspected problems at the mine before the bankruptcy was announced, and had commissioned limited water quality studies of the Alamosa River basin. The State Division of Minerals and Geology and the Water Quality Control Division, following up on a protracted record of problems at the mine—some leading to water quality violations—were in the midst of a negotiated settlement and had just one day earlier received a comprehensive remedial measures plan from the company and its consultants. The State Division of Wildlife knew there were problems in the system, and were investigating mine discharges following fish kills in stock ponds in 1989 and the complete disappearance of fish in the Terrace Reservoir, a DOW-stocked reservoir.

In response to the EPA Emergency Response Action to take over water treatment at the Summitville mine, and particularly in response to local concerns, the Governor of Colorado met with local citizens and the EPA in December, and in short order formed the Governor's Summitville Advisory Committee. By that time the CSU Agricultural Extension Service had begun an evaluation of livestock and had initiated a voluntary low-cost domestic well water sampling program. Local citizens had formed a Technical Assistance Group (TAG) and were meeting regularly to discuss handling of the situation. The Governor's Committee and several State coordinators were put in place to track rumors and disseminate accurate and timely information because, at that time, there was considerable concern that a "food scare" might flare up. Such rumors, if allowed to get out of hand, might have created for the State yet another "Rocky Ford Cantaloupe" or "Alar" scare and agricultural prices would have suffered.

Remarkable for its effectiveness and quick action, the TAG sought relentlessly for attention and helped the agencies focus on potential problems in the agricultural community. Several valley residents testified at a preliminary injunction hearing that failure to maintain the pumps and treatment system might endanger crops and livestock and argued sensibly and knowledgeably about past problems from the mine. So comprehensive was the early response from the Valley citizenry, the U.S. Geological Survey, the CSU Agricultural Extension Service, and local citizens that, much to the surprise of EPA, a lot of what would later be considered the Remedial Investigation of off site damage was completed by non-EPA entities in the first year following bankruptcy.

By fall of 1993, it became apparent to the Editors of this Proceedings that there was a strong scientific commitment on the part of the many researchers involved in the Feasibility Study to exchange information with the other researchers. In October of that year, all met for two days of intense informal presentations of the freshly collected information. At that time, we decided that the diversity and high scientific standards of those presentations called for the works to be collected into a formal proceedings and public forum. Hence, the Summitville Forum '95.

We are grateful to the Colorado State University Department of Civil Engineering for allowing us to produce this forum in conjunction with their yearly Mine Waste and Tailings Conference, and to the Colorado Geological Survey for publishing this Proceedings volume. We are also very grateful to the many researchers and their agencies for providing timely release of the information for publication.

Harry H. Posey
James A. Pendleton
Dirk Van Zyl

ACKNOWLEDGEMENTS

Numerous persons and agencies helped evaluate the Summitville situation, both on and off-site, and many provided access to the study areas. This list, though extensive, only begins to acknowledge those whose participation and interest helped bring about this Forum Proceedings.

The editors wish to give special recognition to citizens of the San Luis Valley whose interest and cooperation have been beneficial. Conejos County and Commissioners Pete Llamas and Lucy Cordova, and the Conejos County Road and Bridge Department. Rio Grande County and Commissioners Vern Rominger and Robert Schaefer. Miguel Lujan and Suzanne Benton. Alamosa County. Alamosa-La Jara Water Conservancy: John Shawcroft, Leroy Valdez. Terrace Irrigation Company: Ron Reinhardt. Rio Grande Water Conservation District: Sarah Jones, Ralph Curtis. Reverend Rudy Breunig, Jeff Stern, Allen Miller, Andrew Valdez, Avelino Muniz. Journalists, Gary Theimer, Mark Hunter, Erin Smith. Public Health Nurse, Lois Booth. And the senior editor thanks Bernie in Capulin for several good haircuts.

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Special thanks to Janet Montera and Verdia Johnson for organizing the Forum. And considerable thanks to Cheryl Brchan for assembling the Proceedings volume.

And finally, thanks to the authors and their agencies for their contributions.

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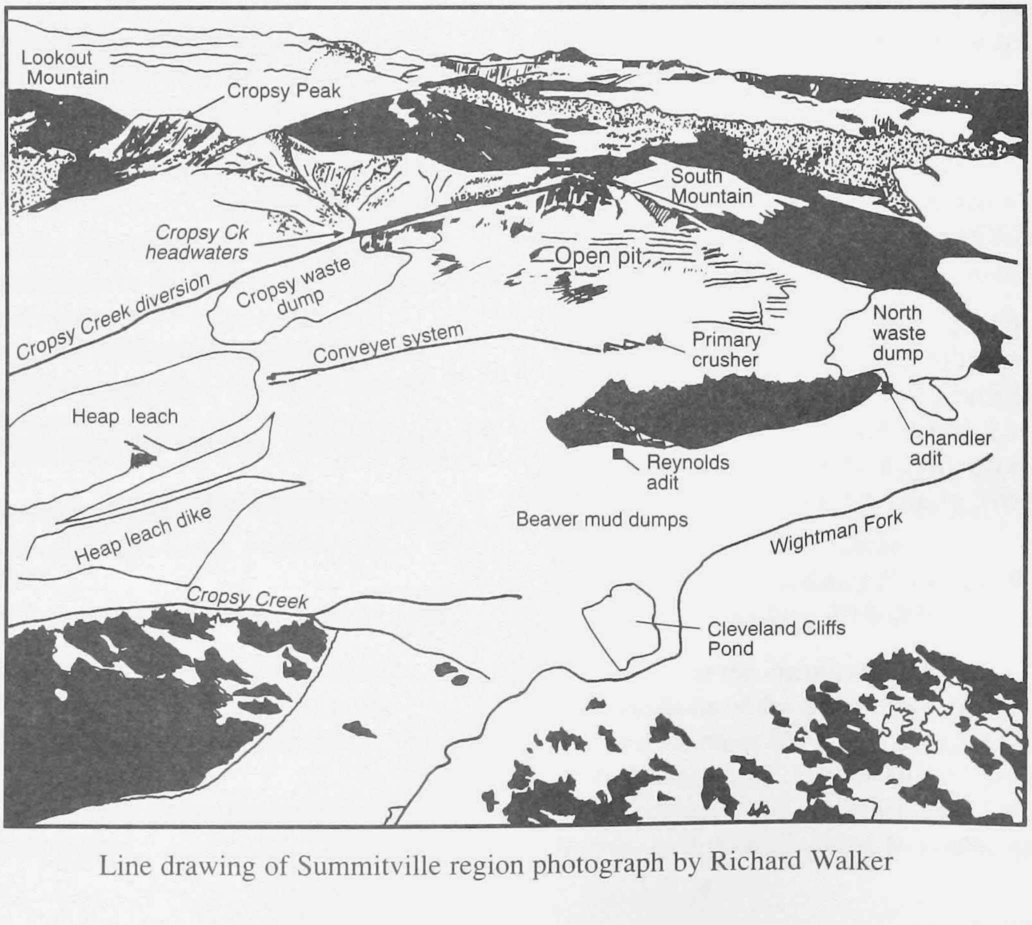
Photograph of Summitville region, October 4, 1991 by IntraSearch, Inc.



Line drawing of Summitville region photograph by Richard Walker

CHARACTERIZING SUMMITVILLE AND ITS IMPACTS: SETTING THE SCENE

By
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INTRODUCTION

At 9:00 pm on December 1, 1992, Galactic Resources Limited (GRL) of Vancouver, Canada notified the State of Colorado of their intent to declare bankruptcy and abandon operation of the Summitville mine effective December 16. The fluid level in the cyanide heap leach pad at that time stood just five feet below the emergency spillway and normal winter precipitation would have caused it to overtop the spillway. Had that happened, cyanide and metal-bearing processing fluid would have overflowed by February of the next year. Within hours of a power outage or mechanical failure, water pumps would have shut down, leaving acidic cyanide water in the heap leach underdrain effluent to overflow the underdrain sump. Effluent from the underdrain would have discharged directly into Cropsy Creek, then Wightman Fork, a tributary to the Alamosa River. On December 4, with no capability to deal with an emergency of this character, the State requested emergency response assistance from Region VIII of the U.S. Environmental Protection Agency (EPA).

Responding quickly, the EPA sent emergency response personnel and contractors to the site to assess the situation. Most of GRL's staff were retained by the EPA's contractors, the U.S. Bureau of Reclamation and Environmental Chemical Corporation, to facilitate the transition. Steps were taken to assure that necessary water circulation and water treatment systems remained operable. Thus, the immediate threat of a direct contaminant release from the site was averted. A technical team comprised of EPA, DMG, and CDPHE personnel and emergency response personnel began assessing longer term consequences of GRL's operations.

For nearly eighteen months prior to bankruptcy, GRL and its daughter company Summitville Consolidated Mining Company Inc. (SCMCI) had been under constant State agency enforcement mandates to evaluate contaminant releases from the site and develop remedial measures to resolve the problems and reclaim the site. Also, state and federal agencies with varying regulatory responsibilities had been monitoring the mine site and its surroundings. As a result, though inadequate to answer the challenge, considerable environmental monitoring data were available with which to evaluate the Summitville Mine and its environmental impacts.

In the six months following GRL's abandonment of the site, a broad selection of environmental characterization and monitoring projects were initiated. Funded by a broad selection of state and federal agencies with differing mandates and authorities, these projects were performed in some cases according to standard EPA protocols for risk assessment and feasibility study, and in other cases in response to different mandates. Several projects were initiated to respond to public concern about risks to health and related potential agricultural product scares. Project personnel, including state and federal workers, contractors, university staff members, private sector technical professionals, water conservancy district officials, local government officials, and concerned citizens sometimes combined their efforts. The projects focused both on potential contaminant generation and potential exposure within the mine area and off-site. Overall, each of these diverse projects addressed some aspect of the characterization of the Summitville mine site and its impacts. It is the purpose of this paper to set the scene for the separate project reports that follow.

BACKGROUND

A general explanation of the physical situation, history, construction of the mine site, and on-site contaminant generation problems will assist the reader's comprehension of the project reports.

Site Location and Description

The Summitville mining district is located about 25 miles south of Del Norte, Colorado, in Rio Grande County (Figure 1). Occurring at an average elevation of 11,500 feet in the San Juan Mountain Range, the mine site is located two miles east of the Continental Divide.

The mine pit occupies the northeastern flank of South Mountain (Figure 2). The permit area occupied by the State's Mined Land Reclamation permit covered 1440 acres, of which approximately 550 acres have been disturbed (Figure 3).

The Site is located in the Rio Grande Drainage Basin near the headwaters of the Alamosa River. The northern part of the Site is bounded by the deserted townsite of Summitville - last occupied in the mid-1930s - and by the Wightman Fork of the Alamosa River. Cropsy Creek, a tributary to Wightman Fork, bounds the site on the east. The confluence of Cropsy Creek and Wightman Fork is located near the northeastern perimeter of the site at the downstream boundary of the site. Wightman Fork enters the Alamosa River approximately 4.5 miles below its confluence with Cropsy Creek.

Climate

The climate of the Summitville mine site is characterized by long cold winters and short cool summers. Snowfall is heavy (commonly 400 inches) and thunderstorms are common in the summer, particularly during the monsoonal season in August. Temperatures range from about 70°F to 17°F in summer and 40°F to -15°F in winter. Annual precipitation averages 55 inches, mostly as snowfall between November and April with annual evaporation of approximately 24 inches.

Topography

South Mountain, the prominent topographic feature of the site, is a relatively steep-faced, faceted surface hosting sparse vegetation in the upper surfaces grading to a gently sloping alpine valley that forms the headwaters of the Wightman Fork. The oversteepened rock faces on South Mountain bear evidence partly of alpine glaciation and of rapidly eroding clay-rich rocks that break down readily in the local climate.

Before 1870, when gold was first mined from the Wightman Fork, the Site consisted of upland surfaces, wetlands and the peak of South Mountain. The predominant ground cover was alpine tundra at the higher elevations with coniferous forest and subalpine meadow in the lower elevations. Since then, mining has altered grossly the local topography. From 1870 through 1873 limited placer mining was conducted in the alluvial deposits of Cropsy Creek and Wightman Fork. Following that was limited open cut mining in several outcrops of gold-bearing quartz veins. From 1873 through 1940 the northeastern flank of South Mountain was mined extensively during several underground mining campaigns. To access the underground, the surface became laced with road cuts and was disturbed by deposition of waste rock in downslope piles near adit portals.

Several mills were constructed at the mine site, including stamp mills and a flotation-cyanidation mill in 1934. Tailings were deposited downslope of each mill. In the late 1960's Wightman Fork was diverted to the north side of the stream valley to accommodate construction of a large tailings pond. Mill tailings at that time were deposited largely on what was to be called later the Beaver Mud Dump, just upslope of the tailings pond, and fine "slimes" were discharged to the pond (Figure 3).

Starting in 1984, SCMCI significantly altered and enlarged the pre-existing disturbed surface over most of the mine site. Waste rock and ore were excavated to form an open pit on the northeastern flank of South Mountain and were dumped into waste rock piles or placed onto a pad for heap leaching. Waste rock from the pit and other locations was used to construct the extensive road system, various building pads, parking lots, sediment ponds, and the earthen embankment that now contains the valley-fill heap leach pad (Dike 1). Cropsy Creek was diverted into a constructed channel upslope of the heap leach pad along the southeastern valley wall of the Cropsy Creek valley. Waste rock and fines were deposited on the Cropsy Waste Pile, the North Waste Pile, the Beaver Mud Dump and the Clay Ore Stockpile.

Several deviations from the original mining plan caused disturbances that might have been avoided. The original mining plan called for the processing of two separate types of ore: clay ore and vuggy silica ore. A separate crusher and conveyor system was installed for each of these ores. The clay ore was to have been agglomerated and leached on a pad upslope of the main heap leach pad, on what is now the Cropsy waste rock dump. However, agglomeration was abandoned, the experimental clay "ore" stockpile remains on the site, and the clay ore crusher and conveyor went virtually unused.

Geology

The Summitville mining district is located near the margin of the Platoro-Summitville caldera complex (Figure 4). Ore-bearing rocks in the immediate area of the mine site consist of the South Mountain Quartz Latite Porphyry (Steven and Ratte, 1960). The porphyry is underlain and surrounded by the Summitville Andesite. The contact between the latite and andesite is intrusive, faulted in some areas, and nearly vertical. The contact on the northern margin of the latite intrusive is marked by the Missionary Fault. South Mountain is bounded on the southwest by the South Mountain Fault, a large northwest trending regional fault. The South Mountain Quartz Latite Porphyry is bounded to the west, on both sides of the South Mountain Fault, by the slightly older Park

Creek Rhyodacite. The latite is overlain at higher elevations in nearby erosional remnants by the Cropsy Mountain Rhyolite.

Emplacement of the South Mountain volcanic dome, hydrothermal alteration, and mineralization occurred in rapid succession approximately 22.5 million years ago (Rye and others, 1990). Stoffregen (1987) concluded that magmatic, hot and highly acidic, sulfate-laden water that suffused from the quartz latite magmas caused extensive alteration of the quartz latite. Hydrothermal alteration consists of four zones, generally occurring in sequence: vuggy silica, quartz-alunite zone, quartz-kaolinite zone, and the clay alteration zone (see Plumlee, and others, this volume, for more details). The vuggy silica zone generally is a porous unit from which most major elements except silica and iron were leached by acidic solutions and replaced in places by excess silica. This zone is comprised of irregular pipes and lenticular pods that generally show greater vertical than lateral continuity. The next outwardly occurring zone, the quartz-alunite zone, contains feldspars of the quartz latite porphyry which have been replaced by alunite. This zone grades outward to a thin quartz-kaolinite zone, which is not always present, and then into an illite-montmorillonite-chlorite zone in which feldspar and biotite crystals were replaced by illite and quartz, with lesser kaolinite and montmorillonite. The quartz-alunite and clay alteration zones are the most volumetrically significant. Fine-grained pyrite is disseminated through the groundmass in all zones (Rye, et.al., 1990). Overall, the alteration mineralogy at Summitville is most similar to alteration near the crest of Cropsy Peak, a lava-capped peak southeast of South Mountain (see King et al., this volume, for more information).

Summitville mineralization is an example of acid-sulfate epithermal Au-Ag-Cu mineralization associated with advanced argillic alteration (see Plumlee et al, this volume). Magmatic water (derived from the magma) mixed with the less acidic and more reducing meteoric water (derived from snowmelt and rainfall), and deposited metal sulfides at relatively shallow depths (less than 1 kilometer). Mineralization is associated mostly with the porous vuggy silica zone, and occurs as covellite + luzonite + native gold changing with depth to covellite + tennanite (see Plumlee and others this volume for an explanation of these minerals). Gold also occurs in a near-surface barite + goethite + jarosite assemblage that crosscuts the vuggy silica zone (Stoffregen, 1987). Numerous minerals comprised of secondary metal salts occur throughout the fractures and groundmass (Plumlee and others, this volume).

Post-volcanic geologic processes have been largely erosional, in part glacial. The two major streams that drain the site, Cropsy Creek and Wightman Fork, tend to follow the quartz latite/andesite contact. Numerous springs and seeps issue along this junction between the fractured quartz latite porphyry aquifer and the underlying dense andesite aquitard. Discharges of iron-rich waters from these springs and seeps, when mixed with air, form ferricrete bogs, concrete-like deposits of iron oxides and iron hydroxides that cement together whatever lies in the path of the mineral water including rock, vegetation, and rarely, wildlife. Site cover material consists of topsoil, silt, clay, and gravel.

Hydrogeology

Ground water at the Summitville mine site is present in several local, shallow, discontinuous perched aquifers. Shallow ground water occurs in surficial deposits consisting of colluvium, "slope wash" alluvium and/or glacial ground moraine, and weathered and fractured portions of the Summitville Andesite. These shallow systems discharge to surface water seasonally. The upper perched aquifer system also contributes to the ground water recharge of the fractured bedrock system. Both the quartz latite and andesite bedrock throughout the mine site are fractured extensively. Several local highly productive wells were installed apparently in zones of high fracture density, and are coincident with surface lineaments. Numerous springs and seeps occur throughout the mine site, the greatest number near the contact zone between the productive, upgradient quartz latite and the surrounding less permeable andesite. Most of these discharge in direct response to the annual precipitation cycle, with high and low flows corresponding to the surface water flows in the area. Rainstorm related discharges, particularly in August, occur at some seeps.

Surface Water Hydrology and Human Occupation

Surface water from the Summitville Site flows past the town of Jasper into Terrace Reservoir, approximately 17 miles downstream from the confluence of the Wightman Fork with the Alamosa River. Below the Terrace Reservoir, the river flows into the western side of the San Luis Valley, past the town of Capulin. Throughout this drainage area, homes, farmsteads and ranches depend on alluvial and bedrock wells or river water for potable and agricultural water production. Additionally, the Alamosa River is used for surface irrigation on lands within a small portion of the Alamosa River Wildlife Refuge (see Balistrieri and others, this volume). Part of the Alamosa River is diverted through the Empire Canal into La Jara Creek. La Jara Creek stream flow and irrigation return water reach the Rio Grande River during several times of year. However, because of irrigation diversion and recharge loss to the alluvial aquifer, the Alamosa River channel rarely has in-channel flow east of U.S. Highway 287, so it does not flow into the Rio Grande at their historic confluence. In places the historic Alamosa River channel has been plowed.

Present Surrounding Land Use

The Summitville Mine occurs mostly on private (patented) land, and is surrounded by lands of the Rio Grande National Forest. Within the mine site are 22 acres of Forest Service land. The Forest Service lands are highly desirable for outdoor sports and recreation, both in winter and summer. Additionally, logging is conducted adjacent to the site and the main access roads. Cattle and sheep are grazed in the surrounding area during summer and autumn the area is heavily hunted.

Production of the Summitville Gold Resource

Placer gold was first discovered in the alluvium of the Wightman Fork of the Alamosa River by J. L. Wightman in 1870. In 1873 the first lode gold deposits were located and claimed on South Mountain. Like many mining communities in the west that are now ghost towns, Summitville materialized overnight to accommodate the miners who worked the mines and mills on South Mountain. Between 1873 and 1949, Summitville yielded approximately 240,000 troy ounces of Gold, worth approximately $7 million at the time of production. Between 1950 and 1984, activities at Summitville were limited largely to exploration. Between 1984 and 1992, SCMCI produced approximately 249,000 troy ounces of Gold. Based on an average price of $325 per ounce, this production represents a value of approximately $81 million. (The price of gold fluctuated during mining operations and what SCMCI recovered in value is not known.)

GRL's Operating Problems

In 1984, GRL acquired the property, completed additional drilling, and proceeded to obtain a permit for a "limited impact" test pit and heap leach. (A limited impact operation, in terms of the Mined Land Reclamation Board, covers less than 10 acres of disturbance and can disturb no more than 70,000 tons of rock per year.) The test project was completed in the summer and fall of 1984 and pronounced a success. GRL formed a local subsidiary, Summitville Consolidated Mining Company Inc. (SCMCI), in early 1984. SCMCI was a wholly-owned subsidiary of Galactic Resources, Inc. (GRI), of Idaho, which was in turn a wholly-owned subsidiary of Galactic Resources, Limited (GRL) of Canada. For simplicity hereafter, we will refer to GRL, the parent corporation, when referring to any of the three corporate entities.

GRL obtained a mine permit for the full scale open pit and heap leach operation in October 1984. However, the depressed gold price during 1985 apparently prolonged the raising of investment capital. Construction commenced in 1985, continued through the winter of 1985, and was completed during the summer of 1986. Considerable difficulty was encountered during construction, due to the extreme winter conditions at 12,000-foot elevation, and this resulted in extensive avalanche damage to the heap leach liner system.

Even though SCMCI produced a reported 249,000 troy ounces of gold, the company's December 4, 1992 U.S. bankruptcy petition reported a net operating loss of approximately $85 million. Complemented by equally unprofitable involvements in the Ridgeway (South Carolina) and Ivanhoe (Nevada) gold mines, Galactic Resources Limited of Vancouver, Canada, SCMCI's parent, reported a combined net operating loss of $297 million in its January 21, 1993 Canadian bankruptcy petition.

SCMCI notified the State of its intention to file for Chapter VII bankruptcy petition by facsimile delivery of a draft press release at 9:00 pm on December 1, 1992. The press release stated that SCMCI intended to seek protection of bankruptcy because it lacked the financial ability to continue operations at the Summitville Mine after December 15, 1992. On the previous day, SCMCI had delivered a revision to their mined land reclamation plan that had been required by the Division of Minerals and Geology (the Division) and the Mined Land Reclamation Board (the Board). This revision application included cost estimates covering several amended reclamation plans; these ranged from $20.6 and $38.6 million. Upon completion of a technical adequacy review, the Division, as statutorily mandated, would have required the operator to submit additional warranty, increasing the bond to an amount equal to the projected reclamation cost. SCMCI filed its petition with the federal bankruptcy court in Denver on the afternoon of December 3, 1992.

ON-SITE CONTAMINANT SOURCES

The Heap Leach

Crushed ore was first deposited in the heap leach, and cyanide solution application commenced in June of 1986. During the first month of processing, cyanide-bearing fluids were detected in the leak detection layer between the primary fabric liner and the secondary compacted clay layer and in the underdrain installed beneath the secondary compacted clay liner. The

Division of Minerals and Geology (the Division) reported the loss of containment to the Mined Land Reclamation Board (the Board). GRL and its retinue of consultants attributed both occurrences to sloppy application of solution which allowed overspray outside the partially lined basin. In addition, GRL presented the rationale that the leak detection system is also an interceptor system because no 45-acre heap could be constructed with zero leakage.[1] The company was allowed to construct a sump (the French drain sump) to capture the contaminated leak detection and underdrain effluent and pump them back into the heap for containment.

The original permit application included a water balance assessment for the Summitville site that projected an excess of evaporation over precipitation. Had that been the case, water from Wightman Fork would have been needed to sustain operation of the heap leach. In fact, water rights covering this project were procured prior to operations. But the water balance projection was later determined to be in error. GRL's consultants contended that the sump fluid, which was pumped back to the heap, would not eliminate the projected water balance deficit within the heap. Additional water would still be required to compensate for evaporative loss.

Records from mid-1987 through the late fall of 1992 show that Summitville mine operations suffered a series of broken pump back pipelines and springs erupting from beneath the heap leach, resulting in releases of cyanide-contaminated fluids. One of the reasons that pumps failed is that acidic waters, which flowed beneath the heap leach pad into the French drain sump had to be neutralized prior to pumping. However, because lime was used to neutralize the acid, and because the solutions dissolved the metals in the pumps quickly, several pumps failed before the operator switched over to sodium hydroxide and stainless steel pumps for more stable operations.

Violations were issued and abatement actions ordered and completed only to encounter further setbacks. The NPDES/CDPS program's original assumption that the mine would be a "zero-discharge" facility was discarded, and GRL was required to install a treatment plant to treat and release the accumulating cyanide-contaminated heap solution. Discharge was essential because there was too much fluid in the heap leach pad and it was affecting recoveries, operations, and ultimate shutdown. But treatment was necessary because every industrial discharge had to meet water quality standards that were established for the discharge.

Throughout a prolonged sequence of events, the operator's attempts to perfect its water treatment plant met no success. During 1989 and 1990 GRL attempted land application to polish and dispose of partially treated effluent. However, the land application project resulted in overland flow due to over application and GRL was cited again for water quality violations. Had the land application water not flowed overland, there might not have been an "unregulated discharge" and application to groundwater might have continued.[2] The volume of fluid inside the heap leach pad grew steadily, inundating the ore, compromising resource recovery, and increasing the eventual risk.

The Waste Rock

Much of the Board's and Division's attention was focused on the heap leach pad, its water balance, land application, and related issues. However, as mining progressed, a significant additional environmental issue developed over acid drainage and metals contamination from the site's waste rock piles. There was a lack of adequate characterization of the overburden and waste rock during the permitting process. The original limited impact permit application stated that because the rocks of the ore body came from the "oxide" zone, they had no acid generating potential. This observation was grossly incorrect.

Like thousands of other deposits in the world, the gold at Summitville formed when hydrothermal solutions deposited sulfide-rich base metal veins. Originally, the gold was extremely finely disseminated within the sulfides and, if not for the process of weathering, probably would not have been technically feasible to mine. Yet, as the cover rock above these ore-bearing deposits eroded, and water and oxygen percolated into the veins, dissolved sulfide minerals, precipitated iron oxide minerals in their place, and in the process left behind higher concentrations of native gold. Native gold in an oxide deposit is eminently more recoverable than gold in sulfide minerals.

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[1] The rationale for leaky liners has its history in federal RCRA regulations that apply to landfills. There it is set out and agreed that landfill liners are expected to leak and in fact are allowed to leak at fixed rates. Given that cyanide heap leach liners and landfill liners are composed of the same materials, it thus must have seemed reasonable to expect leakage. However, revisions to the Colorado Mined Land Reclamation Act do not permit liner leakage.

[2] The regulatory action that issued as a result of overland discharge of fluid from the land application system has been a source of considerable confusion. The discharge was cited for violation because it was an unpermitted discharge. Water pollution was not an issue. The discharged water was treated prior to land application to remove cyanide and metals, but could not meet the discharge limitations for silver. Even so, there is indication that the silver concentrations could not have been accurately measured because of matrix interferences. On the one hand, discharge to the land was acceptable, even though it might be assumed scientifically that the discharge would have made it to streams after some travel distance. However, direct discharge was not acceptable simply because it was not permitted.

In a deposit like this, gold grades are highest and most easily recoverable in the upper, near-surface parts of sulfide veins and diminish downward.

It is generally known that the contact between the upper oxide zone and the sulfide zone below is not a horizontal plane, but rather is an undulating, roughly planar surface which is more or less parallel to the ground surface. It is common to find pockets or pods of sulfide minerals above the water table, even though they reside in the "oxide" zone. Variations in rock permeability allows water and oxygen to reach parts of the veins and restricts them from others.

Because sulfide minerals are not good candidates for cyanide heap leach processing, high sulfide-bearing rock, normally, is disposed without processing. Even at Summitville, grade control was exercised in order to limit the amount of sulfide minerals that reported to the heap. The pit geologist, using visual clues and analytical information from drill hole analyses, decided whether each load of rock was to be ore or waste. Owing to this segregation, the waste rock contains a higher abundance of base metal sulfide minerals than the heap. Unfortunately, these now are being released to the ground and surface waters, due to weathering. GRL discarded extensive amounts of waste rock in several waste rock piles throughout the permit area. They carelessly placed at least one of these piles in a spring fed (groundwater fed) bog which magnified the volume of acid drainage and metallic contaminants released. Had GRL comprehensively evaluated the feasibility of this venture, mining might never have been pursued.

Based on recent water quality monitoring data, it appears that in terms of metal loading, approximately 45% of the mine site's copper metal load (as high as 8,000 pounds per day) comes from the combined French drain sump beneath the heap leach pad, the Cropsy waste pile, the beaver mud dump, and the north waste rock pile.

The Reynolds Adit

At some point in the development of practically every historical mining district in Colorado, there was constructed a dewatering tunnel that lowered the water table to avoid pumping costs and difficulties while mining the deeper levels. In Central City the dewatering tunnel is the ARGO Tunnel; in Cripple Creek, the Carlton Tunnel; in Leadville, the Yak Tunnel; and in Summitville, the Reynolds Adit. The Reynolds Adit, located near the base of South Mountain, was completed in 1897. Prior to plugging in 1994 (Hanley, this volume), the Adit flowed continuously, varying from a low of approximately 100 gallons per minute in the winter to an average high of approximately 400 gallons per minute during spring melt. Abnormally high undocumented snowmelt flows as high as 1,600 gallons per minute have been reported.

Because the Reynolds Adit drains the mineralized portion of South Mountain, historically it has evidenced relatively high metal discharges. Prior to 1988, copper concentrations typically reached 20 to 30 milligrams per liter (mg/L). Beginning in 1989, however, the metals content of the Reynolds Adit effluent began to increase (Golder Associates, Remedial Measures Plan, 1992). In 1992 copper in the effluent reached about 130 mg/L. Even though the mechanism is not completely understood, it appears that GRL's excavation of the open pit, which was not drained and which floored about 300 feet above the Reynolds Adit, stimulated the infiltration of surface water and promoted oxidation of the ore body. Of course, this man-induced activity resulted in an increased release of acid and metals to the Reynolds Adit, following natural processes of weathering. By 1989, the GRL open pit had become an undrained sump.

In June of 1993 the Reynolds Adit effluent reached a maximum documented concentration of 650 milligrams of copper per liter. The past ten years monitoring demonstrate that the highest metal concentrations coincide with the highest flow rates.

Based on recent water quality monitoring data it appears that, in terms of metal loading, as much metal flowed from the Reynolds Adit as from the remainder of the entire mine site, including the waste rock piles. Prior to its plugging in January of 1994, approximately 50% of the metals yield from the entire mine site (as high as 9,000 pounds of copper per day) issued from the Reynolds Adit.

PURPOSES OF CHARACTERIZATION

Rumor Control

An immediate concern voiced by local government officials, business representatives, environmental advocates and local citizens alike, was the need for factual information and the control of misinformation. The EPA and the State desired to disseminate factual and precise information concerning potential health and environmental risks. Testing of municipal and private water supplies was expedited. Representative agricultural produce and animal tissue from areas exposed to potentially contaminated Alamosa River water were analyzed to verify safety of the food supply and to quell potentially damaging food scare rumors. The initial preliminary determinations required thorough and expeditious verification. Most of the results are reported in this volume.

Risk Assessment

In accordance with CERCLA regulations and EPA procedure, complete human health and ecological risk assessments must be completed to define the nature and extent of the risks related to historic and potential contaminant releases from the Summitville mine site. Additional statutes such as the Migratory Bird Treaty and the Threatened and Endangered Species Act also require evaluation of ecological impacts. Both a human health risk assessment and an ecological risk assessment are in progress, and although preliminary indications show minimal risk to human health, aquatic life are severely at risk.

Feasibility Study

CERCLA statutes and EPA superfund regulations also require thorough evaluation of the relative feasibility of proposed emergency response "removal" actions and longer term superfund "remedial" actions. Primary among these feasibility evaluations is the ability of the proposed action to curtail the contaminant release and provide a remedy for the impacts of that release.

Determination of Background Environmental Conditions

CERCLA precludes cleaning up sites to conditions cleaner than those which preceded contaminant release. Provided background water quality and ecological conditions are documented, this can be a relatively straightforward determination. Yet in the case of the Summitville mine site, no comprehensive quantitative environmental monitoring data existed with which to characterize the environmental conditions prior to 1984. The Summitville mine site is probably representative of the majority of historic mine sites in the western U.S. in its paucity of pre-disturbance background data. Many of the characterization projects conducted both on-site and off-site provide insight to deduce environmental conditions which existed prior to contaminant release.

Current methodologies preclude making model determinations about the quality of water prior to anthropogenic disturbances. Although the Clean Water Act provides that streams must consider natural or man-induced pollution caused prior to implementation of the act, such classifications do not consider potential impacts from mines that operated after the act was passed. Summitville, lacking acceptable environmental baseline information, was unable to distinguish pollution caused by their operations from that caused by previous ones, and by natural conditions.

Establishing the Remedial Targets

The majority of the early emergency response and remedial activities implemented at the Summitville mine site have concentrated on the prevention of contaminant release. However, as the remedial projects proceed, the yet-to-be determined pre-disturbance conditions will be approached as subsequent actions are implemented. In order to make efficient and cost-effective decisions between optional technologies and scales of activity, it will become increasingly important to comprehensively characterize the on-site and off-site environmental conditions and impacts of contaminant release. The preliminary results of characterization studies have been instrumental in establishing interim remedial targets for the Summitville mine site. As more comprehensive characterization data are assembled the interim remedial targets will be amended.

Currently, the interim goal is to restore the Terrace Reservoir to fishery status, and meet promulgated in-stream standards in the Alamosa River. The Alamosa is classified as a Class II cold-water fishery, with segments below the Wightman Fork confluence having a seasonal classification for copper.

OTHER ISSUES

Off Site Studies

Much of the information about Summitville pertains not to the site but rather to the off site areas. Studies of the off site areas, most of which are detailed in this volume, pertain to water quality in the Alamosa River, irrigation water, potential effects on crops, on livestock forage, and on crops. Wetlands in the western nether tip of the Alamosa National Wildlife Refuge were examined for potential impacts as well as several palustrine wetlands in the Alamosa River and La Jara Creek. The nature of these studies, though beyond the scope of this review, is impressive for its diversity and complexity. The studies covered disciplines in agronomy, agriculture, water quality, human health, aquatic life biology, aquatic chemistry, geology, geochemistry, limnology, bacteriology, process chemistry, civil engineering, hydrology, hydrological engineering, and terrestrial biology.

Other Contaminant Sources

In the Alamosa River basin are three major areas that have undergone extensive hydrothermal alteration. This alteration formed above and alongside the margins of molten intrusive igneous rocks that formed within a few million years of the Summitville mineralization. Regionally, they are part of the late-stage igneous rock suites that intruded the San Juan volcanic sequence.

The San Juan volcanic field hosts several major calderas where intrusive igneous rocks actually exploded through the overlying volcanic rocks. The extrusions spilled out onto the previously deposited rocks, leaving behind a nearly circular shaped depression that filled in part with other later forming rocks (see Bove and others, this volume, for a more detailed explanation). The Platoro caldera hosts two stocks, igneous intrusive bodies that intruded part way into the crust. These are the Alamosa River stock and the Jasper stock (Figure 4). These stocks are circumscribed in part by zones of hydrothermal alteration, and the altered zones contain anomalous concentrations of minerals, particularly iron sulfide. The hydrothermal alteration zone at Summitville, where the pluton lies at some depth below the surface, is less extensive but obviously well mineralized. Other stocks and hydrothermal alteration zones occur within and adjacent to the caldera (see Bove and others, this volume).

The hydrothermally altered areas are key to understanding the region, geologically, and some may have profound impacts on water quality. At a minimum, the altered areas contain pyrite (iron sulfide), which upon oxidation forms sulfuric acid. The acid, in turn, may dissolve other adjacent minerals, and the process can lead to environmental conditions that in the worst case will not support soil life and which pollutes local streams with acid and metals that were dissolved by the acid.

The rates of physical erosion is generally very high in these altered zones because of the lack of protective soil caps, acidity, and the self-disaggregating nature of some of the rocks. Extreme examples of physical erosion are evident especially in Alum Creek and Burnt Creek, but high erosion rates are also operative in Iron, Bitter, Wightman Fork and Burnt Creeks. The net effects of chemical and physical erosion in these areas has not been quantified, but in all none of the effects serve to generate or preserve high quality aquatic life habitat.

Summitville and the Mining Law of 1872

Numerous accounts of the Summitville situation cite flaws in the 1872 mining law as part of the reason for the present situation. However, the problems at Summitville, environmental problems, are not covered by the 1872 Mining Law, which is a property law that applies to some federal land. Revisions in the royalties to be paid for use of these federal lands, changes in the patent law, or other property provisions would not have affected the problems at Summitville.

CONCLUSION

The Summitville mine bankruptcy has been and will continue to be agonizing for the public, the environment, the mining industry, the State of Colorado, and the EPA for decades to come. Agonizing in terms of impact to the natural environment, public expense, morale, and the conduct of business. It is unfortunate that any lessons must be learned at this extreme an expense. However, it is incumbent upon us to learn the lessons Summitville provides and preclude such from ever happening again. The first step in abating the contaminant releases occurring from the Summitville mine site is to characterize the mine site conditions contributing to those releases and the resulting environmental impacts. With the results of this task in our possession we can begin to perfect the remedy.

If there is a theme to this proceedings volume, it is "The Need for Baseline Data." From an industry's perspective, inadequate baseline could be seen as careless and unprofessional and the first step toward business failure and super regulation. Baseline characterization might also protect against the consequences of "joint and several liability" where baseline conditions are not known, although this thought is merely our personal perspective. For small and intermediate mining companies, without adequate staff and expertise to collect such information, baseline gathering should be part of the essential package of services offered by consulting companies. From the public and regulatory perspective, it should be viewed as essential for environmental and human health protection and necessary for fostering a healthy mining industry. For the environment, it must be seen as the first and most important step toward assessing whether development of resources can proceed in company with environmental protection.

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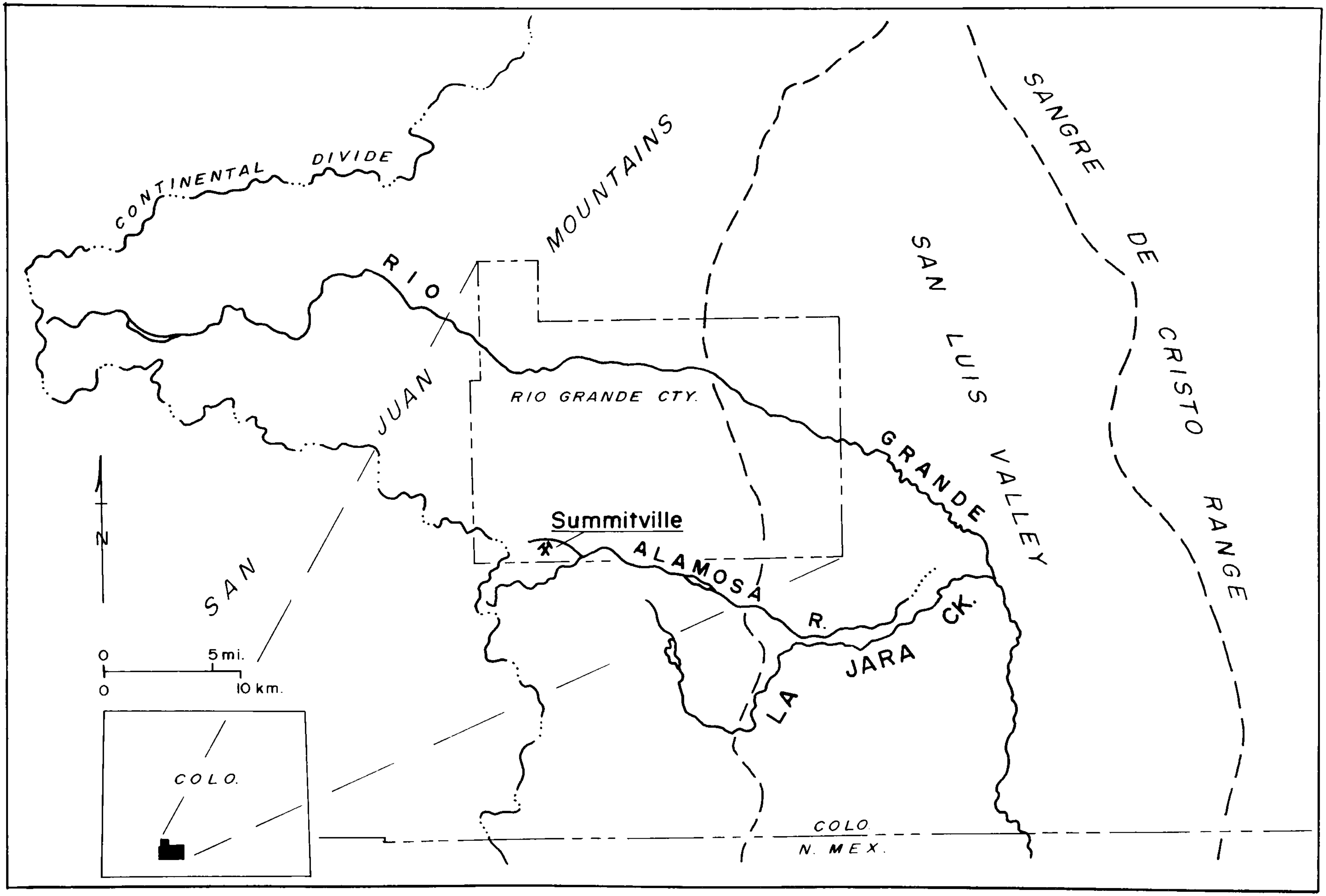

Figure 1. Summitville Area Regional Map

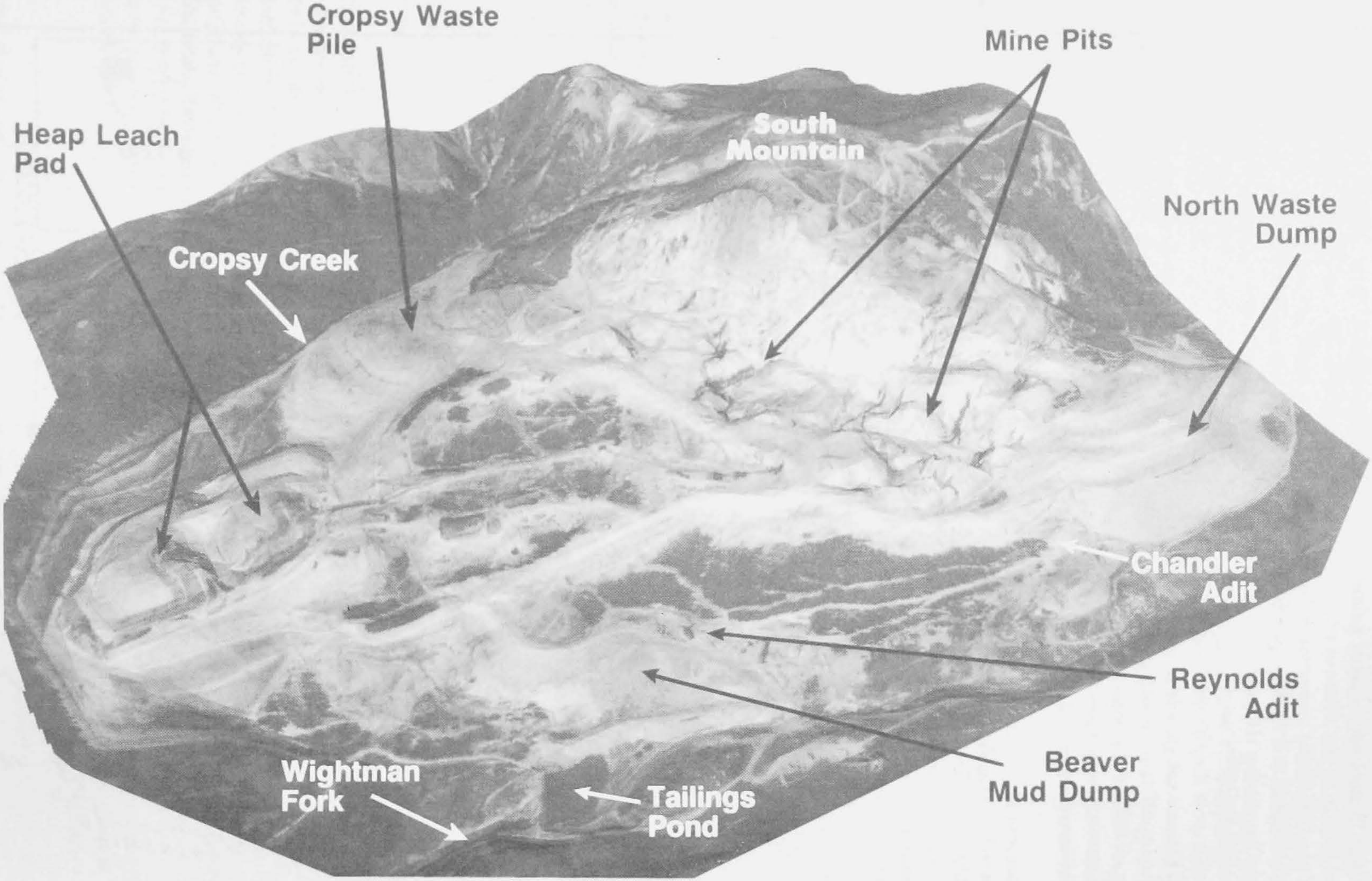

Figure 2. Aerial photograph, Summitville Mine site. Photography by Intrasearch. Photo manipulation by U.S. Office of Surface Mines.

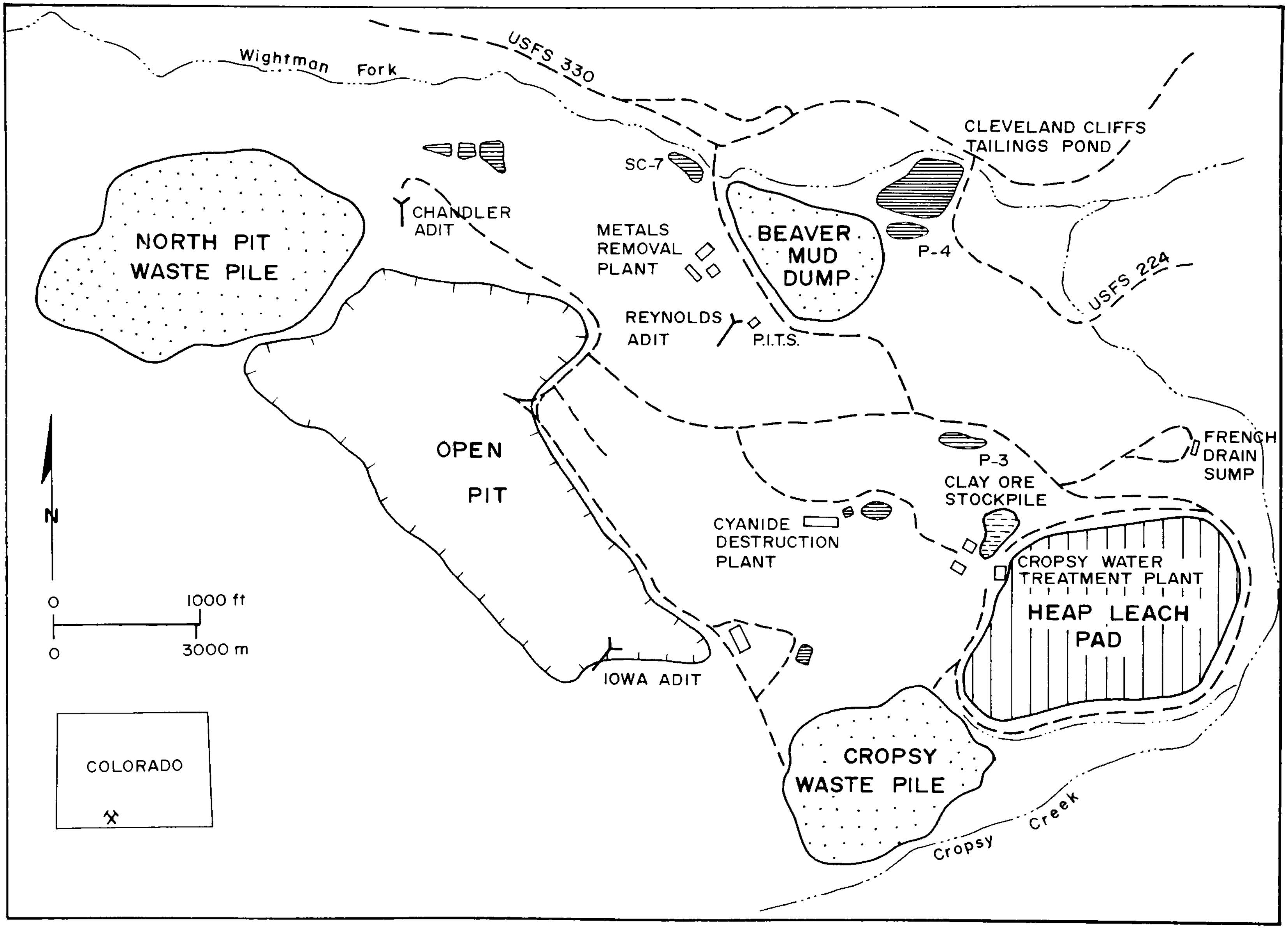

Figure 3. Site plan, Summitville Mine. Modified after Golder Associates, Inc. and Environmental Chemical Corporation.

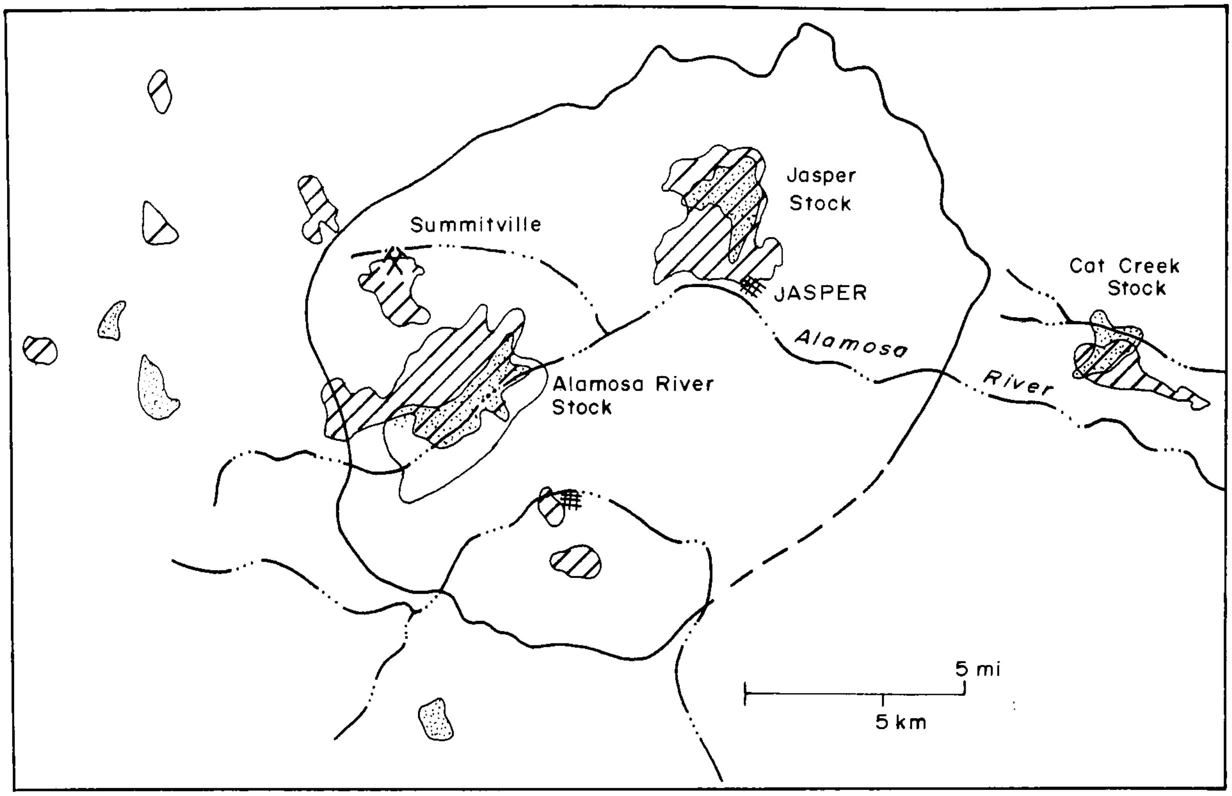

Figure 4. Geologic features of the Platoro-Summitville caldera. Hachures= caldera outline; shaded area = Tertiary intrusive igneous rocks (stock); lined area = hydrothermal alteration, generally associated with igneous intrusives. After Bove and others (this volume).

THE IMPORTANCE OF GEOLOGY IN UNDERSTANDING AND REMEDIATING ENVIRONMENTAL PROBLEMS AT SUMMITVILLE

by
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ABSTRACT

Geologic characteristics of the Summitville mine and vicinity are an important control on the generation of acid-mine drainage, the dominant long-term environmental problem at the site. A good understanding of the environmental geology of the Summitville gold-silver-copper deposit is necessary to: (1) develop the most effective remediation strategies for the Summitville site; and (2) better predict, mitigate, and remediate potential environmental problems at future proposed mine sites with similar geologic characteristics.

Environmentally important geologic characteristics of the Summitville deposit include:

- A high acid-generating capacity resulting from the abundance of sulfide minerals such as pyrite, enargite, covellite, chalcocite, and chalcopyrite.
- A low acid-consuming capacity resulting from intense acid leaching of the volcanic host rocks that occurred prior to the formation of the deposit.
- Intensely altered vuggy silica alteration zones that provided permeability for (a) the mineralizing solutions that formed the deposit, and (b) post-mineralization groundwaters that oxidized sulfides in the vuggy silica zones to depths up to several hundred feet.
- Extensive sulfide-rich clay alteration zones with low permeabilities that were oxidized prior to mining to depths of only several tens of feet.
- Extensive areas of sulfide-rich rocks in clay alteration zones that were exposed to weathering by recent open-pit mining, and that led to increased generation of acid-mine drainage from the site.

Vuggy silica alteration zones and unmineralized faults predominantly controlled shallow groundwater movement prior to mining. Underground mine workings modified the hydrology so that the dominant water outflow occurred from mine-drainage tunnels. Open-pit mining further affected the local hydrology by creating a snow and rain catchment basin that then funneled much greater quantities of water into sulfide rich rocks and mine workings beneath the pit. As a result of the plugging of the Reynolds Adit in late January, 1994, pre-adit hydrologic conditions are largely being re-established.

Extensive deposits of ferricrete (precipitates of iron oxide and hydroxide minerals) mark the location of fossil acid groundwater springs that flowed prior to mining. The locations of ferricrete deposits can be used to help map likely outflow points of springs and seeps renewed by the plugging of the Reynolds adit.

The severe acid drainage problems at Summitville are a direct consequence of the site's geologic characteristics and its climatic setting. Effective remediation will require the isolation of both sulfide-bearing and secondary salt-bearing materials from weathering and oxidation, a formidable challenge given the wide distribution of such materials throughout the site. Future development of deposits geologically similar to Summitville will likely be economically and environmentally difficult unless adequate precautions can be made to mitigate acid-mine drainage.

INTRODUCTION

Geologic characteristics of the Summitville mine and vicinity are an important control on the generation of acid-mine drainage, the dominant long-term environmental problem at the site (Plumlee et al., this volume). A good understanding of the environmental geology of the Summitville gold-silver-copper deposit is necessary to: (1) develop the most effective remediation strategies for the Summitville site; and (2) better predict, mitigate, and remediate potential environmental problems at future proposed mine sites with similar geologic characteristics. This paper summarizes key aspects of Summitville's

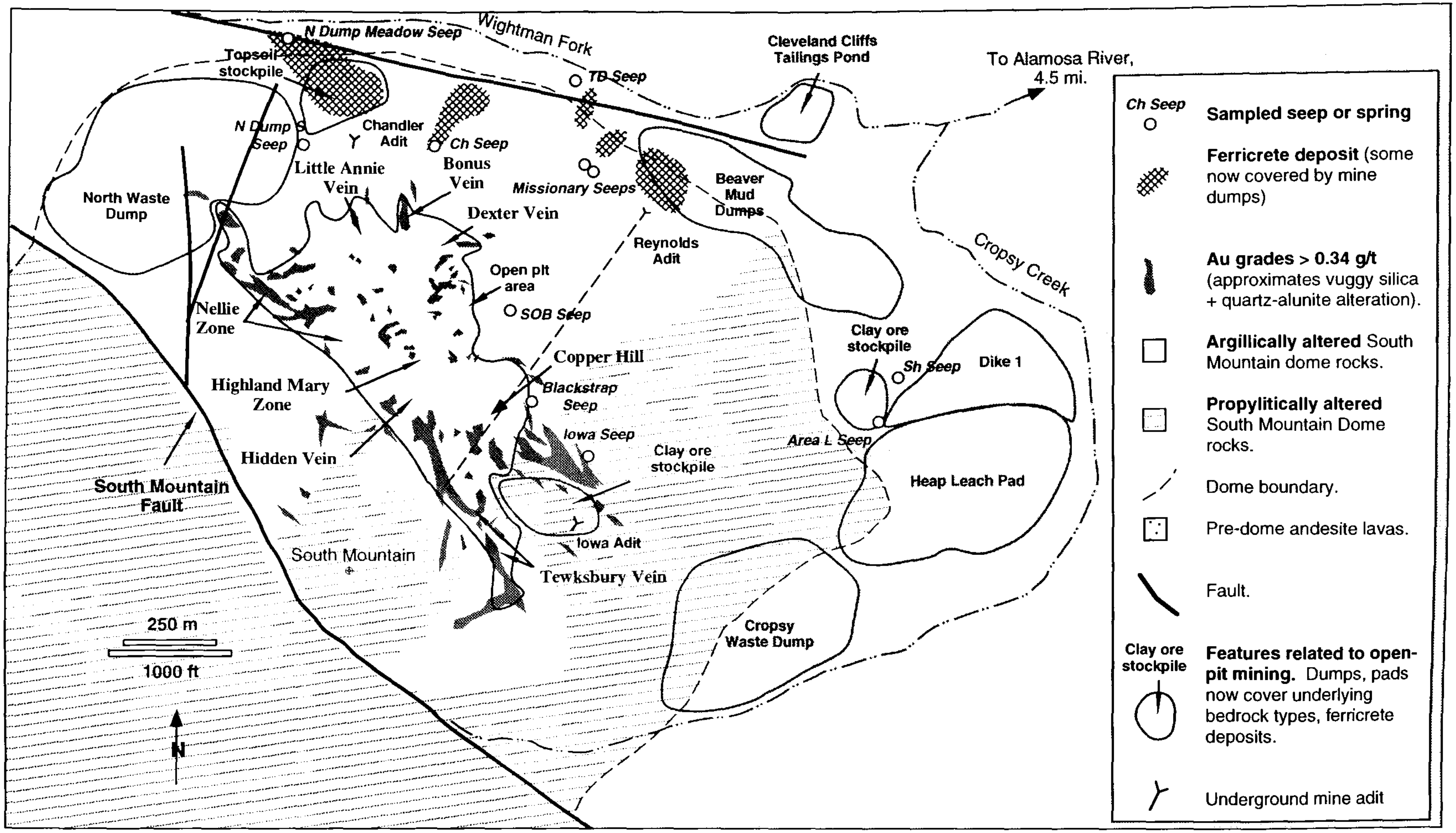

Figure 1. Generalized map of the Summitville mine site showing geologic features (major alteration and ore zones, ferricrete deposits) in relation to past and recent mine features. Also shown are the locations of active seeps sampled for chemical analysis (see Plumlee et al., this volume). The distribution of argillic and propylitic alteration was taken from a surficial geologic map prepared by Mike Perkins and Bill Nieman for the Anaconda Company in the early 1980's. The distribution of acid sulfate alteration (vuggy silica and quartz alunite zones) is approximated by gold grades greater than 0.34 grams per ton (after Gray and Coolbaugh, 1994 in press). The location of ferricrete deposits is approximate based on distributions observed in aerial photographs taken of the site in 1968 and 1980 by Intra-Search, Inc; many of the deposits are now covered by material from the recent open pit mining operations.

environmental geology. For more detailed discussions, the reader is referred to Gray and Coolbaugh (in press), and Gray et al. (in press, 1993).

GEOLOGY

The processes that formed the gold-silver-copper deposit at Summitville ultimately set the stage for the generation of both natural and mining-related acid drainage from the site. Summitville is located in the southeastern portion of the mid-Tertiary San Juan volcanic field, a thick section of volcanic rocks composed in its lower portions of andesitic volcanics and related rocks erupted from numerous stratovolcanoes, and in its upper portions of andesitic to rhyolitic ash flow sheets erupted from numerous calderas (Steven and Lipman, 1976). For a more detailed discussion of the regional geology, the reader is referred to Bove et al. (this volume).

South Mountain volcanic dome

The 22. 4 million-year old Summitville deposit is hosted by the South Mountain volcanic dome (Figs. 1, 2), and formed as a direct result of the magmatic processes that generated the dome (Gray and Coolbaugh, 1994 in press; Rye et al., 1990; Stoffregen, 1987; Perkins and Neiman, 1982; Steven and Ratté, 1960). The dome is composed of quartz latite volcanic lavas that are relatively rich in silica (SiO_2) and have abundant coarse grained crystals of feldspar ($KAlSi_3O_8$). The dome lavas were extruded from a narrow feeder zone (Steven and Ratté, 1960) and pushed outward to form a typical mushroom-shaped silicic lava dome (Fig. 2). Rocks along the contact between the dome lavas and surrounding andesitic lavas were brecciated, creating a zone of higher permeability that is an important control on groundwater movement at the site.

Alteration and Mineralization

As part of the dome-forming cycle, additional magmatic material was intruded into the area beneath the dome. As these magmas crystallized, they released hot gases rich in sulfur dioxide. The gases rose along fractures in the dome rocks and eventually condensed in the shallow portions of the dome, producing fluids rich in sulfuric acid that extensively leached and altered the dome rocks to an advanced argillic alteration assemblage (Figs. 2, 3; Table 1). The greatest amounts of leaching occurred near fractures and left only silica and pyrite in the rock; this alteration zone is called the vuggy silica zone because of the well-formed voids left by the removal of large feldspar crystals. Progressive neutralization of the acidic gas condensates outward from the vuggy silica zones altered the rocks (Fig. 3; Table 1) to successive quartz-alunite, quartz-kaolinite, clay (containing illite, montmorillonite, and pyrite), and propylitic (containing chlorite, pyrite, and some calcite) assemblages. The propylitically altered rocks are very rare in the open pit area, but are more common south and east of the mine.

The advanced argillic alteration event was important in the formation of the Summitville deposit because it provided open space porosity for subsequent sulfide and gold deposition. The advanced argillic assemblage rocks are also environmentally significant because they have a greatly reduced capacity (as compared to fresh, unaltered dome rocks) to consume acid in mine drainage.

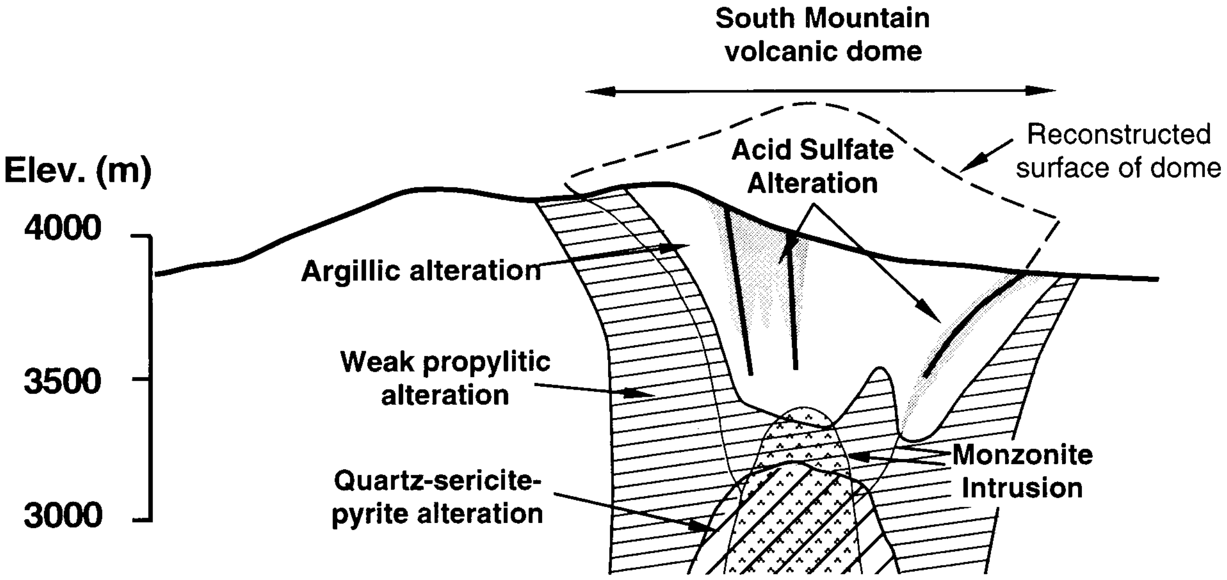

Figure 2. Generalized cross section of the South Mountain volcanic dome showing the geology and distribution of various alteration types. After Perkins and Nieman (1982).

Table 1. Minerals found at Summitville. Minerals listed in bold have the potential to generate acid during oxidation, weathering, or dissolution. Minerals followed by question marks are of uncertain time of origin.

Minerals formed during advanced-argillic alteration

Silica (quartz)	SiO_2	**Alunite**	$KAl_3(SO_4)_2(OH)_6$
Kaolinite	$Al_2Si_2O_5(OH)_4$	Illite	$KAl_4[Si_7, Al]O_{20}(OH)_4$
Pyrite	FeS_2	Woodhouseite	$CaAl(PO_4)(SO_4)(OH)_6$
Smectite	$Na_{0.7}(Al,Fe,Mg)_4[(Si,Al)_8O_{20}](OH_4)\bullet nH_2O$		
Chlorite	$(Mg, Fe, Al)_{12}[(Si, Al)_8O_{20}](OH)_{16}$	Calcite	$CaCO_3$

Minerals formed during hydrothermal mineralization:

Pyrite	FeS_2	**Enargite**	Cu_3AsS_4
Chalcocite (?)	Cu_2S	**Covellite**	CuS
Chalcopyrite	$CuFeS_2$	**Marcasite**	FeS_2
Native sulfur	S°	Gold	Au
Barite	$BaSO_4$	**Sphalerite**	ZnS
Luzonite	Cu_3AsS_4	**Galena**	PbS
Kaolinite	$Al_2Si_2O_5(OH)_4$	**Tennantite**	$(Cu,Fe,Zn)_{12}As_4S_{13}$
Hinsdalite	$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$		

Secondary minerals formed during pre-mining weathering of the deposit:

Jarosite	$KFe_3(SO_4)_2(OH)_6$	Goethite	$HFeO_2$
Limonite	$FeO(OH)\bullet nH_2O$	Scorodite	$FeAsO_4\bullet 2H_2O$
Hinsdalite (?)	$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$	**Chalcocite** (?)	Cu_2S (below water table)

Secondary minerals formed as a result of mining of the deposit (this list will likely expand with further study):

Chalcanthite	$Cu(SO_4)\bullet 5H_2O$	Brochantite	$Cu_4(SO_4)(OH)_6$
Jarosite	$KFe_3(SO_4)_2(OH)_6$	Posnjakite	$Cu_4(SO_4)(OH)_6\bullet 5H_2O$
Hinsdalite (?)	$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$	Halotrichite	$Fe^{+2}Al_2(SO_4)_4\bullet 22H_2O$

Propylitically altered rocks contain minor amounts of carbonate minerals that can help consume acid in mine drainage; however, the propylitically altered rocks occur in such small amounts in the Summitville open pit that they likely have relatively little mitigative effect on acid-mine drainage at the site.

Following the period of intense acid leaching by magmatic gas condensates, Cu- and As-rich sulfide minerals were deposited in the highly altered dome rocks by hot hydrothermal fluids also derived from crystallizing magmas at depth. Minerals deposited in this assemblage include pyrite, marcasite, enargite - luzonite, native sulfur, covellite, chalcopyrite, tennantite, and minor barite, sphalerite, galena, and various phosphate minerals (Table 1; Gray and Coolbaugh, 1994 in press; Stoffregen, 1987). The greatest amounts of sulfide mineralization occurred within rocks altered to vuggy silica because hydrothermal fluid flow was focused in these highly permeable zones; however, appreciable Cu-As sulfide mineralization was also deposited in the quartz-alunite and quartz-kaolinite alteration zones. Multiple generations of hydrothermal brecciation, in which magmatic fluids were explosively released from depth into the dome rocks, also produced some sulfide mineralization. Finally, late-stage sulfide-rich veins were deposited in fractures cutting the highly altered dome rocks (M. Roeber, unpub. data; Gray and Coolbaugh, in press).

Sulfides such as pyrite, marcasite, and enargite are capable of generating large amounts of acid as they weather (Plumlee et al., this volume). The end result of the alteration and mineralizing processes at Summitville was a low-grade gold-silver-copper deposit with the potential to generate large amounts of acid and metals during weathering, but with little capacity to consume this acid.

Structure

The importance of dome-related structures as controls on the distribution of alteration and mineralization zones is illustrated by a map of gold grades of the Summitville mine (Fig. 1); the highest gold grades generally follow the vuggy silica zones of most intense alteration. Vuggy silica zones and coincident gold ore zones radiate outward from the core of the deposit (Fig. 1; Enders and Coolbaugh, 1987). Three northwest fracture trends are present that dip steeply from 65° to vertical. A N30°W ± 20° trend is typified by narrower zones with higher Au grades, such as the Little Annie and Tewksbury zones that were mined underground. A second strong NW structural trend is characterized by N60°W zones that are wider and longer but have lower than average Au grades; examples are the Highland Mary,

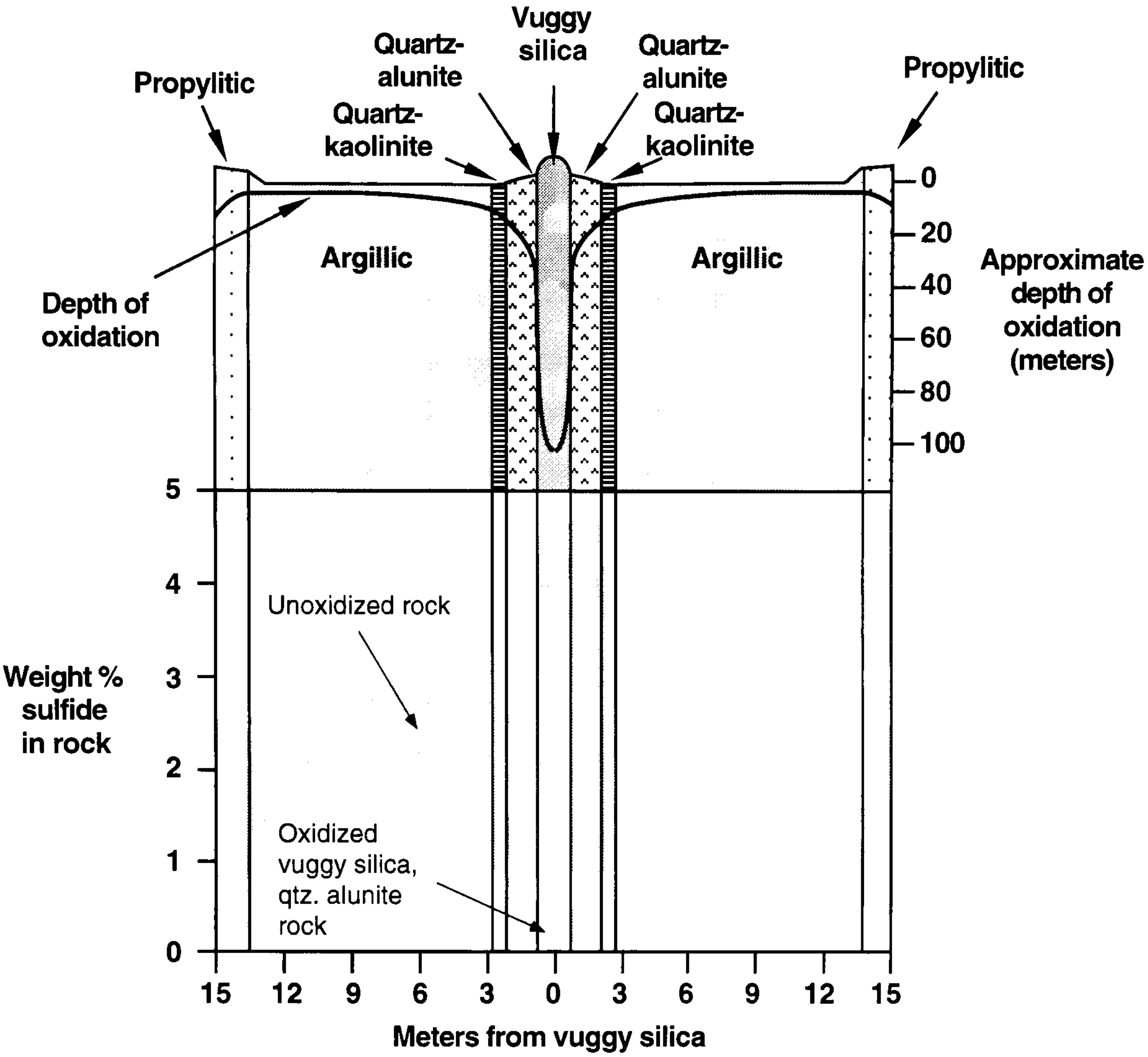

Figure 3. Schematic alteration zoning away from original fractures in the South Mountain dome rocks, showing approximate depth of oxidation (upper plot) and ranges of oxidizable reduced sulfur in weight percent (lower plot). After Gray et al. (1994 in press). Darker stipple shows reduced sulfur ranges in largely unoxidized rocks across all zones. Lightly stippled pattern shows reduced sulfur in oxidized vuggy silica, quartz alunite zones.

Nellie, and Copper Hill zones; these N60°W zones parallel the South Mountain fault on the southwest side of the deposit. A third, less well-developed NW trend strikes N5-10°W and is typified by the Bonus vein east of the Little Annie vein. These three trends intersected near the center of the deposit to form a large ore body approximately 150 by 400 m, the Highland Mary-Copper Hill zone. In addition, some west-trending arcuate ore zones such as the Dexter vein form concentric structures around the core of the deposit on its northern side (Fig. 1). The radial and arcuate structures probably resulted from emplacement of magmas at depth beneath the dome. The well-developed, N60°W-trending structures probably developed along pre-existing regional fractures that were reopened during the Summitville alteration and mineralization.

Unmineralized structures of various orientations crosscut the alteration zones. Largely unmineralized structures mapped in the Reynolds adit (Anaconda Company, unpublished map) generally parallel one of the three northwest trends. These structures produce abundant water in the Reynolds adit, especially during spring snowmelt.

In summary, original dome structures focused alteration by magmatic gas condensates. The alteration zones and some later cross-cutting structures have, in turn, greatly influenced post-mineralization groundwater movement and the extent of weathering prior to mining.

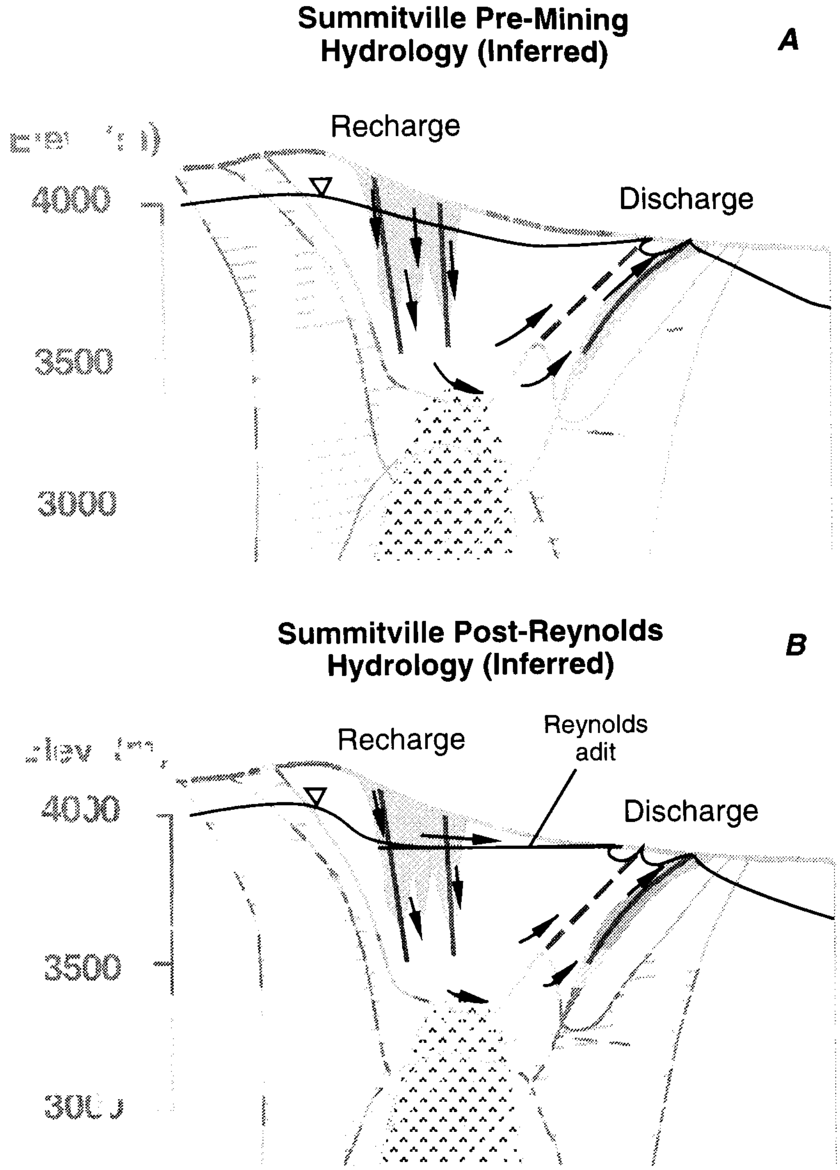

Figure 4. A. Schematic cross section showing inferred hydrology of the Summitville mine area prior to underground mining. Solid black line is water table. Arrows show postulated fluid flow paths. B. Schematic cross section showing inferred hydrology of the Summitville mine area resulting from underground mining. Solid black line is water table. Arrows show postulated fluid flow paths. Flow was reduced from natural discharge points due to increased flow from Reynolds adit. Triangles in each plot show inferred position of groundwater table.

FEATURES OF WEATHERING AND OXIDATION

After the Summitville deposit formed, erosion gradually exposed the deposit to weathering and oxidation by oxygenated ground and surface waters. The most rapid erosion has occurred in the last 5 million years and resulted from a regional uplift of the San Juan Mountains (T. Steven, oral comm., 1993). Weathering and erosion are ongoing, and weathering has been greatly accelerated at the mine site by the recent mining activity.

Pre-mining oxidation and weathering features

Prior to the mining, weathering of the Summitville deposit was focused along the high-permeability vuggy silica alteration zones; pre-mining oxidation of these zones occurred to depths as great as 300 feet below the ground surface (Gray et al., 1993); in fact, gold grades in the vuggy silica zones were enhanced by the oxidation and removal of sulfides. In contrast to the vuggy silica zones, oxidation of rocks in adjacent clay alteration zones occurred only to depths of several tens of feet below the ground surface, due primarily to the greatly reduced permeability of the clay zones to groundwater flow. Some vuggy silica zones and late-stage sulfide veins escaped oxidation if groundwater flow was inhibited by clay-altered rock. Pre-mining weathering and oxidation removed sulfide minerals and left behind variable amounts of iron oxides (hematite and goethite), jarosite (a potassium-iron sulfate), alunite (a potassium-aluminum sulfate), scorodite (an iron arsenate), and gold (Table 1; Stoffregen, 1986). The highly variable nature of the pre-mining oxidation is readily apparent on color aerial photographs of the site (see color photo at front of this volume), with dark brown, highly oxidized vuggy silica zones occurring immediately adjacent to and within larger gray areas of unoxidized, clay-altered rocks.

Features that result from mining

Recent open-pit mining at Summitville exposed to weathering large volumes of sulfide-bearing rocks in the clay alteration zones. It was this exposure of sulfide-bearing rocks in the pit and the storage of these rocks in waste dumps throughout the mine that has led to the increased acid drainage from the site. The acid waters are generated when oxygenated snowmelt and rain waters react with the sulfides to form waters with high contents of sulfuric acid and metals (Plumlee et al., this volume). As the acid waters evaporate during dry periods, they precipitate a complex suite of soluble secondary salts that store metals and acid in solid form until they dissolve during the next period of rain or snowfall. We have observed these salts as surficial coatings on rock materials within the open pit and waste dumps, as coatings on fractures in rocks forming the open pit walls, and as disseminations within sediments left after the evaporation of acid puddles throughout the mine site. In the area beneath the pit, these salts are likely most abundant near airways that allow for evaporation, such as in and near mine workings and in fractured rock immediately beneath the open pit.

Soluble secondary salts are a significant environmental concern at Summitville due to their abundance and the ease with which they can liberate metals and acid into the environment simply by dissolving in rain waters or snowmelt. The types and amounts of soluble secondary salts at Summitville are currently under investigation. Salts identified in limited studies to date include various copper sulfates (including chalcanthite and brochantite), jarosite, and halotrichite. Several phosphate minerals (such as hinsdalite and woodhouseite) have been identified as intergrowths with and as late coatings on primary minerals, and as disseminations within mine-pond sediments. Although in some samples these phosphates are clearly related to the formation of the mineral deposit (Stoffregen and Alpers, 1987), textural evidence suggests that the same suite of phosphates may also be forming as a result of present-day weathering processes. Due to the potentially large number of different salts that may be present, more detailed studies are needed on additional samples to adequately characterize secondary minerals at the site.

Ferricrete deposits

Extensive ferricrete deposits occur primarily along the northern margins of the mine site. These deposits are composed of ferric oxide minerals that were precipitated by acidic, iron-rich groundwaters as they flowed onto the surface from springs. Many of the ferricrete deposits mark the locations of ancient iron springs that flowed prior to mining. The extent of these natural spring deposits can be mapped from aerial photographs taken prior to and during the recent open-pit mining. The ferricrete deposits are localized along the northern contact between the South Mountain dome and surrounding andesitic rocks, along the Missionary fault on the northeastern side of the deposit, and along the northern extensions of NW-trending ore zones such as the Little Annie vein and the Bonus vein (Fig. 1).

Numerous stalactites of hydrous ferric oxides (up to 10 cm long and 1 cm in diameter) were observed in June, 1993, to be actively forming in the Reynolds adit where crosscutting fractures leaked acid water from the adit back. These stalactites form as acidic waters flow from the fractures and become oxygenated; aqueous ferrous iron is then oxidized to ferric iron, which then precipitates as hydrous ferric oxides. As an aside, it is interesting to note that the copper-rich waters draining the Reynolds adit replaced the outer layers of mine rails and anything else made of iron with a thick layer of native copper; analysis of the copper reveals detectable levels of tellurium, indium, and other trace metals.

GEOLOGIC CONTROLS ON HYDROLOGY AND GROUNDWATER FLOW

Summitville's hydrology can be understood qualitatively based on a knowledge of the site's geologic characteristics, limited pumping tests done in 1992, and the monitoring of water table elevations in the pit area since the plugging of the Reynolds adit. However, to adequately predict the long-term response of the site to remedial actions currently underway, more extensive hydrologic pumping tests, downhole geophysical characterization, and tracer and groundwater monitoring studies are required.

Older andesites that surround the South Mountain dome have very low permeabilities and limited groundwater flow near the current ground surface; drilling in the andesites encountered water at depths greater than five hundred feet. The low permeabilities of the andesites, coupled with the higher permeabilities of vuggy silica zones and other fractures in the dome rocks, led to the development of a shallow, perched groundwater system contained largely within the dome.

Prior to mining, vuggy silica zones, unmineralized fractures, and the contact between the dome and surrounding andesites likely served as the dominant conduits for groundwaters at the site (Fig. 4A). Recharge for the groundwater system likely occurred primarily via surface outcrops of the vuggy silica zones. Groundwaters flowed downward along the vuggy silica zones and spread laterally through other intersecting vuggy silica zones and fractures not exposed at the surface. Groundwater discharge occurred primarily along the dome-andesite contact and along limited numbers of fractures that intersected the ground surface; discharge points are documented by the extensive ferricrete deposits discussed previously on the northern side of the mine site. The South Mountain fault west of the deposit was likely also a significant groundwater conduit, and may have fed springs on the northwest side of the South Mountain dome near the drainage divide between the Wightman Fork and Park Creek. It is likely that waters discharged along the dome andesite contact had followed rather deep flow paths (possibly as much or more than 1 km) to reach the contact, and therefore may have had an artesian component.

Inception of underground mining significantly altered the hydrology. Groundwater flow was shifted largely to underground mine workings, which short-circuited the deep flow system along the dome-andesite contact and allowed groundwaters to discharge at a higher elevation along the Reynolds adit (Fig. 4B). Open-pit mining further affected the local hydrology by creating a snow and rain catchment basin that funneled much greater quantities of water into sulfide rich rocks and mine workings beneath the pit and then out the Reynolds adit.

As a result of the plugging of the Reynolds adit in late January, 1994, hydrologic conditions that existed prior to the driving of the Reynolds Adit are largely being re-established. Monitoring by the Environmental Chemical Corporation has shown that water levels beneath the open pit area rose substantially in the months following the plugging and then declined somewhat after spring snowmelt was complete. Reduced flow still continued from the Reynolds adit due to leakage from fractures outside the plug; these fractures are also likely to be feeding active seeps located near the Reynolds Adit (such as the Missionary and TD seeps, Fig. 1). In May, 1994, a plug on the Chandler adit (located approximately 50 m higher than and 800 m northwest of the Reynolds Adit) failed and water began flowing from the adit opening. The flow from the Chandler shows, as expected, that the underground mine workings are much more conducive to fluid flow than the pre-mining fracture systems. However, seeps east and north of the open pit area have also either started flowing or have increased in flow since the Reynolds adit plugging. These seeps typically occur near or within old ferricrete deposits and are located near the dome-andesite contact, along the Missionary fault, or near structures within the dome that intersect the ground surface (Fig. 1). In addition to the seeps located on Figure 1, an intermittent seep on the South Mountain fault (located northwest of the mine at the drainage divide between the Wightman Fork and Park Creek) started flowing again in summer, 1994. The renewed or increased seep activity indicates that groundwaters are once again utilizing natural conduits and flowing from natural discharge points. A number of other seeps are present on the northeastern and eastern side of the deposit; some of these are fed by waters flowing through bedrock fractures (such as the Ch, Missionary, TD, N Dump Meadow, and Iowa seeps), but many are fed by waters flowing through waste material left by the recent open pit mining (such as the N Dump S seep, and seeps from the Beaver mud dumps, clay ore stockpile, and Cropsy waste dump). Chemical compositions of the various seeps are discussed in Plumlee et al. (this volume).

IMPLICATIONS FOR PREDICTION, MITIGATION, AND REMEDIATION

A good understanding of the environmental geology of the Summitville deposit is crucial to: (1) develop the most effective remediation strategies for the Summitville site; and (2) better predict, mitigate, and remediate potential environmental problems at future proposed mine sites with similar geologic characteristics.

Remediation at Summitville

The most significant long-term remedial action needed at Summitville is the mitigation of acid-mine drainage from the site. This requires the isolation of both sulfide-bearing and secondary salt-bearing materials from weathering and oxidation, a formidable challenge given the wide distribution of such materials throughout the site. The current effort to backfill the open pit with acid-generating material and then cap the pit should help significantly reduce acid drainage from the site. However, geologic considerations indicate further efforts and precautions:

- The cap on the pit area must be as impermeable as possible, given the abundance of soluble salts and oxidizable sulfides in the backfill material and the fact that the pit area will continue to drain (although at a greatly reduced level) into the Wightman Fork from reactivated seeps.
- Surface outcrops of vuggy silica zones and faults that are not in the backfilled and capped pit area (Fig. 1) may permit groundwater recharge into the area beneath the cap; these should be identified and, if possible, sealed or capped.
- Seep activity north of the deposit will probably continue and may spread to other areas in which old ferricrete deposits mark pre-mining discharge points (Fig. 1), and to areas where fractures intersect the surface.
- Given the lower-level but pervasive occurrence of acid-generating material throughout the site (on roads, in

soils, windblown into forested areas, etc.), it is likely that some level of surficial acid drainage will bleed from the site over the long term even after the bulk of the waste dump materials have been relocated into the pit. Geochemical and mineralogical surveys of solids from throughout the site are needed to help assess the potential levels of this non-point acid drainage.

- Long-term, field-oriented hydrogeologic, mineralogic, and groundwater monitoring studies are needed to adequately assess the long-term response of the site to remedial actions.

Lessons for the future

The severe acid drainage problems at Summitville were dictated by the site's geologic characteristics (high acid-generating capacity but low acid-consuming capacity of the deposit and its highly altered host rocks) and its climatic setting. The extent of Summitville's downstream effects (acidic, metal-bearing waters persisting more than 60 km downstream; Smith et al., this volume) was also a direct consequence of the surrounding volcanic terrane, which has extensive natural acid drainage from other mineralized areas and relatively small amounts of carbonate minerals to help naturally mitigate the effects of acid drainage. Summitville holds many lessons for the future development and remediation of geologically similar deposits:

- Future development of such deposits will likely be economically and environmentally difficult unless adequate precautions can be made to mitigate the acid-mine drainage.
- At sites in wet climates, extreme care must be taken to adequately isolate mine wastes from surface waters and oxygenated groundwaters. Similarly, the occurrence of alternating wet and dry cycles in mine wastes and workings must be reduced or stopped to prevent the formation of soluble salts and the large-scale flushing of these salts during storm or snowmelt events.
- Unless the climate is so dry as to preclude significant surficial drainage, development of similar deposits in geologic terranes containing rocks with little or no acid buffering capacity will likely be difficult environmentally. These terranes have little nearby material that can be used to mitigate problems on site, and allow the environmental effects of the site to reach much farther downstream without natural mitigation.
- The location of active seeps and fossil seeps (i.e., ferricrete deposits) should be carefully mapped prior to mining, so that acid-generating mine wastes will not be dumped onto active or potentially active springs.
- A detailed knowledge of site geology, hydrology, and the location of potential groundwater outflow points is necessary to better understand the potential effects resulting from plugging of underground mine workings. Mapping of active seeps and fossil seep deposits would help indicate where potential leakage could occur.

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GEOCHEMICAL PROCESSES CONTROLLING ACID-DRAINAGE GENERATION AND CYANIDE DEGRADATION AT SUMMITVILLE

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*Deceased

ABSTRACT

Detailed geochemical studies provide important insights into processes controlling acid-mine drainage and cyanide degradation at Summitville, Colorado. Extremely acidic drainage is the dominant long-term environmental problem at Summitville. Oxidation of sulfides (exposed by the open-pit mining) by oxygenated surface and ground waters, coupled with the lack of acid buffering capacity in the deposit and its highly altered host rocks, is the ultimate cause of acid drainage at the site. The sulfide oxidation is enhanced by processes such as evaporation and bacterial oxidation of aqueous iron. Dissolution of soluble secondary salts (such as iron and copper sulfates) by rainwaters and snowmelt is a major short-term process that generates highly acidic, metal rich waters over much shorter time periods of minutes to days. The salts form by complete or nearly complete evaporation of acidic, metal-bearing waters, and permit a cycling of both acid and metals between solids and waters at the site. The salts contain abundant ferric iron, which, when dissolved, can trigger extensive oxidation of sulfides even without the presence of high levels of oxygen in ground waters or surface waters. The most significant long-term remedial challenge at Summitville will be preventing oxidation of sulfides in acid-generating mine wastes and dissolution of their contained soluble secondary salts by ground and surface waters.

Experimental studies show that the environmental effects of accidental cyanide releases into the Wightman Fork over the course of recent mining were likely mitigated at least partially by the acid drainage from the site. Mixing of the heap leach solutions with the acid waters would likely trigger extensive degradation of cyanide in the heap leach solutions and lead to a relatively short lifetime of cyanide species (except thiocyanate) in the Wightman Fork and Alamosa River, especially if mixing occurred on sunny summer days optimal for maximum cyanide volatilization. However, if leaks occurred in the winter, the cyanide likely could persist considerably farther downstream due to the reduced rates of volatilization. Relatively high concentrations of thiocyanate likely persisted downstream due to its stability in acidic solutions; it is currently unknown how long the thiocyanate persisted, and how it was eventually degraded.

INTRODUCTION

Acid-mine drainage and leaks of cyanide-bearing processing solutions are the two predominant and most widely publicized environmental problems resulting from recent open-pit mining at Summitville. Combined with the geologic characteristics of the Summitville deposit (Plumlee et al., this volume) and the climate at the site, geochemical processes have played an important role in the generation of acid drainage at the site and in the degradation of cyanide leaked from the site. This paper summarizes results of ongoing field-based and laboratory experimental studies that provide insights into some of the geochemical processes influencing environmental problems at Summitville and its downstream environmental effects. For a history of mining operations at the site and other background material, the reader is referred to the summary paper by Posey and Pendleton and other papers in this volume.

ACID-MINE DRAINAGE STUDIES

Sources of mine waters at Summitville (Table 1) include: (1) flows from adits (such as the Reynolds, Chandler, and Iowa adits); (2) flows from seeps or springs draining mine dumps (such as the Cropsy waste dump, North waste dump, and Beaver Mud dumps) and bedrock around the mine site; (3) ephemeral ponds or puddles that form in the open pit after rainfall or snowmelt; and (4) very low-volume flows from seeps within the open pit (such as Blackstrap and Son-of-Blackstrap). For locations of adits, springs, and seeps, the reader is referred to the color aerial photo of the site (this volume) and Figure 1 of Plumlee et al.

(this volume).

This section presents results of an ongoing study of acid-mine drainage at Summitville that was initiated in the fall of 1990 as part of a larger project evaluating geologic controls on mine-drainage composition (Plumlee et al., 1993). Sampling has continued to the present, with extensive cooperation between the USGS and the U.S. Environmental Protection Agency (EPA), U.S. Bureau of Reclamation, and Environmental Chemical Corporation.

Field methods

At each sample site, measurements of water temperature, air temperature, conductivity, pH, and dissolved oxygen content were taken. For samples collected after 1992, acidity and alkalinity titrations were carried out either in the field or in the laboratory immediately on return from the field. Samples collected at most or all sample sites include: filtered and unfiltered waters in acid-washed bottles acidified with nitric acid for analysis of major cations, metals, and trace metals; filtered waters acidified with hydrochloric acid for analysis of Fe^{2+}; filtered unacidified waters in unwashed bottles for analysis of major anions; waters for hydrogen and oxygen isotope analysis; and waters filtered through a glass fiber filter for dissolved organic carbon analysis. At some sample sites, water samples were also collected, filtered , and acidified with nitric acid for analysis of radiogenic isotopes. Filter sizes used over the course of the study varied from 0.1 µm to 0.45 µm, due to variations in the availability of filter types and brands, and due to changing needs of the project. Acid blanks, water blanks, and procedural blanks were also collected. For the 1993 and 1994 sampling, chain of custody procedures have been followed from sample collection through transport, analysis, and storage.

Mine-drainage compositions

The mine-drainage waters at Summitville are among the most acidic and metal-rich in Colorado (Table 1, Fig. 1; Plumlee et al., 1993). For a location map showing the seeps sampled in this study, the reader is referred to Plumlee et al., this volume. Waters draining adits (Reynolds, Chandler; Table 1) and waste dumps (Cropsy, North, SH-1, Area L; Table 1) have pH values from 2.3 to 3.2 and extremely high concentrations of metals and other elements, including: Fe and Al (hundreds to several thousands of parts-per million [ppm] of each; with Fe>Al); Cu and Zn (tens to hundreds of ppm of each; with Cu>Zn); As, Cd, Cr, Co, Li, Ni, rare earth elements (La, Ce, Nd), U, Th, V (hundreds of parts per billion [ppb] to several ppm); Be, Te (tens to several hundreds of ppb). Waters draining the waste dumps generally have somewhat lower pH and higher metal concentrations than waters draining adits. One seep near the Chandler adit (Ch Seep, Table 1) has a composition similar to that of the Chandler adit. Puddles that form in the pit and around the mine site after spring snowmelt and soon after summer rains (NPIT-1; SPIT-1, 2) have generally similar pH values but slightly lower metal contents than those of the adit waters. Low volume seeps within the open pit (Blackstrap, SOB; Table 1) have even lower pH values (as low as 1.7) and higher metal concentrations than those of the waste dumps. As of summer 1994, springs and seeps sampled around the northern periphery of the mine site (TD, Missionary) have generally higher pH values (from 3.8 to 6.8) and lower metal contents than those of the adit waters.

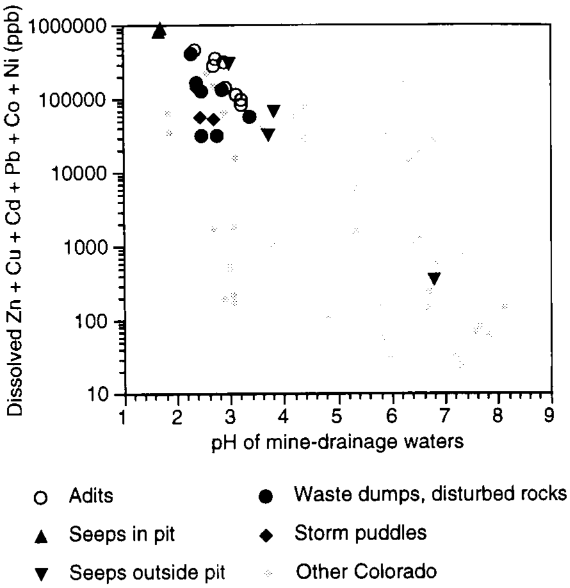

Figure 1. Ficklin plot showing Summitville mine-drainage compositions as compared to compositions of other mine-drainage waters in Colorado.

Both long-term and seasonal variations in drainage water composition occur at Summitville. Copper concentrations in the Reynolds adit waters prior to mining were in the low tens of ppm range (Fig. 2). Soon after open pit mining began , both peak and minimum annual copper concentrations showed a marked increase; this long-term increase showed no signs of abating prior to the plugging of the Reynolds adit in January, 1994. Our data collected since 1991 show that Fe, Al, Zn, As, and other metals exhibit similar increases over time as that observed for Cu. Interestingly, maximum pH values of the Reynolds adit waters, although quite variable, increased somewhat over time from around 2.9 to as high as 3.5 in early 1992 (Golder Associates, 1992).

As shown in Figure 2, pronounced seasonal variations are superimposed on long-term increases in metal content, with the greatest copper concentrations occurring during spring snowmelt, and the lowest concentrations occurring during low-flow conditions in fall and winter. Data collected in 1994 from the Chandler adit show a similar increase in pH (from 2.4 to 2.9) and decrease in conductivity (from 7110 µS/cm to 5800 µS/cm) from early

Table 1. Compositions of selected water samples collected at Summitville over the course of this study. FA - Filtered, acidified; RA - unfiltered, acidified. Anions measured by ion chromatography. Cation concentrations in plat measured by Flame or Graphite Furnace Atomic Absorption Spectrophotometry (AAS). Cation concentrations in bold analyzed by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Cation concentrations in italic measured by Inductively-Coupled Plasma Mass spectrometry (ICP-MS), a screening technique. "Description" gives filter size for filtered samples.

		Reynolds Adit						**Chandler Adit**			**Cropsy Dump**		**North Dump**	**Cleveland Cliffs**
		AD-3	**AD-3**	**AD-3**	**AD-3**	**AD-3**	**AD-1435C**	**Chand-1**	**Chand-1**	**Chand-1**	**Dike 2**	**550D-R**	**S Seep**	**SC12**
Date		10/16/90	10/3/91	6/22/93	8/10/93	7/20/94	6/22/93	6/8/94	7/20/94	8/29/94	10/16/90	6/23/93	8/30/94	6/22/93
	units													
Temperature	°C	4	4.5	4		4	4	4	6	4	6	13.5	7.5	14.5
Description		FA 0.45	FA 0.1	FA 0.45	FA 0.2	FA 0.2	FA 0.45	FA 0.2	FA 0.2	FA 0.2	FA 0.45	FA 0.45	FA 0.2	FA 0.45
pH		3.2	2.9	2.7		3.2	3.3	2.4	2.8	2.9	2.3	2.5	2.4	2.9
Conductivity	µS/cm	2100	3200	5400		1800	10	7110	5530	5820	10300	7650	7500	4100
Diss. O_2	ppm		10	10		10		10	12	12	10	10	10	10
F^-	mg/L				< 0.5	0.67		3.7	0.99	1.6			3.3	
Cl^-	mg/L	int	4.7		2.2	6.5		1.0	1.5	1.3	26		2.5	
SO_4^{2-}	mg/L	2200	1920	4530	4510	1650	2133	15000	6250	12600	23000	8370	11300	3360
Al	mg/L	**112**	**130**	**290**	**230**	**150**	**160**	**430**	**340**	**310**	**2400**	**890**	**710**	**200**
Fe	mg/L	**260**	**310**	**920**	**570**	**190**	**250**	**1400**	**910**	**880**	**5000**	**1100**	**1200**	**540**
Fe^{2+}	mg/L					**177**		**196**	**985**	**760**			**635**	
Mn	mg/L	14	**18**	**31**	**23**	**12**	**10**	**40**	**34**	**35**	**180**	**92**	**65**	**77**
Si	mg/L	**30**	**31**	**30**	**32**	**27**	**28**	**37**	**39**	**42**	**83**	**43**	**60**	**27**
As	ppb	360	**400**	*2900*	*790*	*130*	*460*	*3900*	*1500*	*2500*	**4000**	*190*	*160*	*110*
Ba	ppb	**16**	**20**	*10*	*10*	**20**	*7*	*4*	*5*	*7*	*<2*	*1*	*< 0.1*	*10*
Be	ppb	**24**	**30**	**76**	**50**	*8*	*10*	**120**	**81**	**73**	**300**	**110**	**87**	**37**
Cd	ppb	**180**	**200**	**330**	**300**	**72**	**70**	**440**	**380**	**430**	**1000**	**360**	**400**	**180**
Ce	ppb	**84**	**80**	*80*	*180*	*130*	*20*	*450*	*390*	*380*	**2000**	*200*	*1000*	*150*
Co	ppb	**670**	**700**	**1600**	**950**	**420**	**540**	**2000**	**1400**	**1400**	**7000**	**3000**	**2400**	**1700**
Cr	ppb	**38**	**30**	**110**	**55**	*10*	*20*	**140**	**110**	**99**	**1000**	**280**	**150**	**45**
Cu	ppb	**93000**	**120000**	**234000**	**230000**	**70000**	**84000**	**400000**	**290000**	**260000**	**220000**	**56000**	**100000**	**100000**
La	ppb	**60**	**400**	*30*	*80*	*50*	*7*	*170*	*150*	*140*	**900**	*60*	*320*	*60*
Li	ppb	**20**	*20*	**51**	**38**	*20*	**< 40**	**85**	*20*	*40*	**600**	**230**	**120**	**45**
Nd	ppb	**65**	*80*	*130*	*110*	*60*	*30*	*250*	*230*	*230*	*1600*	*410*	*610*	*190*
Ni	ppb	**760**	**800**	**1900**	**1200**	**550**	**640**	**2600**	**1800**	**1700**	**10000**	**3600**	**2600**	**1400**
Pb	ppb	**370**	*320*	**230**	*320*	*80*	**92**	**< 80**	*310*	*220*	**12**	*< 2*	*0.4*	*5*
Sr	ppb	**228**	**300**	**410**	**310**	**230**	**230**	**400**	**410**	**390**	**600**	**570**	**500**	**1200**
Th	ppb	**6**	*2*	*30*	*4*	*2*	*< 6*	*80*	*40*	*10*	**800**	*100*	*130*	*20*
U	ppb	31	*40*	*140*	*40*	*20*	*40*	*170*	*170*	*100*	1000	*310*	*210*	*60*
V	ppb	**21**	**30**	**110**	**44**	*6*	*20*	**220**	**150**	**100**	**700**	**350**	**220**	*20*
Zn	ppb	**18000**	**20000**	**47000**	**31000**	**12000**	**11000**	**57000**	**47000**	**49000**	**170000**	**61000**	**55000**	**28000**

Table 1 continued.

		Low-volume seeps in open pit		Ponds or puddles in open pit			Seeps or springs in disturbed rock near open pit				Seeps or springs away from open pit		
		Black-strap Seep	**SOB-1 Seep**	**SPIT-1 Pond**	**SPIT-2 Pond**	**NPIT-1 Pond**	**IOWA-1**	**Ch Seep**	**Sh-1**	**AREA L**	**Mission-ary East**	**Mission-ary West**	**TD Seep**
Date		10/3/91	6/23/93	8/10/93	8/10/93	6/8/94	8/10/93	8/30/94	8/30/94	6/8/94	7/20/94	7/20/94	8/30/94
	units												
Temperature	°C	~14	18	19	19	14	5	3	8	10	5	5	4
Description		FA 0.1	FA 0.45	FA 0.45	FA 0.45	FA 0.2	FA 0.45	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2
pH		1.8	1.7	2.5	2.4	2.7	2.8	3.0	3.4	2.5	3.8	6.8	3.8
Conductivity	μS/cm	38000	19500	3300	4600	2510	2800	3670	5090	3090	1450	374	858
Diss. O_2	ppm		10	10	10		10	10	6	10	4.5	1	3
F^-	mg/L			0.70	< 0.25	1.1	< 0.5	<0.5	1.2	1.2	0.51	0.41	0.23
Cl^-	mg/L	240		1.3	2.2	0.59	2.0	0.51	27	2.4	1.1	0.52	10
SO_4^{2-}	mg/L	125800	29850	2320	7890	2140	1900	5000	7310	4820	1540	110	425
Al	mg/L	**5400**	**2100**	**140**	**290**	**180**	**190**	**280**	**210**	**110**	**120**	*0.07*	**5**
Fe	mg/L	**28000**	**12000**	**470**	**840**	**280**	**170**	**540**	**600**	**390**	**150**	*<0.4*	**39**
Fe^{2+}	mg/L					**79**		**338**	**223**	**102**	**169**	*nm*	**35**
Mn	mg/L	**360**	**>100**	**4.2**	**19**	**15**	**19**	**28**	**100**	**14**	**5.8**	**0.7**	**2.4**
Si	mg/L	**84**	**110**	**1**	**1**	**11**	**35**	**27**	**36**	**15**	**19**	**12**	**12**
As	ppb	**15000**	*28000*	*690*	*3400*	*110*	*20*	*80*	*< 20*	*80*	*200*	*< 20*	*190*
Ba	ppb	**50**	*<1*	*1*	*< 0.1*	*5*	*3*	**41**	*< 1*	*8*	**20**	**26**	*20*
Be	ppb	**800**	**220**	*4*	**34**	**30**	**23**	**37**	**54**	11	*4*	*< 3*	*0.9*
Cd	ppb	**3000**	**460**	**73**	**110**	**120**	**81**	**220**	**130**	**39**	**50**	*< 20*	*7*
Ce	ppb	**6000**	*780*	*80*	*220*	*200*	*300*	*260*	*1100*	*330*	*90*	*< 1*	*9*
Co	ppb	**16000**	**7700**	**670**	**1100**	**630**	**460**	**950**	**1300**	**440**	**260**	*3*	**80**
Cr	ppb	**4000**	**2400**	**170**	**170**	**60**	**44**	**58**	*20*	**57**	*10*	*< 10*	*< 1*
Cu	ppb	**460000**	**706000**	**42000**	**120000**	**37000**	**19000**	**270000**	**32000**	**24000**	**58000**	**150**	**28000**
La	ppb	2000	*280*	*30*	*80*	*60*	*140*	*80*	*400*	*110*	*30*	*< 1*	*4*
Li	ppb	2000	**380**	*8*	*20*	*20*	**44**	*10*	*70*	*20*	*10*	*9*	*4*
Nd	ppb	*5100*	*1000*	*60*	*170*	*140*	*160*	*150*	*520*	*170*	*50*	*< 2*	*5*
Ni	ppb	**21000**	**11000**	**860**	**1300**	**830**	**580**	**1200**	**1300**	**570**	**350**	*< 30*	**82**
Pb	ppb	*<200*	< 2	*0.1*	*1*	*1*	*< 0.1*	*180*	*< 2*	*0.6*	*210*	*< 2*	*30*
Sr	ppb	**400**	**830**	*30*	**40**	**95**	**230**	**150**	**1700**	**290**	**250**	**530**	**1300**
Th	ppb	**4000**	*540*	*40*	*80*	*80*	*20*	*6*	*< 3*	*60*	*2*	*< 3*	*< 0.3*
U	ppb	*3600*	*300*	*40*	*90*	*150*	*40*	*70*	*40*	*70*	*30*	*< 1*	*0.3*
V	ppb	**3000**	**340**	**110**	**170**	**57**	*4*	*20*	*30*	**55**	*10*	*< 8*	*1*
Zn	ppb	**390000**	**82000**	**11000**	**20000**	**15000**	**11000**	**29000**	**21000**	**6600**	**6800**	**190**	**2300**

June (a week after the adit started discharging waters) to late August. Most, but not all, elements decreased in concentration from June to late August (Fig. 2); arsenic and zinc, however, decreased in concentration from the June to July sampling, but increased slightly in concentration by late August.

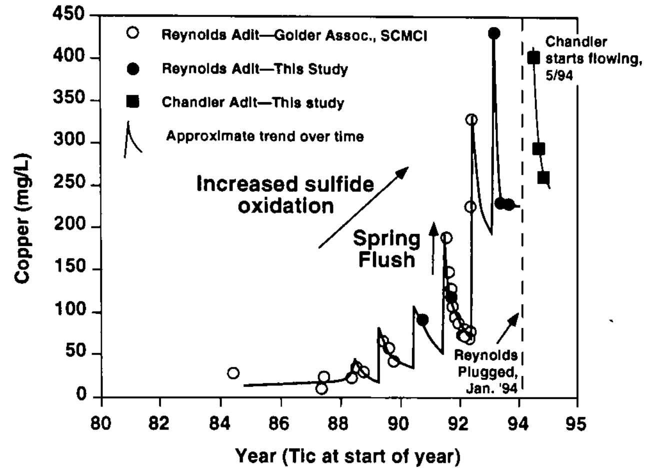

Figure 2. Plot of copper in Reynolds and Chandler adit outflow waters over time. Modified from Golder and Associates (1992) to incorporate results of this study.

Geologic and geochemical controls on mine-drainage composition

The highly acidic, metalliferous mine-drainage waters at Summitville are a predictable result of the deposit's geologic characteristics (Plumlee et al., this volume), in combination with its climate and important geochemical processes.

Background

For details of geochemical processes that control acid drainage generation, see Nordstrom and Alpers (in press), Smith et al. (1994), and Singer and Stumm (1970). When unoxidized sulfides such as pyrite (an iron sulfide) are exposed to oxygenated ground and surface waters, the sulfides initially react with dissolved oxygen in the waters to generate sulfuric acid and liberate metals tied up in the sulfides; in the case of pyrite, reduced or ferrous iron (Fe^{2+}) is the dominant metal produced, along with any trace metals originally present in the pyrite crystal structure. The ferrous iron is then oxidized to ferric iron (Fe^{3+}) with the help of bacteria. Ferric iron can then, in turn, serve as an oxidant that aggressively attacks more sulfides and generates much more acid than simple oxidation by dissolved oxygen. The critical aspects of the process are that sulfide oxidation and acid generation initiated by oxygen dissolved in waters, are greatly enhanced by bacterial action, and can then proceed via oxidation by ferric iron without the presence of abundant dissolved oxygen. In many mineral deposits and their host rocks, minerals are present that can react with and help consume acid generated during sulfide oxidation; these can include carbonate minerals, such as calcite, and rock forming silicate minerals, such as feldspars.

At Summitville, many different sulfides are present (Plumlee et al., this volume) that generate acid and metals during oxidation, including pyrite and marcasite (iron sulfides), enargite and tennantite (copper-arsenic sulfides), covellite and chalcocite (copper sulfides), and chalcopyrite (a copper-iron sulfide). In contrast, there are very few minerals present in the Summitville deposit or its host rocks that can help consume acid. This is a direct result of intense alteration of the host rocks by acid magmatic gas condensates prior to the formation of the deposit (Plumlee et al., this volume). There are some carbonate alteration minerals present in the rocks south and west of the deposit, but these occur in such small amounts within and around the open pit that they do not help mitigate acid drainage (Plumlee et al., this volume). The ultimate cause of the acid drainage problems at Summitville was the exposure and oxidation of sulfide-bearing rocks with high acid generating capacity but negligible capacity to consume acid. However, there are a number of other geochemical processes at work that must be considered as well.

Geologic controls on metal content

The relative proportions of metals and other elements such as arsenic in the drainage are in part a function of the deposit geology. For example, the enrichments of copper relative to zinc in the drainage waters reflect the copper-rich nature of the ores. Similarly, enrichments of arsenic in the drainage waters reflect the abundance of As-bearing enargite and tennantite in the ores (Plumlee et al., this volume). The relatively high levels of trace metals that are more commonly found as low level constituents of host rocks rather than ore deposits (such as U, Th and rare earth elements [Ce, La, and Nd], for example) suggest that some reaction and dissolution of the altered host rocks by the acid waters are also occurring. Co and Ni are also relatively enriched in the Summitville drainage waters. Because these metals are anomalously enriched in the andesitic rocks surrounding the district (T. Steven, oral comm., 1993), their enrichments likely reflect input from both the mineral deposit and its host rocks.

Precipitation and dissolution of secondary minerals

Metals and other elements are brought into solution as a result of sulfide oxidation, acid-generation, and reaction with host rocks. However, the concentrations of some elements are most likely limited when the fluids become saturated with various minerals. Preliminary chemical speciation calculations indicate, for example, that calcium concentrations in most waters are limited by the formation of gypsum (a calcium sulfate mineral). Similarly, silica concentrations are possibly limited by the formation of chalcendony, and iron concentrations in some samples may be limited by jarosite (a potassium-iron sulfate). In most of the waters, concentrations of arsenic and metals such as copper, zinc, etc., are apparently not limited by the formation of mineral phases containing these elements as major constituents.

However, extreme evaporation can cause the waters to become saturated with a broader variety of minerals. As discussed by Plumlee et al. (this volume), our mineralogical studies have identified abundant secondary salts of iron ± aluminum (such as jarosite, a potassium-iron sulfate and halotrichite, an iron-aluminum sulfate), copper (such as chalcanthite and brochantite, copper sulfates), and possibly phosphate (such as hinsdalite). These salts are observed to form during dry periods as surficial coatings on rock materials within the open pit and waste dumps, as coatings on fractures in rocks forming the open pit walls, and as disseminations within sediments left after the evaporation of acid puddles throughout the mine site. The salts store metals and acid until the next rainstorm or snowmelt, at which time they partially or completely dissolve. Once dissolved, the metals are either carried downstream or remain in ponds or in waters wetting fracture surfaces, where they may once again precipitate as soluble salts as the waters evaporate.

The pronounced seasonal variations in metal content, together with the rapid formation of highly acidic, metalliferous ponds and puddles after summer thunderstorms, demonstrate that many of these salts are readily soluble and play an important role in enhancing acid drainage at Summitville. For example, increases in copper concentration in the Reynolds adit waters each spring reflect the snowmelt-triggered flushing of metals from salts formed during the previous fall dry season. The rapidity of the salt dissolution is also apparent in the chemical analyses of acid waters left in puddles and ponds in the open pit after summer thundershowers (samples SPIT-1, 2; Table 1). Samples SPIT 1 and 2 were collected only several days after the start of the summer monsoonal rain season. Prior to the start of the monsoonal moisture, there was a relatively dry period following spring snowmelt. The fact that waters with such acidity and metal content form over the course of only several days shows that the waters are dissolving soluble salts and do not result from sulfide oxidation, a much slower process. The waters have quite high concentrations of all metals and arsenic that are typical of the waters draining workings and dumps at Summitville; mineralogical residences for all of these metals and arsenic have yet to be determined, although it is likely that many reside as trace constituents in the abundant iron or copper salts identified to date.

In addition to being a ready source for dissolved heavy metals and acid, these salts also are a ready source for dissolved ferric iron (for example, compare total iron analyses with ferrous iron analyses in sample NPIT-1). The ferric iron occurs as a constituent of salts such as jarosite. This ferric iron formed by salt dissolution can readily oxidize nearby sulfides and therefore generate copious amounts of acid. Because this can occur without the presence of abundant dissolved oxygen, it shows that isolation of sulfides from atmospheric oxygen cannot alone stop sulfide oxidation, especially if salts containing ferric iron are present.

Alunite dissolution has been proposed as a source for acidity in some mine drainages. However, sulfur isotopic studies of the sulfate in the drainage waters at Summitville show that it does not have the same signature as sulfate in the alteration alunite (Plumlee et al., this volume). Instead, the isotopic composition is the same as that of the original sulfides in the deposit. Thus the sulfate was ultimately derived from sulfide oxidation and not from dissolution of alteration alunite. It is possible that alunite dissolution occurs at slow rates relative to those sulfide oxidation; if so, then alunite may present a potential long-term source of acidity at Summitville.

Although the effects of mineral precipitation and salt dissolution on drainage composition are generally interpretable, much more work is needed to fully understand how these processes help control acid drainage generation at Summitville. For example, chemical speciation, reaction path, and mass balance modeling calculations currently underway will help reveal more details of the processes involved.

Evaporation

As shown in the previous section, evaporation is an important control on drainage chemistry during the summer and early fall months at Summitville. Puddles left after rainstorms or snow melt can dry up quite rapidly on sunny days, leaving mud-cracked sediment flats that contain not only clays and other detrital material, but also secondary salts. Of the samples listed in Figure 1, geochemical evidence of evaporation is present in only three samples: 9/91 Blackstrap, 6/93 Son-of-Blackstrap, and 10/90 Cropsy Dike 2. These waters have elevated chloride concentrations and heavy hydrogen isotopic compositions indicative of evaporation, with Blackstrap showing the most extreme evaporation. Blackstrap and Son-of-Blackstrap are very low volume seep puddles in the open pit, and form as waters seep onto the surface and evaporate before they can flow anywhere. Our preliminary data indicate that evaporation, as expected, has two main geochemical results: it increases concentrations of metals and other elements in solution due to water loss; and it increases the acidity of the waters as they evaporate. Another consequence of the evaporation is that, as ferric iron concentrations increase, the waters may become somewhat more reactive to unoxidized sulfides with which they come in contact, thereby further enhancing drainage acidity and metal content.

METAL LEACHING EXPERIMENTS

To evaluate potential metal mobility from solid mine wastes and the role of secondary salts in acid-drainage generation, we have initiated several leaching experiments of solid materials from the Summitville waste dumps and open-pit area. Samples of material from the North Pit area, South Pit area, and Cropsy waste dump were collected during visits to the site in September, 1993, and June, 1994. During both visits, conditions had been quite dry for at least several weeks prior to the visit, and so extensive buildups of secondary salt coatings were readily visible on all samples collected. All samples are currently undergoing detailed mineralogical analysis to determine the original sulfide and alteration minerals still present in the sample, as well as the mineralogy and trace-element content of the secondary salts.

Experimental procedures

For the first phase of the experiments, a representative 50-gram split of each sample was collected and placed in a 1-liter Nalgene bottle. The samples were not ground or broken so as to best reproduce conditions present in the field. Then, 1000 ml of distilled water were added to each 50-gram solid sample, yielding a water/rock ratio of 20:1. Each sample was gently shaken or stirred by hand periodically over the course of the experiment with the bottle top removed to allow access of atmospheric oxygen. For the first 13 days, the bottle cap was replaced after each sample was shaken, so as to minimize evaporation. On the thirteenth day, the bottle caps were removed to allow evaporation of the waters from the samples. The evaporation was carried out in a laboratory fume hood with the ventilation fan operating.

Measurements of pH and conductivity were taken periodically over the course of the experiments. Filtered water samples for anion and cation analysis were collected 1 day after the beginning of the experiments, and again fifteen days after the start of evaporation.

Results

Plots of pH and conductivity over the course of the experiments are shown in Figure 3. Analytical results for water samples collected are presented in Table 2. Immediate decreases in pH and increases in conductivity demonstrate the rapid rate at which the secondary salts dissolve (Figure 3). The pH of the waters in all samples drops to below 4 within the first ten minutes, and the conductivity also jumps significantly; in the case of the Cropsy wall sample #2, the conductivity exceeds 2000 within the first ten minutes. The most rapid pH and conductivity changes occur approximately within the first hour of the experiments, but pH continues to decrease slowly and conductivity continues to increase slowly over the remaining course of the experiments. With the initiation of evaporation, there is a temporary increase in the rate of pH drop and conductivity increase that occurs over several days.

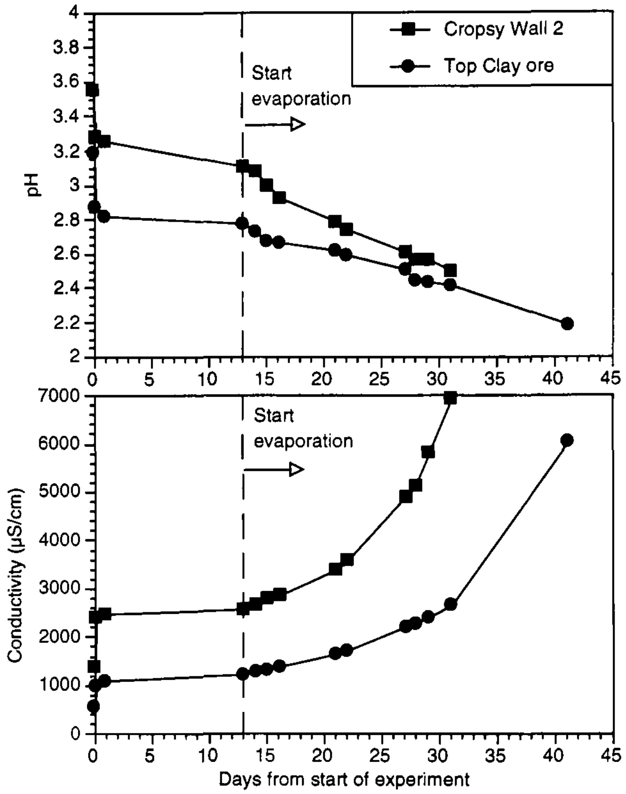

Figure 3. Plot of pH and conductivity results for leaching experiment on two Summitville samples, including one of material from the Cropsy waste dump and one from the top of the Clay Ore stockpile.

The chemical compositions of the leach waters reproduce the general pH range of the Summitville drainage waters, but are usually lower in metal content. This is most notable for arsenic, which occurs in the leach waters in concentrations as much as an order of magnitude lower than those observed in most of the mine waters. Leach waters collected after the first day of the experiment (Table 1; Figure 4) show a wide range in metal content, with the Cropsy waste dump samples having metal contents that most closely approach those of waters actually observed in mine puddles and draining mine waste dumps (Fig. 4). Samples collected after evaporation for 10 days show a marked drop in pH and increase in content of most metals. Interestingly, the leaching data show a steep trend of decreasing pH and increasing metal content (Fig. 4) that merges at its upper end with a shorter but similarly-sloped trend defined by the mine puddle and most mine dump waters. In contrast, the data for most mine workings, seeps, and some dumps show a gentler trend of increasing metal content with decreasing pH (Fig. 4). These two trends intersect at very low pH values and high metal contents. It is possible that these two trends may respectively reflect (a)

Table 2. Analytical results for leaching experiments studying metal mobility from solid mine wastes at Summitville. Experimental techniques discussed in text. Anions measured by ion chromatography. Cation concentrations in plat measured by Flame or Graphite Furnace Atomic Absorption Spectrophotometry (AAS). Cation concentrations in bold analyzed by Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Cation concentrations in italic measured by Inductively-Coupled Plasma Mass spectrometry (ICP-MS), a screening technique. "Description" gives filter size for filtered samples.

		Leaching Experiments															
		Cropsy wall #1		Cropsy wall 3		Cropsy wall 2		North pit 1, solid 3		Seep L bank		Seep L mudflat		Top of clay ore	
Date		6/15/94	7/12/94	6/15/94	7/12/94	6/15/94	7/12/94	6/15/94	7/12/94	6/15/94	7/12/94	6/15/94	7/12/94	6/15/94	7/12/94
	units																
Temperature	°C	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Description		FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2	FA 0.2
pH		3.2	2.6	2.8	2.5	3.3	2.6	3.4	2.8	3.3	2.7	3.1	2.8	2.8	2.4
Conductivity	μS/cm	432	1383	2160	3430	2470	5130	210	785	220	794	416	988	1093	2290
Diss. O_2	ppm	10													
F^-	mg/L	< 0.05	0.51	0.94	<0.5	1.4	2.3	< 0.05	0.09		0.08	0.16	0.32	0.46	0.86
Cl^-	mg/L	0.13	1.3	0.23	<1	2.0	3.7	0.21	0.69		0.42	0.49	1.2	0.38	1.1
SO_4^{2-}	mg/L	159	506	7470	5200	3250	10300	45	185		145	114	460	1270	2620
Al	mg/L	**16**	**46**	**230**	**440**	**290**	**760**	**1.1**	**8**	*<.1*	**3**	**1.3**	**9**	**54**	**120**
Fe	mg/L	**11**	**45**	**140**	**210**	**150**	**190**	**6.7**	**22**	**< 1**	**14**	**12**	**19**	**30**	**75**
Fe^{2+}	mg/L	**3**		**68**		**141**		**2.5**		**0.5**		**3**		**2**	
Mn	mg/L	**0**	**1**	**22**	**44**	**49**	**120**	**0.1**	**0.5**	*< 0.2*	**0**	**1.8**	**4.7**	**4**	**10**
Si	mg/L	**< 1**	**9**	**< 1**	**6**	**< 1**	**9**	**< 1**	**11**	**< 1**	**10**	**2.0**	**23**	**1.0**	**16**
As	ppb	*< 3*	*< 20*	*4*	*4*	*< 3*	*10*	*< 3*	*4*	*< 3*	*< 20*	*3*	*< 2*	*< 3*	*10*
Ba	ppb	*8*	*4*	*< 0.3*	*< 0.1*	*< 0.3*	*< 0.1*	*7*	*10*	*20*	**23**	**29**	*10*	*7*	*6*
Be	ppb	*< 1*	*< 3*	**42**	**86**	**76**	**200**	< 1	*2*	< 1	*< 3*	3	*6*	*5*	*10*
Cd	ppb	*< 2*	*< 20*	**330**	**640**	**260**	**590**	*2*	*5*	*< 2*	*< 20*	*3*	*9*	*10*	*20*
Ce	ppb	*8*	*30*	*6*	*9*	*3*	*6*	*0.4*	*2*	*< 0.1*	*4*	*3*	*20*	*70*	*140*
Co	ppb	**57**	**170**	**1000**	**1900**	**860**	**2000**	**50**	**160**	*1*	*20*	*40*	**100**	**150**	**340**
Cr	ppb	*3*	*20*	*10*	**67**	*9*	**63**	*< 2*	*< 1*	*< 2*	*< 10*	*< 2*	*4*	*20*	**67**
Cu	ppb	**1400**	**5400**	**43000**	**76000**	**20000**	**54000**	**1500**	**6600**	**87**	**1700**	**1700**	**5100**	**8200**	**18000**
La	ppb	*2*	*7*	*1*	*2*	*0.4*	*0.8*	*0.2*	*0.8*	*< 0.1*	*1*	*0.9*	*6*	*10*	*30*
Li	ppb	*0.8*	*7*	*5*	*10*	**85**	**240**	*< 0.6*	*< 0.7*	*0.7*	*< 7*	*3*	*10*	*10*	*40*
Nd	ppb	*6*	*20*	*10*	*10*	*30*	*60*	*0.2*	*2*	*< 0.1*	*3*	*2*	*10*	*60*	*110*
Ni	ppb	**87**	**290**	**1200**	**2200**	**1300**	**3000**	*20*	**100**	*< 2*	*< 30*	**39**	**120**	**190**	**440**
Pb	ppb	*< 0.3*	*< 2*	*< 0.3*	*< 0.2*	*< 0.3*	*< 0.2*	*< 0.3*	*2*	*< 0.3*	*< 2*	*< 0.3*	*0.6*	*< 0.3*	*< 0.2*
Sr	ppb	*3*	**19**	*1*	**< 20**	*1*	*4*	*2*	*7*	*1*	**20**	**43**	**160**	*9*	**32**
Th	ppb	*1*	*< 3*	*10*	*10*	*1*	*2*	*< 0.5*	*0.5*	*< 0.5*	*< 3*	*< 0.5*	*0.6*	*9*	*10*
U	ppb	*4*	*9*	*380*	*440*	*220*	*360*	*4*	*20*	*0.1*	*1*	*3*	*5*	*30*	*50*
V	ppb	*< 0.6*	*< 8*	*10*	*9*	**64**	**46**	*< 0.6*	*< 0.8*	*< 0.6*	*< 8*	*< 0.6*	*< 0.8*	*< 0.6*	*1*
Zn	ppb	**520**	**2600**	**18000**	**38000**	**48000**	**120000**	**320**	**1300**	*20*	**350**	**510**	**1500**	**2100**	**5600**

short-term dissolution of soluble secondary salts with minimal pH buffering, and (b) longer-term interactions of the waters with wallrocks that help buffer pH. However, further experimental studies and chemical modeling of the results are needed to support this possible interpretation.

The leach experiments provide two important insights into processes controlling short-term acid drainage generation. First, they show that very low pH values and very high metal contents can result from the interactions of dilute waters with mine wastes over time periods as short as ten minutes. Second, they indicate that evaporation of acid waters leads to substantial increases in metal content and decreases in pH. Further experimental studies are planned that will better reproduce ambient conditions at the site such as natural sunlight and evaporation.

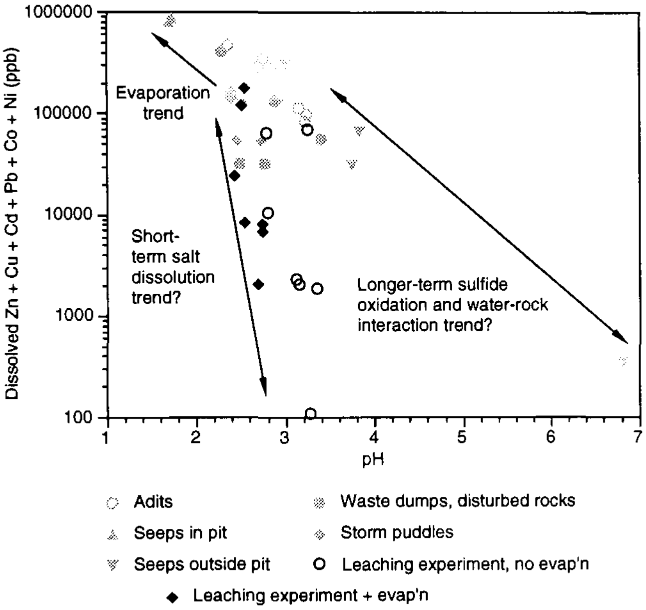

Figure 4. Ficklin plot showing sum of dissolved base metals versus pH for leach experiment waters compared to actual mine-drainage waters.

A PRELIMINARY QUALITATIVE MODEL FOR ACID DRAINAGE GENERATION AT SUMMITVILLE

Based on the results of the mine-water sampling, leaching studies, and mineralogical studies, we have developed a preliminary qualitative model for the generation of acid-mine drainage at Summitville. We stress that further data collection (for example, of ground-water samples from monitoring wells that were inaccessible to us in this study), coupled with detailed chemical modeling and further experimental studies, are needed to begin to develop a quantitative model for the site that can be used to help predict long-term responses of the site to remedial actions.

Pronounced increases in acid drainage from Summitville since the inception of open-pit mining (Fig. 2) clearly reflect the exposure of abundant sulfides by the mining, and the progressive increase in oxidation of these sulfides. The low pH values reflect the lack of appreciable acid-buffering capacity in the deposit or its host rocks; however, slight increases in pH of the Reynolds adit waters since 1984 (Golder and Associates, 1992) may reflect some reactions with, and pH-buffering by, clay-altered rock exposed by the mining. The copper- and arsenic-rich nature of the ores is reflected in enrichments of these elements in the drainage waters. The concentrations of some elements in the waters (such as calcium, barium, and silicon) are apparently limited by saturation with various minerals or amorphous solids). Evaporation during dry summer and fall periods clearly leads to increases in metal content and decreases in pH of the drainage waters; the effects of evaporation are most apparent in low-volume seeps and rain puddles within the open pit, but are also noted in waters draining some mine dumps.

Soluble secondary salts such as chalcanthite, brochantite, and jarosite (Plumlee et al., this volume) clearly play a very important role in metal mobility and the short-term generation of acid drainage at Summitville. These salts form during dry periods in summer and fall from the extreme evaporation of acid mine waters that occur (a) in ponds and puddles, and (b) as wettings on rock surfaces, fracture surfaces, or underground mine workings. The salts store high amounts of metals and acid; the acid occurs both as actual hydrogen ions tied up in the crystal structures and as metals that dissolve to produce hydrogen ions. Any waters that come in contact with these salts, such as spring snowmelt or rain waters, dissolve the salts and pick up considerable acidity and dissolved metals. For example, the spring spike in metal content in the Reynolds adit waters and acid waters draining mine wastes reflects flushing of the dissolved salts. As the salts are largely consumed, metal contents in the waters decrease to some baseline value reflecting slower oxidation of sulfides and dissolution of less soluble salts. Extreme metal concentrations in the Chandler adit waters reflect the flushing of copious salts built up over the last 91 years in the underground mine workings above the Reynolds adit level.

As of late summer, 1993, seeps on the northern periphery of the deposit (Ch, TD, Meadow Pond, and a seep at the headwaters of Park Creek) were showing signs of prolonged flow after snowmelt and general increased flow (Roeber et al., this volume). The waters in the Ch seep near the Chandler adit are similar in composition to those draining the adit itself (Table 1), and likely also come from shallow ground-water flow paths strongly influenced by underground workings and the open pit. Seeps such as the

TD seep, Meadow Pond seep (Fig. 1 of Plumlee et al., this volume), and Park Creek seep have moderately to considerably lower metal contents and higher pH values. Our preliminary interpretation is that these waters (1) followed deep flow paths (Fig. 4 of Plumlee et al, this volume) beneath South Mountain, (2) are therefore older waters that have had time to react with possibly less altered rocks, and (3) are being pushed out ahead of lower-quality waters that recently entered the deep plumbing system in response to plugging of the Reynolds adit. If this preliminary interpretation is correct, then it is likely that water quality in these seeps will deteriorate over time. Further hydrologic and geochemical studies are needed to address this issue.

GEOCHEMICAL PROCESSES CONTROLLING CYANIDE DEGRADATION AT SUMMITVILLE

Among the environmental concerns stemming from recent mining activities at Summitville are past accidental releases of cyanide-bearing heap-leach solutions into the Wightman Fork of the Alamosa River, and the ongoing efforts to remove cyanide from solutions remaining in the heap leach pad. This section presents results of a study in progress that was designed to understand the geochemical processes that (1) controlled the composition of heap leach solutions at Summitville and (2) may have occurred during an accidental release of the heap leach solutions into the Wightman Fork.

Unfiltered heap leach solutions that were being remediated as of summer, 1993, typically had pH values near 9.4 and total cyanide concentrations varying from 120 to 150 ppm. Approximately 100 to 130 ppm of the cyanide was present in weak-acid dissociable (WAD) form as complexes primarily with copper; the remainder was primarily present as free cyanide (CN^-, minor HCN), with lesser amounts as strong complexes with iron, cobalt, and nickel. High copper concentrations (210 ppm) reflect the copper-rich nature of the ores and the strength of the copper complexes with cyanide. Other metals present included: Fe, Co, and Ni (1-2 ppm); Al (0.5 ppm); and Ag, Mo, and Zn (0.1 to 0.2 ppm). High thiocyanate (SCN^-) concentrations (250 ppm) showed that sulfides are present within the heap and are undergoing oxidation. The thiocyanate forms predominantly by the reactions of free cyanide with intermediate-oxidation state sulfur species formed during sulfide oxidation. Heap leach solutions at the time of active mining and cyanide processing had a generally similar pH, approximately twice the levels of WAD cyanide, and somewhat higher thiocyanate concentrations.

Mixing experiments

Any surface leaks from the cyanide heap leach operations that occurred during mining would have flowed into the Wightman Fork. We designed laboratory experiments to model the mixing of the heap leach solutions (remaining as of summer, 1993) with the Wightman Fork water. In the experiments, samples of heap leach solution were mixed with varying proportions of a Wightman Fork water mixture (pH = 3.2) consisting of Wightman Fork water from above the Reynolds Tunnel inflow, Reynolds Tunnel water, and Cleveland Cliffs Pond water. The experiments were conducted both outdoors in open containers (to evaluate the effects of photolytic cyanide degradation) and indoors in closed containers (to allow retrieval of volatilized cyanide gas). Compressed air was bubbled through the mixtures in order to approximate the turbulence that would be encountered during flow along the Wightman Fork.

Results are shown in Figure 5 of one experiment that document the progressive loss of WAD cyanide from the mixture, a transient increase in WAD cyanide associated

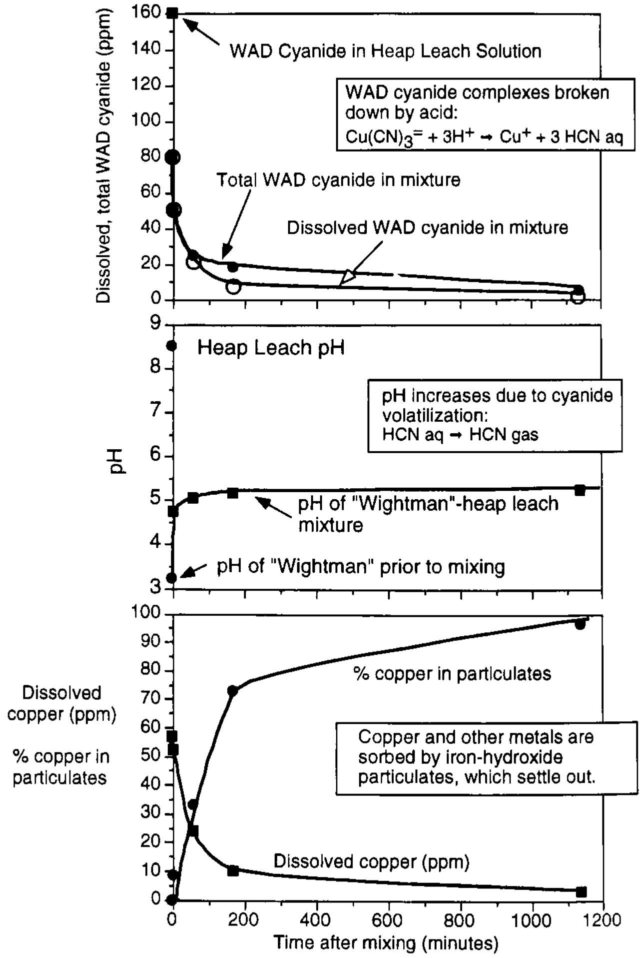

Figure 5. Plots showing changes in WAD (Weak-acid-dissociable) cyanide complexes (top), pH (middle), and copper concentration (lower) in an experiment where heap leach solutions collected in summer, 1993, were mixed with an equal volume of "Wightman Fork" water.

with solid precipitates, and the precipitation of abundant iron hydroxide. We interpret these data to reflect the progressive destruction of the copper-cyanide complexes through acidification by the Wightman Fork waters, and the volatilization of the cyanide as hydrogen cyanide according to the following reaction:

$$Cu(CN)_3^{=} + 3H^+ = Cu^+ + 3HCN\ (g).$$

The temporary shift of WAD cyanide into particulates most likely reflects the precipitation of solid copper cyanide compounds; however, these solid cyanide compounds are also apparently degraded over time. The copper originally complexed with the cyanide is sorbed onto the abundant iron hydroxides that precipitate as a result of the mixing; settling of these particulates would effectively remove the copper and some other metals from solution.

There are several limitations of these experiments that we are addressing in studies currently underway. First, the role of temperature was not evaluated; however, it is likely that the 20°C temperatures of the experiments discussed previously allowed faster rates of cyanide volatilization than would occur at temperatures closer to 0°C (e.g. ambient temperatures if a cyanide release occurred during the winter). The experiments also did not address conditions where cyanide volatilization was inhibited (such as would occur if the mixing occurred under an ice cap in the wintertime). In these experiments we also did not measure total cyanide or thiocyanate concentrations. In addition to the volatilization of cyanide noted previously, it is likely that some of the cyanide was precipitated as a copper-iron cyanide. This conversion may have led to longer-term storage of cyanide in the particulates; however, solid iron-cyanide compounds are well known for their photolytic degradation by the ultraviolet portion of sunlight (see papers contained in VanZyl, 1985). In studies of another mine in Colorado, we have measured very high concentrations of thiocyanate (several hundred ppm) in acid mine waters with pH near 2. Thus, it is apparent that thiocyanate can be quite long-lived in acid solutions (McGill et al., 1985). We are studying further the fate and degradation of cyanide in acid environments.

Our study results to date indicate that mixing with acidic Wightman Fork waters would likely trigger extensive degradation of cyanide in the heap leach solutions and lead to a relatively short lifetime of cyanide species (except thiocyanate) in the Wightman Fork and Alamosa River, especially if mixing occurred on sunny summer days optimal for maximum cyanide volatilization. However, if leaks occurred in the winter, the cyanide could persist considerably farther downstream due to the reduced rates of volatilization. Relatively high concentrations of thiocyanate may have persisted downstream due to its stability in acidic solutions; it is currently unknown how long the thiocayanate persisted, and how it was eventually degraded.

We are currently evaluating the mixing of heap leach solutions with acid-mine drainage as a possible low-cost technique to remediate heap leach solutions and acid-mine drainage at mine sites where both are present.

SUMMARY

The results of geochemistry studies at Summitville demonstrate their utility, especially when integrated with detailed geology and hydrogeology studies, in order to develop the most effective remediation strategies at the site. As discussed by Plumlee et al. (this volume), the most significant long-term remedial challenge at Summitville will be the isolation of large volumes of acid-generating mine wastes from oxidation of sulfides and dissolution of soluble secondary salts by ground and surface waters. The current backfilling of the open pit with mine wastes and capping of the pit area are needed because they will help to significantly reduce both water inflow into the pit area and acid generation from wastes outside the pit area. However, the capping and the resaturation of workings above the Reynolds adit will not totally prohibit ground-water flow into the pit area. Further, the capping and plugging will not inhibit acid generation in the ground waters due to the abundance of ferric iron that can be released from soluble salts and that can then trigger extensive sulfide oxidation. It is therefore likely that low-volume but highly acidic and metalliferous discharge will continue from seeps and springs along the northern boundaries of the site. More detailed ground-water monitoring and chemical modeling studies, coupled with detailed field hydrology studies, are needed to accurately predict how acidic and metal-bearing these waters will be. The leaching studies that we have conducted on solid materials (such as from the Clay Ore stockpile) show that use of such materials from the site as a capping material for the pit area should receive careful scrutiny; their high acid-generating capacity may adversely affect their long-term viability as a capping medium.

It is also likely that lower levels of surface acid generation and discharge will continue across the site, given the wide dispersal of sulfide-bearing materials and soluble salts in surficial material such as soils, road surfaces, etc. This acid discharge will not abate until the sulfides are completely oxidized and all the soluble salts have been flushed. Further leaching studies of surficial material from across the site are needed to help establish the levels of acid drainage that might be anticipated.

Results of the on-site geochemistry studies indicate that low levels of acidic, metalliferous drainage are likely to continue from Summitville, in spite of the necessary ongoing remedial actions. However, these potential long-term acid and metal loadings into the Wightman Fork should be carefully evaluated and compared to metal and acid loadings from other largely natural sources in the upper Alamosa River basin (Miller et al., this volume; Kirkham, this volume; Bove et al., this volume) before more extensive remedial measures are instituted at Summitville.

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GEOLOGY OF HYDROTHERMALLY ALTERED AREAS WITHIN THE UPPER ALAMOSA RIVER BASIN, COLORADO, AND PROBABLE EFFECTS ON WATER QUALITY

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ABSTRACT

The geology of mineralized and altered areas in the vicinity of the Summitville Mine is currently being studied to understand contributions of individual drainages to the downstream contamination in the Alamosa River. These areas, which include the Iron-Alum-Bitter Creek basins (IABC), are essentially undisturbed by mining activity and will offer unique opportunities to characterize background sites adjacent to the Summitville mining area.

Rocks within the upper Alamosa River basin study area are mostly within the Platoro caldera complex. The Platoro caldera, a large volcanic collapse structure, formed about 30 to 29 Ma in response to the eruption of the voluminous Treasure Mountain Tuff. Renewed ash-flow eruption led to the further collapse of a series of calderas nested within the older Platoro caldera. The Platoro caldera complex served as the structural locus of numerous intrusions ranging from monzonite to quartz monzonite in composition. Generally, these intrusions are spatially associated with intense hydrothermal alteration and varied mineralization.

Two main episodes of hydrothermal alteration have been recognized within the upper Alamosa River basin. An early period of alteration (~29-26 Ma) affected rocks within the IABC basins and the Jasper area. A later period of alteration (~23 Ma) affected rocks in the Summitville mining area and postdated the older cycle of alteration by as much as 6 m.y. The zone of hydrothermal alteration around the IABC basins is about 11 km^2. In contrast, younger hydrothermal alteration around the Summitville Mine influenced an area of about 3 km^2.

The Summitville Mine and IABC basins are located along an arcuate fault zone that localized repeated intrusion, hydrothermal alteration, and mineralization. The intrusions related to hydrothermal alteration and mineralization within the IABC basins have been well exposed by erosion. In contrast, the intrusive body associated with the Summitville orebody is present nearly 700 m beneath the surface, buried beneath the quartz latitic lavas of the South Mountain dome.

One of the strong similarities between the Summitville mining district and the IABC basins is the presence of classic acid-sulfate alteration assemblages. Alteration in the Summitville Mine area is characterized by subvertical tabular zones consisting of vuggy silica cores surrounded by successive zones of hydrothermal quartz-alunite and clay. Similarly, small localized zones of quartz-alunite altered rock are present in the Lookout Mountain and Alum Creek areas in the western part of the IABC basins.

The Summitville and Lookout Mountain-Alum Creek areas also show a similar vertical sequence of hydrothermal alteration assemblages. Hydrothermal alteration in both areas grades downward from a magmatically derived acid-sulfate assemblage into underlying zones of quartz-sericite-pyrite alteration with quartz-pyrite stockwork veinlets. Sparse molybdenite is present in the deep assemblage in the Alum Creek area, and copper and molybdenum anomalies have been reported in the deeper levels of the Summitville deposit. Both systems are genetically related to high-level quartz monzonite porphyry intrusions that generated an upper-level acid-sulfate system, which in turn grades into a weak porphyry copper-molybdenum system at depth.

The nature and extent of hydrothermal alteration in the IABC basins contributes to the low pH and the high metal loadings of this part of the Alamosa River. The Alum Creek area, in particular, with its extensive quartz-sericite-pyrite and clay alteration products, contributes water with very low pH, high dissolved metals, and a very large suspended load of potentially acid-generating material. The presence of old iron-oxide cemented conglomerates many feet above modern drainages indicates that the generation of natural metal-rich, acidic drainage has been occurring in the upper Alamosa River basin for many thousands of years prior to mining in the area.

INTRODUCTION

Detailed geologic and geochemical studies of the highly mineralized Iron, Alum, and Bitter Creek areas in the upper Alamosa River basin are critical to understanding the contributions of individual drainages above the Wightman Fork to downstream contamination in the Alamosa River. Studies in these largely unmined or undisturbed areas also offer a unique opportunity to understand the interrelationship between specific rock and alteration types and the local stream geochemistry. As implied by the creek names, water draining from these intensely altered and highly pyritized basins is extremely degraded, with pH and conductivity commonly <3 and >2,000, respectively. Ongoing geologic studies indicate that these extreme acid conditions are generated by the supergene alteration of extensive zones of primary hydrothermal quartz-sericite-pyrite (QSP) altered rocks.

As attested by the characteristic alteration assemblages and the spectacular tan and red, bleached landscape, the Iron, Alum, and Bitter Creek basins are ancient analogs of the active geyser basins at Yellowstone, Wyoming. Downcutting by streams, which sculpted the IABC basins during the last 5 million years (Steven and others, in press), provided spectacular exposure of a complex, multi-level geologic system. Classic quartz-sericite-pyrite alteration related to a very weak molybdenum-copper porphyry system is exposed in Alum Creek and represents the deepest exposed part of the hydrothermal system. These strongly pyritized QSP-altered rocks have been attacked by strongly acidic supergene fluids, which result in the highly degraded water in Iron, Alum, and Bitter Creeks. Several relatively small centers of quartz-alunite altered rock occur about 600 m above the deeper QSP zone. These small quartz-alunite centers in turn grade further upward into an ancient hot spring environment characterized by massive opaline ledges and isolated siliceous sinter deposits.

The purpose of this report is to summarize the geology, mineralization, and alteration within these areas, and to discuss preliminary results of coordinated stream and geologic studies. Measurements of pH and conductivity from over 60 sites demonstrate a good correlation between the type and intensity of alteration and the degree to which the surface and spring waters are degraded. This report draws upon preliminary data--in addition to that from many previously published sources--from roughly two months of field work during the fall of 1993 and the summer of 1994 and provides the geologic framework for related stream geochemical studies in the upper Alamosa River basin.

VOLCANIC HISTORY

The upper Alamosa River basin study area is in the southeastern part of the 25,000 km^2 San Juan volcanic field in southwestern Colorado and adjacent parts of New Mexico (fig. 1). Volcanic activity in the San Juan field commenced about 35 million years ago (Ma) during which time large volumes of intermediate composition lavas were erupted from local stratovolcanoes. At about 29 Ma, the style of volcanism shifted to explosive ash-flow eruptions associated with many large calderas in the San Juan volcanic field. The Platoro caldera complex (fig. 2), which formed about 29 Ma, represents the major source of ash-flow tuffs present in the upper Alamosa River basin study area. A later period of bimodal basalt-rhyolite volcanism, which began about 26 Ma, differs petrologically from earlier volcanic rocks, and is related to crustal extension and opening of the Rio Grande Rift (Christiansen and Lipman, 1972; Lipman and others, 1978). More detailed discussions of the evolution of the Platoro caldera complex and related volcanic rocks in the southeastern San Juan volcanic field is found in Lipman (1975).

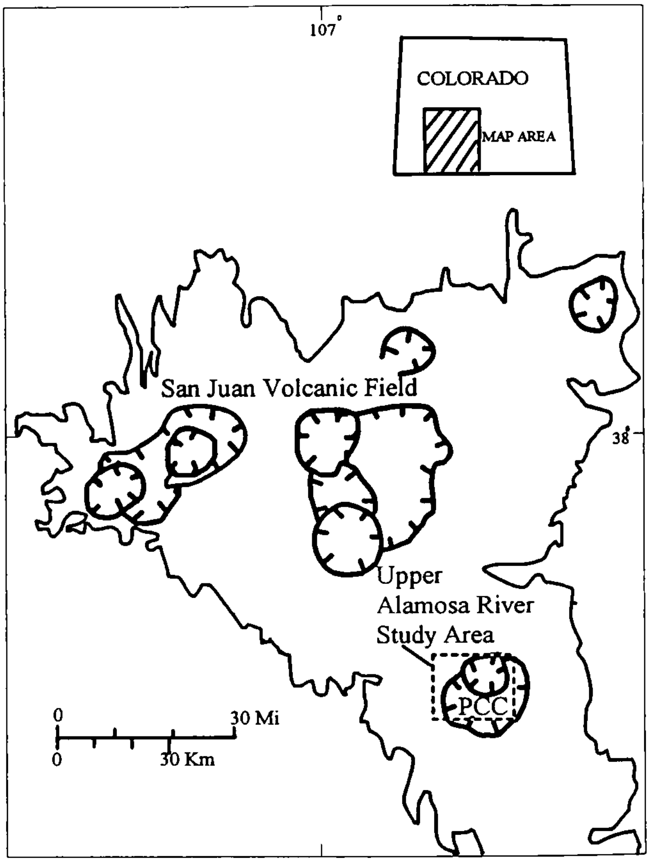

Figure 1. Map of the San Juan volcanic field showing the Platoro caldera complex (PCC), and the upper Alamosa River Basin study area. Major calderas denoted by thick hatched lines. Figure modified from Lipman (1975).

The Platoro caldera complex served as a structural locus for the intrusion of numerous stocks and dikes ranging in composition from monzonite to porphyritic dacite. The

Alamosa River stock (fig. 2), the largest of these intrusions, is an elongate intrusive body measuring about 3 by 7 km. South of the Alamosa River, the stock is mostly unaltered, fine- to medium-grained, equigranular monzonite. However, the northwestern part of the intrusion is petrographically and compositionally more complex and was affected by intense hydrothermal alteration. It is in this area that the Alamosa River stock was intruded by several later pulses of mostly more silicic intrusion. Emplacement of one or more of these later intrusions was responsible for most of the intense hydrothermal alteration in the vicinity of Alum Creek and Lookout Mountain.

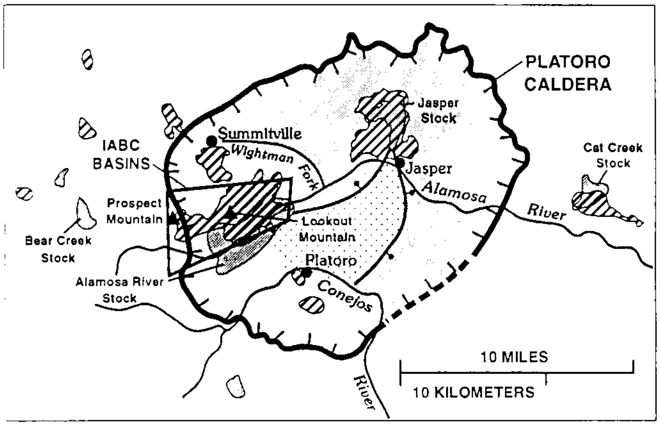

Figure 2. Simplified geologic map of the Platoro caldera complex. Diagonal hatched areas are zones of hydrothermal alteration; white shaded area is intracaldera Treasure Mountain tuff.

Rain and melt water from several large areas underlain by altered, mineralized rock in the Summitville-Platoro area drains into the upper Alamosa River. These areas include the Summitville mining district and the Iron-Alum-Bitter Creek basins (IABC basins). As shown in figure 2, altered and mineralized zones in these areas are closely associated with intrusive centers localized along the structural margins of the Platoro caldera complex.

HYDROTHERMAL ALTERATION AND MINERALIZATION

Early studies by Steven and Rattè (1960) recognized two main episodes of hydrothermal activity in the Summitville-Platoro area. Most of the large masses of altered rock in the IABC basins (fig. 2) were formed about 29-26 Ma during an early period of alteration denoted as Conejos age by Steven and Rattè (1960). Rocks within these areas were altered prior to the eruption of the South Mountain lava dome, which hosts the ore deposit at the Summitville Mine. A later period of alteration, which occurred about 23 Ma (Mehnert and others , 1973), has affected rocks that extend from the north base of South Mountain south to Cropsy Ridge. The main mass of 23 Ma altered rock encompasses most of the South Mountain volcanic dome and envelops the Summitville orebody.

Summitville Area

Discovery of gold in the Summitville area in 1870 led to one of the first large mining ventures in the San Juan Mountains (Steven and Ratté, 1960). Gold, silver, and copper ores in the Summitville area formed in a shallow volcanic environment. Ore is hosted almost entirely by the coarsely porphyritic South Mountain quartz latite dome. The volcanic dome, along with genetically related alteration and mineralization, was emplaced along the northwestern margin of the Platoro caldera complex. Alteration and mineralization at Summitville has been studied in detail and is discussed by Stoffergren (1987) and Gray and others, 1994. Mineralization took place in near-vertical tabular zones and pods of quartz-alunite replaced South Mountain porphyry along northwest-trending fracture zones. Alteration occurred prior to mineralization in these zones and the resultant mineral assemblage grades out from a core of leached vuggy silica through quartz-alunite and a quartz-kaolinite zone, and finally into strong illitic alteration. Ore minerals, mainly pyrite and enargite, fill irregular cavities within the vuggy silica zone. The zone of vuggy silica is generally present within 100-200 m of the surface and appears to be transitional downward into better defined but narrower vein structures. Most of the ore mined at Summitville was from the oxidized zone, which extends to 50 to 100 m below the surface. Ore from this zone generally consists of native gold intergrown with hematite, goethite, and lesser jarosite and barite. High-grade ore beneath the oxidized zone contains covellite, enargite, luzonite, and gold with accessory sphalerite and galena (Stoffregen, 1987).

Isotopic dating in the Summitville area (Mehnert and others, 1973) has established a close temporal association between mineralization and magmatic activity (~23 Ma). The classic acid-sulfate alteration assemblage at Summitville is interpreted by Stoffregen (1987) to have formed by extreme leaching by acid fluids produced by an influx of magmatic SO_2. However, alteration preceded mineralization, the latter being associated with less extreme acid conditions.

Iron Creek, Alum Creek, Bitter Creek (IABC) Basins

The IABC basins (figs. 2 and 3) encompass roughly 11 km^2 of intensely altered and weakly mineralized rock that corresponds spatially with the northern margin of the Alamosa River stock (fig. 2). A later phase of this stock, called the Alum Creek porphyry (Calkin, 1967), is the focus of the most intense alteration in this area and contains zones of anomalously high lead (up to 1060 ppm), copper (up to 250 ppm), molybdenum (up to 600 ppm), and zinc (up to 600 ppm) (Sharp and Gualtieri,1968; Calkin, 1967; Amoco, unpub. data, 1982). A classic porphyry-style, quartz-sericite-pyrite alteration assemblage is centered around the Alum Creek porphyry and is characterized by stockwork quartz-pyrite veinlets containing sparse molybdenite. Pyrite, which occurs ubiquitously throughout altered rocks in the IABC basins, is most prevalent in zones of quartz-sericite-pyrite alteration, where it averages about 1 to 2 volume percent of the rock (Calkin, 1967). The intensity of quartz-sericite-pyrite alteration decreases outward and upward from the center in Alum Creek as denoted mostly by a gradual decrease in both density of quartz-pyrite stockwork veinlets and silica flooding. Unpublished drill core data (Anaconda reference collection housed at the University of Wyoming, Laramie, Wyoming) indicate that the quartz-sericite-pyrite alteration extends several hundred feet below the surface. Unpublished studies by Anaconda during 1982 (Anaconda reference collection housed at the University of Wyoming, Laramie, Wyoming) show that over 70 percent of altered rock from select drill core in the Alum Creek area contains greater than 1 to 2 volume percent pyrite. In contrast, fresh pyrite was detected in only about 35 percent of those samples collected from the surface; however, most of these rocks originally contained pyrite.

Pervasive argillic alteration, characterized by the presence of kaolinite, commonly in the absence of pyrite, is superimposed upon original QSP-altered rocks in the IABC basins. The argillic alteration assemblage was formed by extremely acid supergene fluids generated by the oxidation of pyrite by surface or meteoric water. In general, rocks that have been less intensely silicified by primary QSP altering fluids are more susceptible to secondary argillization; whereas, more silicified QSP-altered outcrops and the pyrite within are typically armored from these acidic fluids. The highly silicified and pyrite-bearing rocks form the characteristic spire and hoodoo-shaped outcrops that are surrounded by less-resistant, argillized rocks that were originally little affected by silicification. Tiny cubed-shaped casts in the rocks indicate that pyrite within these argillized and less resistant outcrops is commonly oxidized and destroyed. Although sometimes indiscernible, the original texture of QSP-altered rocks superimposed by later argillic alteration can be recognized by the presence of stockwork quartz veinlets, silica flooding, remnant sericitized phenocrysts, and oxidized iron-bearing (after pyrite) stockwork.

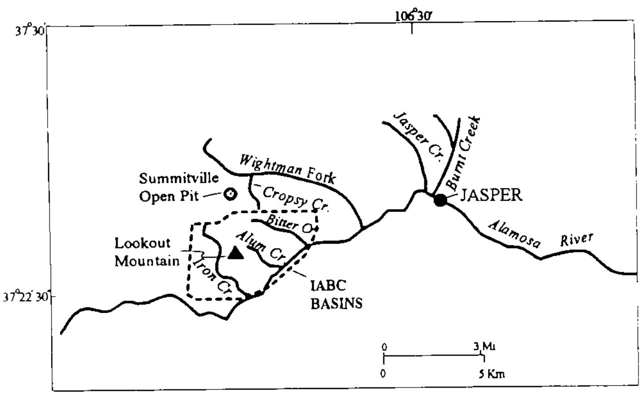

Figure 3. Map of major drainages within the upper Alamosa River basin study area.

Several relatively small centers of quartz-alunite altered rock are located on the south and western slopes of Lookout Mountain, about 600 m above the QSP zone in Alum Creek. There is a general zonation outward from quartz-alunite into QSP-altered rock, the latter having been variably overprinted by an argillic alteration assemblage. These quartz-alunite centers in turn grade further upward into an ancient hot spring environment characterized by massive opaline ledges and isolated siliceous sinter deposits enriched in mercury (up to 16 ppm; Summitville Consolidated Mining Company, unpub. data, 1988). Preliminary sulfur and oxygen isotopic data (R.R. Rye, personal commun.) indicate that the alunite at Lookout Mountain was derived from a SO_4-rich vapor emanating directly from an underlying magma body. Surficial emanation of these sub-volcanic, SO_4-rich fluids resulted in formation of a geyser basin, probably similar in many ways to the active basins in Yellowstone National Park, Wyoming.

Alteration intensity decreases dramatically in all directions outward from the main centers of alteration in the vicinity of Lookout Mountain and Alum Creek. Pyrite concentrations also decreases outward in the peripheral weak argillic-sericitic and propylitic alteration assemblages.

The style of alteration, the occurrence of anomalous copper, lead, zinc, and molybdenum, and the intimate association with a porphyritic quartz monzonite intrusion spurred substantial exploration activity in the Alum Creek area, specifically as a porphyry copper-molybdenum target. However, the IABC basins were considered poor exploration targets for gold and silver (Sharp and Gualtieri, 1968) because concentrations of these metals in over 200 rock chip samples were below analytical detection limits (< 0.1 ppm and <0.5 ppm, respectively), and gold and silver values in exploration drilling did not exceed 0.09 and < 12 oz/ton, respectively (W. Calkin, unpub. data, 1984). The presence of trace to appreciable amounts of gold and silver in altered rocks in the Summitville area (23 Ma alteration) is an important distinction from the IABC basins (29-26 Ma alteration), where altered rock exhibit a general paucity in these metals. Aside from the quartz-pyrite-gold-silver telluride veins mined on a small scale in the Stunner and Gilmore districts at the mouth of Alum Creek (Patton, 1917; Lipman, 1975),these basins are largely undisturbed by mining activity.

PRELIMINARY STREAM PH AND CONDUCTIVITY DATA

During the summer of 1994, a detailed study of spring and surface water geochemistry was conducted in conjunction with ongoing geologic studies in the IABC basins. Guided by our preliminary mapping, and pH and conductivity data provided by Kirkham and others (this volume), approximately 60 spring and surface water sites were selected and subsequently sampled for a wide spectrum of geochemical analyses. The primary goals of this study were to ascertain the degree and type of influence of specific rock and alteration assemblages upon local spring and stream geochemistry, and to characterize the geochemistry of natural waters in this specific type of mineralized, yet relatively undisturbed area. As the majority of geochemical analyses have yet to be completed, our present data set (fig. 4) includes only field pH and conductivity measurements. These data are in good general agreement with the data of Kirkham and others (this volume) from the same general study area, which are discussed in detail within this volume.

Water analyzed from the Alum Creek area, which marks one of the main centers of alteration and mineralization within the IABC basins, is by far the most degraded within the study area, with pH values commonly less than 2.5 and conductivity as high as 2,000 to 10,000 μs/cm. However, the headwaters of the main stem of Alum Creek (pH=5.4, conductivity=20) appeared to contain relatively good quality water (pH= 5.4, conductivity = 20)(fig. 4), with water quality decreasing further downstream. The sample taken at the headwaters of the main stem of Alum Creek was located immediately downstream from a large, fresh plug of porphyritic latite, which is most likely responsible for the relatively good water quality.

Iron Creek at its headwaters appears to be a relatively healthy stream and is the only stream in the IABC basins that is habitat to trout. Even at the confluence of South Mountain and Iron Creeks, which is in close proximity (<0.5 km) to the Summitville Mine, Iron Creek maintains its relatively good water quality with a pH of 6.7 and conductivity of 60 μs/cm (Kirkham and others, this volume). The first significant influx of degraded water originates from a tributary draining highly altered and pyritized rock in the saddle between Cropsy and Lookout Mountains. The intensely altered rocks exposed in this saddle are products of the29-26 Ma period (pre-Summitville alteration) of hydrothermal activity, which also affected rocks in the Iron Creek basin south of the saddle, as well as rocks within Alum and most of Bitter Creek. Water flow in this tributary initiated from a spring with a pH of 2.6 and conductivity of 1380 μs/cm. In addition, highly degraded water with a pH of 2.3 and conductivity of 3870 μs/cm also issues from a spring in the tributary immediately southwest of this saddle. Just below this tributary, the pH of Iron Creek decreases to 4.6, while conductivity increases to 137 μs/cm (Kirkham and others, this volume). Just to the east of Sheepshead, (fig. 4) a prominently altered basin is drained by a tributary with water averaging a pH of about 4.0 and conductivity of about 260 μs/cm. Alteration and accompanying pyritization in this basin is relatively less intense than that around Lookout Mountain and in Alum Creek, and marks the western extent of influence from Conejos age-hydrothermal alteration. Water issuing from a spring just to the south of Sheepshead has relatively good water quality (pH=5.1, conductivity= 8; Kirkham and others, this volume) and reflects the influence of the fresh quartz latite plug making up the large promontory at Sheepshead.

Water quality along Bitter Creek is most adversely affected from relatively acidic water draining from three intensely altered tributary basins on the north side of Bitter Creek, below and flanking Elephant Mountain (fig. 4). While the most degraded water in these side basins has a pH and conductivity of 3.2 and 980, respectively, springs issuing near the fresh rhyolite intrusion at Elephant Mountain were of good general water quality. The water quality in tributaries east of Cropsy Mountain and Cropsy Ridge, are also of general good quality due to paucity of hydrothermally rock in these areas.

Whereas Prospect Mountain delimits the western extent of intense hydrothermal alteration of the older (29-26 Ma) cycle to the west, Bitter Creek generally marks the easternmost limit of the older 29-26 Ma alteration. Later, 23 Ma alteration related to mineralization around Summitville was largely confined to rocks north of Cropsy Ridge. With the exception of relatively insignificant volummetric contributions from two degraded tributaries (pH=3.8, conductivity= 790) around a small altered intrusion near the mouth of the Wightman Fork (fig. 2), natural waters are of relatively good quality between Bitter Creek and the altered areas around Jasper and Burnt Creeks.

DISCUSSION

The Summitville Mine and IABC basins are all localized along an arcuate fault zone, generally referred to as the ring fracture zone of the Summitville caldera (Lipman 1975; Stoffregen, 1987). This fault zone, from Summitville south to the Alamosa River and east to Jasper is marked by repeated

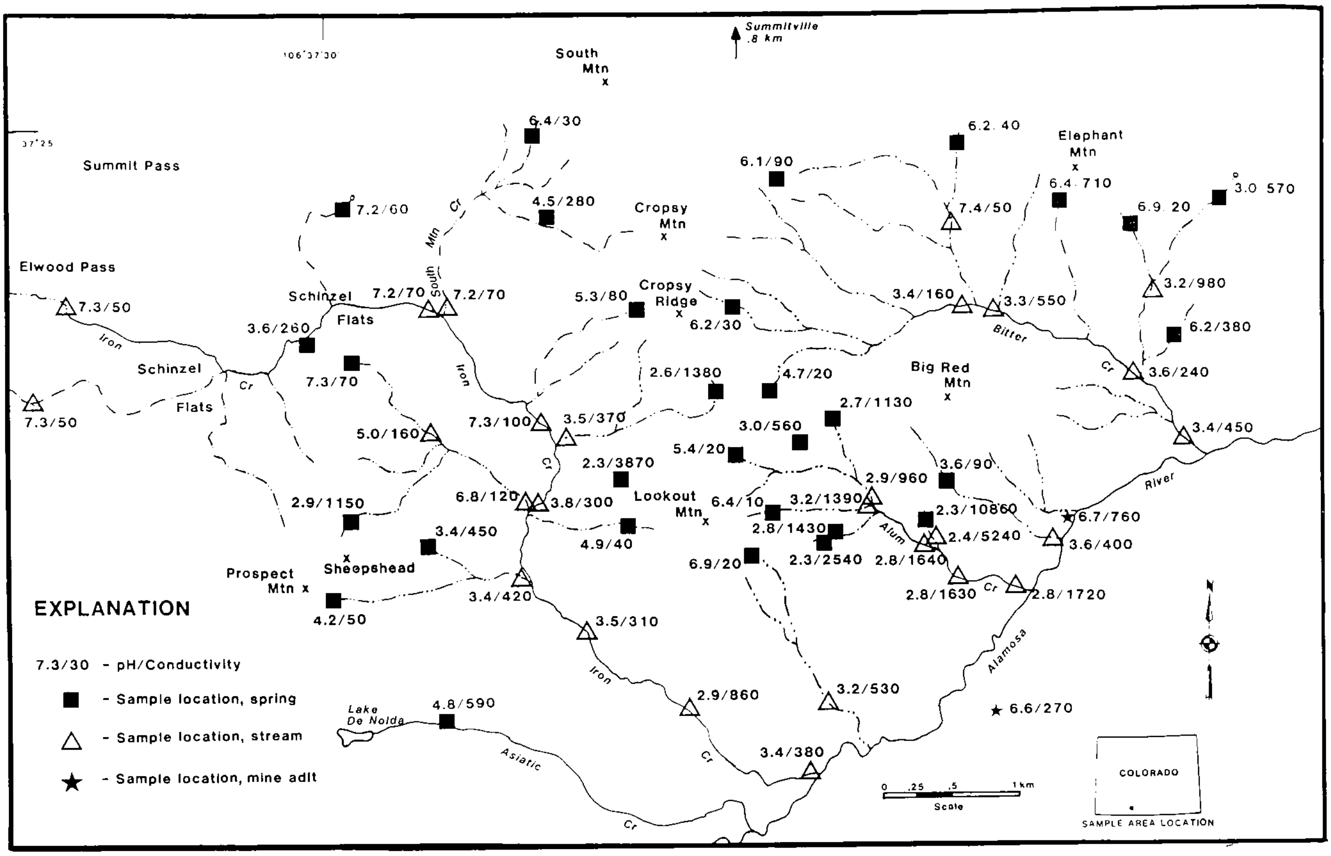

Figure 4. Sample locality map showing pH and conductivity data from springs and surface water in the IABC basins

intrusion, hydrothermal alteration and mineralization. As shown in figure 2, there is an intimate association between hydrothermal alteration, mineralization, and shallow intrusion of monzonite to monzonite porphyry stocks. The intrusions related to hydrothermal alteration and mineralization within the IABC basins have been well exposed by erosion; in contrast, the younger quartz monzonite intrusion(s) associated with the Summitville orebody is present about 700 m beneath the surface, buried by a thick accumulation of quartz latitic lavas of the South Mountain extrusive dome.

One of the striking similarities between the Summitville mining district and the IABC basins to the south is the presence of classic acid-sulfate alteration assemblages. Mineralized and altere rocks in the Summitville area are in fault-controlled, subvertical tabular zones consisting of vuggy silica cores surrounded by successive zones of quartz-alunite, quartz-kaolinite, kaolinite-sericite, and smectite-chlorite. Similarly, small localized zones of quartz-alunite altered rock also are present in the Lookout Mountain and Alum Creek vicinities in the western portion of the IABC basins (fig. 3). However, unlike the Summitville mining area, these zones are not mineralized and lack a central zone of vuggy silica rock.

The vertical progression of hydrothermally altered rocks in the Summitville and the Lookout Mountain-Alum Creek areas is also strikingly similar. Alteration related to both hydrothermal systems grade downward from acid-sulfate altered rock of magmatic derivation (Rye and others, 1992; R.O. Rye oral commun.) into underlying zones of quartz-sericite-pyrite alterered rock with accompanying quartz-pyrite stockwork veinlets. Sparse molybdenite is present within the deeper quartz-sericite-pyrite assemblage in the Alum Creek area, and anomalous copper and molybdenum are reported in the deeper levels of the Summitville deposit (Gray and others, 1993). Both the Summitville and Lookout Mountain-Alum Creek hydrothermal systems are characterized by upper level acid-sulfate and deeper level, weak "porphyry" copper-molybdenum systems. In both areas, these hydrothermal systems were genetically related to high-level quartz monzonite intrusions.

From these data it is apparent that the depth of erosion--relatively shallow in the Summitville area compared to the IABC basins--is an important factor when comparing specific geologic and geochemical characteristics of the Summitville mining district to the IABC basins. For example, it would be misleading to compare the geochemical characteristics of water from the Alum Creek drainage to waters from upper

Cropsy Creek in the Summitville area (fig. 3) because different levels of the alteration assemblage are exposed in each area. Although no quantitative data are yet available, one would expect significantly higher pyrite and related metal abundances within the deeply dissected Alum Creek area relative to the higher level alteration assemblage drained by upper Cropsy Creek.

Besides depth of erosion, areal distribution of alteration is another important factor when comparing the degree of water degradation associated with the older(29-26 Ma) versus younger (23 Ma) periods of hydrothermal alteration. Since the area of altered rock around the Summitville deposit (3 km^2) (23 Ma alteration) is less than one-third of that associated with the older alteration in the IABC basins (11 km^2), it is not surprising that alteration intensity and degree of water degradation diminish in South Mountain (pH=4.5-6.4, conductivity =30-280) and upper Cropsy Creeks (pH= 4.4-7.3, conductivity =50-460; Miller and McHugh, 1994), which are about 0.5 km from the mine site.

Finally, geochemical sampling of highly altered rock in the Summitville and IABC basins (Sharp and Gualtieri, 1968) show extensive lead anomalies in both areas with smaller anomalies of copper, molybdenum, and zinc. The acidic nature of the creeks, and probably shallow groundwater, in the IABC basins results in high solubility of these metals and significant contributions to trace metal loadings in the Alamosa River. The numerous terraces of iron-oxide cemented conglomerates as much as 100 m above modern drainages in the IABC basins indicate that natural acid drainage has been active in the IABC basins for thousands, if not millions of years. In all likelihood, these acid stream conditions existed ever since the beginning of stream downcutting and associated regional uplift and tilting in the central San Juan Mountains, approximately 5 million years ago (Steven and others, in press).

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SOURCES OF ACIDITY AND HEAVY METALS IN THE ALAMOSA RIVER BASIN OUTSIDE OF THE SUMMITVILLE MINING AREA, COLORADO

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ABSTRACT

Mining-related and naturally occurring sources of acidity and heavy metals degrade the Alamosa River basin within the San Juan Mountains of south-central Colorado. The recently abandoned Summitville gold mine has been attributed as the major source of contamination, but it is also evident that other long-inactive mines and also natural degradation in Iron, Alum, Bitter, Burnt, and Jasper Creeks could be responsible for at least a portion of the problem. As part of a state-wide mine inventory on U.S. Forest Service lands, mines and natural sources of degradation were inventoried in the Alamosa River basin outside the Summitville mine area in the summer and fall of 1993 and spring of 1994. During this inventory 219 mine openings and 130 mine dumps were visited, field water tests for pH and conductivity were performed at 344 locations, thirty-one mine openings with standing or draining water and three dump seeps were discovered, and dozens of naturally occurring acidic, metal-rich springs (NOAMS) were observed during the inventory. NOAMS ranged from tiny individual seeps to extensive seepage areas a few hundred feet long to prominent springs which have formed large, sometimes beautiful, mounds of ferrosinter (iron-rich precipitate from springs). Historic mining has caused a moderate amount of the contamination in Iron Creek, and it constitutes a small part of the degradation in Burnt Creek. No definitive evidence of mining-related water chemistry problems was discovered in either Alum or Bitter Creek, suggesting most or all degraded water in these two watersheds results from natural processes. Mineral exploration activities could arguably be responsible for a very minor amount of the problem in Alum Creek. Presence of "fossil" NOAMS, terraces of ferroconglomerate (iron-cemented alluvium) at least 30 feet above stream level in Iron, Alum, Bitter, and Burnt Creeks, and NOAMS only a few hundred feet below drainage divides indicate that the naturally occurring degradation has been ongoing for at least thousands, and perhaps tens of thousands of years or longer. Debris-flow activity in Alum Creek and other creeks is capable of depositing large quantities of pyritic material in the Alamosa River.

A conservative estimate of the maximum possible contribution of mining to the degradation of the Alamosa River above the confluence with Wightman Fork can be made if it is assumed that all dissolved metal associated with draining mines and dump seeps in the area is entirely a result of mining and that it eventually reaches the river and stays in solution. Under this scenario the abandoned mines could be responsible for nearly 11% of the iron and almost 18% of the aluminum, but only around 1% of the copper, manganese, and zinc in the river above the confluence with Wightman Fork at the time of sampling, with the balance of these dissolved constituents being attributable to natural degradation. The relative loadings due to mining probably vary seasonally and with precipitation.

INTRODUCTION

As part of the Abandoned Mine Land Inventory (AMLI) of U.S. Forest Service lands within Colorado, the Alamosa River basin (Figure 1) was investigated by the Colorado Geological Survey (CGS) for mining-related environmental problems and physical hazards during the summer and fall of 1993 and spring of 1994. The AMLI typically addresses only mining sites, but to insure adequate characterization of the Alamosa basin our inventory was expanded to address both mining and natural degradation. Included within the study area is the Summitville gold mine, whose operator filed for bankruptcy and abandoned the site in December, 1992, leaving behind a variety of environmental problems. Because the Summitville mine was under consideration for designation as a Superfund site and the subject of extensive studies, it was specifically excluded from our investigation.

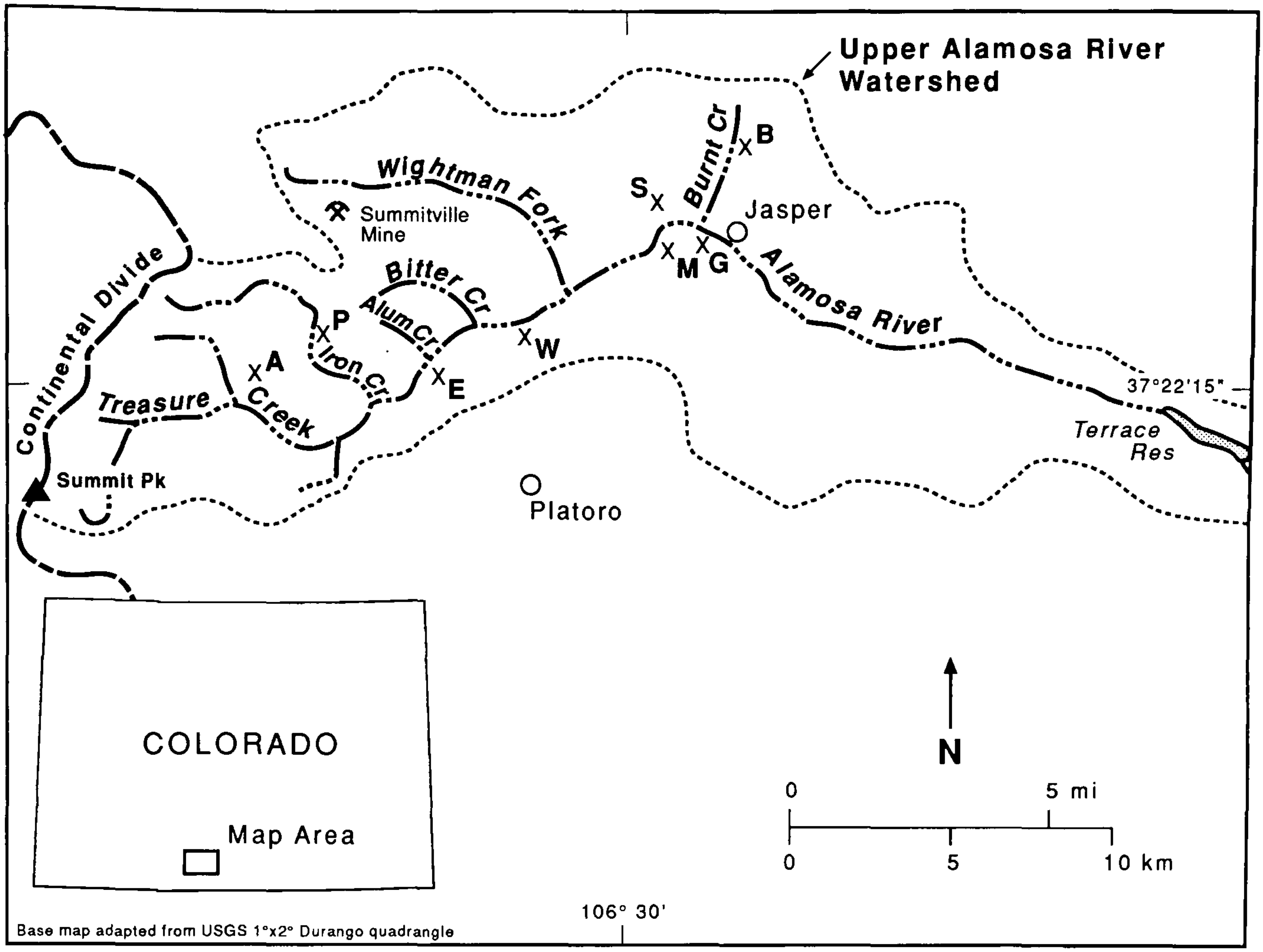


Figure 1. Extent of Alamosa River watershed above Terrace Reservoir, showing the locations of the main tributaries, larger mines, and those mines mentioned in the text but not shown on other maps. (P = Pass-Me-By, A = Asiatic, E = Eurydice, M = Miser, G = Guadaloupe, B = Burnt Gulch mines, S = Sanger mine, and W = Watrous claims)

Our inventory included review of published and file information on mining, examination of aerial photography, and several months of field investigations. All known mines and nearly all prospects within the basin were visited. Field tests for pH and conductivity were performed on mine drainage, natural springs and seeps, and streams at 344 locations as part of the inventory. All acidic tributaries within Iron, Alum, Bitter, and two unnamed creeks, and most within Burnt and Jasper Creeks were investigated to determine the source of their acidic water.

Twenty-three water samples were collected for laboratory analysis. Fifteen water samples were obtained from draining adits, one was collected from a dump seep, two were gathered from Iron Creek above and below the inflow from the Pass-Me-By mine, and five were obtained from naturally occurring acidic, metal-rich springs (NOAMS). Several samples were analyzed by the Colorado Department of Health as part of the AMLI project. Other samples were analyzed by the U.S. Geological Survey (USGS) Branch of Geochemistry, SLV Analytical Services, and the USGS Water Resources Division. Dissolved water samples were filtered using a 0.45 um filter, except for four samples that were collected cooperatively for our investigation by staff from the Branch of Geochemistry, who used a 0.2 um filter.

Total and dissolved metal concentrations were obtained for some samples, while only dissolved concentrations were obtained for others. All samples were analyzed for iron, aluminum, manganese, copper, zinc, lead, cadmium, chromium, and nickel, but only part were tested for arsenic, barium, beryllium, boron, calcium, cobalt, gallium, lithium, magnesium, molybdenum, potassium, selenium, silicon, silver, sodium, strontium, sulfate, vanadium, and zirconium.

Table 1 lists the field parameters and dissolved concentrations and loadings for iron, aluminum, manganese, copper, and zinc for the sampled waters. Wherever feasible, discharge rates for the sampled sites were measured using a cutthroat flume or by timed catchment. Discharge rates for the Lower Orinoco mine and for Lower Iron and Burnt NOAMS had to be estimated due to the difficulty involved in collecting all the water at a single measuring point. Water issuing from Burnt adit infiltrated into a steep hillside before reaching a suitable collection point. All water samples were collated during August 1993, except that from Bitter Spring, which was sampled in June 1994.

MINING-RELATED SOURCES

Historic mining activities in the Alamosa basin were concentrated in the Summitville mining district. Mining outside the Summitville area consisted of numerous prospects, several very small mines, and a few small to moderate-sized mines. Patton (1917) provides the most complete description of mining activities within the basin and includes mine locations shown on a generalized topographic map. Other mines and prospects were shown by Calkin (1967), Lipman (1974), and AMOCO (1982). We attempted to locate all mine features and most prospects described in these references. When a mapped feature was not found, the hillslope below the plotted location was traversed for evidence of acidic drainage. If acid drainage was encountered, it was followed upstream to determine its source. As the summer progressed, we realized that the unnamed mines and prospects shown by Patton (1917) were in most instances very small features. Prospects were typically only a few feet deep, while unnamed shafts and adits were at most a few tens of feet deep and frequently less than 10 feet deep. Some features were so subdued that they were difficult to recognize even at close range. In a few very remote areas that were drained by streams with good quality water, we elected not to expend the field work necessary to locate such features because of their very low potential for environmental degradation.

A total of 219 mine openings and 130 mine dumps were inventoried, most of which were prospect features. Locations of the more important mines are shown on Figures 1, 2, 3, 4, and 5. Most dumps contained less than an estimated 1000 cubic yards (cy) of material, and in many instances less than 100 cy. Based on the estimated dump size the Pass-Me-By mine, with a dump slightly in excess of 10,000 cy, is believed to have the greatest amount of underground workings, followed by the Miser mine, an unnamed mine in Burnt Gulch, and the Eurydice mine. Dumps with around 1000 cy of material were found at the Asiatic, Guadaloupe, Globe, Red Mountain no. 1, and Sanger mines, and also at unnamed mines at the Watrous claims south of Government Park, two adits near Stunner campground, an adit beneath Forest Road 250 between Bitter and Alum Creeks, and an adit adjacent to Forest Road 250 north of Terrace Reservoir.

A fairly large disturbed area is present in Alum Creek where a jeep road enters the creek bed. It has been suggested that hydraulic mining may be responsible for this disturbed area, but it also coincides with a location where several mineral exploration test holes were spudded and is likely a result of grading activities related to the drilling. Sections of rusted, often twisted, small diameter steel pipe observed in Alum Creek could potentially have been used for hydraulic mining, but the pipe more likely served as a water line for a mineral exploration test hole drilled on the drainage divide at the head of tributary B. A shallow shaft in Alum Creek described by Calkin (1967) was not located during our study. The shaft apparently was buried, backfilled, or destroyed when the staging area was built for the exploration drilling effort.

Water was draining out of or standing within thirty-one of the inventoried mine openings. Acidic water seeped from the toe of three of the mine dumps, one at an unnamed mine in Burnt Gulch, another within the Watrous claims near Government Park, and a third at the Pass-Me-By mine. Mine drainage locally contained significant concentrations of iron and aluminum, but when compared to many other mining districts the concentrations of most other metals generally were not significantly elevated. Water draining from or standing in the mine openings ranged in pH from 3.0 to 7.8, and conductivity varied from 164 to 2060 µS/cm. Drainage from the Pass-Me-By mine was the most acidic, had the second highest conductivity (1100 µS/cm), and apparently is toxic to conifers, judging from the number of dead trees present in the outflow area. The highest measured conductivity (2060 µS/cm) related to mining was associated with a tiny, 0.1 gpm seep at an adit just below Forest Road 250. The seep had a pH of only 6.9 and it promptly infiltrated into the ground a short distance from the collapsed portal. Dump seeps ranged from pH 2.5 to 7.4 and their conductivity varied from 306 to 2430 µS/cm. The seep at the Pass-Me-By mine was by far the most acidic and had the highest conductivity, but its flow rate was only 0.4 gpm and it rapidly infiltrated into the ground. A prominent zone of dead trees occurs below the Pass-Me-By dump seep. Perhaps the dump seep is responsible for killing the trees, but their death more likely relates to the fact that the drainage from the Pass-Me-By mine formerly flowed through this area. Several of the mine openings with draining or standing water have less than 100 linear feet of total underground workings based on their dump size and on underground observations. Water issuing from such mine openings may represent natural ground water intercepted by the shallow workings. Chemical modification of natural ground water as its passes through such small mines is likely very limited.

Table 1. Field parameters and dissolved metal concentrations and loadings for draining mines, dump seeps, NOAMS, and in-stream water samples.

Location	pH	Cond uS/cm	Q gpm	Fe mg/L	Fe load g/day	Al mg/L	Al load g/day	Mn mg/L	Mn load g/day	Cu mg/L	Cu load g/day	Zn mg/L	Zn load g/day
Upper Alamosa Mines													
Asiatic	6.00	480	5.8	0.79	25.0	1.00	31.6	0.420	13.3	<0.040	0.00	<0.040	0.00
Pass-Me-By	3.02	1,100	26.9	140.00	20,524.7	59.00	8,649.7	0.310	45.4	0.078	11.44	0.180	26.39
Gilmore Meadow	5.29	276	0.8	2.90	12.6	0.10	0.4	0.220	1.0	0.010	0.04	0.150	0.65
Smuggler	6.10	361	0.2	2.20	2.4	0.12	0.1	0.339	0.4	<0.001	0.00	<0.010	0.00
Globe	6.40	304	1.5	0.81	6.6	0.06	0.5	1.000	8.2	<0.004	0.00	0.240	1.96
Lower Orinoco	7.44	442	1.5*	2.14	17.5	<0.04	0.0	0.941	7.7	<0.001	0.00	0.019	0.16
Ferrocrete	3.98	682	0.8	61.00	266.0	11.00	48.0	2.400	10.5	<0.004	0.00	0.250	1.09
Adit under FR250	6.91	784	1.1	17.00	101.9	0.57	3.4	1.100	6.6	<0.001	0.00	<0.010	0.00
Red Mountain	6.58	991	2.3	17.90	224.4	0.42	5.3	1.541	19.3	<0.001	0.00	0.041	0.51
Queen Bird	5.52	476	0.4	0.58	1.3	0.13	0.3	0.381	0.8	<0.001	0.00	0.048	0.10
Watrous	3.14	846	0.0	35.00	0.0	3.20	0.0	0.470	0.0	1.400	0.00	0.160	0.00
Mines in Wightman Fork (excluding Summitville)													
Grape	5.65	277	0.7	0.22	0.8	<0.10	0.0	0.120	0.5	0.002	0.01	0.370	1.41
Mines near Jasper													
Miser	5.85	620	126.0	1.50	1,030.1	<1.00	0.0	0.280	192.3	<0.040	0.00	0.041	28.15
Burnt Dump Seep	4.83	589	2.6	<1.00	0.0	2.00	28.3	0.220	3.1	<0.040	0.00	0.067	0.95
Burnt Adit	3.10	649	0.1*	5.00	2.7	5.00	2.7	0.460	0.3	0.100	0.05	0.058	0.03
Guadaloupe	6.39	962	1.9	22.20	229.9	0.33	3.4	3.464	35.9	0.105	1.09	2.511	26.00
NOAMS													
Upper Iron Spring	2.53	2,590	6.7	160.00	5,842.4	120.00	4,381.8	0.240	8.8	0.990	36.15	0.260	9.49
Lower Iron Spring	2.94	622	20.0*	26.00	2,834.0	9.00	981.0	0.650	70.9	<0.040	0.00	0.130	14.17
Spring on FR 250	2.75	2,600	3.9	70.00	1,487.9	38.00	807.7	15.000	318.8	0.350	7.44	0.930	19.77
Burnt Spring	3.82	2,040	18.0*	70.00	7,063.2	31.00	3,041.1	4.200	412.0	0.058	5.69	0.810	79.46
Bitter Spring	3.27	214	1.6	1.92	0.0	1.42	12.4	0.049	0.3	0.077	0.67	0.138	1.20
In-Stream													
Iron Cr. Above PMB	4.25	181	1,500.0*	0.88	7,194.0	1.90	15,532.5	0.140	1,144.5	0.012	98.10	0.028	228.90
ron Cr. Below PMB	4.22	210	1,500.0*	2.70	22,072.5	3.00	24,525.0	0.150	1,226.3	0.012	98.10	0.030	245.25

* = flow rate is estimated

Drainage from the Pass-Me-By mine contained by far the highest dissolved concentrations of aluminum (59 mg/L), iron (140 mg/L), cobalt (0.12 mg/L), and nickel (0.1 mg/L) of any of the sampled mine drainages, whereas the Guadaloupe had the highest concentrations of manganese (3.5 mg/L) and zinc (2.5 mg/L), and the Watrous was highest in copper (1.4 mg/L). Lead was above detection limits only for the adit under Forest Road 250 (0.06 mg/L) and Smuggler (0.05 mg/L). Dissolved iron, aluminum, and copper loadings from the Pass-Me-By mine at 20,500 g/day, 8600 g/day, and 11.4 g/day, respectively, far exceeded the loadings for these metals from any other mining source. The Miser mine accounted for the most manganese loading (192 g/day), but the Pass-Me-By at 45 g/day and the Guadaloupe at 36 g/day were also responsible for appreciable amounts. Approximately equal dissolved zinc loadings were generated by the Miser (28 g/day), Pass-Me-By (26 g/day), and Guadaloupe (26 g/day).

When visited on August 5, 1993, about 1 gpm was issuing from collapse debris that entirely blocks the main portal at the Pass-Me-By mine. Water seeped out of the debris about three feet above the original portal floor, suggesting the adit was at least partially flooded. An additional 20 gpm issued from the ground about 25 feet in front of the collapsed portal. On August 11 seepage from the collapse debris had ceased, only a damp spot was present, and all the mine drainage surfaced at the location in front of the adit. Drainage from the Pass-Me-By mine had been recently channelized such that it flowed over the north end of the mine dump, down the hill, and into Iron Creek. An extensive deposit of reddish brown, indurated precipitate had formed along the flow path below the Iron Creek road, and conifers within this area were dead.

Over 100 gpm of water with a strong odor of hydrogen sulfide issued from collapsed debris at the Miser mine, leaving behind a heavy deposit of soft, bright reddish orange precipitate as it flowed over the collapsed debris. The water vigorously discharged out the collapse debris about 15 feet above the estimated original adit roof, indicating that the workings were flooded at least to that elevation. The mine drainage flowed into a series of two beaver ponds before entering the Alamosa River. The pH of the water increased from 5.9 at the collapsed portal to 7.4 below the beaver ponds.

As at the Pass-Me-By and Miser mines, the portal of the Guadaloupe mine also was completely collapsed shut. Water slowly seeped from collapse debris about 20 feet above the estimated original adit roof, suggesting the underground workings are at least partially flooded. A thick deposit of soft, reddish orange iron precipitate blanketed the collapse debris and mine dump along the flow path of the mine drainage, which infiltrated into the ground before reaching the Alamosa River.

NATURAL SOURCES

Naturally occurring water quality degradation in the Alamosa basin has been recognized by several previous investigators (Moran and Wentz, 1974; Kirkham and Holm, 1989; Hamilton, 1989; and Miller and McHugh, 1994). Acidic tributaries within Alum, Iron, Bitter, and two unnamed creeks, along with most tributaries in Burnt and Jasper Creeks, were investigated to determine their source of contamination. This was accomplished by following their acidic tributaries to where either the pH and conductivity of the tributary improved to near normal levels or to where the acidic headwater flow within the tributary first emerged from the ground. Many of the NOAMS observed while inventorying these watersheds were field tested for pH and conductivity and their discharge rate was estimated to assess their potential contribution to stream chemistry.

Dozens of NOAMS exist within the basin. They were observed only in areas underlain by intensively hydrothermally altered rock such as those near Lookout Mountain, Sheepshead, Cropsy Ridge, Elephant Mountain, and north of Jasper, with the poorest quality water being associated with unvegetated exposures of weathered, highly altered bedrock. NOAMS had pH values as low as 1.4 and conductivities as high as 6410 µS/cm, values that suggest the NOAMS issue water that is more degraded than the worst sampled mine drainage. NOAMS range from tiny individual seeps to extensive seepage areas hundreds of feet long to large springs that have formed huge mounds of ferrosinter (iron-rich chemical precipitate from springs), some of which are beautiful features that support unusual ecosystems. (Note that the use herein of the modifier "ferro" does not refer to the ionic state of the iron precipitate). Lower Iron and Burnt NOAMS have brightly colored ferrosinter mounds and discharge directly into live streams. NOAMS occur at elevations ranging from about 10,000 to nearly 12,000 feet. Some are found in the uppermost reaches of watersheds, while others are at stream level near the mouths of the creeks. Many of the ferrosinter mounds entomb organic debris that falls on them, providing abundant datable material throughout the vertical extent of the deposit. "Fossil" (presently dry) ferrosinter mounds were noted at several locations. Cessation of flow may result from blockage of open fractures by precipitating minerals or from changed hydrologic conditions related to episodes of erosional downcutting, glaciation, or perhaps interception of the degraded water by underground mine workings.

Water from the Upper Iron, Lower Iron, Burnt, and Bitter NOAMS, along with the NOAM spring on Forest Road 250, were sampled for chemical analysis (Table 1). The sampled NOAMS commonly had higher concentrations of iron and aluminum than the draining mines. Metal concentrations reported for the Lower Iron NOAM spring may be somewhat low, as it was raining heavily the day it was sampled and not possible to segregate rain water from the spring water before collecting a sample. Manganese concentrations in four of the NOAMS were within the same range as many of the draining mines, but the NOAM spring on Forest Road 250 had a concentration about four times higher than any draining mine. Concentrations of most other metals were similar in both the NOAMS and the draining mines. However, of all the water samples analyzed for this study the highest concentrations of iron, aluminum, manganese, cobalt, nickel, calcium, lithium, magnesium, and sodium were associated with NOAMS. Water discharging from the smaller mines and prospects may in large part represent naturally degraded ground water intercepted by the mine that has been only slightly modified chemically by passage through the limited underground workings. Even at the largest mine in the area, the Pass-Me-By mine, most dissolved metal concentrations were lower than those in the nearby Upper Iron NOAM spring.

At least part of the NOAMS are associated with ground water seepage along sub-horizontal fractures within altered bedrock. At the head of Burnt spring acidic water was observed discharging out of a sub-horizontal fracture in altered bedrock. The linear alignment of seeps issuing from the head of Upper Iron spring also suggests ground water discharges along a sub-horizontal fracture. Field tests run on the various seeps at the Upper Iron spring indicate the acidic water moving through bedrock mixes with relatively clean, shallow ground water in the alluvial aquifer along a small tributary. The pH of the springs drops and the conductivity increases with distance from the tributary.

Deposits of ferroconglomerate (iron-cemented alluvium) are forming actively in several areas within the Alamosa basin. Terraces of ferroconglomerate were observed at various elevations above Alum, Iron, Bitter, and Burnt Creeks, suggesting that naturally degraded water has existed in these watersheds for thousands of years. Naturally degraded water has probably existed in these watersheds for much of the Quaternary Period (past 1.6 million years). NOAMS may have originated shortly after initial erosion cut into the altered rock and created suitable hydrologic conditions that allowed precipitation falling in the upper reaches of the watershed to flow by gravity through the altered rock and discharge at a lower elevation. Because some modern NOAMS occur less than 300 feet below nearby drainage divides, the amount of downcutting required to create suitable hydrologic conditions need not be great.

CHARACTERISTICS OF WATERSHEDS

Iron Creek: Iron Creek is the largest watershed to contain NOAMS (Figure 2), and its degraded quality results from both mining-related and natural sources. Based on our field tests and the distribution of trout, Iron Creek appears to be a fairly healthy stream above tributary G even though iron precipitate is locally prevalent in Schinzel Flats. The pH and conductivity of the mainstem above tributary A were 6.3 and 36 µS/cm, with the values for tributary A being very similar. Although several small prospects occur along tributary B, the pH of this tributary was 6.8 and conductivity was 54 µS/cm. Small prospects were also observed in the vicinity of Schinzel Flats, including one from which an estimated 0.5 gpm of pH 3.7 water with conductivity of 195 µS/cm was draining. This tiny prospect adit has a small dump and probably extended underground only a very short distance. The water draining from this feature likely represents naturally degraded ground water intercepted by the prospect adit. The pH and conductivity of tributary C at the mainstem were 6.7 and 92 µS/cm, while the mainstem had a pH of 7.0 and conductivity of 47 µS/cm below tributary C.

One might anticipate that South Mountain Creek would be significantly degraded, based on its proximity to the Summitville hydrothermal alteration zone. Immediately north of the center of section 36, three forks merge to form the mainstem of South Mountain Creek. The northwest fork heads at a relatively low saddle, the northeast fork drains the back side of South Mountain, and the eastern fork drains the west flank of Cropsy Mountain. The northwest and east forks contain healthy looking streams with pH of 6.2 to 6.3 and conductivity of only 28 to 34 µS/cm. Surprisingly, the northeast fork which heads on South Mountain was only slightly degraded, having a pH of 5.4 and conductivity of 106 µS/cm. NOAMS along the north bank of the creek about 1000 feet below the confluence of the three forks contributed moderately acidic water to the creek, but even at its confluence with Iron Creek South Mountain Creek only had a pH of 6.7 and conductivity of 60 µS/cm. Tributary D, which drains a small basin containing one prospect and a NOAM spring issuing from a bleached altered outcrop, had creamy orange to tan precipitate in its headwaters, but stream pH was only 6.5 and conductivity was 114 µS/cm at the confluence with the mainstem. Trout were observed in Iron Creek between tributaries D and E, and the creek maintained its reasonably good quality as it received inflows from tributaries E and F and as it passed through a narrow canyon cut into altered bedrock from which several small springs issued.

The first significantly degraded water entered Iron Creek at tributary G, which drains the saddle between Cropsy Ridge and Lookout Mountain. Headwater flow in tributary G initiated at a NOAM spring high on Cropsy Ridge in an area of weathered, altered bedrock, and it received inflows from several other NOAMS along its reach. A small tributary inflow from a less altered area on the north flank of Lookout Mountain had a pH of 5.4 (H. Posey, 1994, pers. comm.). At the mainstem the pH

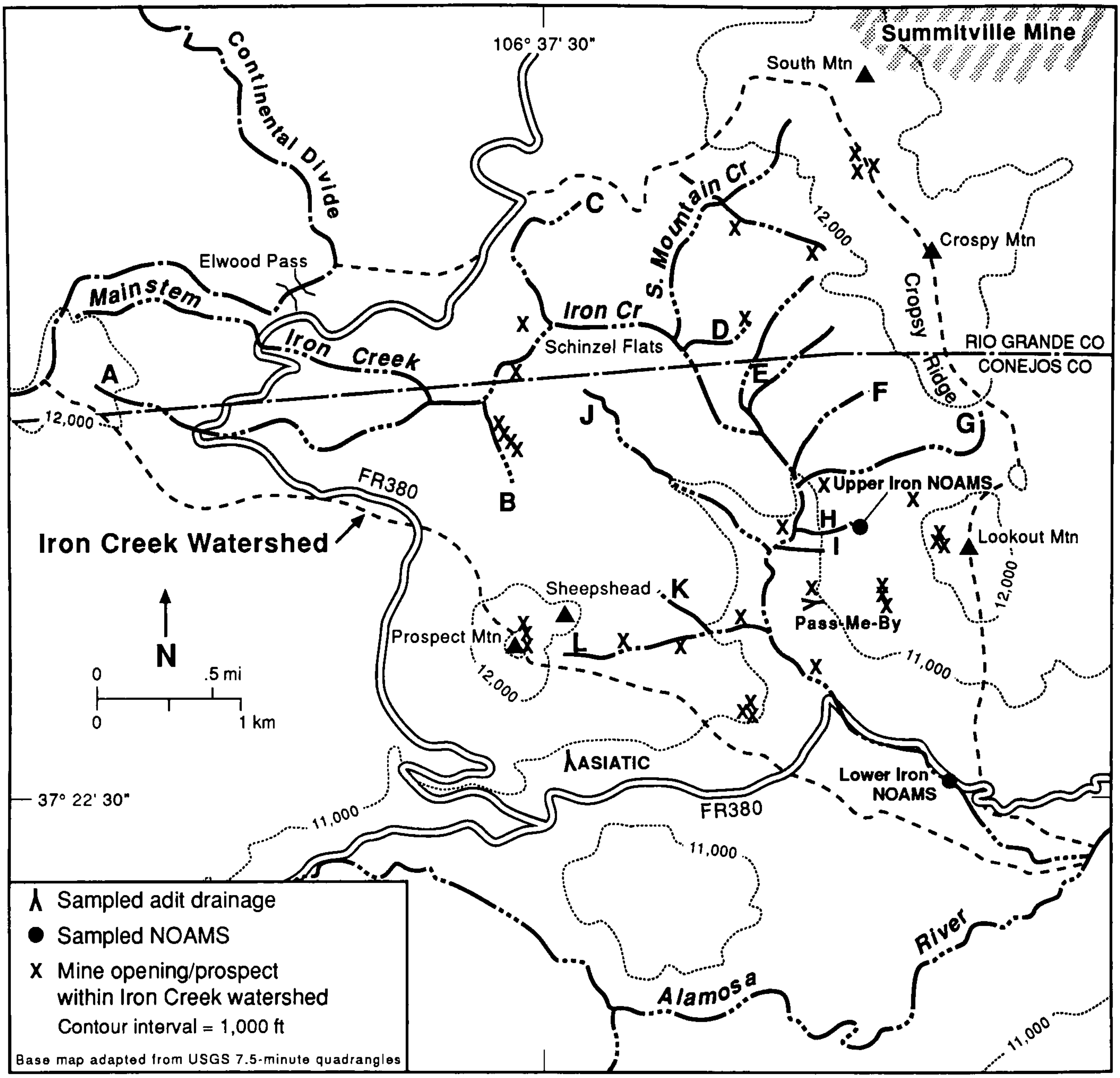


Figure 2. Map showing outline of Iron Creek watershed. Tributaries with surface flow that were investigated during this study are highlighted and labeled. Draining mines and NOAMS in or near the watershed that were sampled are labeled. Other mine openings within the watershed are indicated by "X".

and conductivity of tributary G were 3.5 and 317 µS/cm. Iron Creek dropped to pH 5.2 as a result of tributary G. Another significant inflow of degraded water occurred at tributary H, which includes discharge from Upper Iron spring. The pH of Iron Creek fell to 4.6 and its conductivity increased to 137 µS/cm below tributary H. Other NOAMS occur in tributary I, and they furthered the degradation of Iron Creek. Tributary J provided a relatively clean inflow (pH 6.8; conductivity 112 µS/cm), but Iron Creek remained fairly degraded, having a pH of 4.8 and conductivity of 149 µS/cm.

The uppermost important source of water degraded by mining in Iron Creek was discharged from the Pass-Me-By mine. Iron Creek experienced a very slight pH drop from 4.25 to 4.22 and an increase in conductivity from 181 to 210 µS/cm as a result of this inflow. Sampling by Kirkham and Holm (1989) in 1986 indicated that the total recoverable metal concentrations in Iron Creek increased from 4.2 to 5.6 mg/L for iron and from 2.8 to 3.5 mg/L for aluminum, but the concentrations of other tested metals remained fairly constant and some even decreased as a result of the Pass-Me-By inflow. Dissolved water samples were collected during our investigation from Iron Creek above and below the drainage from the Pass-Me-By mine. Dissolved iron raised from 0.88 to 2.7 mg/L and aluminum increased from 1.9 to 3.0 mg/L. Manganese and zinc showed slight increases from 0.14 to 0.15 and from 0.028 to 0.030 mg/L, respectively. Other tested metals (arsenic, barium, cadmium, chromium, copper, lead, nickel, and silver) either remained relatively constant or were below detection limits.

Immediately below the drainage from the Pass-Me-By mine, acidic inflows from Sheepshead Creek (tributaries K and L) enter Iron Creek. In the headwaters of tributary L the water was slightly acidic (pH 5.1), but had very low conductivity (8 µS/cm). Degradation of Sheepshead Creek resulted from NOAMS, some of which form seep areas adjacent to and above the creek and others that issue directly into the stream bed. The "No Name" adit described by Calkin (1967) had a prominent accumulation of iron precipitate within it. This adit was dry when visited, but it may contribute to the degradation of Sheepshead Creek if and when it discharges water.

Numerous NOAMS occur along Iron Creek between Sheepshead Creek and the Alamosa River, with nearly all being east of the creek along the base of Lookout Mountain. South of the Forest Road 380 crossing there are sections where tiny seeps issue from the east channel wall for hundreds of feet. The impressive Lower Iron NOAM spring, was discovered on the east bank about midway between the Alamosa River and Forest Road 380. Immediately above the Alamosa River Iron Creek had a pH of 3.4 with conductivity of 284 µS/cm. The Alamosa River looked healthy above Iron Creek, but it was obviously impacted by the inflow from Iron Creek. A conspicuous mixing zone was observed immediately below the confluence, with bright reddish orange precipitate dropping out along the north bank, but promptly evolving to a creamy orange and white precipitate a short distance downstream.

Alum Creek

Much of Alum Creek watershed is underlain by pyrite-rich altered bedrock that rapidly weathers to a gravelly, clayey soil which is generally unvegetated, highly erodible, and readily mobilized during debris flows. A few small mines and prospects were found within the watershed of Alum Creek, and exploration drilling also has been conducted within the watershed. No definitive evidence of mining-related water quality degradation was observed therein. Degraded water in Alum Creek appears to largely result from natural processes, although mineral exploration efforts might arguably have contributed in a minor way to the problem. Because Alum Creek is a very active debris flow basin, it is capable of depositing large quantities of pyritic soils to the river during intense thunderstorms.

As shown on Figure 3, the mainstem of Alum Creek heads in the saddle north of Lookout Mountain. In its headwaters the mainstem contained fairly good quality water based on our pH and conductivity tests. The headwater flow in tributary A, however, initiated at a spring that issued from a prominent ledge of ferrocrete where pH 3.2 water with conductivity of 650 µS/cm seeped to the surface. Similarly, the headwater flow of tributary B, which heads in the saddle west of Little Red Mountain, started at a NOAM spring that discharged pH 2.6 water with conductivity of 1650 µS/cm. A fairly clean, pH 5.7 seep with conductivity of 31 µS/cm comprised the headwater flow in tributary C, but it was degraded by a series of NOAMS downstream. Headwater flow in tributaries D and E also began at NOAMS.

Mainstem Alum Creek initiated as fairly clean water, but became degraded as it passed across the unvegetated outcrop of weathered, altered bedrock and by the inflows from tributaries A, B, C, D, and E. Based on our field tests, the most degraded water within the Alamosa basin was associated with a series of NOAMS located on the west bank of Alum Creek below the inflow from tributary C. These seeps, which ranged in pH from 1.4 to 2.2 and in conductivity from 2950 to 6410 µS/cm, may issue from a fault zone mapped by Lipman (1974) and AMOCO (1982). This segment of Alum Creek was severely eroded during a debris flow event in 1994, subsequent to which the distribution and character of the NOAMS were altered. Alum Creek received additional inflows from NOAMS as its passed through the remaining altered rock areas, and at its confluence with the river had a pH of 2.8 and conductivity of 1550 µS/cm.

Analyses of the water in lower Alum Creek have been reported by Moran and Wentz (1974), Kirkham and Holm (1989), USF&WS and USEPA (1994), and Miller and McHugh (1994). These studies report that Alum Creek generally contains the highest metal concentrations and metal loadings of any of the tributaries discussed herein.

Bitter Creek

The primary tributaries of Bitter Creek, extent of the watershed, and locations of nearby draining mines and NOAMS that were sampled are indicated on Figure 4. Several small prospect pits and adits, along with the Blue Bell shaft described by Patton (1917), were found within this watershed. None of the observed mine features in Bitter Creek appear to contribute to the degraded water found in this watershed. Most of the water quality problems in Bitter Creek apparently relate to inflows from tributaries I, H, and D, and to NOAMS occurring along the mainstem in the lower half of the basin.

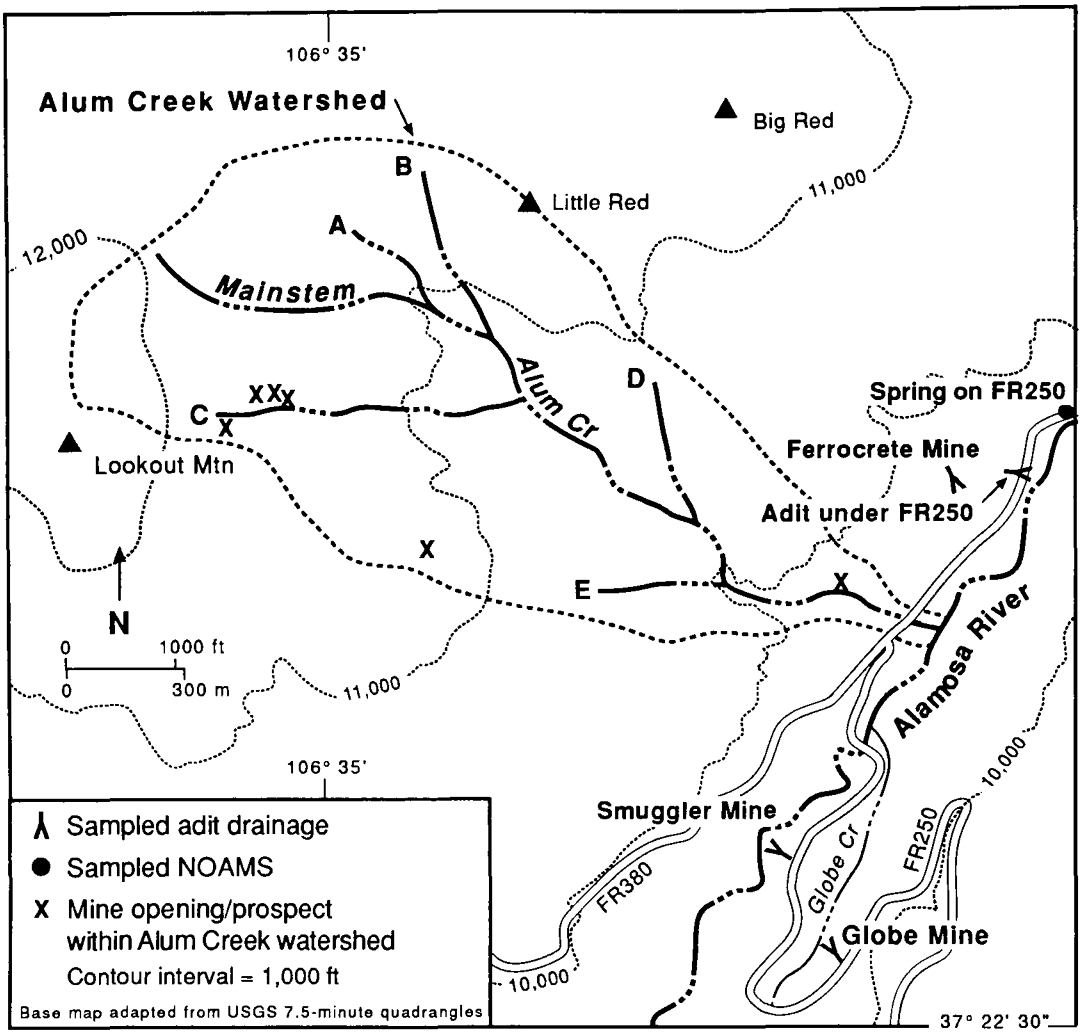


Figure 3. Map showing outline of Alum Creek watershed. Tributaries with surface flow that were investigated during this study are highlighted and labeled. Draining mines and NOAMS in or near the watershed that were sampled are labeled. Mine openings within the watershed are indicated by "X".

Water within tributary A and in the mainstem above tributary B had low conductivity and only a slightly depressed pH. The first poor quality inflow (pH 3.6; conductivity 258 µS/cm) to the watershed occurred at tributary B. Several very small prospect adits were noted in tributary B, including one adit where the ground was damp in front of its collapsed portal, and a group of four shallow adits (deepest was about 10 feet deep), the lowermost of which contained standing water. This portion of tributary B consists of outcrops of unvegetated, weathered, altered bedrock from which a nearly continuous series of acidic seeps issue along a subhorizontal alignment. A large seep herein referred to as the Bitter NOAM spring occurred about 30 feet below the group of four small adits. A water sample collected from this spring during 1994 contained the lowest metal concentrations of all sampled NOAMS.

Small NOAMS along the mainstem between tributaries B and C provided additional inflows of acidic water. The northerly fork in the headwaters of tributary C contained pH 4.2 water with conductivity of 143 µS/cm, while in the southerly fork the water had a pH of 4.7 and conductivity of only 47 µS/cm. Several NOAMS are present along both sides of tributary C above its confluence with the mainstem, and the quality of the tributary worsened with each natural acidic inflow. One of the NOAMS on tributary C has a large ferrosinter mound that occurs just above the mainstem confluence and extends uphill about 100 feet from the creek. An estimated 2 gpm of pH 3.5 water with conductivity of 415 µS/cm issued from this spring. Below the inflow from tributary C, the mainstem had a pH of 4.0 and conductivity of 168 µS/cm.

Tributary D was discharging about 2 gpm of pH 4.4 water with conductivity of 49 µS/cm, while tributary E

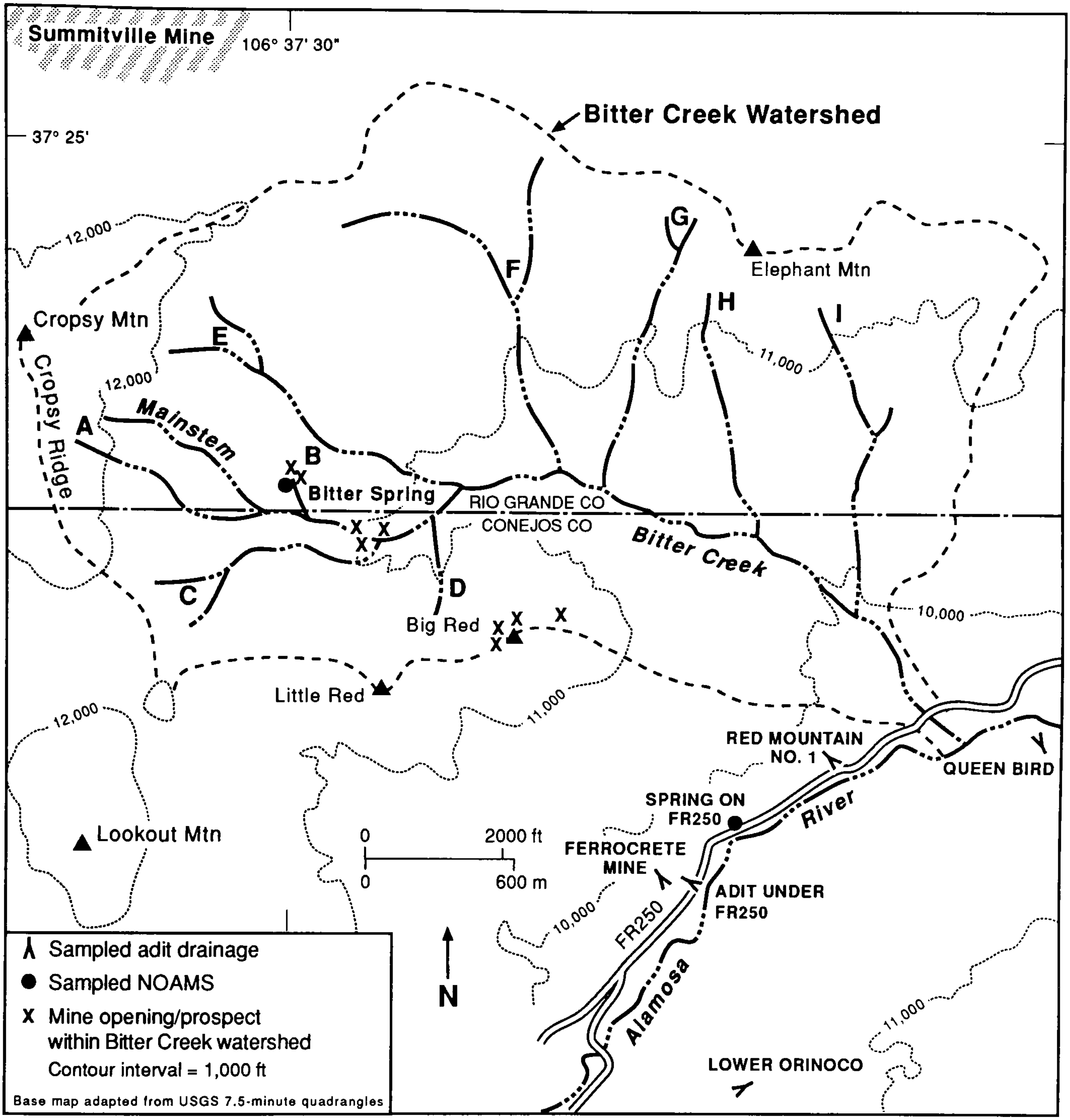


Figure 4. Map showing outline of Bitter Creek watershed. Tributaries with surface flow that were investigated during this study are highlighted and labeled. Draining mines and NOAMS in or near the watershed that were sampled are labeled. Mine openings within the watershed are indicated by "X".

issued about 5 gpm of water with a pH 5.4 and conductivity of 53 µS/cm, both of which caused little effect on the mainstem. A few small NOAMS issued into the mainstem between tributaries E and F, but the tributaries were fairly low in conductivity and had only slightly depressed pH. The inflow from tributary F improved the pH and conductivity of the mainstem. NOAMS with pH of 3.2 to 3.3 and conductivities of 420 to 594 µS/cm formed the headwater flow in tributary G, but the quality of water in tributary G was similar to that in the mainstem at their confluence. Several NOAMS were noted along the mainstem between tributaries G and H.

Headwater flow in tributary H initiated at a series of NOAMS having pH from 2.5 to 2.6 and conductivity from 894 to 953 µS/cm. Other NOAMS occurred along tributary H, and its quality remained poor to the mainstem confluence. Below tributary H the pH of the mainstem was 3.7 and conductivity was 286 µS/cm. Headwater flow in tributary I began at springs with near neutral pH (6.2) and low to moderate conductivity (31 to 66 µS/cm), but several very acidic NOAMS (pH 2.1 to 2.5) occurred along tributary I, causing the stream to degrade. At its confluence with the mainstem, tributary I had a pH of 3.2 and conductivity of nearly 1000 µS/cm, which caused the pH of the mainstem to drop slightly (3.63 to 3.49) and the conductivity to increase abruptly from 296 to 412 µS/cm. The pH and conductivity of Bitter Creek remained fairly constant to the Alamosa River.

Burnt Creek

An outline of the Burnt Creek watershed and its various relevant features is shown in Figure 5. The entire watershed, except for a very small area on Marble Mountain, is underlain by hydrothermally altered rock (Lipman, 1974). Both natural and mining-related sources degrade the water within Burnt Creek. Burnt Gulch frequently experiences debris flow activity in which pyritic soils are mobilized during thunderstorms. Although 35 field tests were performed in Burnt Creek, it was not investigated with the same thoroughness as the other three watersheds. The stream segment between the two waterfalls shown on Figure 5 was not inventoried because traversing the falls required technical rock climbing. Tributaries C and D were tested only at their confluence with the mainstem.

Surface flow in the uppermost headwaters of the mainstem had a pH of 6.4 and conductivity of 166 µS/cm, and its banks were well vegetated and tree lined. Headwater flow in tributary A, however, initiated at a NOAM spring discharging pH 3.6 water with conductivity of 1562 µS/cm that is located in an unvegetated outcrop of weathered altered rock. Below the confluence with tributary A the mainstem had a pH of 4.2 and conductivity of 523 µS/cm. A greenish cream colored precipitate was present on the rocks below the water level, while white precipitate occurred on rocks above water level. Several small, but very acidic NOAMS issued into the mainstem between tributaries A and B, and the pH and conductivity of the mainstem reflected these acidic inflows. Immediately below one of the NOAMS in this reach the precipitate in the mainstem turned bright reddish orange and minor ferroconglomerate was present.

A headwater spring in tributary B had a pH of 6.0 and conductivity of 212 µS/cm. The spring water infiltrated back into the ground a short distance downstream, but resurfaced just above the mainstem, at which point it had a pH of 5.6 and conductivity of 895 µS/cm. The field parameters for the mainstem actually improved as a result of the inflow from tributary B, but moderately thick, reddish orange precipitate abruptly developed below the confluence. Very unusual precipitate patterns were present along the mainstem below tributary B. At one location the creek splits into two branches as it spills over a small rock outcrop. The western branch had reddish orange precipitate in it, whereas the eastern branch had a greenish cream-colored precipitate. Below another acidic inflow the precipitate was creamy orange, while at other locations only white precipitate was present.

Water in the mouth of tributary C had a pH of 3.7 and conductivity of 1015 µS/cm, but time did not allow for thorough examination of this tributary, which contains bare outcrops of altered rock. Neither Patton (1917) nor Lipman (1974) indicate any mine features within this tributary, so its degraded water is probably the result of natural processes. Another prominent deposit of reddish orange precipitate developed in the mainstem below the inflow from tributary C. Several acidic inflows from NOAMS further degrade the mainstem between tributary C and the upper impassable waterfall, where a large boulder jammed between the narrow canyon walls creates a fall about 50 feet high. Lower Burnt Creek was investigated by following the creek upstream from Jasper to where the lower impassable waterfall was encountered. The inventory work in the upper and lower reaches were separated in time by about five weeks and the discharge rates of the creek had changed by about an order of magnitude, so the data collected during the two different time periods are not directly comparable.

About 600 feet below the lower falls is a striking ferrosinter mound formed at the Burnt NOAM spring. When sampled on August 31 the spring had a pH of 3.8 and conductivity of 2040 µS/cm, while on July 9 its pH was 3.2 and conductivity was 2340 µS/cm. The NOAM spring consisted of water with very low dissolved oxygen content that issued from a sub-horizontal fracture in altered bedrock about 75 feet above stream level. Mineral precipitate developed a locally overhanging mound of ferrosinter that included numerous tiny terracettes retaining little pools of water. The rim of each terracette was a light brown color, and the pool floor was a deep, dark reddish brown. Various colored mineral precipitates had formed on rocks in different portions of the mound. This spring contained high concentrations of iron, aluminum, and manganese (Table 1), and it had the highest metal loading for manganese and zinc and the second highest iron loadings of all sampled NOAMS, draining mines, and dump seeps in the study area.

Tributary D enters Burnt Creek about 500 feet below Burnt spring. It had a pH of 3.9 and conductivity of 1950 µS/cm when tested in July, and a huge mound of soft, reddish orange precipitate occurred at its mouth. A cursory examination of the lower few hundred feet of the tributary did not reveal the source of the water. Tributary

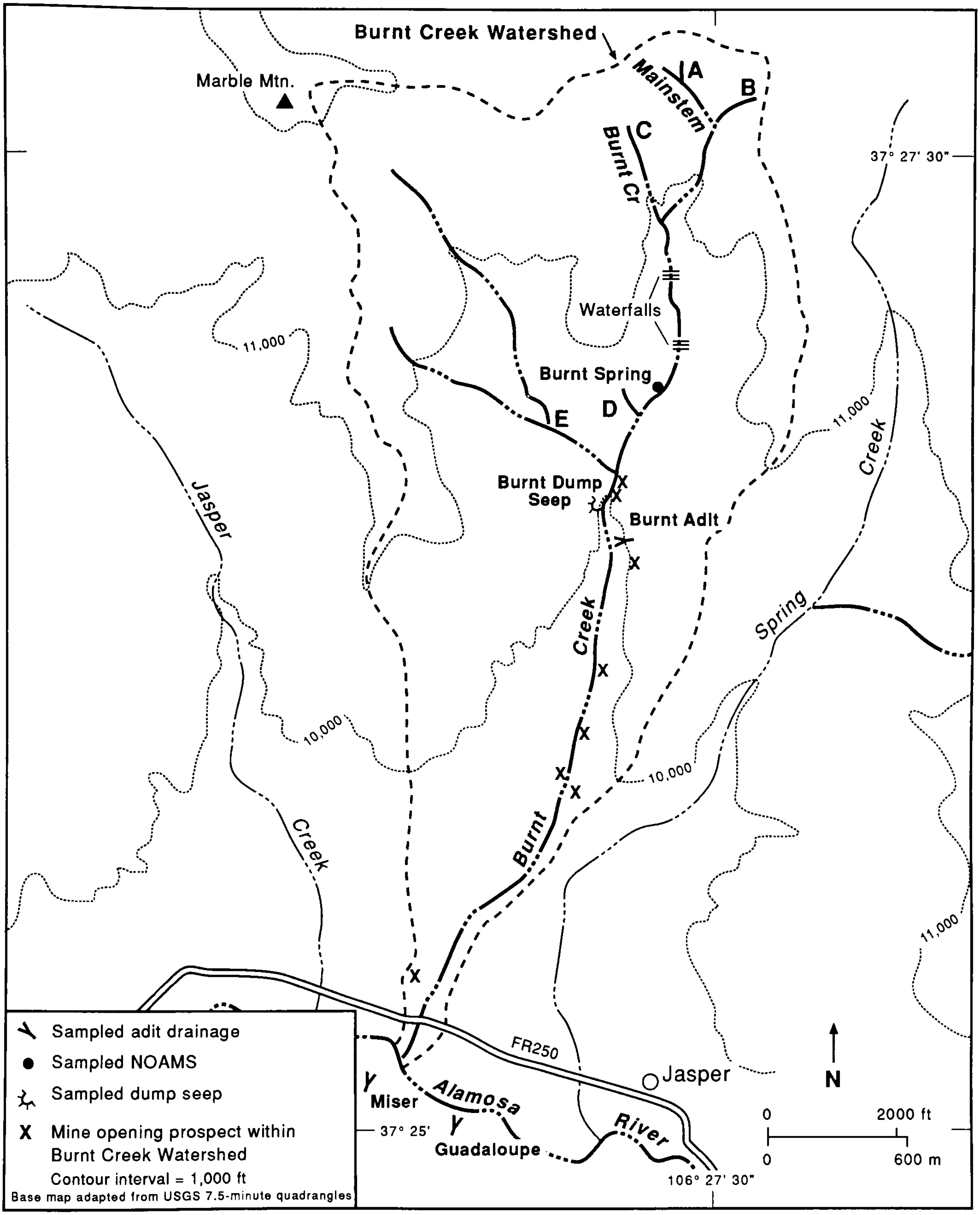


Figure 5. Map showing outline of Burnt Creek watershed. Tributaries with surface flow that were investigated during this study are highlighted and labeled. Draining mines and NOAMS in or near the watershed that were sampled are labeled. Other mine openings within the watershed are indicated by "X".

D should be thoroughly explored to determine whether mining contributes to the degradation, although neither Lipman or Patton report any mines within it. A short distance below tributary D a NOAM spring whose field parameters were similar to those of Burnt spring discharged into Burnt Creek. The creek had a pH of 3.7 and conductivity of 1617 µS/cm below this point. Tributary E drains a well vegetated basin, which was reflected by its pH of 5.8 and conductivity of 272 µS/cm.

The uppermost known mine features in Burnt Creek lie immediately downstream of tributary E. The Burnt dump seep issued from a moderate-sized mine dump (volume estimated at 4,000 cy) on a terrace several feet above stream level. The dump seep had an average pH of about 5.0 and conductivity of up to 589 µS/cm. It contained appreciable concentrations of aluminum (2.0 mg/L) and manganese (0.2 mg/L), but metal loadings are relatively insignificant compared to that of Burnt NOAM spring (Table 1). Burnt adit, which drained acidic (pH 3.1 to 3.3) water with high conductivity (649 to 1228 µS/cm), is just downstream from the dump seep. When visited in July it was discharging an estimated 1 gpm and did surface flow to the creek, but when sampled on August 31 most of the flow infiltrated into the hillslope below the portal and was not measurable. Drainage from Burnt adit contained 5 mg/L of iron, 5 mg/L of aluminum, 0.5 mg/L of manganese, 0.1 mg/L of copper, and 0.06 mg/L of zinc, but its metal loadings are very low due to its very low discharge rate. Other mines are present along Burnt Creek below Burnt adit, but none appeared to contribute to the degradation of the creek. However, the NOAMS present within this reach were sources of contamination.

As Burnt Creek leaves its bedrock canyon and flows over the debris fan above Jasper, it promptly infiltrates into the unconsolidated fan alluvium. In July the creek was flowing up to an estimated 150 gpm within the bedrock canyon, but at only 30 gpm about 500 feet below the fan head. The creek was dry only 1000 feet below the fan head and where it crosses Forest Road 250. Burnt Creek does have surface flow to the Alamosa River during spring runoff and during heavy summer thunderstorms, such as on August 31, 1993 when it had a pH of 4.2 and conductivity 628 µS/cm at Forest Road 250.

Ideally, degraded Burnt Creek water that infiltrates into the debris fan deposits should improve in quality as it travels through the material before reaching the Alamosa River alluvial aquifer. Hamilton (1989) reports that poor quality water has been produced from bedrock in Jasper, and local well drillers have described similar problems. An investigation of ground water chemistry in the Jasper area would make an interesting study that might resolve whether Burnt Creek plays a substantial role year around in the degradation of Alamosa River water quality and assess the long-term ability of earthen materials to remediate metal contamination in the subsurface.

Jasper Creek

Where it crosses Forest Road 250 Jasper Creek typically contains water with a pH of 6 to 7. Several small mines and prospects occur within this watershed, but none were draining degraded water. Naturally degraded, low pH water enters the mainstem of Jasper Creek from tributaries on the east side of the mainstem that flow over intensely hydrothermally altered rock.

Unnamed Tributaries

Acidic water within the unnamed tributary on the south flank of Lookout Mountain between the watersheds of Iron and Alum Creeks is degraded solely by natural processes. Debris flows carrying pyritic soils occur frequently in this tributary. The valley that heads on the south side of the saddle between Little Red and Big Red Mountains was dry when visited in 1993, but likely contains naturally acidic water when it does flow in its headwaters. During August 1993 the headwater surface flow in this tributary resulted from drainage at the Ferrocrete adit.

IN-STREAM WATER QUALITY

Figure 6 depicts the iron, aluminum, manganese, copper, and zinc loadings in each of the four watersheds at their confluence with the Alamosa River based on the July 8, 1993 sampling by the USF&WS and USEPA (1994) and also the mining-related sources sampled during August for this study. The portion labeled "Mining Above WTMN" represents the loadings calculated in this study for mines located in the basin above the confluence with Wightman Fork, while that labeled "Total Mining" indicates the loadings due to all sampled mines within the basin, except for Summitville. Note that the mines upstream from the Wightman Fork confluence are responsible for most of the iron and aluminum loadings resulting from mining, but the mines below Wightman add appreciably to the manganese and zinc loadings. The two sets of mining data illustrate the maximum possible loadings due to mining sources at the time of sampling.

Wightman Fork contributed higher loadings for the five metals than did the total mining sources or the three upstream tributaries during July, although during the October, 1993 sampling Alum Creek was higher for iron and aluminum. Loadings for the five metals were greater in each of Iron, Alum, and Bitter Creeks than was the total for all sampled mining sources. Alum Creek had higher loadings for all five metals than did Iron or Bitter Creeks.

To evaluate the relative inputs from natural versus mining sources in Iron Creek a comparison between the loadings from the two sampled NOAMS with drainage from the Pass-Me-By mine can be made (see Table 1).

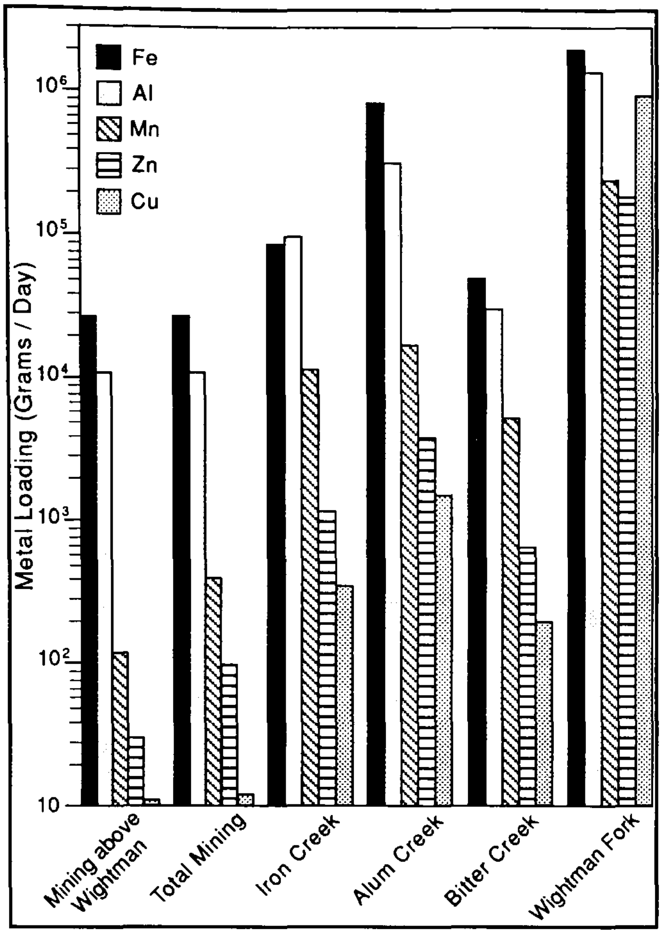
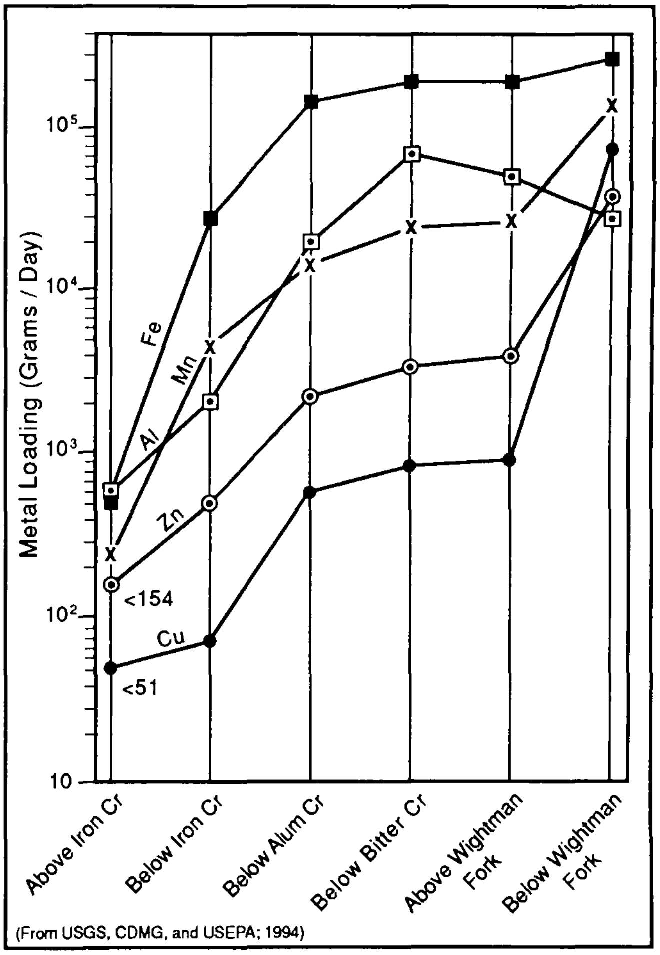


Figure 6. Dissolved metal loadings from mining sources and tributary streams (data on mine loadings from this study; data on tributaries from July 8, 1993 sampling by USF&WS and USEPA, 1994). Columns labeled "Mining above Wightman" represents the loadings from all sampled mine drainage in the upper Alamosa River basin above the confluence with Wightman Fork. Columns labeled "Total Mining" indicate loadings due to all sampled mine drainage in the basin.

The mine contributes appreciably more iron and aluminum to Iron Creek than does either spring; it even exceeds the combined loadings from both NOAMS for these metals. The Pass-Me-By mine provides about an equal amount of zinc as do the two NOAMS, but the NOAMS are responsible for greater manganese and copper loadings. If one assumes that all of the dissolved metal contained in the drainage from the Pass-Me-By mine enters Iron Creek and remains in solution until the creek reaches the Alamosa River, then the mine could account for up to 21 to 31% of the dissolved iron and 8 to 13% of the dissolved aluminum in the creek at its mouth, based on the July and October data in USF&WS and USEPA (1994). Significantly less of the other dissolved metals at the mouth of Iron Creek are due to the Pass-Me-By mine.

Figure 7 graphically illustrates the dissolved iron, aluminum, manganese, copper, and zinc loadings in the Alamosa River on August 10 and 11, 1993 at various locations (data from USGS, CDMG, and USEPA, 1994). Above Iron Creek all loadings were fairly low. Below Iron Creek, which is affected by both mining and natural sources, the loadings for iron, aluminum, and manganese jumped, and zinc also showed a moderate increase. Loadings for all five metals rose sharply below the inflow from Alum Creek, a naturally degraded stream. Moderate increases in metal loadings occurred in the reach where Bitter Creek entered the river, but metal loadings remained fairly constant in the reach between Bitter and Wightman. Copper, zinc, and manganese loadings dramatically rose below the inflow from Wightman Fork, iron increased somewhat, and aluminum dropped.

A conservative quantitative evaluation of the contributive effect of mining to the degradation of the Alamosa River above its confluence with Wightman Fork can be made by comparing the loadings from the draining



(From USGS, CDMG, and USEPA; 1994)

Figure 7. Dissolved metal loadings in the Alamosa River on August 10 and 11, 1993 (from USGS, CDMG, and USEPA, 1994).

mines as determined through our data with the August 1993 sampling of the river above Wightman Fork by USGS, CDMG, and USEPA (1994). Assuming that all of the dissolved metals in the draining mines is entirely resultant from mining-related degradation and that it eventually reaches the river and remains in solution, then the abandoned mines could be responsible for nearly 11% of the iron and almost 18% of the aluminum, but only around 1% of the copper, manganese, and zinc in the Alamosa River above its confluence with Wightman Fork. This comparison is highly conservative and represents the maximum possible contribution of the mining sources at the time of our sampling because 1) at least part and perhaps much of the dissolved metal contained in the draining mines may result from naturally degraded water that was intercepted by the mine workings, 2) dissolved metals, especially iron and aluminum, tend to precipitate seasonally as the water flows through the basin, and 3) drainage from several mines infiltrate into the ground before reaching a live stream and may be remediated while passing through the soil. For total metal loadings the relative contribution from mining is even less, because the mine dumps are generally stable and add little to the sediment load, especially when compared to the erosion that affects outcrops of weathered, altered bedrock.

SUMMARY

The Alamosa River Basin is affected by both natural and mining-related sources of acidity and metals outside of the Summitville mining area. Iron, Alum, Bitter, and Burnt Creeks, along with two unnamed creeks, provide inflows which degrade water quality in the Alamosa River. Mine drainage is responsible for a moderate amount of the iron and aluminum in Iron Creek and for a small part of the contamination in Burnt Creek. Mine drainage also formed the headwater flow in one of the unnamed tributaries. However, no unequivocal evidence of mining-related sources was discovered in either Alum or Bitter Creek. A very minor portion of the degradation in Alum Creek may arguably be attributed to the exploration drilling conducted therein. Alum Creek and others are capable of depositing large amounts of pyritic soils in the Alamosa River during debris flows triggered by intense thunderstorms. Much of the dissolved iron and aluminum and virtually all of the manganese, copper, and zinc in the Alamosa River above its confluence with Wightman Fork apparently results from natural processes. Wightman Fork is the primary source of dissolved copper and zinc loadings to the Alamosa River. It also contributes a major amount of manganese loading and a smaller percentage of the iron and aluminum loadings.

ACKNOWLEDGEMENTS

We thank the U.S. Forest Service, particularly Vern Schmitt, for financial and professional support which enabled this investigation to be undertaken. Geoff Plumlee, the late Walt Ficklin, and Kathy Smith with the USGS Branch of Geochemistry arranged to have four of our water samples analyzed, collected additional water samples at several locations recommended by us, and made valuable suggestions which improved our investigation. Harry Posey and Jim Pendleton, Colorado Division of Minerals and Geology (CDMG), and Paul Von Guerard, USGS Water Resources Division, facilitated the analysis of several of our samples through the joint USGS/CDMG/EPA investigation of the Alamosa basin. These samples were analyzed by Katie Walton-Day, USGS Water Resources Division, whose promptness and patience are appreciated. Mary Mueller with SLV Analytical Services kindly analyzed water from Bitter Spring and also provided recommendations that aided our study. Geoff Plumlee and Harry Posey also edited this paper.

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CALCULATIONS OF PRE-MINING GEOCHEMICAL BASELINES AT THREE STREAM JUNCTIONS FOR WIGHTMAN FORK AND CROPSY CREEK NEAR SUMMITVILLE, COLORADO

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Remediation of environmental problems associated with the Summitville mining site has raised questions as to what were the pre-mining geochemical baselines of stream waters in the vicinity and downstream from the Summitville site. The presence of fossil iron bogs, particularly along the northeast base of South Mountain, indicates that prior to mining, natural acid drainage was generated by the oxidation of sulfides at Summitville. Thus, geochemical baselines of Wightman Fork and Cropsy Creek prior to mining were likely lower in pH and elevated in metals such as Fe, Al, Cu, and Zn, compared to streams draining unaltered areas within the Wightman Fork drainage basin.

This paper calculates the most likely pre-mining geochemical baselines of stream waters in the Summitville area. Geochemical baselines are calculated by combining chemical modeling of water-rock interactions in the stream channel with mass-balance calculations. The input of surface waters from the mineralized areas in the Wightman Fork drainage basin is determined using chemical data of stream waters collected from similarly mineralized but undisturbed areas in similar physical and geologically equivalent environments to Summitville. The input of stream waters from the unmineralized areas is determined directly by stream waters collected from unmineralized and undisturbed areas within the Wightman Fork drainage basin. The results are compared to amounts and attenuation of dissolved species in stream waters draining the Calico Peak altered area near Rico, Colorado, which is undeveloped and geologically and physically similar to Summitville.

The worst case scenario is determined by assuming chemistry of streams draining the Summitville area prior to mining to be equivalent to streams draining advanced argillic altered areas south of Summitville, such as the Alum Creek drainage. The concentrations of base metals are assumed to have been originally greater at Summitville. The most likely scenario is determined by using water chemistry of streams draining several equivalent mineralized areas in Colorado and the literature. The geochemical baselines prior to mining were calculated for stream waters at: (1) Cropsy Creek at the junction with Wightman Fork; (2) Wightman Fork above the junction with Cropsy Creek; and (3) Wightman Fork at the junction with the Alamosa River. The geochemical baseline was determined for pH, Fe, Al, SO_4, Cu, Zn, and conductivity. The details and results of the calculations are shown in a USGS Open-File Report, in press.

REMOTE MINERAL MAPPING USING AVIRIS DATA AT SUMMITVILLE, COLORADO AND THE ADJACENT SAN JUAN MOUNTAINS

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INTRODUCTION

Most naturally occurring and man-made materials absorb and scatter sunlight at specific wavelengths. The spectral information is a measure of how reflected sunlight interacts with a surface. It is these absorptions that produce the colors sensed by the human eye. For instance, absorption by plants produces the green color observed by the human eye. Just as every human has a characteristic thumb-print, each mineral and manufactured material has a unique spectral signature that is related to chemical composition, grain size, degree of crystallinity, or temperature of formation. Subtle differences in the reflectance spectra of minerals can indicate major differences in chemistry or some physical parameters. Spectral information can be gathered from laboratory samples, remotely sensed by aircraft or satellite systems, therefore providing a powerful mapping tool.

Imaging spectroscopy is a new mapping technique and represents a part of the next generation in remote sensing technology. The narrow spectral channels of an imaging spectrometer form a continuous reflectance spectrum of the Earth's surface, which contrasts with the 4 to 7 channels of the previous generation of imaging instruments, for example the Landsat Thematic Mapper (TM) and Multispectral Scanner (MSS) instruments. Systems like Landsat can distinguish general brightness and slope differences in the reflectance spectrum of a surface. However, imaging spectroscopy has the advantage of providing compositional information based on the presence and position of absorption bands, as well as contributing data on brightness and slope.

The system used to collect data for this study is the NASA "Airborne Visible and Infra-Red Imaging Spectrometer" (AVIRIS) instrument. AVIRIS acquires data in the spectral range from 0.4 µm to 2.45 µm in 224 continuous spectral channels. The instrument is flown in an ER-2 aircraft (a modified U-2 spy plane) at 19,800 meters (~65,000 feet). The swath width is approximately 11 kilometers and the swath length can be as great as 1000 kilometers.

The image is composed of many data points, called pixels (614 pixels in a 11 kilometer swath width). Each pixel is a three-dimensional data point consisting of an X-, Y-, and Z- component. Each pixel represents a surface area (the X- and Y-components) approximately 17 meters square and contains information on the chemical and mineralogical character of the material (the Z-, or spectral component). Spectra acquired by remote measurements are interpreted by comparison with laboratory spectra from well characterized samples.

Clark *et al.*, (1990a, 1991) developed a new analysis algorithm that uses a digital spectral library of known reference materials and a fast, modified-least-squares method of determining if a diagnostic spectral feature for a given material is present in the image. This algorithm is called "tricorder." The tricorder analysis compares continuum-removed spectra (Clark and Roush, 1984) from the remotely sensed data, to a database of continuum-removed spectral features from the reference spectral library (Clark et al., 1993). Multiple features from multiple materials are compared and the material with the closest match is mapped. The algorithm does not force a positive match which makes if different from many other algorithms in use. The tricorder algorithm attempts to map only minerals included in the reference database.

IMAGING SPECTROMETER DATA

We have analyzed AVIRIS data for the Summitville mining district and the adjacent San Luis Valley, in Colorado. The data were acquired on September 3, 1993. A combined method of radiative transfer modeling and empirical ground calibration site reflectance were used to correct the flight data to surface reflectance (Clark *et al.*, 1994). This method corrects for variable water vapor in the atmosphere and produces smooth spectra with spectral channel to channel noise approaching the signal to noise of the raw data. Thus, the data can be compared to standard laboratory measurements. The calibration site is a plowed field approximately 18 kilometers SW of Alamosa. The calibration site soil samples were obtained on the day of the overflight and measured on the USGS laboratory spectrometer (Clark *et al*, 1990b). The spectra of the calibration field are spectrally bland and serve as an ideal calibration standard.

TRICORDER ANALYSIS

For the present study we mapped minerals based on the presence of absorption features in the ~0.45 µm to ~1.0 µm, 1.5µm, and 2.2 µm to 2.3 µm wavelength region, which represent the visible and near-infrared portions of the electro magnetic spectrum. In this dataset we looked for 64 different minerals.

Absorption bands in the visible portion of the spectrum (~0.4-0.8µm) are caused by electronic processes including crystal field effects, charge transfer, color-centers, and conduction bands. The absorptions resulting in the visible portion of the spectrum involve elements of the first transition series which have an outer unfilled d-shell in their electronic distribution. The energy levels are determined by the valence state of the element, its coordination number and its site symmetry. Differences in these parameters are manifested in individual diagnostic absorption bands. Absorptions in this wavelength region are commonly associated with the presence of iron in the mineral structure.

Near-infrared radiation (1-2.45 µm, in this study) absorbed by a mineral is converted into molecular vibrational energy. The frequency or wavelength of the absorption depends on the relative masses and geometry of the atoms and the force constants of the bonds. There are two main types of molecular vibrations: stretching and bending. A stretching vibration is a movement along the bond axis which either increases or decreases the interatomic distances. Bending vibrations consist of a change in the angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule, but without movement of the atoms in the group with respect to one another (Silverstein et al., 1981). Only vibrations that result in a change in the dipole-moment of the molecule will be infrared active.

Absorption features in the 2.2 to 2.3-µm region result from a combination of the OH-stretching fundamental with either the AL-O-H bending mode absorbing at approximately 2.2 µm, or Mg-O-H bending mode absorption at 2.3 µm. At high resolution these bands also appear as characteristic multiple, complex absorption features. Based on previous work (King and Clark,1989, Clark et al., 1990b, Clark et al., 1993), it is known that the strength, position and shape of these features is a function of the mineral chemistry.

In this study we searched for 22 minerals with absorption features at wavelengths near or less than 1.0 µm. We successfully mapped 7 of these 22 potential minerals. The minerals we detected include: amorphous iron-hydroxide, ferrihydrite, goethite, hematite, K-jarosite, Na-jarosite, and an Fe-bearing material that spectrally matches the processed sludge removed from the Reynolds Tunnel. Figure 1 shows their distribution at, and near, the Summitville mine. Comparison of spectra of these minerals extracted from the remotely sensed data with our laboratory standards shows no differences. We have detected spectral difference that allow us to discriminate between the amorphous iron-hydroxide and ferrihydrite, based on our laboratory standards, however, it is possible that these two materials are chemically similar. It should be noted that the most reliable method of identifying amorphous iron oxides is mossbauer spectroscopy.

Samples of the processed Reynolds Tunnel sludge, collected at the mine site, were used as laboratory standards to identify this material in the remotely sensed data. In Figure 1, its distribution is depicted in yellow. In this case the algorithm maps solid Fe-bearing material and red-stained water puddles in the mine pit. Several days of rain occurred prior to the day of data acquisition, thus it is likely there was standing water in the pit. Other investigators have reported the occurrence of red-puddles (for example, Black Strap and Son of Black Strap; see Plumlee et al., this volume) in the pit resulting from precipitation or melting snow.

To detect the presence of minerals that have absorption features in the 2.2-2.3 µm wavelength region we used 48 mineral standards. These 48 standards included phyllosilicates, sulphates, carbonates, and cyanide compounds. Of these 48 standard minerals we detected 8 different phases of significant areal extent. Figure 2 shows the distribution of 6 of the 8 mineral phases detected (not shown are muscovite and dickite). Subtle spectral differences allow for the discrimination between K and Na alunites and poorly-crystalline and highly-crystalline kaolinites. The occurrence of Na-montmorillonite is depicted in yellow in this image. However, because of spectral similarities and limitations of the mapping algorithm, some of the material mapped as Na-montmorillonite may be muscovite or sericite. Recent modifications to the mapping algorithm have eliminated this inconsistency.

Spectral data contained in the AVIRIS pixels are very similar to the spectral standards measured in the laboratory. Figure 3 shows the spectrum of a montmorillonite pixel detected near Alum Creek compared to a laboratory spectrum of a standard montmorillonite. Breaks in the spectra of the AVIRIS data occur at the wavelengths where absorptions from atmospheric gases occur. The absorption features in the montmorillonite spectrum from the AVIRIS data are identical to the diagnostic absorption features in the laboratory standard at wavelengths near 2.2 µm. The AVIRIS data shows that the montmorillonite is mixed with an Fe-bearing mineral phase because of an absorption near 0.8 µm (this

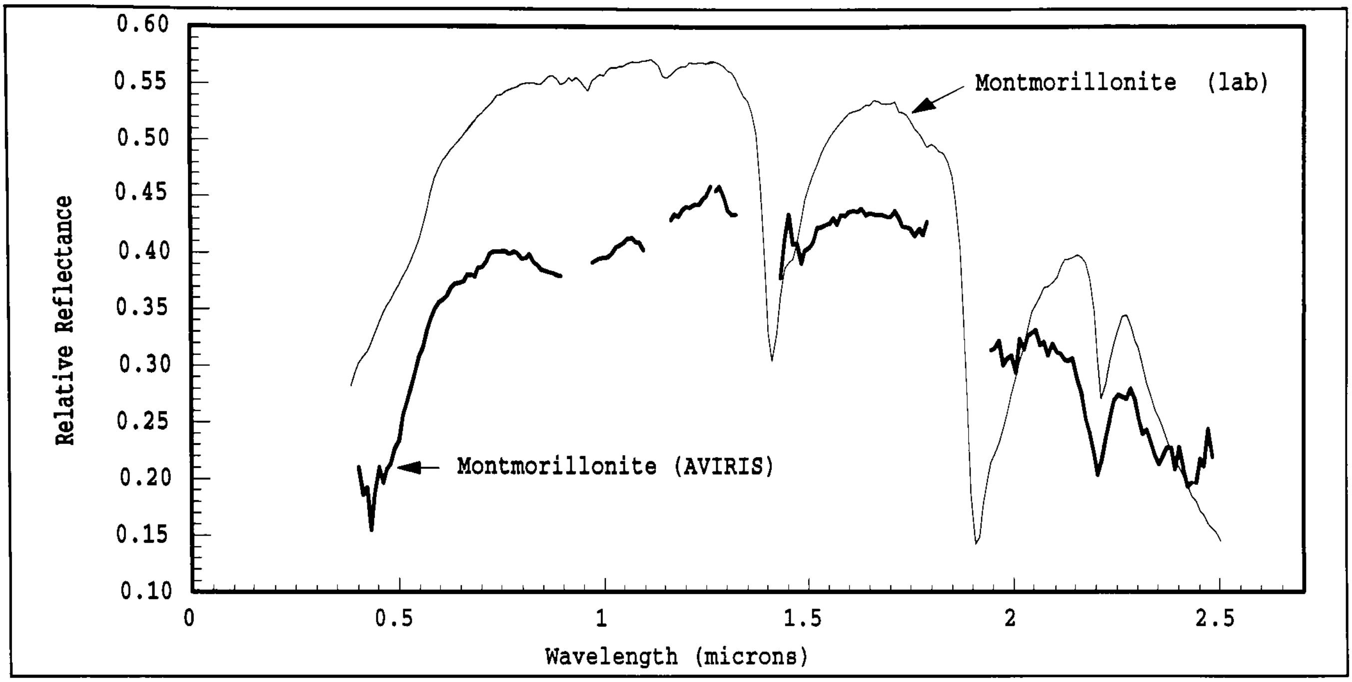

Figure 3. Spectra of montmorillonite measured in the laboratory and montmorillonite detected by AVIRIS near Alum Creek.

absorption feature would be mapped with the Fe-bearing minerals). Similarly, Figure 4 shows the spectrum of a goethite mixed with alunite from the AVIRIS data and laboratory spectra of alunite and goethite. The diagnostic absorption features associated with the alunite occur near 1.5 μm, 1.7 μm, and between 2.1 μm and 2.4 μm, whereas the absorption from goethite is near 0.9 μm.

The mapping of the halloysite or kaolinite-smectite mixtures from the AVIRIS data has been less certain because of inconsistencies in both the spectral data and supporting x-ray analysis. Initially, the areas in red (Figure 2) were mapped as halloysite, based on laboratory standards. However, X-ray data indicated that the material contained kaolinite and other unidentified phases, but did not contain either halloysite or illite (Stephen Huebner, personal communication, 1994). The spectral data of the material (collected in the field) clearly indicates that crystalline kaolinite is not present and that absorption features very similar to illite and halloysite are present. Thus, we believe that the material is likely to be a supergene weathering product, a mineral for which we do not have either spectral or X-ray standards, or a new mineral. Therefore, caution should be applied in interpreting the presently-mapped areal distribution of this phase.

DISCUSSION

Imaging spectroscopy data of the Summitville mine and the Iron, Alum and Bitter Creek basins were used to identify minerals associated with alteration. Hydroxyl-bearing materials, including clays, show discrete distribution patterns at both the mine site and within the Iron, Alum and Bitter Creek basins. Mineralogic differences between the open pit and the heap leach pile at the mine site can be distinguished (Figure 2) and discrete mineralogical boundaries in the Iron, Alum and Bitter Creek basins can also be detected.

Perhaps the most interesting observation is that the Summitville mine apparently does not contribute OH-bearing minerals via the Wightman Fork to the Alamosa River. In contrast the mineralized area in Iron, Alum and Bitter Creek basins do contribute OH-bearing minerals to the Alamosa River. This observation is based on the spectral characteristics of the exposed fluvial sediments along Alum Creek and Bitter Creek and lack of OH-bearing fluvial sediment along the Wightman Fork. The unmined mineralized areas are believed to contribute OH-bearing materials to the Alamosa River due to the porous character of the well-exposed rock, which allows altered materials to be eroded easily and deposited along the

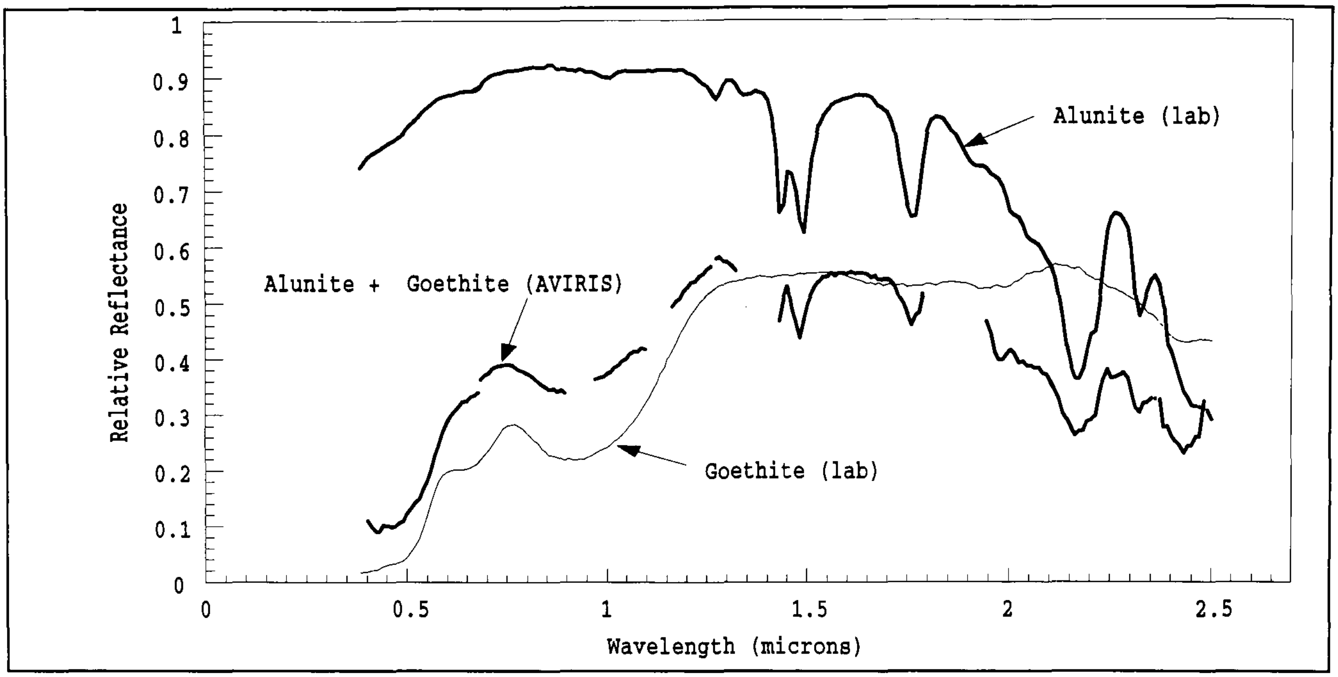

Figure 4. Spectra of alunite and goethite measured in the laboratory and alunite + goethite detected by AVIRIS near Summitville.

stream banks. If hydroxyl-bearing materials, and associated contaminants, are being supplied to the Wightman Fork by the Summitville mine, the material must be carried as a very fine-grained aqueous suspension which cannot settle onto the creek banks.

Images show that both the Summitville mine and Iron, Alum and Bitter Creek basins are sources of iron-bearing sediments to the Alamosa River (Figure 1). These sediments give a reddish-brown color to stream banks, a characteristic typically associated with acid drainage, and are potential carriers of heavy metals to locations downstream. Consequently, in assessing the environmental impact of mining at Summitville, it is an important to recognize that both the Summitville mine site and the Iron, Alum and Bitter Creek basins contribute this type of sediment to the Alamosa River.

SUMMARY

In summary, we have demonstrated the unique utility of imaging spectroscopy in mapping mineral distribution. In the Summitville mining region we have shown that the mine site does not contribute clay minerals to the Alamosa River, but does contribute Fe-bearing minerals. Such minerals have the potential to carry heavy metals. This application illustrates only one specific environmental application of imaging spectroscopy data. For instance, the types of minerals we can map with confidence are those frequently associated with environmental problems related to active and abandoned mine lands. Thus, the potential utility of this technology to the field of environmental science has yet to be fully explored.

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Note: Figures 1 and 2 are on pages 369–370.

INITIAL VEGETATION SPECIES AND SENESCENCE/STRESS INDICATOR MAPPING IN THE SAN LUIS VALLEY, COLORADO USING IMAGING SPECTROMETER DATA

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ABSTRACT

Spectroscopic analysis of Airborne Visual and Infra-Red Imaging Spectrometer (AVIRIS) data is presented to show vegetation species and senescence/stress mapping. AVIRIS data were acquired over the San Luis Valley up to the Summitville abandoned mine in Colorado on September 3, 1993. The data were first corrected to surface reflectance using a combined radiative transfer model plus empirical ground calibration. Reference spectra were extracted from the AVIRIS data set over known crops and in adjacent pasture land. Continuum-removed spectral features from the reference spectra were compared to each spectrum in the AVIRIS data set using a modified least-squares spectral feature matching algorithm. Ground truth data were compared to the resulting identifications and the method proved to be 96% accurate.

A method of analyzing the position of the blue shift of the chlorophyll absorption red edge is presented. Shifts smaller than 1% of the bandwidth of the spectral data can be detected. In the case of AVIRIS, that corresponds to 0.1 nm. The shift was mapped for the data set and numerous fields were found to have varying degrees of shift. Some were in senescence, some had been sprayed with a defoliant, and in others the shift may be caused by lack of water or other nutrients. This analysis shows the AVIRIS instrument wavelengths are stable to better than 0.1 nm over at least one 512 line scene.

INTRODUCTION

Vegetation covers a large portion of the Earth's land surface. Obtaining quantitative information about vegetation with remote sensing has proven difficult. To first order, all vegetation is chemically similar, and most healthy plants are green showing absorption bands that are almost identical. Plant species are generally characterized by the leaf and flower or fruit morphology, not by remote sensing spectral signatures. However, to the human eye, many plants show varying shades of green, so there is direct evidence for spectral differences between plant types. Quantifying these subtle differences in a predictable manner has not been easy, and has been made more difficult by lack of adequate instrumentation.

Imaging spectroscopy is a new mapping tool and the next generation in remote sensing technology. The narrow spectral channels of an imaging spectrometer form a continuous reflectance spectrum of the Earth's surface. That contrasts with the 4 to 7 channels of the previous generation of imaging instruments, like the Landsat Thematic Mapper (TM) and Multispectral Scanner (MSS). While systems like Landsat can distinguish general brightness and slope differences in the reflectance spectrum of the surface, imaging spectroscopy not only does that, but also resolves absorption bands in the spectrum which can be used to identify specific species. Spectroscopic analysis of imaging spectroscopy data allows any material to be mapped, whether mineral, vegetation, manmade, water, snow, or other if it displays unique absorption features in the measured spectral region (e.g. see Clark *et al.*, 1993a, Clark *et al.*, 1992) .

NASA is now flying the "Airborne Visual and Infra-Red Imaging Spectrometer" (AVIRIS) instrument. AVIRIS acquires data in the spectral range from 0.4 to 2.45 μm in 224 spectral channels. The instrument is flown in an ER-2 aircraft (a modified U-2) at 19,800 meters (65,000 feet). The pixel spacing on the ground is ~17 meters, with a 20-meter square pixel, the swath width is about 10.5 kilometers (614 pixels) and the swath length can be up to about 1000 kilometers with the current tape recorder capacity on the aircraft.

Clark *et al.*, (1990a, 1991) developed a new analysis algorithm that uses a digital spectral library of known materials and a fast, modified-least-squares method of determining if a single spectral feature for a given material is present. This algorithm, now called "tricorder," compares continuum-removed spectral features (Clark and Roush, 1984) from the imaging spectrometer data set to corresponding continuum-removed spectral features from a reference spectral library. Multiple features from multiple materials are compared and the closest match is selected. The algorithm does not force a detection like many other algorithms. For example, many algorithms take a set of curves and best fit them to the observed data, often requiring a set of parameters (like mineral fraction) to sum to one. The tricorder algorithm has no such constraint. If the materials do not exist in a given pixel, such that there are no spectral features from those or similar materials, the algorithm produces zeros, indicating they are not detected.

The human eye sees different plant leaves as shades of green, as characterized by the "green peak" in reflectance spectra. The eye/brain color system differentiates shades of green under different lighting conditions. For example, under indoor incandescent light, there is a strong red slope to the spectral signal received by the eye due to the red spectral shape of the light source (as compared to the same plant in direct sunlight). We are still able to distinguish the plant as green and distinguish different plants as various shades of green.

The tricorder algorithm is very sensitive to the shape of spectral features and has the potential to distinguish more subtle differences in the visible spectrum of plants than the human eye. We have applied this method, along with reference spectra of specific plants, to map vegetation species in AVIRIS scenes.

The continuum removal to isolate diagnostic spectral features is an important step, particularly when a pixel contains spectral information from green plants, dry vegetation, and soil. In such a case, the combination of materials within a pixel changes the color perceived by the human eye. However, by isolating absorption features with continuum removal, the position and shape of the continuum removed spectral feature remains constant, although its depth changes with absorber fractional areal coverage in the pixel. The tricorder algorithm normalizes the absorptions so that overall shape is compared.

IMAGING SPECTROMETER DATA

We analyzed AVIRIS data obtained over agricultural areas in the San Luis Valley of Colorado. The data were acquired on September 3, 1993. A combined method of radiative transfer modeling and ground calibration site reflectance were used to correct the flight data to surface reflectance (Clark *et al.*, 1994a). This method, called Radiative Transfer Ground Calibration, or RTGC, corrects for variable water vapor in the atmosphere and produces spectra free of artifacts with spectral channel to channel noise approaching the signal to noise of the raw data. The calibration site soil samples were obtained on the day of the overflight and measured on our laboratory spectrometer (Clark *et al*, 1990b). The site was near the center of the AVIRIS scene and the spectra of the soil is spectrally bland, especially in the region of the chlorophyll absorption in the visible portion of the spectrum.

The center of the scene is located at approximately 106^o 03' longitude, 37^o 23' latitude, and the scene covers about 92 square kilometers. This scene is one of 28 in the area for a general project to study the Summitville abandoned mine site in the mountains above the San Luis Valley and its effects on the surrounding environment.

VEGETATION SPECIES AND REFERENCE SPECTRA

The study area includes farmland producing potatoes, alfalfa, barley, oat hay, canola, and open fields containing chico, and other unidentified weeds. Ideally, one would have a digital spectral library of reference spectra of the plant species to be mapped. Such a library does not exist for vegetation, as it does for minerals (e.g. Clark *et al.*, 1993b). It is not known how many spectra as a function of growing season would be required to represent the changing spectral signatures.

Some plant species were measured with a portable field spectrometer, but due to windy conditions and limited availability of the instrument, sufficient data to form a library of all crops could not be obtained. The main objective of the field operations was to provide spectral information on sites with detailed geochemical analysis. Because of the limitation of obtaining field spectra, reference spectra were obtained for sites of known species directly from the AVIRIS data. AVIRIS, having been well calibrated to surface reflectance, is an excellent field spectrometer, providing data for large areas. The reference spectra obtained from the AVIRIS data set are shown in Figure 1. The alfalfa, canola, oat hay, and nugget potato spectra (Figure 1a) show the plants to be green and healthy. The barley had lost all its chlorophyll signature (Figure 1b). The Norkotah potatoes were not being irrigated as they were about to be harvested, and consequently they showed a weak chlorophyll and cellulose absorptions with soil (clay) absorptions from exposed soil. These potatoes were also being sprayed with a defoliant. Thus, they should show decreased chlorophyll absorption along with a shift of the red edge of the absorption to shorter wavelengths. The chico and pasture spectra show combinations of chlorophyll and cellulose (dry vegetation) absorptions. There was rain in the valley in the few days before the flight so the chico/pasture may not show much water deprivation stress (being native plants they are hardy and can also withstand some reduced precipitation compared to the crops).

TRICORDER ANALYSIS

The continuum-removed chlorophyll-containing spectra are shown in Figure 2. The shape differences between each species enable the tricorder algorithm to discriminate between them. The tricorder algorithm produced maps of the distribution of each material. If there are other plants present in the image with similar spectral features, they could be misidentified as one of those in Figure 1. Thus, it is important to have a complete set of reference spectra. The extensive work by many workers on the Summitville project provided knowledge of the crops in the area, thus our spectral library for this case should be complete for crops. As the time of data acquisition was early fall for this mountain valley (elevation ~7650 feet, 2330 meters), some crops and/or pasture are senescing. The crops are changing spectrally, so this is a difficult test, and it was not known how representative a single reference spectrum for each crop would be. Each crop exists in several fields, each of which may have been in a different stage of senescence.

The tricorder algorithm examines the spectrum of each pixel in the image and chooses the best match to the set of reference spectra. The images from each crop/soil/pasture match were then color coded and a color coded map produced (Figure 3). Results of field checking of crops in the area were used to produce a color coded map of what Figure 3 image might look like if completely correct (Figure 4, "the answer map"). Field verification data was supplied by Maya ter Kuile of Argo Engineering (1993, personal communication), and our own work. Every crop and field could not be checked due to limited resources for the large area.

Examination of Figures 3 and 4 shows the tricorder-derived map to be highly accurate. Of 43 verification fields (not including chico/pasture), 7 included the sites of our reference spectra, 33 were identified correctly, another 3 were identified as mixed by the tricorder analysis (but were indicated as one crop type in the field data), and no fields were incorrect. The fields identified as mixed were of two species, one of which was correct in each case. The field check was done by driving the roads and identifying the crops visually. Because of the time required to develop this analysis (AVIRIS data receipt followed by calibration to surface reflectance in January, 1994, initial mapping in February, 1994), and the fact that it was winter, we were unable to investigate the cause of the discrepancies in the three fields mapped as mixed. If we give a score of half to the three fields identified as mixed, the success score of 96% shows the method is accurate.

The accuracy is made even more impressive when one considers several fields were mapped correctly even though they had already been harvested. There was apparently enough plant material still left on the fields to still make a correct identification. This is again possible because the algorithm normalizes the absorptions, so even though the vegetation cover may be only a few percent, a correct identification can be made. The harvested areas can be identified in Figure 5 in circular plots where the colored pixels are sparse and/or low in intensity. Clark *et al.*, (1992) was also able to differentiate vegetation communities on the arid Colorado Plateau, another sparsely vegetated case. The harvested areas should also be under stress, and are indicated as such in the senescence/stress map (below).

Canola was mapped in many of the areas known to be pasture. While it is possible that canola seeds have been blown into surrounding fields and are growing, it is more likely that the canola spectral signature is close to other (native?) plants in those open fields. Complete discrimination of crops and surrounding wild vegetation requires a more complete set of reference spectra, beyond the scope of this initial study.

SENESCENCE/STRESS MAPPING

The long-wavelength side of the chlorophyll absorption (~0.68 to ~0.73 μm) forms one of the most extreme slopes found in spectra of naturally occurring common materials, plant or mineral (see Figure 1). The absorption is usually very intense, ranging from a reflectance low of less than 5% (near 0.68 μm) to a near infrared reflectance maximum of ~50% or more at ~0.73 μm). The properties of reflectance spectra (e.g. Clark and Roush, 1984) indicate such an absorption band is "saturated." In such a case, the absorption band minimum will not change much with increased or decreased absorption, but the wings of the absorption will change. When the chlorophyll absorption in the plant decreases, the overall width of the absorption band decreases. The short wavelength side of the chlorophyll absorption is not observed in reflectance as is the long wavelength side because of other absorptions in the ultraviolet (UV). The result of this combination appears as a shift to shorter wavelengths as the chlorophyll absorption decreases. This has popularly become known as the "red-edge shift" or the "blue shift of the red edge" and can be caused by natural senescence, water deprivation, or toxic materials (e.g. Collins *et al.*, 1983; Rock *et al.*, 1986).

The ratio of two spectra, one shifted in wavelength, the other not, and each with steep slopes as seen at the "red edge," will produce a spurious feature when there is only a small shift between the two. If the blue shifted spectrum is divided by an unshifted spectrum, a peak will be observed in the ratio. For a spectrum of green vegetation (from Figure 1a), a 1 nm shift will produce a residual feature of about 6%. The AVIRIS data have a signal to noise of several hundred in this spectral region, so red-edge shifts of less than 0.1 nm are possible to detect. We used field spectrometer spectra for the San Luis data set, and computed a ratio cube which would show a peak when a shift occurs.

The red-edge shift was mapped using the tricorder algorithm (Figure 5). The fact that the resulting image shows no horizontal scan line striping attests to the superb wavelength stability of the AVIRIS instrument. As indicated earlier, the senescence/stress crop fields are those which have been harvested, sprayed with a defoliant, deprived of water, or may have other toxic influences. The area covered by this scene is not affected by acid mine drainage from the Summitville mine, thus it provides a control for the region of what might be expected for normal conditions. There is a curious senescence/stress indication along the banks of the stream that enters the image at the top middle of the image to the lower left. (stream flow is to the southeast). The other stream, flowing from the bottom middle of the image to the right middle edge (also flowing to the southeast) shows no similar anomaly. The cause is as yet undetermined.

CONCLUSIONS

Vegetation species mapping is possible with high precision using spectral feature analysis of data from airborne imaging spectrometers. Once calibrated, and after reference spectra have been selected, species mapping, along with senescence/stress indicator mapping can be achieved in less than 1 second of CPU time per square kilometer per species (or soil/mineral) on a 10 million floating point operation per second (MFLOP) workstation.

Imaging spectroscopy data can be used for environmental application, monitoring vegetation cover and its health, monitoring vegetation species, and providing a rapid overview of large areas. When applied to large areas, the cost to derive these maps is low in cost relative to field checking and monitoring on the ground. The species maps might be used for more accurate crop yield predictions.

Space limitations prevent us from presenting the entire AVIRIS data set of the Summitville and San Luis Valley study area in this paper, and processing is not yet complete. Additional areas, including vegetation species and senescence/stress indicator maps for more of the study area will be shown at the meeting.

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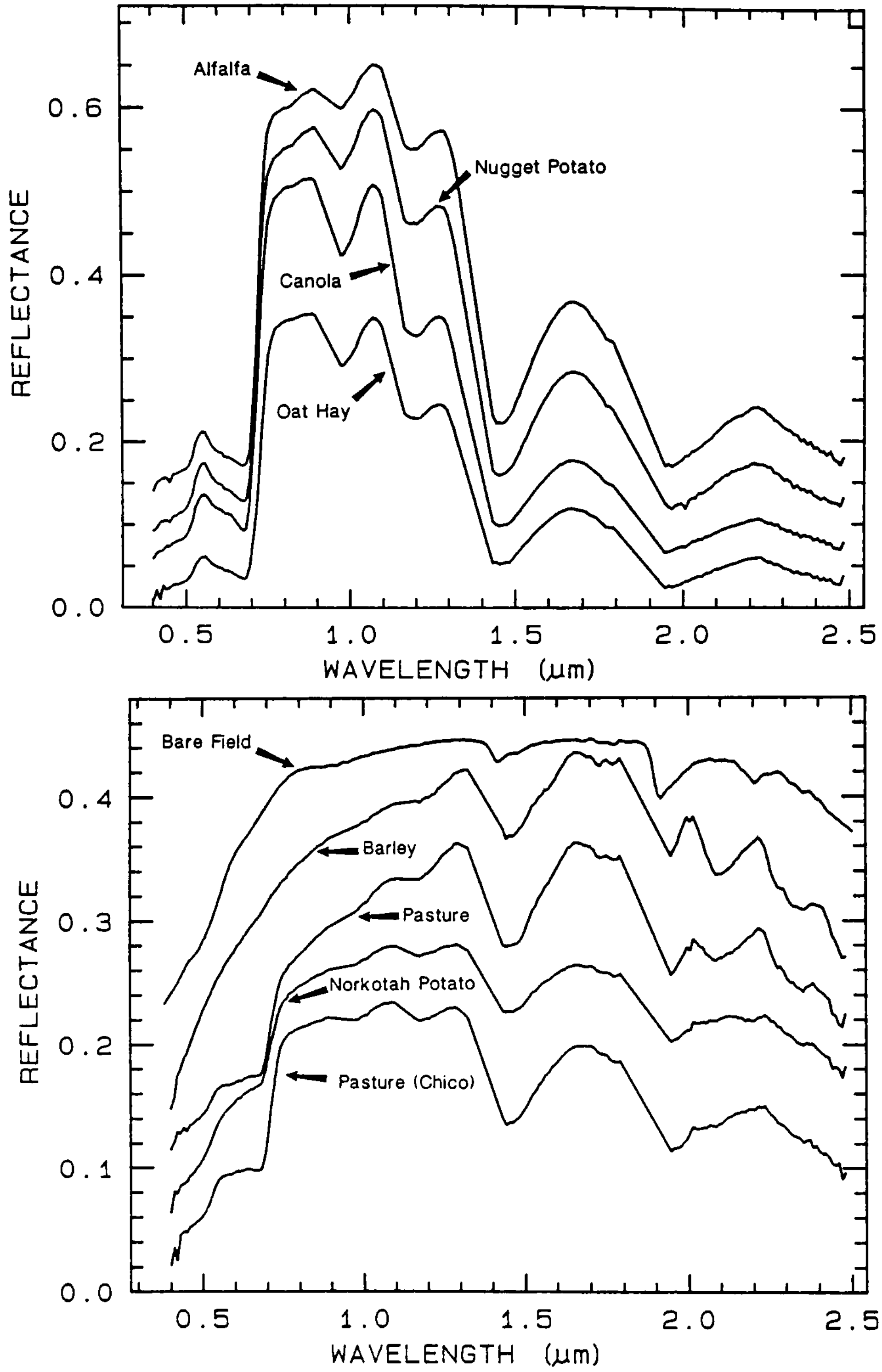

Figure 1. Reference spectra used in the mapping of vegetation species. The field calibration spectrum is from a sample measured on a laboratory spectrometer, all others are averages of several spectra extracted from the AVIRIS data. Note that the noise is extremely low, comparable to the lab spectrum of the field calibration site. In Figure 1a (top), each curve has been offset from the one below it by 0.05. In Figure 1b (bottom), each spectrum has been offset by 0.04 from the one below it, except the top spectrum is offset 0.06. The offsets are cumulative, so the field calibration spectrum is offset a total of 0.18 for clarity.

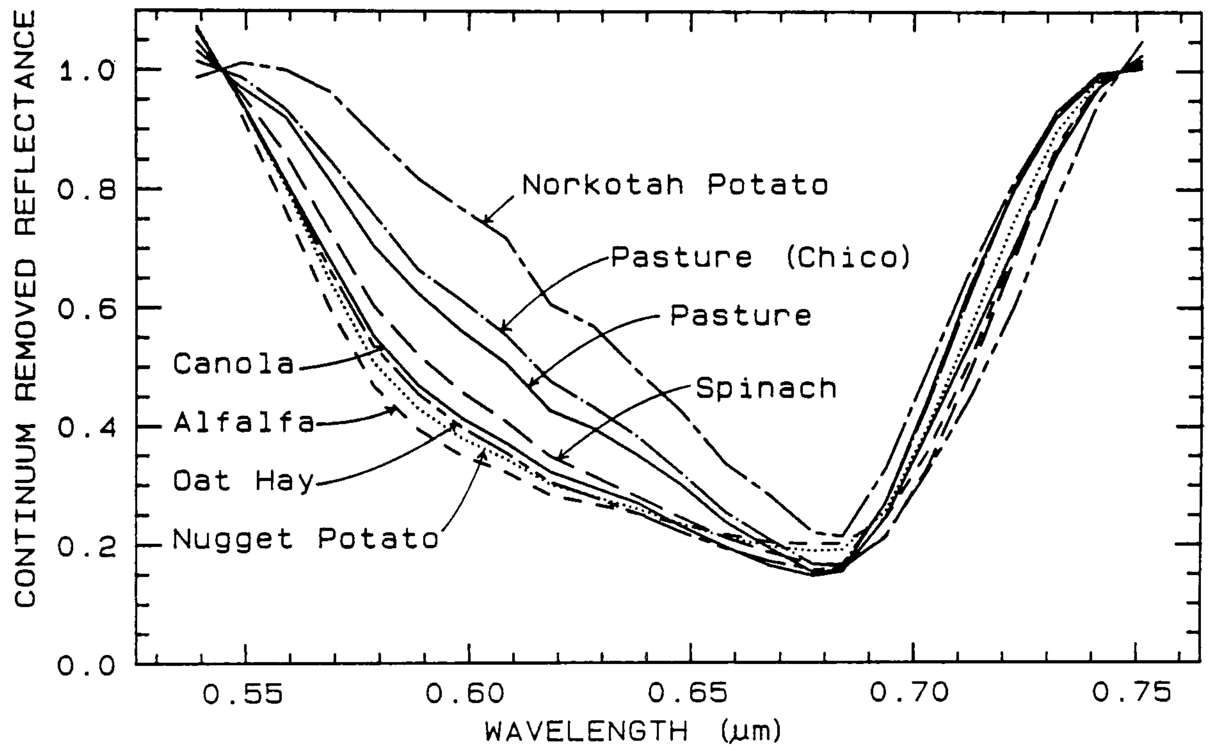

Figure 2. The continuum-removed chlorophyll absorption spectra from Figure 1 are compared. Note the subtle changes in the shapes of the absorption between species.

Note: Figures 3, 4, and 5 are on pages 371–373.

CORRELATION OF ELECTRICAL GEOPHYSICAL DATA WITH LITHOLOGY AND DEGREE OF ALTERATION AT THE SUMMITVILLE MINE SITE

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ABSTRACT

In 1993 the US Geological Survey made 18 Schlumberger dc electrical soundings at the Summitville mine site. Interpretation of the resistivity data indicate that high resistivities (>140 ohm-m) correspond to the quartz-alunite alteration zone, medium resistivities (30-100 ohm-m) are related to argillic alteration and including clay, and that the lowest resistivities (<45 ohm-m) are associated with areas of very poor quality water and/or very high clay content. Field measurements on the Summitville Andesite indicate a small resistivity range (70-140 ohm-m) for the unaltered unit. A geoelectrical cross section across the mine area is markedly different from a cross section across the heap leach pad. The areal extent of high-silica alteration is shown on a resistivity depth map of 30 meters.

INTRODUCTION

In 1993 the U.S. Geological Survey made 18 dc electrical resistivity soundings, using the Schlumberger array, at the Summitville mine site in southern Colorado. The survey area is at an average elevation of about 11800 feet and covered about 1.25 square miles. These soundings were made to determine if surface electrical techniques could delineate structure, alteration zones and ground-water quality. Although the area is mountainous, access was good along mining roads and trails. Sounding expansion was limited to a maximum of 8000' between the current electrodes by the length of available road and the length of wire available. Figure 1 shows the station locations, some mapped geologic features, and generalized topography of the area.

Schlumberger sounding is a dc resistivity

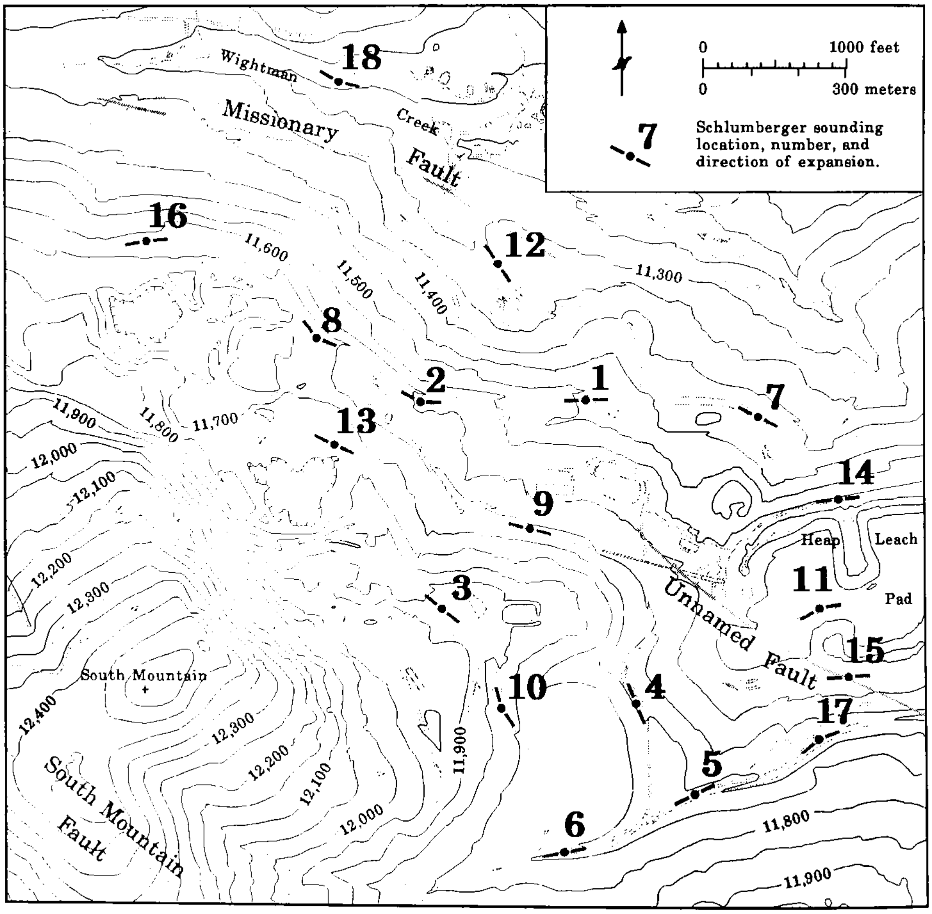

Figure 1. Map showing the location, number, and direction of expansion of the Schlumberger sounding stations. Topographic contours shown at an interval of 50 feet.

geophysical technique that uses variations in the electrical properties of earth materials to help detect buried geologic structures. Dc resistivity (the inverse of conductivity) is a fundamental rock property that varies because of rock type, clay content, porosity and the quantity and quality of the water contained in the rock. Resistivity is normally expressed in ohm-m. In many volcanic areas the resistivity of the rock is primarily dependant on the quality and quantity of water and the amount of clay present in the rock rather than on the actual lithology. For instance, the resistivity of Hawaiian basalts varies from 40000 ohm-m for dry basalts, to 300-500 ohm-m for fresh water saturated basalt, to about 30 ohm-m for salt-water saturated basalt (Zohdy and Jackson, 1969). Generally speaking, unfractured rocks have higher resistivities than fractured/weathered rocks; higher clay content lowers the resistivity of a rock; the poorer the quality (higher TDS and/or chlorides) of the interstitial water the lower the resistivity.

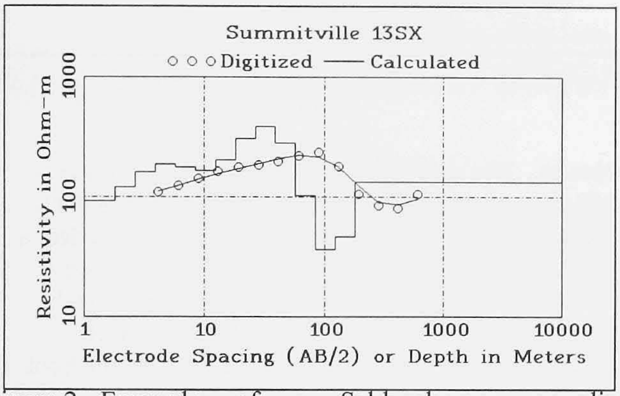

Figure 2. Example of a Schlumberger sounding interpretation.

Schlumberger sounding is a method that uses a symmetric electrode array to vertically explore the subsurface. The name Schlumberger derives from Conrad Schlumberger, an early proponent of the array geometry. Schlumberger soundings are interpreted by computer modeling of the sounding data as a series of horizontal layers (Zohdy, 1989 and Zohdy and Bisdorf, 1989). Figure 2 shows a typical computerized Schlumberger interpretation (sounding 13) of the Summitville data. The circles show digitized observed data points, the stepped line shows the resistivity model, and the smooth line shows a sounding curve calculated from the model. The calculated curve is presented to show how well the model fits the observed data. More detailed explanations of processing and automatic interpretation procedure can be found in Bisdorf (1985) and Zohdy and others (1993). A series of individual soundings can be combined to generate either a geoelectrical cross section or a map view of interpreted resistivity. Cross sections, which can be thought of as vertical slices through the ground, similar to a road cut, are easier to interpret than individual soundings and show lateral as well as vertical variations of resistivity. Maps of interpreted resistivity show areal distributions at a particular depth, which can be thought of as horizontal slices through the earth.

GEOLOGY

The Summitville area consists primarily of Tertiary volcanic rocks. Quartz latite, quartz monzonite, and andesite (Steven, and Ratté, 1960; and Grey and others, 1993) are the primary rock types. The Summitville ore deposit is structurally controlled

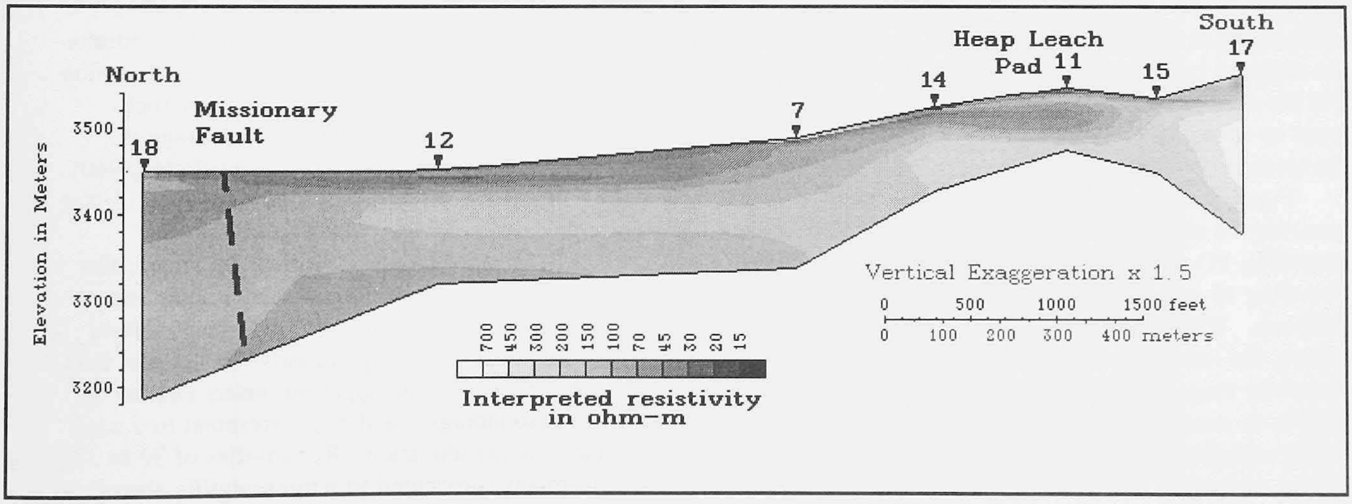

Figure 3. North-south interpreted resistivity cross section (soundings 18-17). Grays represent interpreted resistivities in ohm-m. Sounding locations are indicated by the triangles.

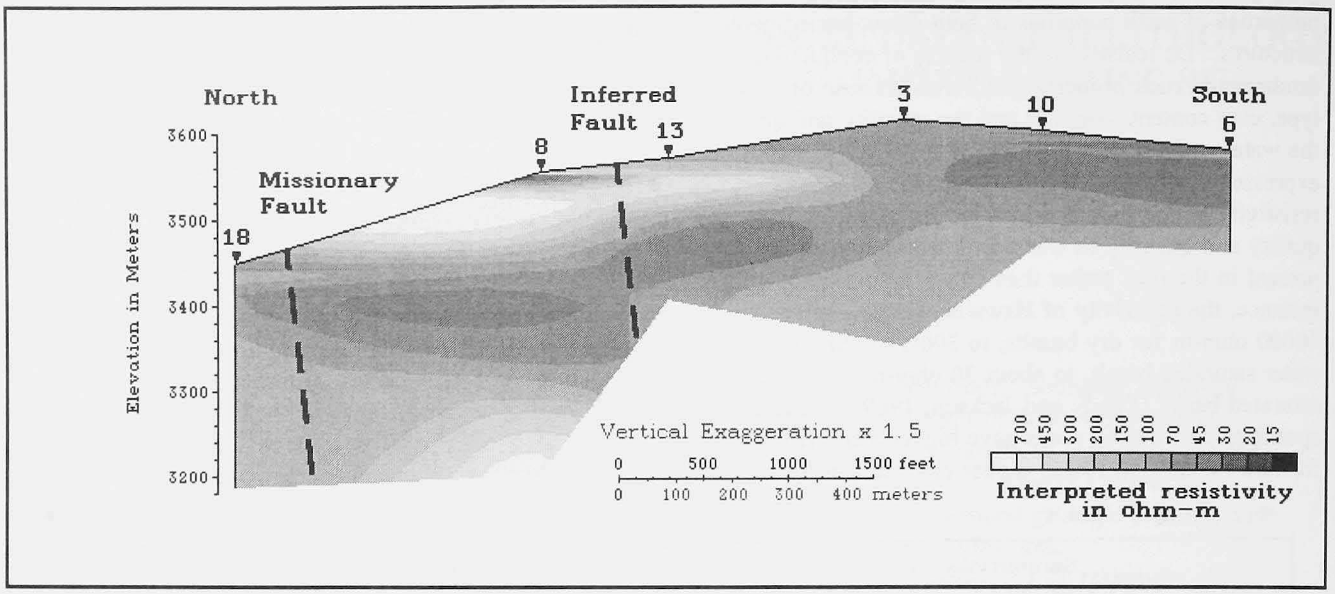

Figure 4. North-south interpreted resistivity cross section (soundings 18-6). Grays represent interpreted resistivities in ohm-m. Sounding locations are indicated by the triangles.

and many of the "veins" strike northwest, parallel to the South Mountain Fault, partially shown on figure 1. Figure 1 also shows the South Mountain Fault, Missionary Fault and an unnamed fault. Parts of the area are highly altered and consist of a quartz-alunite zone, an opalized zone, an argillic zone and a propylitic zone. In the survey area, opalized alteration zones are rare, mostly occurring to the west.

RESISTIVITY CROSS SECTIONS

Resistivity cross sections are generated from individual sounding interpretations. Each sounding interpretation is sampled in a manner to approximate a continuous vertical distribution of resistivity with depth (Bisdorf, 1982). This vertical data is then horizontally interpolated to create a grid. Gray scale or color values are assigned based on the interpolated resistivity values and the desired contour levels. Topographic information, input as sounding elevations, is represented by connecting the surface location of the soundings by straight lines.

Figure 3 shows a cross section that extends from sounding 18 on the north, across the heap leach pad (sounding 11), and ending at sounding 17 on the south. Sounding 18 is located over predominantly Summitville Andesite. With the exception of the weathered upper 10 meters, the interpretation of sounding 18 shows a resistivity range for the Summitville Andesite of 70 to 140 ohm-m as seen in the cross section as two shades of gray. Under soundings 12 and 7 the resistivity is somewhat higher, indicating that this material is slightly different, but not significantly so, than that under sounding 18. This layer becomes more resistive and higher in elevation until under sounding 17 it has a resistivity of greater than 150 ohm-m. The change in elevation of the top of the > 150 ohm-m contour between soundings 7-14 and 11-15, could be attributed to faulting or it might reflect a previous topographic surface. The heap leach pad is indicated by resistivities of 30 to 70 ohm-m, which reflect the presence of conductive fluids. Under sounding 12 lower resistivity material is present from the surface to a depth of 20 to 30 meters and probably represents clay- and/or water-saturated sediments.

Because of the high resistivity of the rocks under the heap leach pad, and if the elevation differences in these rocks are due to erosion then heap leach overflows are not likely to leak into the ground water aquifer through the impervious andesite (rhyolite?). Leaking fluids would tend to flow along the andesite surface downhill to either the Cropsy Creek diversion or Wightman Creek. If the high resistivity rock surface is faulted and not eroded then leakage is possible through the faults. Steven, and Ratté (1960) show a northwest striking fault near sounding 15 (see figure 1).

Figure 4 shows a north-south cross section that starts south of the Cropsy waste pile, crosses next to the open pits, and ends just on the northern side of Wightman Creek. The high resistivities (greater than 200 ohm-m) seen in the upper 80 meters next to the open pits (soundings 8 and 13) correspond to a zone of quartz-alunite alteration. Resistivities of 30 to 100 ohm-m might correspond to a more argillic alteration zone, where the increase in clay content has decreased the resistivity. A deep (about 250 meters deep) high resistivity zone is seen under sounding 8. This area may represent a less altered rock, such as the quartz-latite porphyry or even the core quartz monzonite porphyry. Sounding 18 was made just north of the mapped position of the Missionary Fault, on what is mapped as the Summitville Andesite. The cross section doesn't indicate a fault here, implying that the mapped fault has offset rocks of similar resistivities. However, it is possible to interpret the thinning and apparent offset of the 30 to 100 ohm-m zone between soundings 8 and 13 as a fault.

RESISTIVITY DEPTH MAP

Resistivity depth maps are made by sampling the continuous vertical resistivity variations described above, at the desired depth. Combining this value with the x-y location, an xyz file is created and gridded using a minimum curvature algorithm (Webring, 1981). Gray scale or color values are assigned based on the grid value and the desired contour levels. The Kolor-map and section program (Zohdy, 1993) uses similar procedures and provides a discussion of the nuances of resistivity map generation.

Figure 5 shows a map of interpreted resistivity for a depth of 30 meters, in which the resistivity value at each location is the resistivity value 30 meters below the surface elevation. The high resistivity zone in the vicinity of soundings 8 and 13 and possibly extending out to soundings 16 and 12, probably represents quartz-alunite alteration with its high silica content. This is the same shallow resistive zone seen in the cross section of Figure 4. Resistivities surrounding sounding 18 represent the Summitiville Andesite, which grades into higher resistivity rock toward sounding 14, suggesting a less porous rock. The lowest resistivities on this map, under soundings 9, 11, and 4 may represent an argillic alteration zone or material with high clay and/or water content. Sounding 4 is located at the base of Cropsy waste pile where odd colored water discharges. Other maps and cross sections indicate that this lower resistivity zone extends deeper under sounding 9 and exists at depth under sounding 2 possibly indicating a zone where hydrothermal fluids might have

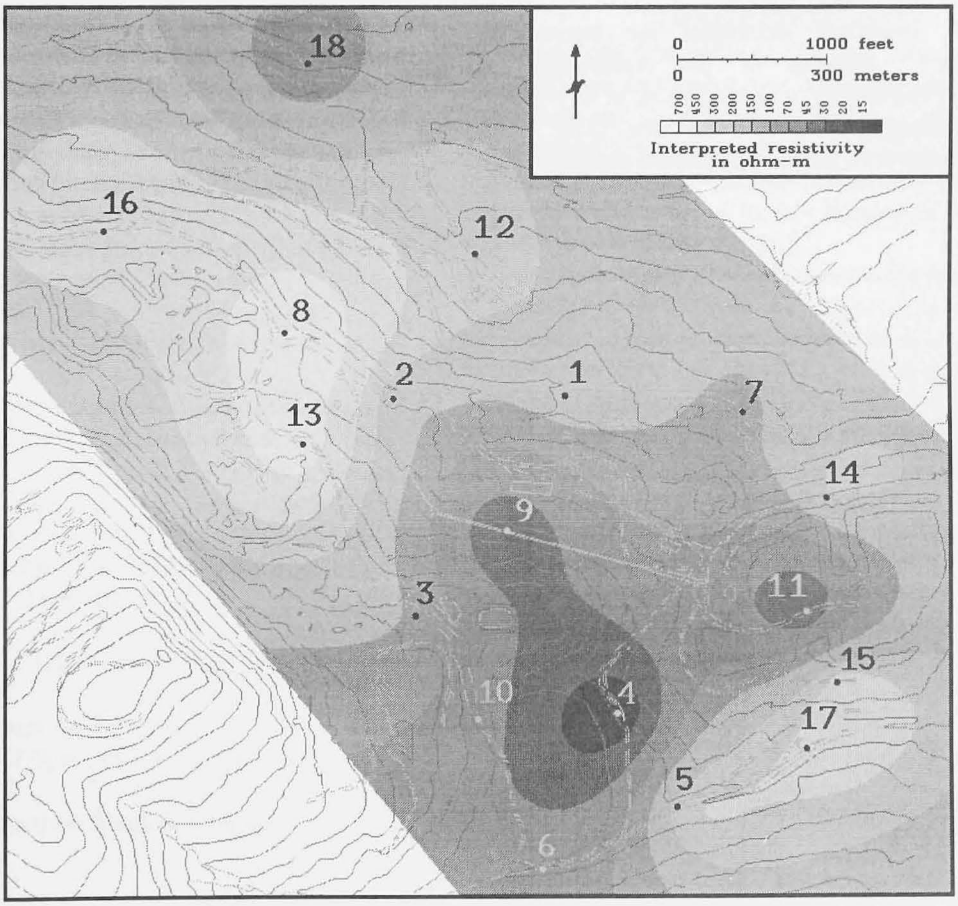

Figure 5. Map of interpreted resistivity at a depth of 30 meters. Grays represent interpreted resistivities in ohm-m. Circles indicate the Schlumberger sounding locations.

concentrated and increased the quantity of clay. Higher resistivities under soundings 5, 17, and 15 correspond to unaltered volcanic rocks probably andesite or rhyolite, and tend to mimic the edge of the altered rocks.

SUMMARY

Resistivity depth maps can show the areal distribution of resistivity and cross sections can show the vertical and lateral distribution. Possible faults were indicated on the cross sections, but resolution is limited by the spacing of the soundings. The resistivity data appears to have mapped an area of high silica content, possibly some combination of the vuggy quartz silica, quartz-alunite, and possibly quartz-kaolinite alteration zones. Lower resistivity zones are believed to correspond to argillic alteration zones. The lowest resistivities such as those detected at the heap leach pad and at the base of Cropsy waste pile, probably related to rock saturated with poor-quality water.

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SUMMITVILLE SITE WATER QUALITY CHARACTERIZATION AND MODELING

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INTRODUCTION

Summitville Consolidated Mining Company Inc. (SCMCI) negotiated an Amended Settlement Agreement and Compliance Plan (SA&CP) in July, 1992 with the Colorado Department of Health Water Quality Control Division (WQCD) and the Colorado Department of Natural Resources Division of Minerals and Geology (DMG). The SA&CP contained several requirements which, in total, were intended to achieve substantial remediation and reclamation of the Summitville site. The SA&CP required goals in document submittal as well as development of goals for on-site work. The first goal of the SA&CP was submittal of a Progress Report identifying and defining plans for implementation of remedial measures by August 31, 1992. Submittal of the final Remedial Measures Plan by November 30, 1992 was the second major submittal goal of the SA&CP. Both the Progress Report and Remedial Measures Plan were compiled by a group of consultants which included: Adrian Brown Consulting, Inc; Environmental Solutions Inc.; Geochimica, Inc.; Geraghty & Miller, Inc.; Golder Associates Inc.; and, Times Limited. Four papers in this volume have been extracted directly from the Remedial Measures Plan and Technical Revision to the Reclamation Plan (SCMCI, 1992). These papers are:

- "Summitville Site Water Quality Characterization and Modeling";
- "Geohydrology and Adit Plugging";
- "Geochemistry of Spent Ore and Water Treatment Issues"; and,
- "Remedial Alternatives Identification and Evaluation".

The four papers present a synopsis of the engineering and scientific approach for development of final Remedial Measures Plan. The authors recommend the four combined papers be read to gain an understanding of the scope and effort expended to prepare the Final Remedial Measures Plan. These papers are presented in the present tense although only some of the measures described were finally implemented by the EPA during their activities.

BACKGROUND

Summitville Consolidated Mining Company, Inc. (SCMCI) was required by the Amended Settlement Agreement and Compliance Plan of July 1992 to submit a Final Remedial Measures Plan to Colorado Department of Health Water Quality Control Division (WQCD) and Colorado Department of Natural Resources, Division of Minerals and Geology (DMG).

The purpose of the Final Remedial Measures Plan was to present the methodology and engineering designs to implement the requirements of the Amended Settlement Agreement to achieve compliance with in-stream constituent criteria compiled in substantial compliance with the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The format necessitated review of the Settlement Agreement (Agreement) requirements, performance of technology screening pertinent to remediation of the site, description of the technologies which can be implemented for remediation and, design of remedial activities based on the applicable technologies.

The applicable requirements for the remedial activities are the in-stream Numeric Criteria Limits (NCLs) downstream of the site set forth in the Amended Settlement Agreement and Compliance Plan. Therefore, instead of establishing conventional effluent limitations at each discharge of potentially contaminated water from the facility, in-stream standards at the downstream boundary of the site have been established to improve over exiting water quality conditions of Wightman Fork as that stream leaves the site. The NCL criteria are based on the

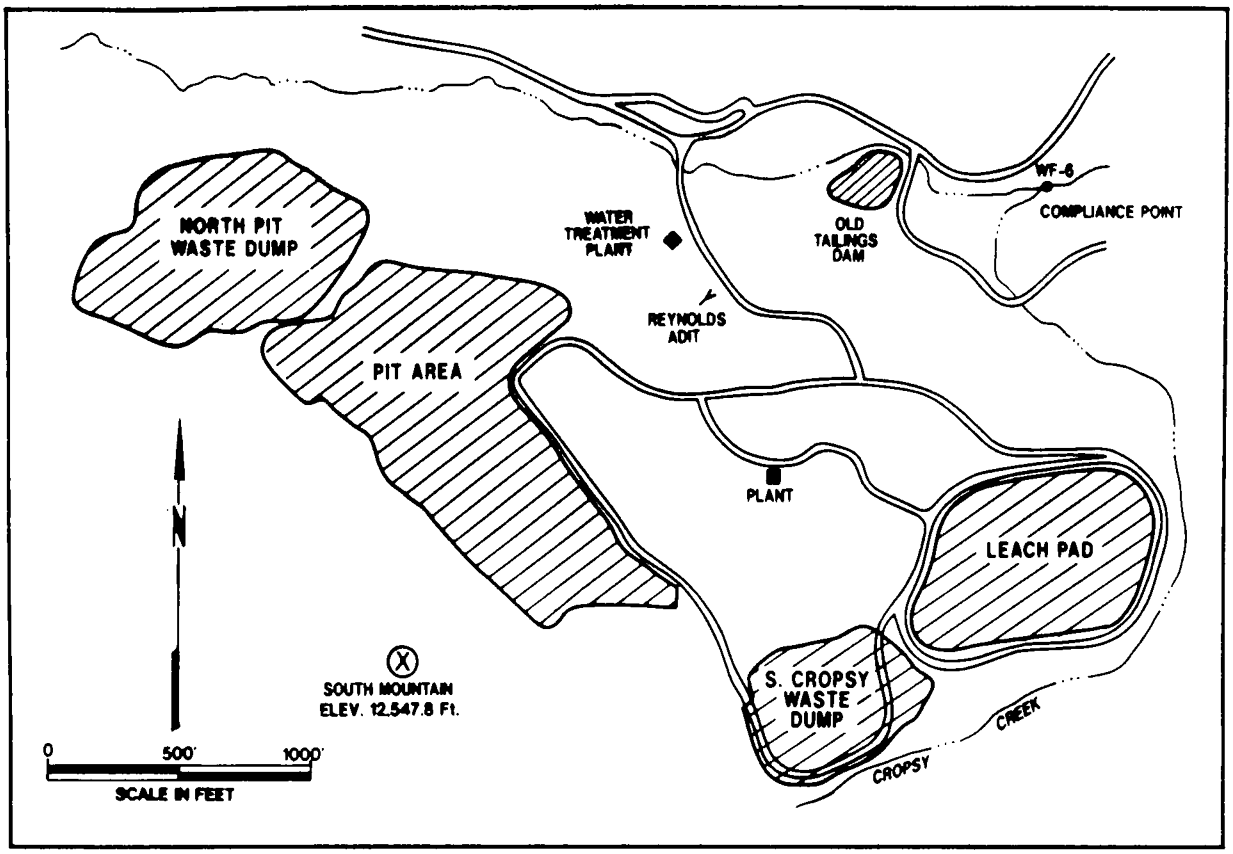

Figure 1. Compliance Point Location

Colorado Discharge Permit System (CDPS) methodology for water quality effluent limitations and were derived using the conventional mass balance calculation with the 1981 Alamosa River water quality standards and the estimated critical low flows for the basin.

The single downstream surface water monitoring location at the property boundary is WF-6 which, for the purposes of the NCLs, has been designated Outfall 004. The compliance point location (WF-6) is shown on Figure 1. The compliance criteria approach has also been termed the "bubble approach" because of the single in-stream monitoring location at the property boundary. Such a "bubble" concept should allow SCMCI the flexibility to operate the site as a single unit by conducting reclamation and remedial activities and, to treat and/or release water from the site at its discretion to attain the NCLs at WF-6. The Remedial Measures Plan was prepared to fulfill the reporting requirements specified in the Amended Compliance Plan (ACP), identified as Exhibit C of the July 1, 1991 Settlement Agreement. The ACP required the following four major tasks:

- On or before August 31, 1992, SCMCI shall submit a Progress Report on the identification and planned implementation of remedial measures to achieve compliance with the final NCLs by December 31, 1993. The progress report shall, at a minimum, include the following information:

1. a preliminary summary of the loadings for metals and cyanide currently coming off the Site during each season for each source identified;
2. preliminary plans for reducing the loading and description of the methods being considered for inclusion in the Remedial Plan;
3. a description of steps that need to be taken and what needs yet to be done to finalize the Remedial Measures Plan by November 30, 1992;
4. a time schedule for development of the Remedial Measures Plan; and,
5. a preliminary outline of the monitoring plan for each remedial measure.

- On or before November 30, 1992, SCMCI shall submit a Remedial Measures Plan, identifying remedial measures which SCMCI will take to achieve compliance with all the final NCLs at Outfall 004[1] by December 31, 1993. The Remedial Measures Plan shall include, at a minimum:

1. a description of remedial measures which shall be capable of meeting the NCLs at Outfall 004 by no later than January 1, 1994, each measure proposed shall include a removal efficiency associated with it;
2. a final analysis of loadings to be removed;
3. each measure proposed must include a monitoring component for assessing the measure's effectiveness and efficiency;
4. sediment controls until reclamation is complete;
5. all the elements outlined in the original Compliance Plan, Exhibit D of the Agreement;
6. a description of active treatment until reclamation measures result in continued compliance with the NCLs at Outfall 004 without the need for active treatment;
7. a description of staffing and resources needed for implementation of the Remedial Measure Plan; and,
8. a schedule for implementation of the proposed remedial measures.

- On or before November 30, 1992, SCMCI shall submit a complete and adequate application for a permit amendment or technical revision, if appropriate, to revise the following aspects of the existing reclamation plan and permit. The permit revisions shall comply with all applicable requirements. The amendment shall revise the plan to detoxify and reclaim the heap leach, and shall include:

1. Standards for heap processing solution detoxification;
2. Schedule for detoxification and dewatering of the heap;
3. Maintenance of the water balance and saturated surface within the heap to ensure prevention of line overtopping;
4. Final grading and configuration of the heap;
5. Subsoiling, topsoiling, revegetation and maintenance of the heap;
6. Final disposition of all underdrains, sumps and pump back facilities;
7. Chemical characterization of the heap before and after detoxification.

- The reclamation plan shall include the results of an investigation of the potential hydrologic connection between the mine pit and the Reynolds and Iowa Adits. The investigation of the potential hydrologic connection will be submitted to the MLRD and WQCD by August 31, 1992. SCMCI will also evaluate feasible alternatives to reduce the potential for the hydrological conditions of the mine pit to contribute to an exceedance of the NCLs at Outfall 004. The report will also include an evaluation of the feasibility of reconfiguring the mine pit to increase runoff and decrease precipitation infiltration to ground water. Nothing in this Paragraph shall be construed as modifying SCMCI's obligation to comply with the NCLs established by the WQCD at WF-6.

The Remedial Measures Plan has also been developed to ensure that the identification and screening of remedial alternatives is in substantial compliance with the process used in the NCP. Generally, to satisfy these requirements, remedial actions must:

- be protective of human health and the environment, utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable and be cost-effective; and,
- attain applicable or relevant and appropriate requirements (ARARs). The NCLs are equivalent to the principal ARARs for the Remedial Measures Plan.

The interim and final NCLs established for WF-6 are presented in Table 1.

Compliance with the NCLs will be at sampling point

Table 1. Numeric Criteria Levels

Parameter	**Interim Numeric Criteria Levels**	**Final Numeric Criteria Levels**
T.R. Zinc, mg/l	2.9	0.70
T.R. Copper, mg/l	3.0	1.6
T.R. Lead, mg/l	n/a	0.12
T.R. Silver, mg/l	n/a	0.0015
Total Mercury mg/l	n/a	0.001
T.R. Cadmium, mg/l	n/a	0.019
T.R. Manganese, mg/l	n/a	5.6
T.R. Iron, mg/l	n/a	50
Weak Acid Dissociable (WAD) Cyanide, mg/l	n/a	0.05
pH, s.u.	n/a	2.5 - 9.0

T.R. = Total Recoverable

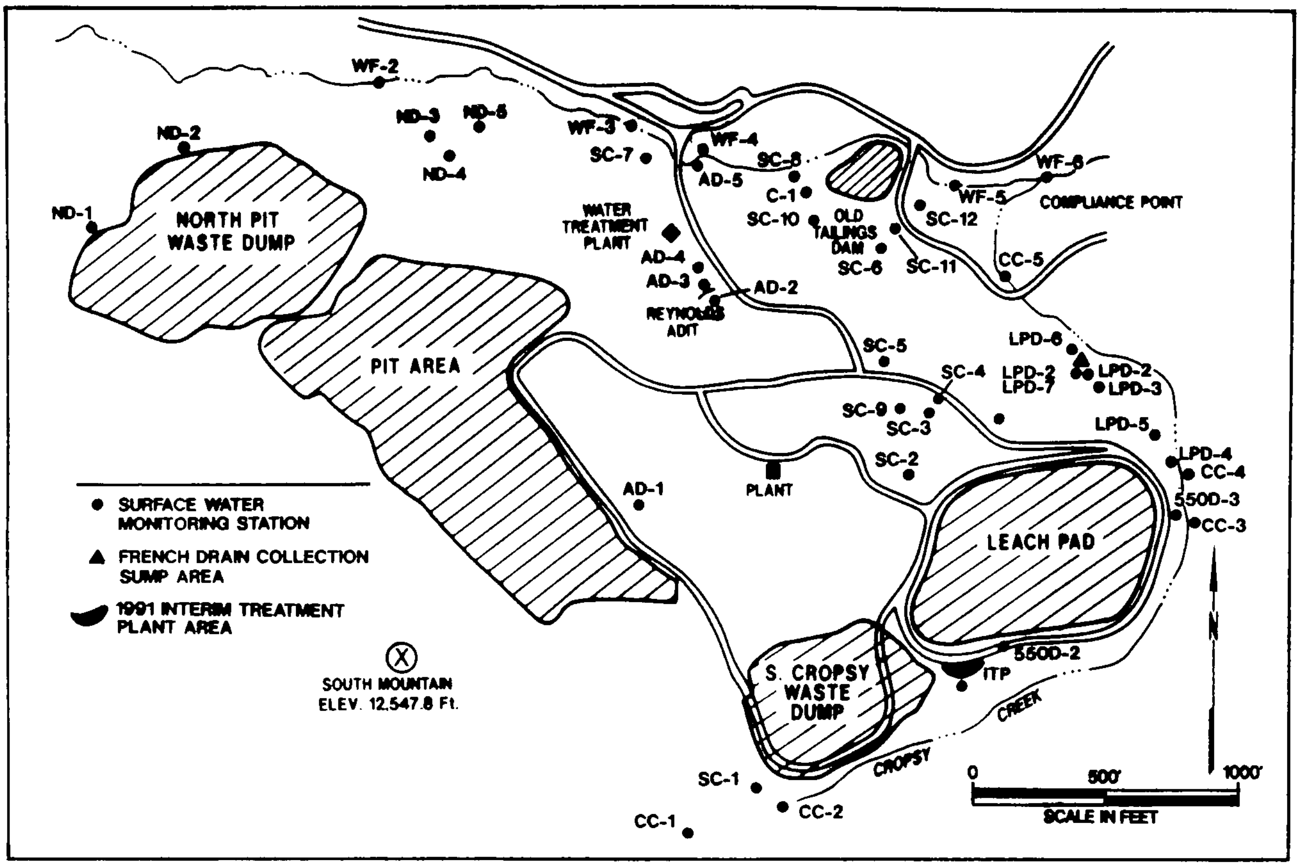

Figure 2. Monitoring Locations

WF-6. This sampling point is located on the Wightman Fork at the boundary of the patented claims block immediately downgradient of the SCMCI mine site and below the confluence of Wightman Fork and Cropsy Creek.

SITE METAL LOADING

A detailed water sampling program was implemented by SCMCI beginning July 1991 to determine the relative metal load contributions by runoff and seepage from individual known point sources such as the Reynolds Adit and ditches, as well as diffused loadings from small catchment areas at the site. The sampling program has been conducted in accordance with the Water Sampling Protocol For The Summitville Mine (EIC, 1991) and focuses primarily on sampling surface water monitoring locations and groundwater wells.

Monthly surface water sampling included flow measurements and analysis for all parameters specified by the Water Sampling Protocol which include general chemistry and a range of total and dissolved metals. Figure 2 shows the locations of all the on-site sampling stations. Data from these stations have been compiled for a twelve month period and incorporated into a metal load model as described below.

Prior to implementation of the water sampling program in July 1991, limited water quality data was available for the Summitville Mine and the Wightman Fork drainage dating back to October 1981.

POST-1991 WATER QUALITY DATA

The current surface water sampling program specified surface water monitoring stations at various locations including:

- Two locations upgradient and downgradient of the confluence of the Alamosa River and Wightman Fork designated (AR);
- Thirteen locations along Wightman Fork designated (WF);
- Five locations along Cropsy Creek and the relocated Cropsy Creek drainage designated (CC);

- Five locations along the North Pit Waste Dump diversion ditch designated (ND);
- Five locations along the diversion ditch collecting flows from the Iowa and Reynolds Adits designated (AD);
- Six locations downgradient of the heap leach pad Dike 1 including outlets of the leach pad underdrains designated (LPD); and,
- Eight locations along the on-site surface water diversion structures designated (SC).

Surface water sampling locations for the sampling program were selected to allow monitoring of water quality upgradient and downgradient of stream confluences and potential load source areas. Additional in-stream sample locations were selected that correspond with potential diffused load sources such as waste rock pile areas and point load sources such as the historic Reynolds Adit. This approach allowed evaluation of metal loading for specific stream segments and identification of areas contributing significant metal loadings.

Table 2 details the location of all water monitoring sites designated in the revised water sampling protocol. Monthly samples and flow measurements were taken for all monitoring locations when accessible and when flows were present. Two additional sample locations are the French Drain Sump (FD) located below the heap leach pad dike and the Interim Treatment Plant (ITP) located at the toe of the Cropsy Waste Rock Dump. Flow measurements and water samples were collected by SCMCI environmental staff.

COPPER AS AN INDICATOR

Copper loads will be used as an indicator for evaluating remedial alternatives in terms of their potential effects on reducing Copper loads. This metal was used as the basis of the evaluations for the following reasons:

- Silver, mercury, WAD cyanide, and pH are already either in, or very close, to compliance with the NCLs;
- Copper is the metal whose current concentration exceeds the proposed NCL value by the highest proportion. This indicates that the remedial actions at the site will be driven by the need to reduce copper loadings (and concentrations in-stream at WF-6). Therefore, modelling remedial actions in terms of their reductions in copper loading will always produce estimates of resource commitments (in terms of time, effort and costs) that would exceed the estimates generated by the use of any other NCL parameter.
- Load reductions for key metals can be predicted reliably on the basis of projected load reductions in copper. Copper concentration is an excellent predictor of the concentrations of zinc, lead, cadmium, manganese, and iron.

A geochemical analysis was made of the water quality data at WF-6 to investigate the relationship between copper concentrations and those for other constituents. Table 3 shows the statistics of the multiple, bivariate correlations of the NCL compounds for all samples collected at WF-3, WF-4, WF-5, WF-6, AD-3 and CC-5 from July 1991 to February 1992, representing 58 sampling events, of which 40 events included all ten parameters on the same physical water samples. All correlations greater than 0.50 (or less than -0.50) have p-values less than 0.001 and are therefore statistically significant. All values of zinc, copper, lead, cadmium, manganese and iron substantially exceed the quantitation limit for each metal, indicating that the statistics will not be confounded by issues of data censoring. It also shows that the presence of these metals at values one or more orders of magnitude above the quantitation limit indicates that the reported values should be quite precise. The correlation of silver to mercury (r=.45) is an artifact of setting concentrations equal to quantitation limit for each of these metals.

The geochemical behavior of the species, given the ranges of values, correspond well with the statistical correlations. Because the sample solutions are acidic (pH 3.2 - 4.7) and oxidized (all were surface water samples collected from shallow, flowing waters), all six metals are expected to be present in solution predominantly as divalent ions[2]. The somewhat lower (but still significant) correlation between copper and manganese (as well as between manganese and the other divalent metals) may be related to the probable existence of manganese in solution as the manganate ion (MnO_4^{2-}) whereas the other metals are expected to be present in solution as simple Me^{2+} cations. This inference is supported by the fact that the metals with the highest correlation coefficients with manganese are the amphoteric metals zinc and cadmium.

Low correlations (e.g., between copper and silver or mercury) are expected when one parameter has meaningful values (e.g., values for copper that are always well above the quantitation limit) while the values for the other parameter are censored (e.g., the majority of the silver and mercury values set at the analytical quantitation limit). The poor correlation between copper (and the other divalent metals) and WAD cyanide is due in part to censoring of cyanide data and in part to the fact that the basic inorganic chemistry of cyanide is sufficiently different from that of copper that little or no fundamental relationship is expected in solution and also that cyanide is released only from the leach pad. It is considered that the significant correlation between pH and the metals is due to a common cause (i.e., both are present in solution because of the oxidation of pyrites and subsequent leaching of metals.) However, the correlation is lower than that between the metals because hydrogeochemical

Table 2. Surface Water Monitoring Sites

Monitoring ID	Location
WF-1	Wightman Fork just upstream of the limit of SCMCI disturbance
WF-2	Wightman Fork approximately 100 feet downstream of the corner of sections 24, 19 and 30
WF-3	Wightman Fork just downstream of Land Application Area B
WF-4	Wightman Fork just downstream of discharge of adit water
WF-5	Wightman Fork downstream of the confluence with the tailings pond spillway discharge
WF-6	Wightman Fork downstream of confluence with Cropsy Creek
WF-7	Wightman Fork downgradient of the confluence with Sawmill Creek
WF-8	Wightman Fork downgradient of the confluence with Big Hollow
WF-9	Wightman Fork downgradient of the confluence with Palmer Gulch
WF-10	Wightman Fork downgradient of the confluence with unnamed tributary
WF-11	Wightman Fork downgradient of the confluence with Whitney Gulch
WF-12	Wightman Fork downgradient of the confluence with Smallpox Gulch
WF-13	Wightman Fork upgradient of the confluence with Alamosa River
AR-1	Alamosa River upgradient of confluence of Wightman Fork
AR-2	Alamosa River downgradient of confluence of Wightman Fork
CC-1	Cropsy Creek upstream of site disturbance
CC-2	Cropsy Creek near the head of the diversion
CC-3	Cropsy Creek upstream of the 550 Ditch
CC-4	Cropsy Creek downstream of the 550 Ditch outlet
CC-5	Cropsy Creek just downstream of diversion confluence with natural channel
ND-1	North Dump north drainage ditch above subsurface drain outlet
ND-2	North Dump north drainage ditch below subsurface drain outlet
ND-3	North Dump north drainage ditch upgradient of the sediment ponds
ND-4	North Dump south drainage ditch upgradient of the sediment ponds
ND-5	North Dump drainage from the sediment ponds
AD-1	Drainage from the Iowa Adit
AD-2	Drainage ditch carrying Iowa Adit flows just upstream of the confluence with the Reynolds Adit
AD-3	Drainage from the Reynolds Adit
AD-4	Downstream of the confluence of the Reynolds and Iowa Adits
AD-5	Ditch carrying combined flows upstream of the confluence with Wightman Fork
550D-1	550 Ditch upstream of the confluence with underdrain flows
550D-2	550 Ditch downstream of the confluence of the ditch with the underdrain flows
550D-3	550 Ditch upstream of the confluence with Cropsy Creek Diversion
LPD-1	Underdrain flows outletting on the north abutment of Dike 1
LPD-2	Underdrain flows outletting on the north abutment of Dike 1
LPD-3	Underdrain flows outletting on the west abutment of Dike 1
LPD-4	530 Underdrain flows
LPD-5	510 Underdrain flows
LPD-6	Surface water flows in natural Cropsy Creek channel upstream of the Cropsy Creek Diversion
SC-1	Outlet of road drainage upgradient of the South Cropsy Dump
SC-2	Outlet of road drainage at the generator plant
SC-3	Road drainage upgradient of Gomperts Ponds on the west side
SC-4	Road drainage upgradient of Gomperts Ponds on the east side
SC-5	Outlet from Gomperts Ponds
SC-6	Drainage ditch from the main topsoil stockpile
SC-7	Pre-existing sediment pond near Wightman Fork west of guard station
SC-8	Sediment pond at the mud containment area below the Beaver Mud Dump

Table 3. Water Quality Correlations (r(x,y) for NCL Parameters

	Zn	**Cu**	**Pb**	**Ag**	**Hg**	**Cd**	**Mn**	**Fe**	**WAD CN**	**pH**
Zn	1	.99	.92	-.15	-.07	.97	.75	.99	-.09	-.61
Cu		1	.92	-.14	-.13	.96	.67	.98	-.12	-.57
Pb			1	-.11	-.03	.98	.60	.88	-.11	-.51
Ag				1	.45	-.12	-.07	-.13	-.01	.27
Hg					1	-.03	.00	-.07	.11	.01
Cd						1	.69	.94	-.08	-.57
Mn							1	.70	.11	-.58
Fe								1	-.11	-.58
WAD CN									1	.22
pH										1

Note: Statistics calculated in CSS:STATISTICA; values rounded to two significant places for use in this table only.

processes can effect the pH of the solution within the range of 2.7 to 6.7 without differentially affecting the concentrations of the six metals.

The statistics given in Table 3 are consistent with the expected physical chemistry of the metals in the existing aqueous solutions at Summitville. Calculation of mass loading reduction for the remedial measure of plugging the Reynolds Adit performed for all the NCL metals show that for equivalent load-reduction factors, NCL metals produce predicted in-stream loads that are consistent with the trends predicted using copper (Table 4). In a more simplified fashion, consider the data for WF-6 from July, 1991 through September, 1992 as shown on Table 4. The low flow observed during this period was in February, 1992, when flow at WF-6 was only 147 gpm, which is very close to the critical flow value used to compute the NCLs. At that time, the concentration of copper was 13.7 mg/l, the concentration of zinc was 4.41 mg/l, and the concentration of iron was 51.6 mg/l. Assuming the that the corrective measures reduce the copper concentration to the NCL of 1.6 mg/l, equivalent loading reductions for zinc would produce a concentration of 6.03 mg/l. Concentrations for zinc and iron, based on loading reductions, would meet the respective NCL values of 0.7 mg/l and 50 mg/l.

Laboratory-scale testing of water treatment options and industry experience shows that the cyanide concentrations can be lowered to levels that meet discharge permit requirements and NCL compliance at WF-6. Laboratory testing of attenuation that could be achieved in the South Mountain area by modifying the mine hydrology indicate that 90 to 99% lower copper concentrations can be achieved by natural attenuation. The same testing program shows that the zinc and iron concentrations also can be attenuated by up to 90% so long as the pH of the solutions along the flow path remains above pH 5. Therefore, it is considered that copper alone can be used as an indicator metal in the screening of alternatives.

It is therefore concluded that by using copper as the indicator species in the model, the potential metals loading reduction through implementation of the remedial actions produces the most conservative estimates (time, effort and costs) of resource commitments to achieve the NCL parameters.

METAL MASS BALANCE EVALUATIONS

The objectives of conducting the metal mass balance evaluations are as follows:

- To rank the point and diffuse source areas in terms of their metal loads to assure that remediation activities focus on the major causes of the elevated metal concentration WF-6;
- To provide information on seasonal (monthly) and annual metal loadings for the various areas and point sources within the site to characterize the types of loads reporting to monitoring location WF-6. The seasonal distribution of load provides clues as to whether the load is predominantly due to surface flows, waste pile leachate, or deeper groundwater seepage. This knowledge in turn is useful in the planning and design of remedial measures; and,
- To provide a tool that allows the beneficial impacts of reclamation and remedial alternatives in terms of reduced metal loads at WF-6 to be

Table 4. NCL Metals and Equivalent Load Reduction Comparison

NCL Parameter	Range of Concentration at AD-3[1] (mg/l)	Range of Concentration at WF-6[1] (mg/l)	Reduced Concentration at WF-6 when AD-3 is Removed[2] (mg/l)	NCL Level (mg/l)	Number of Months Exceeding NCL
Cadmium	0.21-0.396	0.018-0.062	0.0025-0.03	0.019	4
Copper	69.6-332	7.27-30.0	0.09-12.7	3.0 (INCL)	4
Cyanide	[3]	0.002-0.075	-	0.05	1
iron	220-754	30-88	10-60	50.0	1
Lead	0.33-0.64	0.014-0.087	[4]	0.12	0
Manganese	13-33	5.7-18.0	3.4-16.6	5.6	11
mercury	< =0.001[5]	<0.0005[5]	-	0.001	0
Silver	-	<0.0025	-	0.0015	-
Zinc	15-44.4	2.5-6.56	0.4-5.8	2.9 (INCL)	3

Notes:

1 Range of concentration for samples collected at monitoring locations WF-6 and AD-3 for the period between July 1991 to September 1992.

2 Reduced concentration is calculated from load analysis when 99 percent of AD-3 loading is removed from WF-6 loading.

3 Indicates that the concentration for this parameter was found to be below the detection limit of 0.005 mg/l.

4 The lead concentration of samples taken at sample pint WF-6 for the period from July 1991 to September 1992 are all below the NCL level.

5 The mercury concentration of samples taken at sample points AD-3 and WF-6 for the period from July 1991 to September 1992 are all below the NCL level.

6 Silver concentrations were generally below detection limits at WF-6, all silver concentrations for AD-3 were below detection limits. The detection limits for silver ranged from 0.1 to 0.0002 mg/l.

quantitatively estimated as needed.

The water quality data collected during the July 1991 to September 1992 period was compiled to form a metal loading model. The in-stream metal loads were calculated as pounds per day from the metal concentration (mg/l) and the flow rate (gpm) for each monitoring location. Figure 3 presents the structure for the flow load model. The model addresses separate stream segments associated with potential load source areas at the mine site. This concept includes the Wightman Fork drainage, the Cropsy Creek drainage, the North Pit Waste Dump Diversion, the 550 Diversion and the Adit Drainage. Each of these segments are further divided where monitoring sites are located up and downgradient of potential load sources. Monitoring locations are associated with potential source areas as follows:

- North Pit Waste Dump - ND-1, ND-2, ND-3, ND-4, ND-5, ND-1A, and ND-1B;
- Iowa Adit-AD-1;
- Reynolds Adit - AD-3;
- Beaver Mud Dump - SC-8, SC-6 and WF-5;
- Clay Ore Pile - SC-5;
- Heap Leach Pad - FD, LPD-2, LPD-6 and CC-5; and,
- Upper Cropsy Waste Rock Dump - ITP, 550D-1, 550D-2 and 550D-3.

By using such data for load modelling, it is assumed monthly flow measurements and water samples are representative for the entire month during which the sample was collected. The difference in the metal load between adjacent monitoring stations was used to determine source loadings for the various areas and their relative contribution.

Copper was selected for the purposes of these analyses as the representative indicator metal constituent. Differences in copper load between stations (delta copper loads) are presented in Table 5 for each sample location and reflect the load contributed from a source area associated with each stream segment for a twelve month period. The total copper load to WF-6 is calculated as the sum of the delta copper loads and was found to be greater than the in-stream loads found at WF-6. This difference between the calculated sum and the measured in-stream loads at WF-6 is due to several factors including:

- Treatment of waters currently being collected (i.e. French Drain Sump, Interim Treatment Plant) prior to reporting to WF-6;
- Underflow component in the Wightman Fork

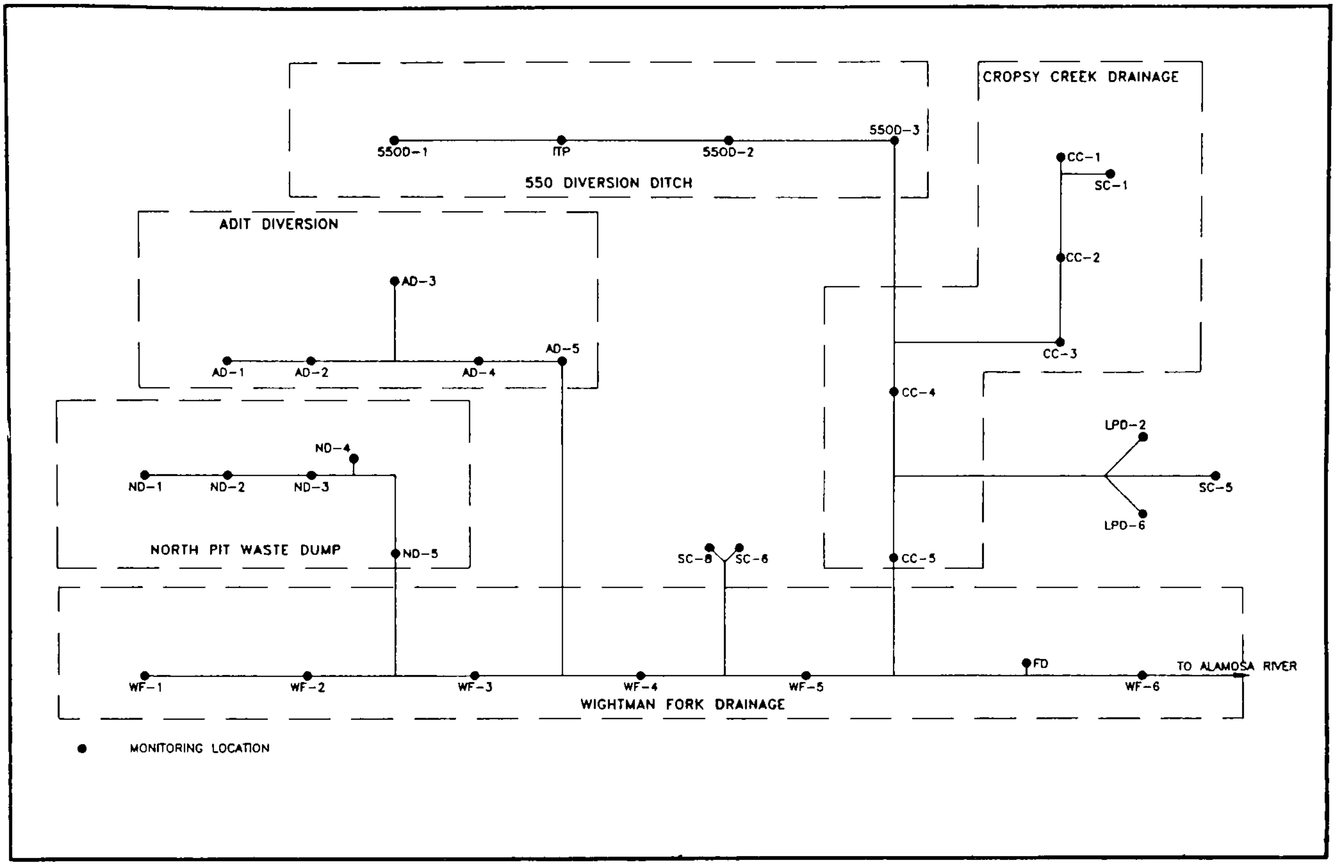

Figure 3. Structure for Flow Load Model

channel; and,

- Possible geochemical reactions occurring between source areas and WF-6.

For example, during August 1991 the total delta copper load at WF-6 is 795 lbs/day as presented in Table 5. The measured copper load at WF-6 for the August 1991 sample was 571 lbs/day. An additional 139 lbs/day was removed from flows being collected and treated at the FD and ITP during this same period and is included in the 795 lbs/day value. This leaves 85 lbs/day or approximately 10 percent of the 795 lbs/day total delta copper value unaccounted. The remaining 10 percent may be attributed to underflow and other uncertainties. Therefore the total delta copper load values for WF-6 presented in Table 5 account not only for the copper load measured at WF-6 but account for copper loads currently being removed by treatment and uncertainties. This approach is conservative and allows for a more complete accounting of metal loading at the mine site. The annual copper load is calculated as the sum of the calculated monthly totals.

As discussed above, monitoring station WF-6 was selected as the compliance point for metal loading on Wightman Fork. The location of WF-6 is downgradient of areas impacted by current and historic mining activities at the Summitville Mine site. During the period of record, July, 1991 through September, 1992, flows at WF-6 ranged from a high of 7,219 gpm during May, 1992 to a low of 147 gpm for February, 1992. The total calculated copper load at WF-6 ranged from a high of 2,406 lbs/day during June 1992 to a low of 110 lbs/day during February 1992. It should be noted that peak copper calculated loading occurs during the months of May, June, and July with copper loads exceeding 1,600 lbs/day. During this time period, peak streamflows were also noted at the WF-6 monitoring site.

The relative contributions of delta copper load for each monitoring station as a percent of the total calculated copper load at WF-6 can be calculated. The percentage values represent the incremental loading occurring between each monitoring point. This comparison is useful in identifying the most significant contributors of

Table 5. Delta Copper Loads (lbs/day)

Station	Jul 91	Aug 91	Sep 91	Oct 91	Nov 91	Dec 91	Jan 92	Feb 92	Mar 92	Apr 92	May 92	Jun 92	Jul 92	Aug 92	Sep 92
WF-1	0.07	0.29	0.03	0.01	0.00	0.00	0.00	0.00	0.00	10.00	0.03	0.00	0.01	0.00	0.02
WF-2	0.89	0.77	0.81	0.94	0.61	0.25	0.15	0.14	0.12	0.22	1.23	4.57	1.84	0.00	1.24
ND-1	-	-	3.68	-	-	-	-	-	-	0.00	0.00	0.00	6.29	0.00	1.99
ND-2	-	-	(1.96)	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
ND-3	-	-	(1.31)	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
ND-4	-	-	-	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
ND-5	-	1.28	-	-	-	-	-	-	-	0.00	152.65	198.53	(2.96)	0.00	(1.77)
WF-3	15.88	8.01	7.02	7.40	4.08	2.34	0.71	2.05	1.67	1.76	(125.48)	(33.89)	9.88	4.92	5.47
AD-1	11.00	7.46	3.32	1.32	0.24	-	-	-	-	0.00	11.66	39.52	6.01	0.00	6.09
AD-2	-	-	0.29	-	-	-	-	-	47.52	0.00	0.00	0.00	0.00	0.00	0.00
AD-3	739.95	268.65	234.39	159.24	159.24	84.62	61.45	64.78	-	55.11	843.12	1719.97	463.06	0.00	365.57
AD-4	-	-	37.02	-	-	-	-	-	(24.22)	0.00	0.00	(163.34)	(469.06)	0.00	9.90
AD-5	(99.11)	(52.66)	(38.34)	-	-	(13.64)	(37.98)	(20.87)	24.00	(28.70)	(68.57)	71.84	573.79	703.75	(33.04)
WF-4	252.36	114.08	42.5	(55.48)	(55.48)	15.41	10.04	(6.76)	-	20.40	(207.39)	(151.59)	(193.40)	(708.67)	10.82
SC-8	-	-	6.31	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
SC-6	-	-	0.14	-	-	-	-	-	1.65	0.00	0.00	0.00	0.00	0.00	0.00
WF-5	(61.37)	166.21	6.13	36.04	36.04	(7.08)	(14.76)	9.88	0.00	21.69	121.37	275.77	88.12	0.00	(213.93)
CC-1	0.12	0.03	0.02	0.00	0.00	0.00	0.00	0.00	-	0.01	0.03	0.03	0.07	0.04	0.13
SC-1	-	-	0.00	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
CC-2	(0.03)	0.01	(0.00)	(0.01)	(0.00)	(0.00)	0.00	(0.00)	-	(0.00)	0.06	0.04	0.01	(0.04)	(0.05)
CC-3	0.41	0.17	0.03	0.00	0.01	0.00	-	0.00	-	0.00	1.29	3.34	0.13	0.09	(0.00)
550D-1	-	-	-	-	-	-	-	-	-	0.00	0.00	-	0.00	0.00	0.00
ITP	52.39	85.56	-	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
550D-2	-	-	0.58	-	-	-	-	-	-	-	0.00	-	0.00	0.00	0.00
550D-3	28.56	0.92	(0.06)	0.48	0.28	-	0.01	0.00	0.01	0.78	13.15	1.08	0.45	0.72	0.26
CC-4	(4.14)	(0.520	(0.02)	(0.02)	(0.02)	0.03	-	(0.00)	(0.01)	(0.07)	(3.20)	1.10	0.07	(0.81)	0.20
LPD-2	6.87	5.63	4.94	3.08	2.55	1.66	1.53	4.10	5.69	3.17	5.88	10.85	3.61	0.00	1.39
FD	56.25	53.44	50.63	50.63	50.63	50.63	45.53	28.78	32.54	72.50	402.25	56.25	56.25	56.25	56.25
LPD-6	78.97	4.38	0.08	-	-	-	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00
SC-5	21.41	10.22	2.69	0.47	-	0.38	0.12	0.13	4.19	4.04	142.19	23.32	5.69	0.00	0.00
CC-5	(108.36)	68.25	2.15	(1.40)	3.12	(0.62)	(0.98)	(3.56)	(9.09)	(6.81)	(101.68)	(0.83)	0.11	18.94	4.03
WF-6	383.31	(32.23)	2.02	(38.14)	33.46	0.77	21.09	(25.67)	(8.47)	8.81	(155.49)	(114.63)	(32.51)	212.83	72.49
TOTAL (lb/day)	1648	795	405	293	290	156	141	110	117	188	1695	2406	1215	998	536
MONTHLY (lbs)	51102	24657	12143	9083	8708	4839	4359	3076	3639	5654	52542	74592	37677	30924	16076
ANNUAL (lbs)	254,394														

copper loading to the Wightman Fork. For example, the delta load at WF-5 during August 1991 represents 20.9 percent of the total calculated loading at WF-6. This delta load includes the increase in load that enters the Wightman Fork between the WF-4, SC-8, SC-6, and the WF-5 monitoring locations presented in Figure 3.

A review of the copper loading data expressed as a percentage indicates that the major contributor of copper load is AD-3, the Reynolds Adit, which amounts to between 34 percent (in August 1991) and 71 percent (in June 1992) of the calculated load at WF-6. Significant copper contributions also occur in the drainage areas upgradient of WF-5, and CC-5 for all recording periods.

SELECTION OF COPPER AS THE KEY INDICATOR CONSTITUENT

As discussed above, the model uses copper as the key indicator species to evaluate current loadings to the surface and ground water systems and to predict the improvements in water quality as a result of potential remedial actions. The ACP identifies the ten parameters listed in Table 1 which must meet designated NCL values at the conclusion of the remedial program. This section presents an evaluation that supports the use of copper as the representative key indicator species with respect to achieving compliance with all the NCL parameters.

CURRENT DATA AT WF-6

Table 6 presents the data at WF-6 for the ten NCL constituents set for the period July 1991 to September 1992. The table provides the arithmetic and geometric means of the data and for comparative purposes, the NCLs. While it is understood that during the compliance period (i.e., after the final NCLs become effective), the Agreement requires that in- stream concentrations at WF-6 meet the final NCL values on a 30-day average for all months, the annual average water quality data are considered appropriate for use in this preliminary evaluation as they represent the currently anticipated long-term behavior of the NCL parameters in the system.

As shown by Table 6, the water at WF-6 currently meets the final NCL values for lead, mercury, and pH for all sampling events. The geometric mean value for silver is 0.0016 compared to a final NCL of 0.0015; this difference is not analytically significant. In addition, the geometric mean concentration of WAD cyanide at WF-6 meets the final NCL value on an annual average basis and exceeds the final NCL on a monthly basis only in two out

Table 6. Water Quality Data at WF-6: July 1991 - June 1992 (all data in mg/l except pH in s.u.)

	Zn	Cu	Pb	Ag	Hg	Cd	Mn	Fe	WAD CN	pH
Jul 91	7.4	31.0	.041	<.0002	<.0001	.052	10.0	88.0	<.005	3.25
Aug 91	4.4	15.0	.020	<.0002	<.0001	.032	8.4	55.0	.025	3.33
Sept 91	4.4	14.5	.022	<.0002	<.0001	.034	9.2	51.5	<.005	3.34
Oct 91	6.5	28.0	.071	<.0002	.0002	.059	12.0	55.0	.007	3.46
Nov 91	5.9	18.5	.054	.0007	.0002	.069	11.0	72.0	.579	3.68
Dec 91	4.4	14.3	.059	.0016	.0003	.044	9.9	46.3	<.005	3.53
Jan 92	2.7	9.1	.048	.0013	.0004	.039	6.0	33.0	.048	4.67
Feb 92	5.1	15.4	.020	<.01	<.0001	.053	13.8	33.1	.075	3.70
Mar 92	3.1	16.0	.076	<.01	.0002	.048	10.0	36.0	<.010	3.94
Apr 92	5.7	12.9	.018	<.01	<.0001	.049	18.9	80.9	.002	3.20
May 92	2.6	7.3	.011	<.01	<.0001	.019	6.6	35.1	.003	3.28
Jun 92	5.4	27.7	.018	<.01	<.0001	.040	8.9	86.0	<.002	3.22
Min	2.6	7.3	.011	<.0002	<.0001	.019	6.0	33.0	<.002	3.20
Max	7.4	31.0	.076	.0016 (<.01)	.0004	.069	18.9	88.0	.579	4.67
Arithmetic Mean	4.8	17.5	.038	.0045	.0002	.045	10.4	56	.064	3.55
Geometric Mean	4.6	16	.032	.0016	.0001	.043	9.9	52.5	.012	N/A
FNCL	0.70	1.6	0.12	0.0015	0.001	0.019	5.6	50	0.05	2.5-9.0

Notes: 1. In calculating statistics, values less than the quantitation limit were set at the quantitation limit.

2. For months in which more than one sample was collected, the value represents an arithmetic average of all measured values, where this value is taken to be a thirty-day average within the meaning of the Settlement Agreement.

of twelve months of the current record. It is indicated that long-term compliance with the final NCL for WAD cyanide can be achieved by leach pad decommissioning activities, including oxidative destruction of cyanide and enhanced natural attenuation. Of the remaining five NCL-limited parameters, only zinc, copper and cadmium exceed the NCL by more than a factor of 2 on an annual average basis.

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Logsdon, M. and Mudder, T., 1994, Geochemistry of Spent Ore and Water Treatment Issues. Tailings and Mine Waste '95 and Summitville Forum, Colorado State University, Fort Collins, Colorado.

Summitville Consolidated Mining Company, Inc., 1992, Technical Revision to the Reclamation Plan and Final Remedial Measures Plan.

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1. Colorado Department of Health Water Quality Control Division identifies WF-6 as Outfall 004.

2. All six metals have two electrons in the outer shell. Binding energy for *3d* electrons and *4s* electrons in copper are nearly identical, and one can represent copper as having two *4s* electrons and nine *3d* electrons as well as having one *4s* electron and ten *3d* electrons (e.g., Pauling and Pauling, 1975; Cotton & Wilkinson, 1988). This ambiguity in energy levels corresponds with the empirical data that cuprous ion (i.e., Cu^{+1}) is unstable in oxidized solutions with respect to cupric ion (i.e., Cu^{2+}).

GEOHYDROLOGY AND ADIT PLUGGING

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INTRODUCTION

Summitville Consolidated Mining Company Inc. (SCMCI) negotiated an Amended Settlement Agreement and Compliance Plan (SA&CP) in July, 1992 with the Colorado Department of Health Water Quality Control Division (WQCD) and the Colorado Department of Natural Resources Division of Minerals and Geology (DMG). The SA&CP contained several requirements which, in total, were intended to achieve substantial remediation and reclamation of the Summitville site. The SA&CP required goals in document submittal as well as development of goals for on-site work. The first goal of the SA&CP was submittal of a Progress Report identifying and defining plans for implementation of remedial measures by August 31, 1992. Submittal of the final Remedial Measures Plan by November 30, 1992 was the second major submittal goal of the SA&CP. Both the Progress Report and Remedial Measures Plan were compiled by a group of consultants which included: Adrian Brown Consulting, Inc; Environmental Solutions Inc.; Geochimica, Inc.; Geraghty & Miller, Inc.; Golder Associates Inc.; and, Times Limited. Four papers in this volume have been extracted directly from the Remedial Measures Plan and Technical Revision to the Reclamation Plan (SCMCI, 1992). These papers are:

- "Summitville Site Water Quality Characterization and Modeling";
- "Geohydrology and Adit Plugging";
- "Geochemistry of Spent Ore and Water Treatment Issues"; and,
- "Remedial Alternatives Identification and Evaluation".

The four papers present a synopsis of the engineering and scientific approach for development of final Remedial Measures Plan. The authors recommend the four combined papers be read to gain an understanding of the scope and effort expended to prepare the Final Remedial Measures Plan. These papers are presented in the present tense although only some of the measures described were finally implemented by the EPA during their activities.

BACKGROUND

Prior to the SCMCI mining period, the Summitville ore zone had been mined since the last century, using underground methods. This mining has left an extensive network of adits, drives, workings, and stopes at the base of South Mountain. Access to these workings was in general by horizontal adits driven into the side of the mountain from the north. The principal access to the underground workings is the Reynolds Adit, which was collared at an altitude of 11,320 feet, and which proceeds in an approximately west-south-west direction to the ore zone. The Reynolds adit is approximately 2,500 feet long, and is essentially straight. The Reynolds is joined close to the exit point by the Dexter Adit, which connects the adit system in the north of the ore zone with the Reynolds Adit, providing a common egress from the prior workings. The general adit system which is known to have existed is presented in Figure 1.

The adit system which provided access to the underground mines during their active periods today provides drainage from the mine workings and the north flank of South Mountain. Reaction of infiltrating meteoric water with residual mineralization, particularly under the desaturated conditions of the drained adit system, has produced acidic, high-TDS, high-metals waters that are currently - and have been for many years - discharging from the Reynolds system. Prior to the implementation of the portable interim treatment system (PITS), this discharged water was directed to Wightman Fork, where it comprised the majority of the metal and acid loading of the creek.

The plugging of the adits is intended to:

- Prevent currently acidic flow from directly reaching Wightman Fork;
- Raise the water table in the ore zone, to reduce

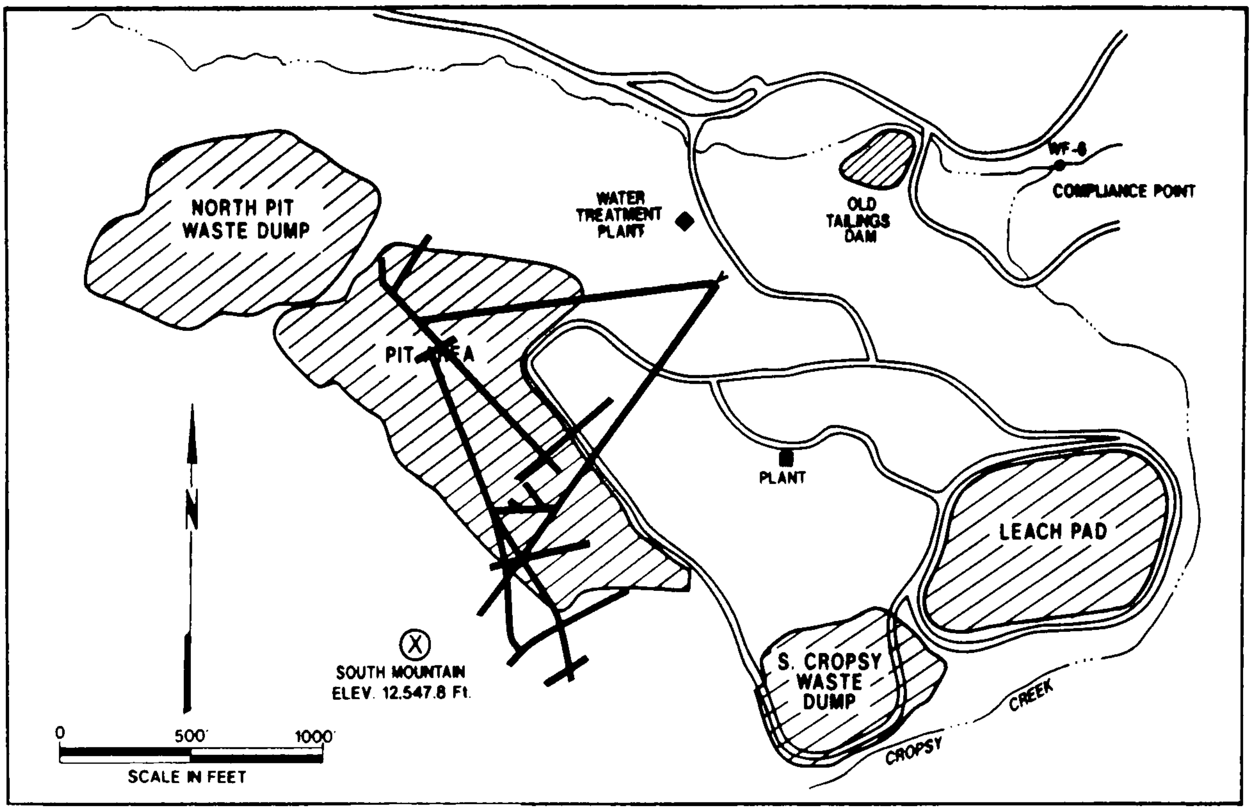

Figure 1. Location of Reynolds and Dexter Adits

or eliminate the formation of further acid from the oxidation of the ore zone; and,

- Drive any seepage from the ore zone through the rock and alluvial materials between the ore zone and Wightman Fork, to reduce the concentration and load of metals in the water by both increasing pH and attenuation by the rock mass between the ore zone and the creek.

GEOLOGY

The geology of the Summitville Mine site is relatively complex, as shown by Figure 2. The upper cross-section in Figure 2 shows the general geology of the area looking to the west, while the lower cross-section in Figure 2 shows the concentric rings of the orebody which are located within the porphyry between Wightman Fork and South Mountain. The site is located at the intersection of two major structures; the Platoro fracture zone and the ring fractures of the Platoro-Summitville caldera complex. The South Mountain composite volcanic dome consists of at least four phases of quartz latite porphyry. There are six major alteration assemblages associated with the epithermal gold-silver-copper mineralization, the most important alteration zone being the silica zone, which hosts the silver/gold orebody. Argillically altered rock is the most abundant material on South Mountain and appears to be more resistant and probably more permeable than the orebody host material. To the north of the orebody, approximately bordered by Wightman Fork, is a zone of andesitic rock which is essentially unaltered.

GENERAL HYDROGEOLOGIC DESCRIPTION

As it relates to the groundwater flow regime the geology of the Wightman Fork area seems to be relatively simple. It comprises altered volcanics in the South Mountain area, with the degree of alteration decreasing to the north to Wightman Fork, and essentially unaltered andesites just south and to the north of Wightman Fork.

The hydrogeological setting of the volcanic porphyry within which the Summitville Mine area presents a rather uniform medium. The hydraulic conductivity of the rock in the vicinity of the orebody has been evaluated by a series of permeability tests in monitor wells drilled into bed rock, the results of which are shown in Table 1.

The direction of groundwater flow in the South Mountain area appears to be north-east towards Wightman Fork. Groundwater flows and hydraulic heads are greatly influenced by the Reynolds Adit which appears to drain the entire north-east side of South Mountain, including the pit area. The Iowa Adit, located at an elevation of approximately 11,730 feet, drains a portion of the east side of South Mountain. It is estimated that the average

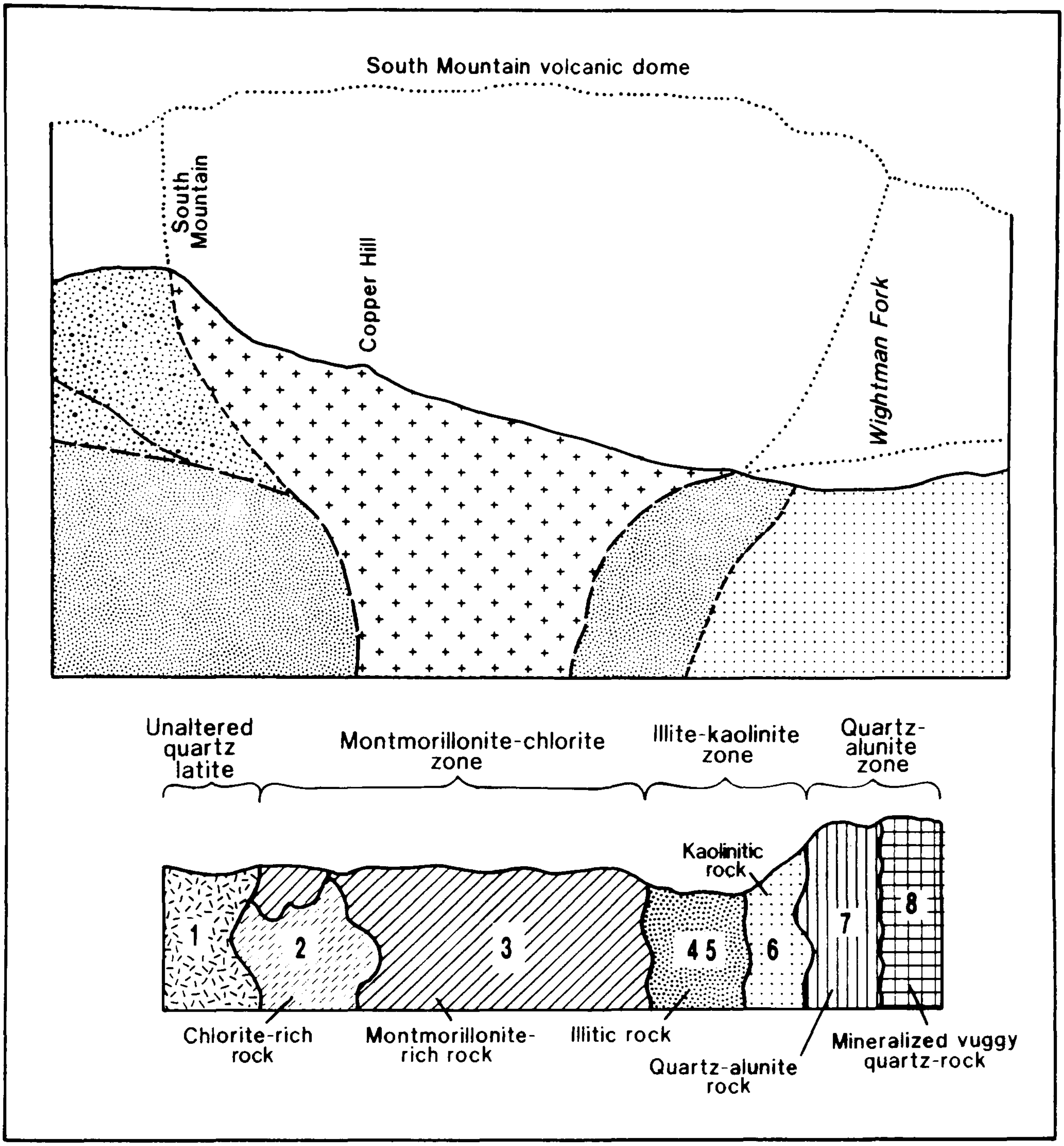

Figure 2. Geology of the Summitville Mine

Table 1. Hydraulic Conductivity in ABC Observation Wells

Site	Water Depth (ft)	Q (gpm)	K (cm/s)
ABC-MW1	182	10.0	1.1×10^{-5}
ABC-MW2	149	8.8	2.2×10^{-4}
ABC-MW3	292	9.6	9.5×10^{-5}
ABC-MW4	123	12.0	6.0×10^{-6}
ABC-MW5	182	14.0	1.1×10^{-3}
ABC-MW6	87	5.3	4.7×10^{-5}

flow from the Reynolds Adit is between 200 and 400 gpm, with high flows during spring runoff. Shallow groundwater from the mined area also reaches the ground surface as numerous seeps around the Reynolds and Iowa portals.

CURRENT LOAD

The load to Wightman Fork from the Reynolds Adit can be computed from information collected over the years by SCMCI and its predecessors at the site. The information available for this evaluation is flow and

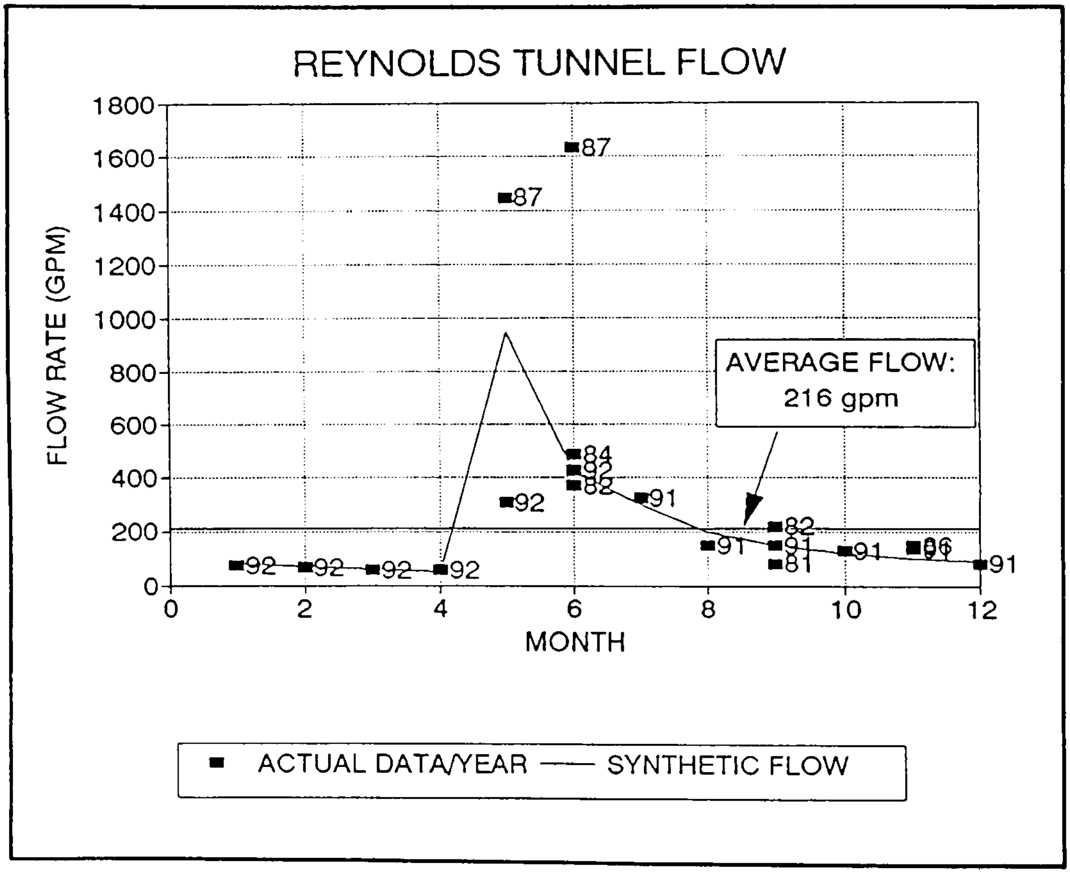

Figure 3. Measured Flows at the Mouth of the Reynolds Adit

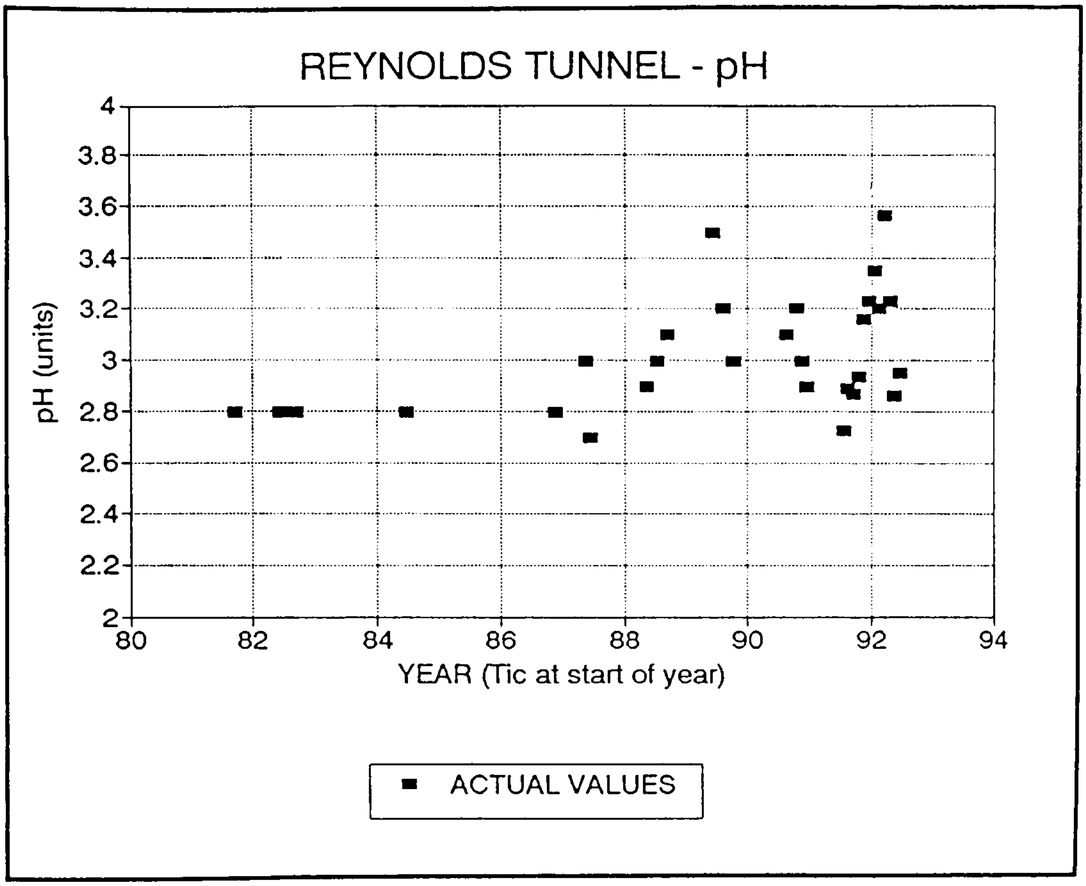

Figure 4. pH of Reynolds Adit Waters

chemical data taken at the mouth of the adit.

The flow from the Reynolds adit has varied over the times at which it has been monitored over the last decade. The flows by month at the adit are illustrated in Figure 3, presented in the months that the flows were measured. Based on these data, a synthetic estimated hydrograph for the year has been developed, as shown by the solid line on the curve in this figure. Based on this synthetic flow, the average flow from the adit has been approximately 220 gpm.

pH, total dissolved solids (TDS), copper and zinc are considered to be indicative of the overall chemistry of the system, these will be evaluated below.

pH

The pH of the Reynolds Adit water had shown considerable variability over the last decade, with the range of values falling between 2.7 and 3.6 (Figure 4). The median pH is about 3.

TDS

The TDS of the adit water has increased over the last five years, from about 1,000 mg/l in 1987, to about 5,000 mg/l present, with spikes to near 6,600 mg/l at times. The majority of this TDS is sulfate.

Copper

The copper concentrations in the Reynolds Adit flow are presented in Figure 5. They have increased from about 20 mg/l in the mid-eighties to a peak of near 340 mg/l in 1992. Concentrations are highest during the spring runoff, and drop rapidly during the year.

The mass flux of copper to Wightman Fork from the Reynolds Adit averages about 75 tons of copper per year. Prior to the SCMCI development, based on the limited data available, the average copper load may have been about 30 tons per year. The prevention of the copper flux to the stream will remove the 75 tons per year, providing a reduction of up to 30 tons per year from the pre-SCMCI condition.

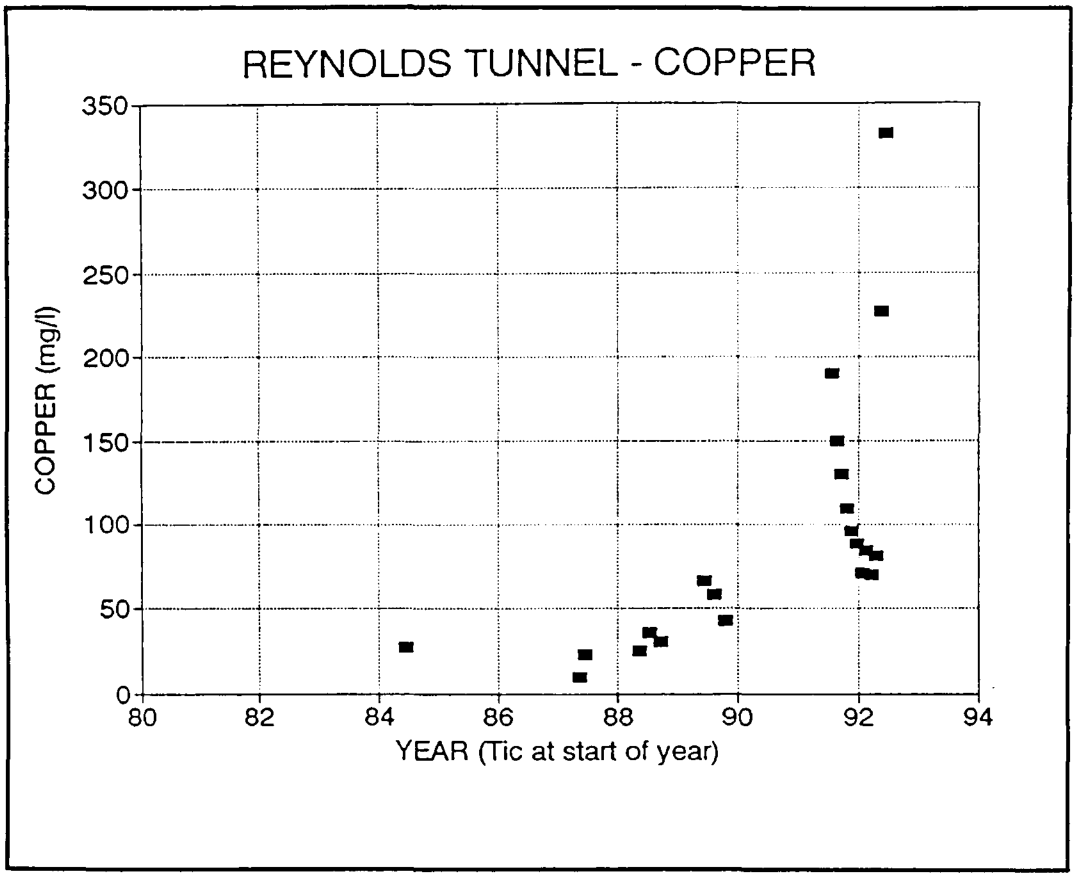

Figure 5. Copper Concentration in the Reynolds Adit Flow

Zinc

Data available for zinc shows groundwater concentrations less than 45 mg/l, with concentrations directly related to flow volume.

LOAD REDUCTION ACTIONS

The load reduction activity proposed for the Reynolds Adit is the plugging of the adit. This action will result in the following:

- The direct flow from the adit system will immediately cease.
- Flow that previously exited the adit will be forced to travel through the groundwater system, thus maximizing the opportunity for precipitation and attenuation[1] of metal species.
- The groundwater level, currently significantly below ground surface in the area of the ore zone (due to the drainage which occurs through the Reynolds Adit), will rise toward the ground surface. This will decrease the rate of direct oxidation of pyrites by oxygen, thus reducing and perhaps largely eliminating acid generation and leaching of metals in the submerged sulfide ore zone.
- Modelling of the groundwater system after the Reynolds Adit is plugged shows the mine pits filling but not overtopping the rim of the pit.

The plugging of the Reynolds Adit will be achieved by the installation of engineered acid-resistant concrete plugs in the main stem of the adit. The proposed design concept is illustrated in Figure 6. The plug will be designed to withstand the maximum possible static head which could be exerted by the water behind it in the Reynolds Adit with a factor of safety of at least 2. The plug will be fitted with monitoring devices, so that the water pressure and water quality behind the plug may be monitored after the installation of the plug. In addition, the plug is fitted with a drainpipe, so that the water may

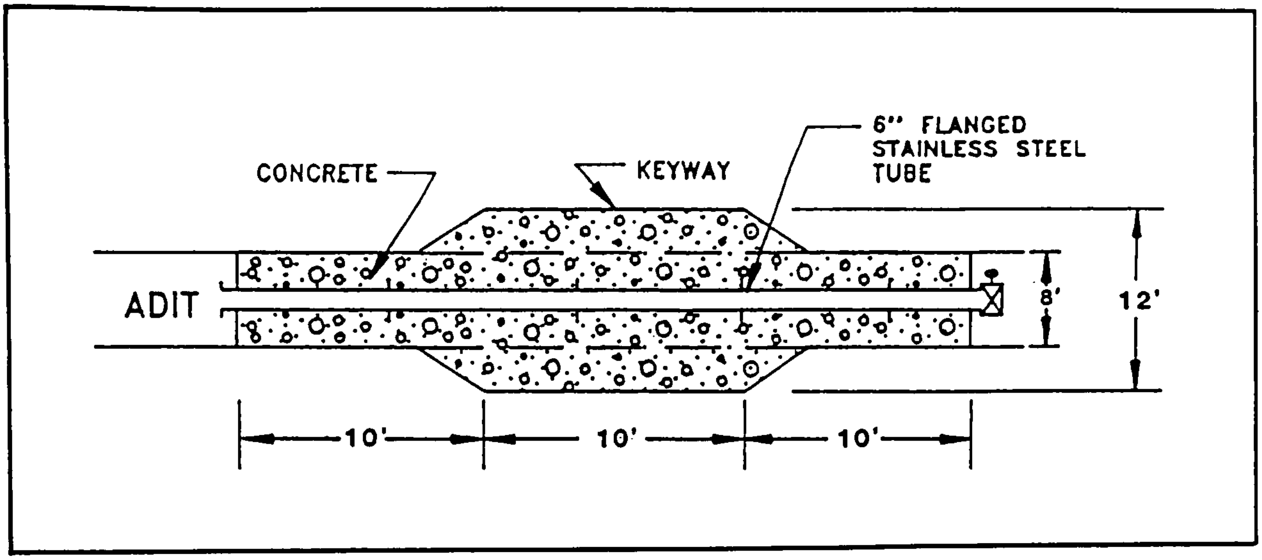

Figure 6. Proposed Design of Reynolds Adit Plug System

In conjunction with the plugging of the Reynolds Adit, it is proposed that the Dexter Adit also be plugged. The Dexter, which joins the Reynolds approximately 120 feet inside the existing Reynolds portal, also connects with the mine workings at the same elevation as the Reynolds Adit, but at the northern end of the workings. Currently, however, the Dexter Adit has been plugged by natural processes. The natural plug has withstood an estimated 150 feet of head since the early 1980's without significant leakage, and currently the flow from the adit is less than one gpm. The plugging of the Dexter Adit is anticipated to take advantage of this existing plug, and to provide insurance from a catastrophic failure of that plug. To protect against such a failure, an engineered acid-resistant concrete plug is proposed in the open portion of the tunnel, avoiding the disturbance of the existing natural plug.

EFFECTIVENESS OF LOAD REDUCTION ACTIVITIES

Hydraulic Effectiveness

The hydraulic effectiveness of the adit plugging program has been evaluated using a finite element model of the groundwater flow system.

The flow system is modelled as a groundwater aquifer, with flow in the model originating as infiltration, moving through the system, and exiting into the streams in the topographic lows. The Reynolds Adit, and the underground workings to which they are attached, are modelled as line sinks, with head controlled within the system. All flow is conserved; any flow that enters the model domain exits in Wightman Fork.

The model was constructed by reviewing the topography, meteorology, hydrology, and geology of the site area. A model domain comprising the surface water catchment of the stream gauging location WF-7 was selected for analysis, including the entire upper Wightman Fork basin, as well as Cropsy Creek, the northern portion of South Mountain, and the southern portion of North Mountain. The model was calibrated by applying the infiltration rate, and setting the hydraulic conductivities of the different geologic materials so that the model reasonably simulated the groundwater heads and Reynolds Adit flows observed prior to the SCMCI mining activity (SRK, 1984) and at the present. After a reasonable match was obtained flow from the Reynolds Adit was eliminated and the resulting head and flow conditions observed.

Conclusions drawn from the Reynolds Adit plugging analyses are as follows:

- Nearly all of the existing rock mass will be re-saturated after the plug is installed and equilibrium is established. It should take up to seven years to reach equilibrium after the adit is plugged;
- After plugging the adit, the South pit system should fill in about two years and overflow into the North pit should occur at the rate of about 20 gpm. The pit system will not overflow, however;
- Groundwater flow through the bedrock from the ore zone to Wightman Fork should increase from its current 220 gpm to about 400 gpm;
- Transit time for groundwater flow to reach Wightman Fork from the ore zone is about 20 years; and,
- The groundwater flow through the Beaver Mud

Dump at the toe of the slope will be approximately 40 gpm.

The precision of the flow analysis is considered adequate for design and regulatory support, but actual performance of the plugged system may vary from the predicted behavior.

In summary, the plugging of the Reynolds Adit is expected to re-saturate the north slope of South Mountain, flood the underground mine workings, and cause most groundwater flow from the workings to pass through the rock mass which is located between the ore zone and Wightman Fork.

Effectiveness in Preventing AMD

The mine workings that are drained by the Reynolds/Dexter system lie in sulfide ore. The sealing of the Reynolds and Dexter Adits should substantially mitigate the long-term acid-mine drainage (AMD) by limiting the initiating oxidation of pyritic sulfides once the new, saturated condition is established. The generation of acid from sulfide oxidation requires three components: sulfide, water, and an oxidant (generally atmospheric or dissolved oxygen). Of these, the supply of oxygen or another oxidant is the critical component, given the presence of sulfides (Brown and Logsdon, 1991). The complete flooding of the sulfide-bearing minerals remaining in the vicinity of the pit, and the submergence of the pre-SCMCI underground workings will almost totally deprive the acid generation reaction of oxygen. Once saturated conditions have been reestablished, the groundwater is the only medium capable of carrying oxygen into the system; the maximum concentration of dissolved oxygen is about 10 ppm. The low flux of oxygen through the saturated system will limit the oxidation of pyrite, thus mitigating the long-term acid-generation potential of the re-saturated ore zone. Additional oxidants such as ferric iron would also be present in limited quantities but are not expected to have a significant effect on the oxidation of pyrite over time. The reduction of acid generation then will limit the leachability of base metals from the sulfides and iron from the direct dissolution of iron sulfides.

Effectiveness in Limiting Copper and Zinc in Wightman Fork

After the groundwater flow system has reached its new equilibrium, the groundwater table slope will have increased, and somewhat more groundwater will be flowing to Wightman Fork from the general mine area than previously (it had been flowing down the Reynolds Adit instead). Prior to the plugging of the adit, the groundwater flow rate from the pit area to Wightman Fork is estimated to be about 220 gpm and the flow from the Reynolds Adit is about 200 gpm. After plugging the adit, groundwater flow is computed to rise to approximately 400 gpm. The groundwater in the rock material adjacent to the creek has been measured to contain less than 1 mg/l of dissolved copper. When this material flows into Wightman Fork, the copper load to the stream from the pit area is computed to be less than 1 ton per year, a net reduction of about 74 tons per year, or about 99% of the current load from the adit.

After the plugging of the adit, groundwater will infiltrate into the mined area, and into South Mountain upgradient of it, and will tend to flush the existing groundwater in the mined area towards Wightman Creek. The current groundwater concentrations in the most recently drilled wells are presented in Table 2; the locations of the wells, and the copper concentrations in them, are indicated in Figure 7.

This information suggests that the rock in the vicinity of the ore zone (ABC-MW2 and ABC-MW3) has no further neutralizing capacity, allowing acid generation and subsequent metal mobilization. The higher pH values and

Table 2. Field Parameters for Groundwater Wells

Site	Depth To Water (ft)	Temp. °F	pH	EC μs/cm	SO_4 mg/l	Cu mg/l
ABC-MW1	188.50	46	6.1	200	125	0
ABC-MW2	285.35	46	3.2	2600	3000	310
ABC-MW3	202.88	44	2.8	2500	2750	90
ABC-MW4	37.56	46	4.1	1200	750	1
ABC-MW5	14.30	46	6.0	200	65	0
ABC-MW6	16.10	48	6.9	2200	1400	0
Reynolds		43	3.2	2700	2700	180

Note: Data taken in period August 11-14, 1992

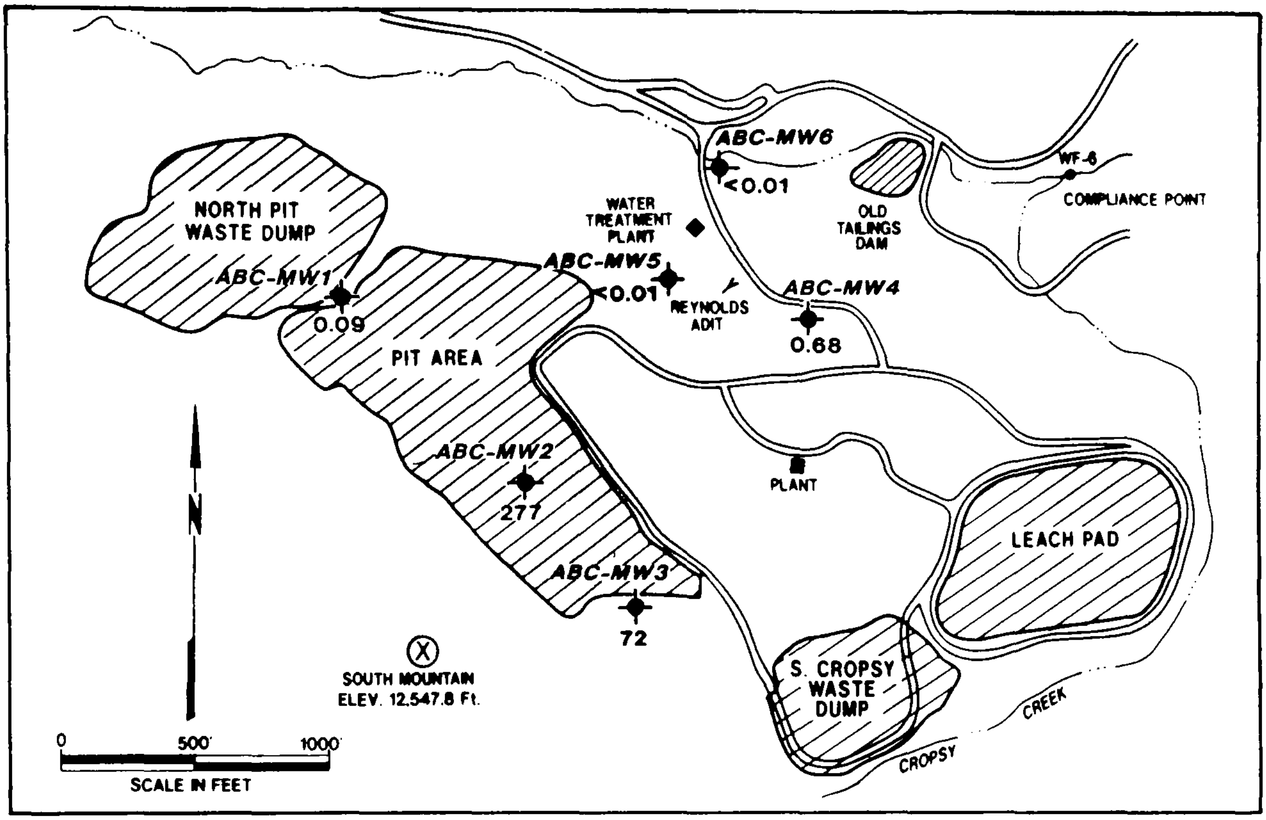

Figure 7. Groundwater Observation Wells and Copper Concentrations (1992)

the lower field copper values in ABC-MW4 and ABC-MW6 suggests the rock between the ore zone and Wightman Creek appears to have neutralizing and attenuating capacity. The presence of sulfate in ABC-MW4 and ABC-MW6 suggests that the groundwater in these locations was previously acid and has been partially or largely neutralized in transit from the mine area to the creek.

The transit time for groundwater to move from the pit to Wightman Fork is estimated to range up to 20 years, based on the calibrated model and an estimated porosity of 5%. During that time, the acidic groundwater will interact with the rock between the ore zone and the creek, resulting in some neutralization of the seepage, and the attenuation of metals, particularly copper and zinc. The effect of these processes will be to reduce the concentration of copper and zinc and other metals in the groundwater, and thus to reduce the load of copper and zinc and metals to Wightman Fork.

To evaluate the response of acidic, metal-bearing waters as they flow through the formation, a geochemical testing program was undertaken. Based on the results of sequential leach tests of rock samples obtained from the drill holes located between the orebody and Wightman Fork (ABC-MW4 through ABC-MW6), an empirical model of copper and zinc removal from groundwater was developed for the site. This model was applied to groundwater flow through rock in that zone and produced the following results:

- The total attenuative capacity of the rockmass for copper is at least 135,000 tons using only the attenuation limits found in the batch tests-the batch tests were not taken to the point at which no further copper or zinc were attenuated, a point in excess of the 4:1 water:soil ratio. This exceeds the calculated mass of copper in the entire orebody above the elevation of Wightman Fork (105,000 tons). Thus, the rockmass has the capacity to prevent all of the copper from reaching Wightman Fork, should it oxidize.
- The total attenuative capacity of the rockmass for zinc at a water:soil mass ratio of 4:1 is at least 12,000 tons based on the same attenuation testing. This constitutes about 25 percent of the

zinc present in the orebody above the elevation of the Wightman Fork (16,500 tons).

- For both copper and zinc, the amount of metal which can actually be mobilized after the successful plugging of the Reynolds Adit is limited (to about 12 tons per year for copper and 2 tons per year for zinc). The attenuative capacity of the rock is sufficient to contain such generated dissolved metals for several thousand years without breakthrough.

In both cases, the attenuative capacity of the rockmass far exceeds the amount of copper and zinc currently computed to be in the orebody groundwater system (850 tons and 80 tons, respectively), which provides excellent protection against this existing metal load from ever being felt in Wightman Fork. This model assumes the groundwater will flow through the bedrock as a porous medium, and that the randomly collected samples are representative of the bedrock geochemistry. Groundwater seeping into Wightman Fork from the orebody via the rockmass is expected to have an insignificant effect on metal mass fluxes in Wightman Fork.

Based on these evaluations, it appears that the rockmass has the capacity to permanently reduce significant metal transport from the orebody to Wightman Fork by the groundwater pathway.

SUMMARY OF EFFECTIVENESS

Based on the detailed hydrological and chemical evaluation discussed above it is concluded that the installation of the plug in the Reynolds Adit should achieve the following effects:

- Substantial reductions of direct discharge of acidic, metal-bearing water from the adit;
- The remaining orebody materials will largely or totally saturate over a seven-year period, thus reducing further acid generation and metal mobilization; and,
- Existing acid, metal-bearing groundwater in the underground workings and the adjacent rock will move downgradient towards Wightman Fork. Interaction between this water and the bedrock through which it is flowing will result in: the attenuation of copper, zinc, and other metals to levels which will be insignificant with respect to meeting the remedial objectives; and a modest increase in the pH of the groundwater.

Accordingly, successful plugging of the Reynolds Adit system is expected to reduce groundwater-borne metals contributions to Wightman Fork immediately.

POTENTIAL NEGATIVE EFFECTS AND PROBLEMS

Potential negative effects and problems associated with plugging of the Reynolds Adit, and the response that has been developed to mitigate them, are as follows:

- *Re-saturation of the surface.* The increase of the water table level to the ground surface may locate seeps and alter the forest cover which exists now, or which might re-establish on the reclaimed surfaces. However as the slope was probably flooded with groundwater prior to the original mining, this is considered to be a return to the natural condition, and is not likely to be a negative impact.
- *Pit outflow.* There may be a small flow from the existing pit depressions to the surface water system. It is likely that this flow will be acid, and may carry some dissolved metallic load.
- *Possibility of plug failure.* There is a potential that the plug to be emplaced in the adit system may fail. This would cause the water in the adit system to discharge suddenly into Wightman Fork. This possibility has been rendered remote by the design of the plug system. If failure were to occur discharge would enter the existing dam on Wightman Fork, where solids would settle out. After this, the flow would mix with the Wightman Fork flow, and would pass downstream and become increasingly dilute reducing downstream impacts.
- *Possibility of flow from another adit.* A considerable amount is known of the adit system at Summitville. Many of the original adits have now been mined out in the current mining campaign. The Reynolds emerges from the mountainside at considerably the lowest elevation, 11,320 feet. Table 3 shows the relationship of other adits to the Reynolds Adit. It is likely that the construction of the Reynolds Adit plug, along with a protective bulkhead in the Dexter Adit to prevent a catastrophic failure of the natural plug now in place, will be the only plugging necessary.
- *Possibility that the re-saturation of the slope will be incomplete.* It is possible that, despite the results of the analysis of the re-saturation of the slope, there will be portions of the near-surface material which will remain unsaturated after the adit plugging is complete. In this event, there may be some opportunity for continued acid generation in the subsurface. It is considered

Table 3. Elevations of Historic Adits

Adit	Elevation (ft)	Comment
Reynolds	11,318	Open
Chandler	11,498	Natural plug
Ida	11,604	Open
Dexter	11,513	Above Reynolds, natural plug
Narrow Gauge	11,677	May be mined out or covered over by the North Pit Waste Dump - Status Unknown
Oding	11,687	Mined out
Montroy	11,765	Mined out

that this can at most be a minor volume of material, and that any acid generated, and metal liberated, will be minor compared to the original mass load of metal from the adit system. Such flow will pass through the groundwater system, and will interact with the existing rock, providing some reduction in metal concentration and increase in pH.

- *Possibility of increased seepage in vicinity of the Reynolds Adit.* The plugging may induce increased seepage at the surface near the Reynolds Adit. However, as this seepage may have to pass considerable rock cover, it is expected it will be somewhat neutralized and the copper and zinc levels lowered by sorption. No major problem is expected.

In evaluating the possible negative effects and problems associated with mine plugging, an evaluation of the adit plugging activities at the Eagle Mine in Summit County, Colorado was undertaken. The plugging of the Eagle Mine resulted in flow from other adits, incomplete saturation of the mountain, and numerous seeps of poor quality water. It appears that the problems associated with the Eagle Mine are a result of:

- The placement of the bulkheads was too close to the ground surface of the mountain allowing for water pressure to exceed the confining pressures of the overlying materials;
- The location of the workings within the stratified formation allowed for discrete flow pathways through the sedimentary formations to the surface; and,
- Fracturing of the formation provided numerous pathways for water to surface.

In addressing these modes of failure relative to Summitville, the Reynolds plug location is 1200 feet within the adit allowing for several hundred feet of confining materials to support the increased water pressure. The workings lie within a relatively uniform formation with low permeability. Similar circumstances to these are found in the Walker Mine in Plumas County, California where the plugging of the mine showed very positive results. There the placement of the bulkhead was 2700 feet within the adit and the formation to be flooded was relatively uniform.

PIT RECONFIGURATION

The plugging of the adits will create the potential for the disposal of acid generating material in the area from which material was removed during the pit development. An analysis was performed to evaluate the amount of material that could be placed in the pits, and on top of the pit area at the same hydraulic conductivity as the *in-situ* material and still remain saturated by groundwater after the plugging of the adit. The volume of material which could be disposed of in a saturated condition is approximately 7 million cubic yards (10 million tons), based on this computation. This available capacity can be utilized to store acid-generating materials that present a significant metals load and must be effectively remediated by other engineering measures.

IOWA ADIT

In addition to the Reynolds Adit, the Iowa Adit produces a measurable surface flow May through November. The average flow for these months is approximately 27 gpm, with a high of 80 gpm during June. The water quality is acidic (pH 3 or 4), with TDS running between 3,000 mg/l and 10,000 mg/l, copper between 20 mg/l and 50 mg/l, and zinc between 12 mg/l and 25 mg/l, the concentrations being directly related to flow volume. The location of the Iowa Adit is topographically higher than the South pit rim, the flow from the Iowa will be directed into the pit to mix with waters from the lower groundwater system created by the plugging of the Reynolds Adit.

ENVIRONMENTAL MONITORING AND EFFECTIVENESS OF REYNOLDS ADIT

Monitoring activities after adit plugging will consist of the following:

- Monitoring of the bedrock wells ABC-MW4 through ABC-MW6;
- Hydraulic head measurements of water within the Reynolds and Dexter Adits;
- Visual inspection of the Reynolds, Dexter and Iowa Adits; and,
- Annual spring and seep survey.

The existing hydrogeologic model indicates that the actual effectiveness of the adit plugging activities will not be fully known for three to four years. It is estimated that South Mountain will resaturate in approximately seven years. During this evaluation of new springs and seeps or increased flows at existing springs and seeps will indicate the quantity of solution bypassing the natural neutralizing and attenuation capacity of the bedrock.

Groundwater quality monitoring, if the adit plugging is successful, should indicate that the existing poor mine water is being pushed through the bedrock towards Wightman Fork. This should take a minimum of three to four years.

Hydraulic head measurements at the Reynolds and Dexter Adit plugs will be performed to document the rate of resaturation. The Iowa Adit will be visually monitored for the presence of flow.

OBSERVATIONAL APPROACH DECISION CRITERIA

The effectiveness of the Reynolds Adit plug in reducing metal loads to Wightman Fork will be evaluated in two stages, the short-term and long-term effectiveness. The short-term effectiveness in reducing the metal load to Wightman Fork should be immediate. However, should a large increase in spring and seep flow in the mine area develop after plugging indicating that South Mountain will not resaturate and hydraulically encapsulate the sulfide rock, then a contingency plan will be implemented during Phase II. The contingency plan would involve collection and treatment of acid drainage from the Reynolds Adit.

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Miller, S., Van Zyl, D.J.A., and McPherson, P., 1994, Summitville Site Water Quality Characterization and Modeling, Tailings and Mine Waste '95 and Summitville Forum, Colorado State University, Fort Collins, Colorado.

Steffen, Robertson & Kirsten, 1984. Galactic Resources Inc. Regular Operations 112 Permit Application, Summitville Project.

Summitville Consolidated Mining Company, Inc., 1992, Technical Revision to the Reclamation Plan and Final Remedial Measures Plan.

1.In reference to metals removal, it is hypothesized that at least part of the removal of metals from solution occurs by the following process: 1) a modest increase in pH is effected by contact between acid water and the rockmass, 2) an iron hydroxide precipitate is formed which scavenges metals from solution. To simplify references to the removal process, it will simply be referred to as attenuation (of metal species) within this document.

GEOCHEMISTRY OF SPENT ORE AND WATER TREATMENT ISSUES

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INTRODUCTION

Summitville Consolidated Mining Company Inc. (SCMCI) negotiated an Amended Settlement Agreement and Compliance Plan (SA&CP) in July, 1992 with the Colorado Department of Health Water Quality Control Division (WQCD) and the Colorado Department of Natural Resources (Division of Minerals and Geology (DMG). The SA&CP contained several requirements which, in total, were intended to achieve substantial remediation and reclamation of the Summitville site. The SA&CP required goals in document submittal as well as development of goals for on-site work. The first goal of the SA&CP was submittal of a Progress Report identifying and defining plans for implementation of remedial measures by August 31, 1992. Submittal of the final Remedial Measures Plan by November 30, 1992 was the second major submittal goal of the SA&CP. Both the Progress Report and Remedial Measures Plan were compiled by a group of consultants which included: Adrian Brown Consulting, Inc; Environmental Solutions Inc.; Geochimica, Inc.; Geraghty & Miller, Inc.; Golder Associates Inc.; and, Times Limited. Four papers were taken directly out of the final Remedial Measures Plan and Technical Revision to the Reclamation Plan (SCMCI, 1992). These papers are:

- "Summitville Site Water Quality Characterization and Modeling";
- "Geohydrology and Adit Plugging";
- "Geochemistry of Spent Ore and Water Treatment Issues"; and,
- "Remedial Alternatives Identification and Evaluation".

The four papers present a synopsis of the engineering and scientific approach used in development of final Remedial Measures Plan. The authors recommend the four combined papers be read collectively to gain an understanding of the scope and effort expended to prepare the Final Remedial Measures Plan. These papers are presented in the present tense although only some of the measures described were finally implemented by the EPA during their activities.

DESIGN AND OPERATION OF HEAP LEACH SYSTEM

The heap leach system was designed as a zero discharge facility to recover precious metals from crushed rock contained in the Summitville orebody. The heap leach system consists of a lined permanent pad, two dikes or retention embankments, the solution application and collection piping and pumping equipment, a series of lined ponds, water diversion structures, a metallurgical processing facility for recovery of metals, and access roads. In addition, there are waste rock disposal areas and the open pit.

The general operating plan for the heap leach system was to load ore from each year of mining onto the existing heap on a protective synthetic liner behind a rock-filled dike. Upon placement of the ore, a dilute solution of cyanide was applied to the leach pad and ore through sprinklers to dissolve the gold and silver as their cyanide complexes. After percolation through the ore, the solution was collected by gravity at the bottom of the pad and removed by pumping from a series of wells located within the pad. The gold and silver bearing solution was pumped to the metallurgical facilities for processing, with the barren solution being recirculated onto the pad to continue the leaching process.

The construction of the containment dikes and installation of liners was initiated in late 1984 and completed in early 1988. The design of the containment dikes was modified again in 1986. In addition to the other components discussed, a diversion channel was excavated around the south and east sides of the leach pad to divert natural Cropsy Creek flows around the pad and to intersect surface runoff.

A permanent underdrain system consisting of geofabric wrapped coarse rock and perforated pipe, remains under the double liner to collect natural seepage from the bedrock underlying the leach pad area. The collected seepage is directed through the underdrain placed beneath the leach pad to a pumpback station located at the toe of the dike. The contamination of the underdrain seepage with leach solution is a problem which has been examined and is discussed in a subsequent section. At the upper end of the heap leach pad, the valley center drain (VCD) consists of an 18-inch diameter perforated and corrugated plastic pipeline buried in crushed bedding material and drain rock, all of with is enclosed in a geotextile wrap. Associated with the main underdrains are the finger drains which were originally located by visual examination of the prepared ground surface. The VCD discharges at the toe of Dike 1 at the French Drain sump.

In addition to the underdrain system, two other systems were constructed for the heap leach pad. The first drainage system was a temporary cutoff to intercept runoff upgradient of the leach pad during its construction. The second system was a permanent cutoff to divert runoff around the road which was intercepted upgradient. The present 550 diversion ditch is the permanent cutoff to intercept runoff and drainage between the Cropsy diversion and the top of the completed leach pad.

The heap leach system was originally designed as a zero discharge facility. However, with the introduction of the cyanide-bearing return flow from the French Drain sump in 1986, SCMCI began to experience a positive water balance in the heap leach pad. Two computer-modeled water balance projections were conducted (Klohn-Leonoff, 1987 and Golder Associates Inc., 1988) for SCMCI. Both water balance models indicated that the Summitville heap leach pad was in a positive water balance and would, at some point in the future, exceed design containment requirements. At the end of 1988, there was approximately 80 million gallons of excess solution stored within the heap leach pad. This positive water balance was largely a result of pumping the French Drain flows back into the heap leach pad.

SCMCI performed feasibility testing of various water treatment scenarios in 1988 and filed an application for a CPDS permit to authorize discharge of treated excess water from the heap leach system in 1989. After several months of discussion with WQCD, a CPDS permit was issued in May 1989. In the fall of 1989, a water treatment facility was brought on-line to treat and release excess solution from the heap leach pad to reduce the solution storage volume.

The heap leach pad operated as a closed system. Inflows were from direct precipitation, snowmelt, discharge from the interim water treatment plant (IWTP) and return flow from the French Drain sump. Outflows include spray evaporation and discharges from the recently modified water treatment plant (WTP) which have been treated to meet effluent limits at Outfall 004.

HEAP LEACH PAD DECOMMISSIONING

Heap leach pad decommissioning involved a step-by-step approach. The first step was to evaluate the spent ore material chemical stability for in-place, long-term closure. Once the feasibility of in-place chemical stabilization of the solids was established, evaluation of long-term solution management, and short-term dewatering and treatment were addressed. The "bubble concept" of establishing a single in-stream compliance point below the operation allowed SCMCI the flexibility to remediate the site by treating and releasing water from the site to attain the water quality criteria. After closure, long-term solution management of the leach pad was to be incorporated into the site "bubble" to allow the most efficient use of resources while still achieving the objective of meeting site-specific in-stream water quality criteria at one downgradient point.

The goal of decommissioning was to comply with the site-specific closure standards in an economical and practical manner. To accomplish the goal of decommissioning, a combination of physical reclamation, water treatment, and rinsing is usually required.

The purpose of physical reclamation is to minimize the infiltration and generation of potentially poor quality solution through its contact with the pad solids. The act of physical reclamation usually involves recontouring and capping of the pad with low permeability liners and/or compacted soils. The final surface of the pad is then revegetated to maximize runoff and minimize infiltration.

The purpose of treatment and rinsing is to produce an effluent of acceptable quality for release into the environment without causing unacceptable impacts to surface and ground waters. Treatment can be accomplished through one of several chemical, biological, or physical processes such as hydrogen peroxide oxidation, microbial degradation, or volatilization. The combination of microbial degradation and volatilization are often referred to as natural attenuation. These processes discussed later can often be enhanced artificially through addition of chemical reagents and microbial seeds. Treatment and rinsing can be combined by either recycling or discharging treated effluent generated through continuous application of fresh water onto the pad.

In the event recycling or treated effluent is used to rinse the pad, the solution eventually must be either discharged or evaporated. If the recycled or continuous fresh water used in rinsing must be discharged following treatment, compliance with the in-stream standards or existing discharge permit is mandatory.

The constituents of concern a the Summitville Mine with respect to the pad solids and solution included the metals, WAD cyanide, and pH for which in-stream Numeric Criteria Limits (NCLs) have been established in Wightman Fork at sampling station WF-6.

Solution Management

There are two goals associated with solution management within a spent leach pad, short-term and long-term. The short-term goal is to dewater and/or rinse the pad sufficiently to achieve compliance with the specified closure standards and to allow discharge of the residual solution. The long-term goal is to minimize the infiltration of water and the generation of additional poor quality solution.

In order to increase the treatment and discharge of pad solution, the existing water treatment facility has been retrofitted according to a plan presented in the July 1, 1992, Plan for Compliance. The plan utilized the barren and filtration ponds at the gold plant for WAD cyanide destruction using hydrogen peroxide instead of chlorine, and then feeding the partially treated water to the retrofitted wastewater treatment plant for final metals precipitation and polishing using sulfide reduction.

The WAD cyanide remaining in the recirculating pad solution could be systematically reduced over time using one of two approaches. The first approach would involve addition of hydrogen peroxide to the entire recirculating solution in a quantity to completely destroy the WAD cyanide, using the recently installed Degussa treatment system.

A second approach would involve enhanced biological degradation through the addition of specifically adapted microbial seeds and the necessary nutrients to the recirculating solution. The results of a preliminary bench-scale investigation indicated that a significant reduction in WAD cyanide was achieved following the passing of a few pore volumes of microbially spiked solution through a column of pad material at the lower solution temperatures anticipated at the site. An evaluation to conduct full-scale, enhanced, natural microbial attenuation of WAD cyanide within the pad during the dewatering phase was performed. Since the discharge of water during dewatering must meet the existing CDPS permit with respect to WAD cyanide, and the cost of biological degradation is significantly less than chemical treatment, this is the process of choice at the present time.

Solids Management

In conjunction with the management, treatment, and discharge of solutions, there remains a need to minimize the long-term generation of poor quality solution through contact of precipitation, runoff, and snowmelt with the residual pad solids. There are two specific aspects of solids management which must be addressed during decommissioning. The first aspect is to classify the solids as to their nature and their potential release of metals and other constituents at undesirable levels.

Following rinsing, the primary source of additional metals release arises from the generation of acid and the oxidation of sulfides. With knowledge of the chemical aspects of the solids, a physical reclamation plan can be devised to minimize the extent of infiltration and solution movement within the pad. Of particular importance at the Summitville Mine, is the introduction of acidic drainage into the pad from the upgradient South Cropsy Waste Rock Pile

Physical reclamation can be accomplished in one of several manners including capping with low permeability liners and/or soils, and recontouring the sides and surfaces to maximize runoff. In the case of the Summitville Mine, there was an additional option to allow permanent submergence of a portion of pad under water to impede acid generation, if this process is shown probable. In this case, establishment of a wetland on top of the recontoured pad may be a viable approach, although it would raise additional issues regarding geotechnical stability of Dike 1. Since partial or complete submergence of the pad probably would not be a viable or acceptable approach, then maintaining only a minimal hydraulic head on the liner would be the preferred.

HEAP LEACH PAD GEOCHEMISTRY

To determine the long-term impact of the leach pad drainage and geochemistry on water quality in Wightman Fork at the compliance point, SCMCI undertook a detailed geochemical evaluation of the behavior of the pad solids. The evaluation included mineralogical and chemical analyses of samples of the different types of the pad solids and a laboratory testing program to evaluate the long-term chemistry of leachate produced under two alternative leaching scenarios. The first leaching test evaluated the chemistry of leachate derived from reacting the pad solids with acidic drainage such as would be anticipated from the upgradient Cropsy Waste Rock Disposal Area. the second leaching test evaluated the chemistry of leachate derived from reacting the pad solids with de-ionized (DI) water as a surrogate for rain or snowmelt.

Six bulk samples of the leached ore or pad solids were collected by SCMCI in February 1992 as representative of the types of materials that exist on the pile. These samples were initially evaluated for static acid-base accounting (ABA) parameters, and EPA Method 1312 leaching characteristics in April 1992. In this program, the spent ores or pad solids were tested on both an "as-received basis" and after rinsing with DI water to remove the easily solubilized alkaline rinds. The samples were rinsed at a water:rock ratio of 5:1 on a volume basis until either a total ratio of 80:1 had been reached or the pH and conductivity of the rinsate had fallen below 7.0 and 100uS, respectively.

A second phase testing program included the following elements:

▸ Initial characterization tests on "as-received" materials. The characterization tests include measurement of pH, conductivity, Eh and ferrous iron (Fe^{+2})on a 2:1 (water:rock) paste, and analysis of total metal concentrations for calcium, magnesium, sodium, potassium, silicon, aluminum, sulfur, iron, arsenic, barium, cadmium, chromium, cobalt, copper, manganese, lead, mercury, nickel, selenium, silver and zinc.

▸ Preparation of an equal-mass composite of the six ore types and retesting of the initial characterization on the composite pad.

▸ Detailed testing of the composite sample and a specific sample of high-S ore, selected to be sample LPO-4. The detailed testing included:

- Static acid-base accounting (ABA) on an "as-received" material. Results are presented in Table 1.
- Rinsing the crushed ore until the conductivity of the rinsate fell below 100uS.
- Repeating the acid-base accounting tests on the rinsed ore samples. Results are presented in Table 1.
- EPA Method 1312 leaching of the rinsed splits with analysis for alkalinity/acidity; pH; Eh; SO4; chlorine, calcium, magnesium, sodium, potassium, silicon, aluminum, sulfur, iron, Fe^{+2}/Fe^{+3}, arsenic, barium, cadmium, chromium, cobalt, copper, manganese, lead, mercury, nickel, selenium, silver, and zinc.
- Sequential leach testing with chemical analysis of leachates and solids. Each sample was leached with both DI and with Reynolds Adit water. The DI tests were performed to simulate leaching with rainwater/runoff, as would be expected if the pad materials are isolated form drainage from the Cropsy waste dump. Results are presented in Table 2. The Reynolds tests were performed to simulate leaching that could occur if acid water (e.g, drainage from the Cropsy dumps) moves through the pad. Results are presented in Table 3. Figure 1 is a schematic diagram of the sequential testing procedure. The sequence of tests allows evaluation of the leaching that could occur at water:rock ratios ranging form 0.25:1 to 4:1.

A bulk sample of low pH, mineralized water from the

Table 1. Leach Pad Ore: Acid-Base Accounting

Parameter	**LPO-4 (as received)**	**LPO-4 (washed)**	**LPO-COMP (as received)**	**LPO-COMP (washed)**
Total S (%)	3.02	3.46	2.47	1.90
Pyritic S (%)	0.22	0.27	0.26	0.21
Total S (ton $CaCO_3$/Kton)	94.4	108	77.2	59.4
Pyritic S (ton $CaCO_3$/Kton)	6.9	8.4	8.1	6.6
Acid Neutralizing Potential (ton $CaCO_3$/Kton)	4.0	5.2	5.2	3.7
ANP-Pyritic S (ton $CaCO_3$/Kton)	-2.9	-3.2	-2.9	-2.9

Table 2. LPO-COMP Sequential Batch - Leachates (DI)

Batch	**pH**	**EC**	**SO4**	**Aluminum**	**Copper**	**Iron**	**Zinc**
D1	7.36	3090	2380	0.80	1.10	4.37	0.04
C1	7.30	2820	1970	1.25	1.13	4.32	0.05
B1	6.78	2340	1650	3.05	1.06	5.38	0.05
A1	6.99	1560	774	0.91	0.60	1.31	0.03
A2	5.85	493	148	0.18	0.04	0.61	<0.01
A3	6.80	321	84	0.20	0.02	0.71	<0.01
A4	6.36	228	44	0.29	0.02	1.48	<0.01
1312	6.71		<10	0.17	<0.01	<0.03	<0.01

Table 3. LPO-COMP Sequential Batch - Leachates (Reynolds)

Batch	pH	EC	SO4	Aluminum	Copper	Iron	Zinc
D1	7.28	3420	2440	0.57	1.06	5.45	0.05
C1	6.96	3180	2340	3.34	1.19	9.63	0.19
B1	6.85	2870	2360	0.70	0.81	32.6	0.06
A1	4.26	2580	2450	0.12	0.86	217	0.83
A2	3.78	2240	2380	0.8	0.62	503	6.06
A3	3.77	2040	2270	0.7	0.42	660	8.25
A4	3.72	1970	2040	0.7	0.45	765	8.75

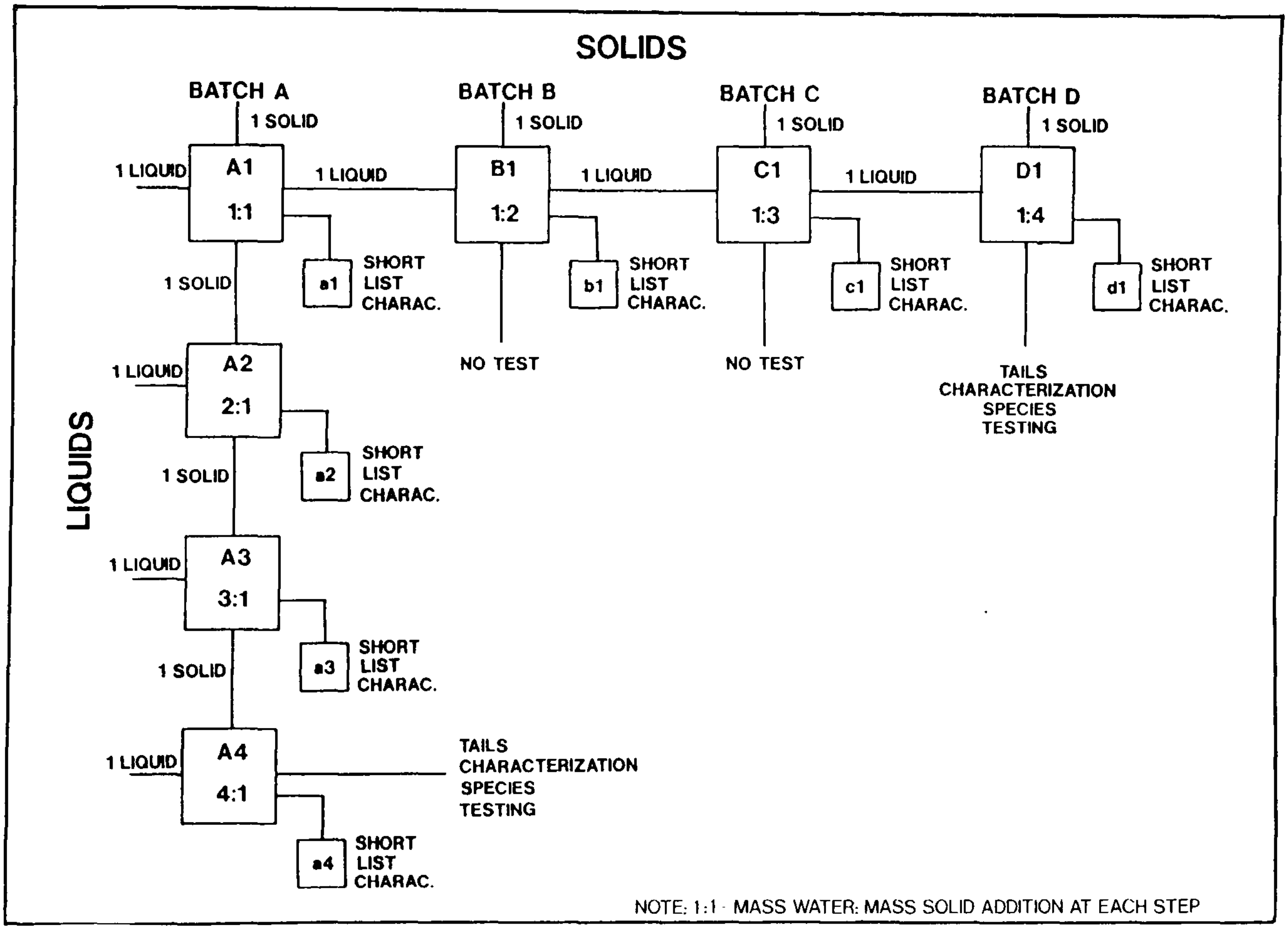

Figure 1. Schematic Diagram of the Sequential Testing Procedure

Reynolds Adit was collected and analyzed using standard EPA methods, consistent with the methods used in the current SCMCI sampling and analysis program. This bulk sample was used in the sequential batch leaching tests to simulate acidic waters from across the site.

The chemistry of a leachate from the decommissioned leach pad will depend upon predominantly the acidity of the fluid that enters and leaches the solids. If the lixiviant is quite acidic like the Reynolds Adit water, then the residual alkalinity of the leach pad ores will be removed, relatively rapidly, and the leachate will be a low pH (<4), high TDS, high metals solution that will contain at a minimum cadmium, iron and zinc concentrations above the NCL limits.

However, if the lixiviant is infiltrating precipitation, which is simulated by de-ionized water the Method 1312

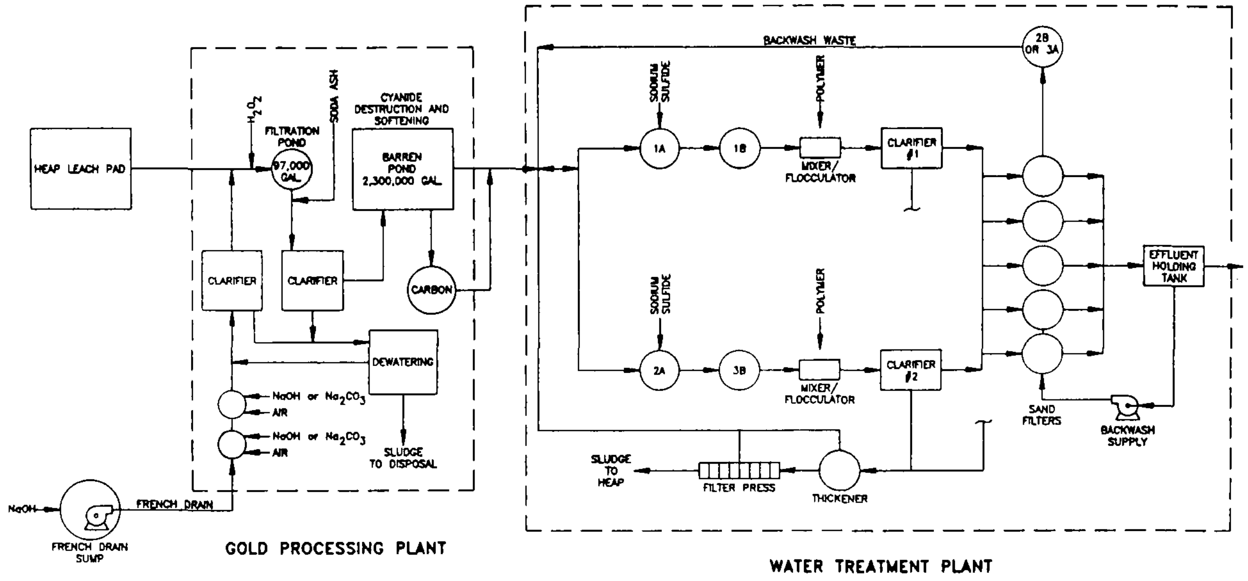

Figure 2. Proposed Process Flowsheet

extractions, then the decommissioned leach pad should not go acid and high concentrations of NCL metals should not appear over time. Given a final cover with an in situ saturated hydraulic conductivity of 1×10^{-6} cm/s (Cover Option #1), the total steady-state recharge through the pile would be about 24.5 acre-feet/year. At this rate of recharge, the interstitial water will turn over at a rate of about 1 pore volume per 36 years. For a final cover with an in situ saturated hydraulic conductivity of 1×10^{-7} cm/sec (Cover Option #2), the total recharge would be about 6.0 acre-feet/year. For Option #2, one pore volume would be exchanged per 147 years. The short-term chemical behavior of the pad, which is dominated by the residual alkalinity produced by the leaching and the addition of lime $CaCO_3$ to the ore to create a high pH would be expected to produce neutral to alkaline pH leachate, and low concentrations of metals. Based upon the laboratory results, this short-term geochemical condition would be expected to persist for at least 90 pore volumes of water exchange, or several thousand years.

The long-term behavior would be dominated by the low reactivity of the leached ores, which contain very little sulfide mineralization and low total metals concentrations. The low ionic strength infiltrating water does not react significantly, and the result is a low TDS, pH 6.0-6.5, low alkalinity solution with very low concentrations of dissolved metals.

Based on these results, a properly capped and recontoured leach pad which is not inundated by acidic water will produce a minor metals load to Wightman Fork and would provide an environmentally acceptable closure approach with respect to the heap leach pad.

HEAP LEACH PAD DETOXIFICATION

The collection and routing of French Drain water and barren heap leach pad solution flows, as well as the treatment plant design have been modified to allow an increase in WAD cyanide detoxification, and metals removal capabilities during dewatering and an emergency situation. The proposed process flowsheet is presented on Figure 2. The new wastewater treatment system (WTS) includes the cyanide destruction circuit at the site of the

Gold Plant, and the sulfide precipitation circuit at the site of the water treatment plant. The heap leach pad detoxification standards are discussed in the Technical Revision to the Reclamation Plan (SCMCI, 1992). There are two options for rinsing or detoxifying the WAD cyanide in the heap leach pad. Two concentrations have been derived based on the need to satisfy the in-stream WAD cyanide NCL at WF-6. These two concentrations are 0.7 mg/l, which will be acceptable for a cover having a saturated hydraulic conductivity of $1x10^{-6}$ cm/sec, and 2.5 mg/l when a cover hydraulic conductivity of $1x10^{-7}$ cm/sec is used.

The hydrogen peroxide cyanide destruction first stage has been modified to accommodate a maximum combined flow of French Drain and barren solution of 1,500 gpm. Discharge from the first stage flows by gravity to the second stage at the existing water treatment facility, which has been modified to accommodate an average flow rate of 400 gpm and peak flow of 540 gpm by conversion of its single train configuration to dual train operation.

To maximize treatment performance, the French Drain solution is being treated first for removal of iron and manganese prior to combination with the heap leach pad solution for cyanide destruction, softening and additional metals removal. The iron and manganese are removed first to decrease the subsequent demand for hydrogen peroxide in the cyanide detoxification process. Iron and manganese are commonly removed by oxidation followed by either sedimentation or filtration. Typical oxidants used in iron and manganese removal include air (oxygen), chlorine, potassium permanganate, and hydrogen peroxide. To minimize the addition of chemicals that result in increased TDS, air is used in the primary oxidant during iron and manganese removal.

The WTS involves addition of the hydrogen peroxide using an in-line static mixer and a chemical dosing system and storage system leased from a chemical distributor. Soda ash is being added to increase alkalinity and promote precipitation of hardness as calcium carbonate. The chemically treated solution will then enter the existing barren pond to provide sufficient residence or hydraulic retention time to complete oxidation of cyanide and settling of the sludge. The sludge will be disposed in accordance with currently accepted and permitted practices, although alternative sludge disposal scenarios are being evaluated and are discussed below.

At a design flow of 1,500 gpm, the 2.5 million gallon barren pond provides a minimum of one day (24 hours) of residence or oxidation time as well as short-term storage for precipitated sludge. Following chemical precipitation of the metals and oxidation of WAD cyanide, the treated solution is routed to the second stage. Conveyance of the pre-treated solution is through a newly installed pipeline from the first stage to the pumphouse with designed flow capacity of approximately 600 gpm and then to the second stage through 2 existing 4-inch pipelines. The excess detoxified solution that cannot be discharged is routed back to the leach pad for spraying to rinse the leached ore.

Soda ash softening is a proven technology used in treatment of drinking waters for hardness removal. Calcium concentrations are reduced to <100 mg/L as $CaCO_3$ in typical water treatment. The reduction in calcium concentration will aid in reducing the possibility of scaling problems in the WTS. The softening process produces a considerable volume of sludge that is settled in a clarifier or in the barren pond. The sludge is co-mingled with the sludge generated from the cyanide destruction process and currently disposed on the lined heap leach pad.

Additionally, it is proposed to biologically detoxify the spent ore by applying solutions of treatment bacteria in a drip application, percolation leach. Enhanced biological degradation or detoxification of WAD cyanide in the leach pad moisture and on the retained solids at the Summitville Mine will consist of the following steps:

- Production of bacteria designed to oxidize cyanide in spent ore and the pore moisture of spent ore.
- Application of dilute solutions of the treatment culture.
- Analysis of drain-down solutions and spent ore to verify biological degradation of cyanide.

The process is operated as a closed-circuit with recycling and with no discharge to the environment. The process bacteria populations and nutrients are natural and non-toxic.

Once the accumulated pad water is removed and detoxification completed, the pad will be rinsed if needed to achieve the specified closure standard for cyanide. In the event the specified standard has not been achieved, then chemical treatment using hydrogen peroxide would be needed to destroy the residual cyanide to the rinse standard. Rinsing could be accomplished either by recycling biologically or chemically treated water or by continuously passing fresh water through the pad. In general, fresh water rinsing is not practical at the Summitville Mine due to the limitations on water availability and the problems associated with storing, treating, and discharging large volumes of water.

ACTIVE WATER TREATMENT OF ACID DRAINAGE

Active water treatment of acid drainage at the Summitville Mine is being performed at the portable interim treatment system (PITS). The PITS is currently treating flow from the Reynolds Adit, the Iowa Adit and other groundwater seeps. The PITS has been designed and constructed with a flow capacity of 150 gpm.

The chemistry of the acidic site waters is dominated by metals including aluminum, iron, manganese, zinc, and copper, the concentrations of which can range from several tens to hundreds of mg/l. Of major concern are the potential long-term changes in site water chemistry resulting from generation of acid drainage.

There are four primary issues relating to the efficiency and success of long-term active water treatment:

- Current and future water chemistry;
- Current and future water volumes;
- Type and degree of water treatment; and,
- Volume and chemical nature of the sludges produced during treatment.

The range of water chemistry and flows determine the design capacity of an active treatment system. Design and construction of a treatment system with no consideration of storage or flow equalization would require a very large capacity to accommodate flows generated during the short runoff period, while only a fraction of the capacity would be needed during the remainder of the year.

The initial concentrations of the constituents and the required reduction in metals loading will dictate the complexity and degree of treatment required. In the event only minor reductions in metals loading are required a conventional active treatment facility employed either alone or in combination with a passive treatment system may be sufficient to attain the necessary efficiency.

A conventional neutralization and metals precipitation facility in general can achieve a 95 percent or greater reduction in metal load.

The long-term active treatment of water is generally not considered a viable option for site remediation due to cost and the generation of large volumes of sludge. The current and future water chemistry and volume will be controlled by the success of site reclamation and closure, in conjunction with other potential remedial actions.

One area of particular concern with respect to water treatment involves the long-term disposal of chemical sludges, for which the options are on-site and off-site disposal. One off-site disposal option would involve dewatering and possibly drying the sludge for shipment to a non-hazardous waste repository. For this approach to be successful the sludges must pass the traditional USEPA SW-846 TCLP analysis. A second off-site disposal option would involve shipment of the sludge to a smelter for recovery of metals, if the economic value is acceptable.

The current on-site disposal method involves placement of the sludge on the heap leach pad in accordance with an approved State protocol. However, long-term disposal of sludges may not be feasible or consistent with the long-term reclamation objectives. The preferred on-site disposal options include: underground disposal within the historical mine workings and/or within the open pit.

PASSIVE WATER TREATMENT OF ACID DRAINAGE

Three passive treatment alternatives were considered. They include wetlands, engineered anoxic systems, and direct land application. These alternatives are considered passive due to their increased reliance upon natural versus manmade components as the center of the treatment system. Although these systems are not maintenance free, their operational costs are generally less than those associated with conventional or advanced treatment systems.

These systems could be of value in treating small water flows requiring only periodic and/or partial metals removal. In general, the operational life of direct land application and wetlands systems are finite due to the available metals loading capacity of the soils and organic matter associated with the systems.

Once the metals loading capacity of either wetland or direct land application systems is exhausted, the soils and/or organic matter must be removed and replaced if continued use of the systems is desired.

SLUDGE DISPOSAL

Chemical sludge is produced in the active water treatment process at the Summitville site. Under the process flow scheme at the water treatment system (WTS), sludge is produced in three separate process steps: 1) iron and manganese removal, 2) softening, and 3) sulfide precipitation. Sludge is also produced in the treatment of waters from the Reynolds Adit and other groundwater seeps through the portable interim treatment system (PITS).

Sludge Characteristics and Volume

During the course of water treatment involving processes such as chemical oxidation, neutralization, and softening, chemical sludges are produced through the precipitation of metal hydroxides and carbonates. In addition, there is a minor quantity of sulfide sludge produced during advanced treatment and removal of trace metals. Currently, the sludges are dewatered to about 30% solids by weight using two filter presses and deposited on the heap leach pad.

Based upon the levels of metals remaining in solution following primary and secondary treatment, the total quantity of sulfide sludge produced per day in the second stage has been estimated to be about 100 pounds or less. At an estimated solids underflow concentration of 3%, the volume of sludge would only be about 400 gallons per day (gpd). Although the sulfide sludge does exhibit the necessary characteristics to be acid generating, it is commingled each day with thousands of pounds of hydroxide and high alkalinity and high pH chemical sludges which are not acid generating. As a result, the primary concern from a short and long-term perspective related to the disposal of the high volumes of metal hydroxide and softening (calcium carbonate) sludges.

Disposal Alternatives

Off-site sludge disposal alternatives including hauling to an approved disposal facility or hauling sludge to a smelter for metals recovery were evaluated. However, the cost of off-site sludge disposal is extremely high, and recovery of copper or other metals only provides a short-term solution. Therefore, other alternatives were evaluated with particular emphasis on on-site disposal.

The current on-site sludge disposal practice involves placement of dewatered filter cake on the heap leach pad in accordance with a State-approved method. However, long-term disposal of sludges in this manner is not consistent with the heap leach pad closure plan. The other on-site disposal alternatives include construction of a disposal facility, or disposal in the old mine workings after plugging of the Reynolds adit.

A lined impoundment could be constructed for disposal of sludge as an alternative. Following completion of active water treatment, the impoundment could be capped with low-permeability soils and revegetated. To accommodate the sludge produced for a period of only 3 to 4 years, it is estimated that about 2 to 3 acres of area would be required assuming a final depth of sludge of 20 to 30 feet.

The preferred on-site disposal alternative involves placement of the sludges without dewatering, into the old mine workings following plugging the Reynolds adit. The advantages of this alternative include providing both a short and long-term solution of sludge disposal, the potential for neutralization of the acidic water as it enters the workings and possibly decreasing metals levels, and an approach to significantly reduce the cost of decommissioning and closure of the leach pad and ultimately the entire mine site.

Another advantage to this approach is the potential opportunity to ensure that adequate buffering capacity is provided in the deposited sludge to neutralize not only the acidity in the Reynolds Adit water, but also the acidity produced as the result of the precipitation of metals such as aluminum and iron. Based upon the flows of French Drain water and barren heap leach pad solution and their corresponding chemical characteristics, the total alkalinity available in the combined sludges during two years of treatment, which corresponds to the estimated time required to fill the workings, would be about 3,580 tons as calcium carbonate.

Since an excess of buffering capacity or alkalinity, above the anticipated acidity in the water filling the working, of about 620 tons or 17% is anticipated following disposal of sludges underground, the alternative appears acceptable. Based upon experience, however, a ratio of about 1.5:1.0 for alkalinity to acidity is often needed to raise the low pH water from below 4.0 to about 7.0.

Using a ratio of 1.5:1.0, more alkalinity expressed as calcium carbonate was needed in addition to the excess 620 tons anticipated to neutralize the incoming acidity. At a combined French Drain and barren solution flow of 0.58 MGD, the additional excess tonnage of alkalinity corresponds to an increase in feed dosage for soda ash of 700 mg/l. The preferred approach would be to carefully monitor the alkalinity, hardness, and sludge production, to determine the appropriate dosage requirements, and add further alkalinity accordingly.

With respect to residual WAD cyanide in the sludge, the results of the recent chemical evaluations of the sludge obtained from treatment of the French Drain water without cyanide destruction indicated that the cyanide was associated with the liquid and not the solid phase of the sludge. Therefore, following treatment of the various waters for removal of WAD cyanide, very low WAD cyanide levels are anticipated in both solids and solutions. Assuming all of the WAD cyanide in the 3% sludge was associated with the solids, a total cyanide concentration of about 40.0 mg/l based upon recent analyses of the French Drain water, and a ratio of sludge to Reynolds adit water of about 0.15 (i.e. 30/200), the resultant WAD cyanide level in the mine workings without any treatment would be about 0.18 mg/l, or less than the drinking water standard.

Environmental Monitoring of Heap Leach Pad

During the detoxification and dewatering process, operational monitoring will be performed to determine water levels and success of cyanide destruction. Following the detoxification of the heap leach pad, five auger drillholes will be sampled and analyzed to verify that the facility solids and solutions meet the closure standards. These auger samples will also be evaluated for the potential to generate acid drainage. The potential for acid generation of the heap leach spent ore will determine the permeability requirements for the cover materials. Some downgradient monitoring points will be established to analyze for cyanide. The acid drainage under the heap leach pad was evaluated as part of the Cropsy groundwater and surface water diversion task. Quarterly monitoring of the French Drain solution for cyanide will continue through Phase I.

Subsoil and Topsoil for Heap Leach Pad Reclamation

This section presents the cover designs which are presented in the Technical Revision to the Reclamation Plan (SCMCI, 1992).

To establish a cover with a hydraulic conductivity of $1x10^{-7}$ cm/sec the following sequence was proposed. After regrading of the heap, 242,000 cu. yds. of rinsed spent ore should be removed and stockpiled for future use. Bentonite admixture (it is estimated that up to 12% bentonite may be required) will then be mixed in the upper one foot of the regraded spent ore. Such addition can be done by spreading the bentonite on the surface and disking it in or by using a pugmill batch plant operation. The amended material will be place in lifts and compacted, so that a continuous low permeability soil liner is formed. To prevent frost damage to this low permeability liner, it will be covered by a three foot blanket layer of the stockpiled spent ore. A three foot thick layer will be sufficient to insulate the clay liner and prevent frost damage. The blanket layer will be covered by a one foot thick layer of growth medium prior to seeding. Approximately 81,000 cu. yds. of growth medium will be placed using front-end loaders, haul trucks and dozers. The surface of the topsoil layer will be slightly compacted through equipment passes. This process will allow for better water retention and reduce erosion on the topsoil layer.

It has been the experience at the Summitville Mine that fine clayey materials can be placed and compacted to a hydraulic conductivity of $1x10^{-6}$cm/sec. The cover construction to obtain a hydraulic conductivity of $1x10^{-6}$ cm/sec will consist of the following. Material from the Dexter clay stockpile will be placed using front-end loaders, haul trucks and bulldozers with compaction provided by construction traffic as well as compactors if needed. This material will be placed in a one foot thick lift. This compacted layer of low permeability material will be covered with a one foot thick layer of topsoil which will be handled in the same way as described above. It must be noted that a blanket layer is not included in this cover design, because experience on-site has shown that clayey materials such as the Dexter clay stockpile will maintain a permeability of about $1x10^{-6}$ cm/sec in the freeze/thaw conditions experienced at the mine.

Observational Approach Decision Criteria

The heap leach pad decommissioning will be performed during Phase I by achieving detoxification standard for WAD cyanide and then regrading and capping the facility. The success of revegetation will be monitored and corrective measures applied if necessary. Evaluation of the long-term geochemical behavior of the spent ore will be performed during subsequent Phases. A primary goal of the heap leach pad decommissioning is to minimize infiltration and flow through the spent ore, to prevent removal of the buffering capacity, and to reduce the potential for generation of acid drainage.

The wastewater treatment system will be partially dismantled and removed from the site once the heap leach pad has been successfully detoxified. The first stage hydrogen peroxide cyanide detoxification system will not be required. Should acid drainage treatment requirements be greater than the capacity of the PITS, the sulfide precipitation circuits of the second stage will be left in operation until the flows can be reduced to comply with PITS design capacity.

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REMEDIAL ALTERNATIVES IDENTIFICATION AND EVALUATION

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INTRODUCTION

Summitville Consolidated Mining Company Inc. (SCMCI) negotiated an Amended Settlement Agreement and Compliance Plan (SA&CP) in July, 1992 with the Colorado Department of Health Water Quality Control Division (WQCD) and the Colorado Department of Natural Resources Division of Minerals and Geology (DMG). The SA&CP contained several requirements which, in total, were intended to achieve substantial remediation and reclamation of the Summitville site. The SA&CP required goals in document submittal as well as development of goals for on-site work. The first goal of the SA&CP was submittal of a Progress Report identifying and defining plans for implementation of remedial measures by August 31, 1992. Submittal of the final Remedial Measures Plan by November 30, 1992 was the second major submittal goal of the SA&CP. Both the Progress Report and Remedial Measures Plan were compiled by a group of consultants which included: Adrian Brown Consulting, Inc; Environmental Solutions Inc.; Geochimica, Inc.; Geraghty & Miller, Inc.; Golder Associates Inc.; and, Times Limited. Four papers in this volume have been extracted directly from the Remedial Measures Plan and Technical Revision to the Reclamation Plan (SCMCI, 1992). These papers are:

- "Summitville Site Water Quality Characterization and Modeling";
- "Geohydrology and Adit Plugging";
- "Geochemistry of Spent Ore and Water Treatment Issues"; and,
- "Remedial Alternatives Identification and Evaluation".

The four papers present a synopsis of the engineering and scientific approach for development of final Remedial Measures Plan. The authors recommend the four combined papers be read to gain an understanding of the scope and effort expended to prepare the Final Remedial Measures Plan. These papers are presented in the present tense although only some of the measures described were finally implemented by the EPA during their activities.

SCOPE

This paper integrates the findings of the other three papers and provides a basis for identifying the most cost-effective combination of remedial measures. The key aspects of this paper include:

- A brief summary of the acid rock drainage (ARD) issues at the Summitville Mine site.
- Identification of the types of remedial technologies and process options that could be applied at the site.
- A discussion of the basis used to evaluate the alternative remedial measures.
- The evaluation of the alternative remedial measures.
- A description of the selected remedial measures and the associated implementation approach.

The selected measures incorporated the most cost-effective alternatives that achieve significant reductions in metal loading. Implementation involves a phased approach which allows field verification of the effectiveness of the measures as these are being installed.

The basic procedures outlined in the National Contingency Plan (NCP) were followed. The NCP represents the federal guidelines (USEPA, 1988) for conducting remedial investigations and feasibility studies at Superfund sites, and contains formalized requirements for: identifying remedial technologies and process options; "screening out" those that are infeasible; developing remedial alternatives from the remaining technologies; and conducting detailed evaluations of these alternatives.

SUMMITVILLE MINE ISSUES

The problems at the Summitville Mine (Figure 1) were the result of solid mine waste management plans that did not include any special provisions for ARD from the ore and waste rock, and, additionally, the absence of an

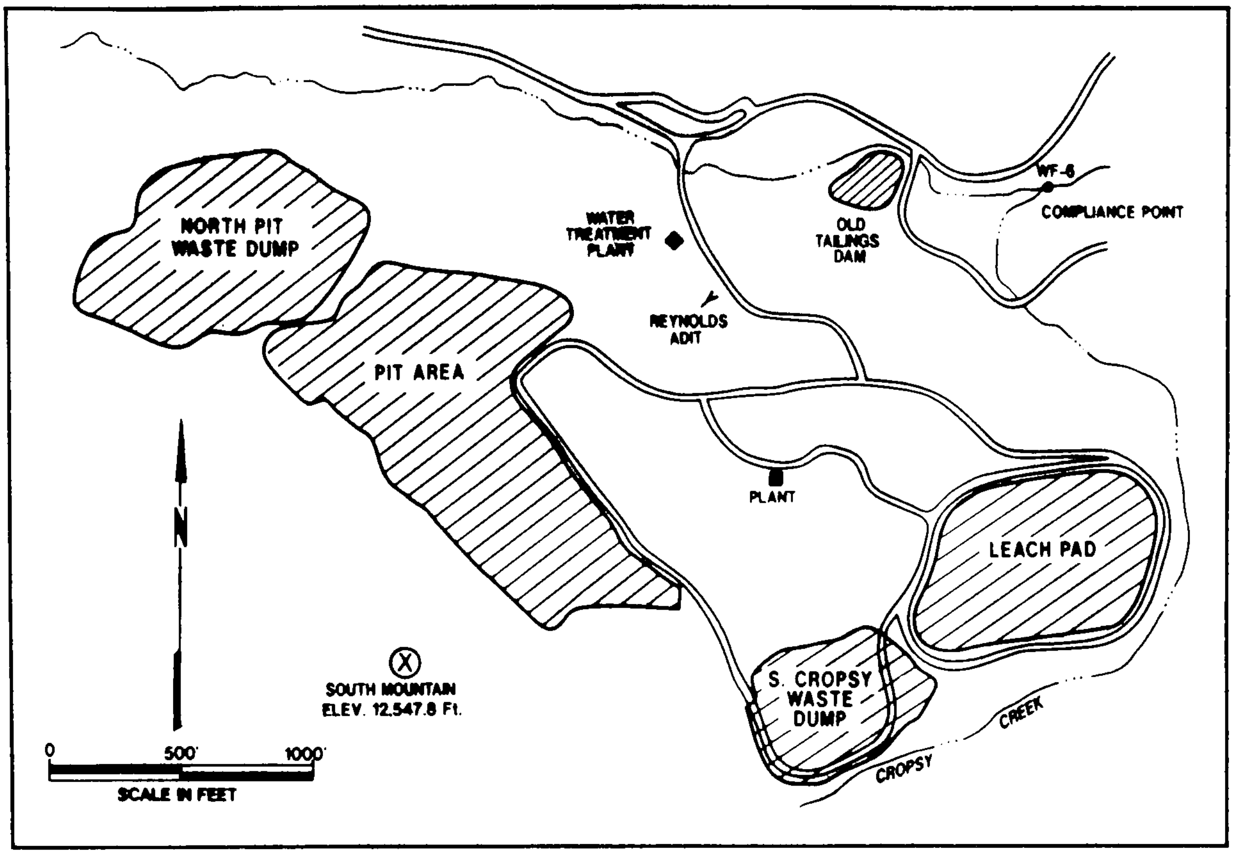

Figure 1. Site Map and Compliance Point Location.

effective water balance management plan for controlling (without spilling) and ultimately disposing the water and process fluids stored in the valley heap leach operation. In addition, the mine was faced with having to deal with the historic acidic discharge from the Reynolds Adit. As a result, towards the later phases of mining, the operators had to contend with acidic discharges from the underground adit, acidic seeps from the various waste piles, including the valley leach embankment which was constructed of waste rock with ARD potential, and an increasing water volume accumulating in the valley leach impoundment. Furthermore, upon closure of the mine, the mine operators were faced with having to control future acid runoff and seepage that would accumulate in the pit.

The important mine features are depicted in Figure 1, while Figure 2 provides a flow sheet that illustrates the major discharge and seepage pathways. The approximate annual zinc and copper loadings associated with the various discharges and seeps are summarized in Table 1. The associated impact on the water quality of the main receiving stream, Wightman Fork Creek at gauging station WF-6, is illustrated in Table 2.

Copper is the main constituent of concern and can be used to characterize the mine's major environmental impact, i.e., impact on fisheries in the receiving streams which include Wightman Fork Creek and the Alamosa River. As discussed later, copper is also used as the key constituent for the evaluation of the alternative remedial measures.

SELECTION OF REMEDIAL ALTERNATIVES

The settlement agreement with the State of Colorado, referred to in the introduction, required that the remedial measures achieve interim (by the end of 1993) and final (by September 1995) aquatic life-based numeric criteria levels (NCLs) in the lower reaches of Wightman Fork Creek (i.e., at station WF-6). This is an innovative "bubble" concept to achieve water quality standards, in that it does not include any discharge standards for individual mining facilities, and, therefore, allows the mine to select the best mix of upgradient remedial technologies. However, the NCLs were relatively arbitrarily set and did not consider site-specific values necessary to protect aquatic life, or values that were

Table 1. Current Metal Loads to Wightman Fork

Source Area (subbasins)	Mine Facilities Contained in Source Area	Total Load for Period July 1991 through June 1992 (lbs)		Ranking in Terms of Copper Load
		Zinc	Copper	
AD-3 (Reynolds)	Portions of the Mine Pit and the Underground Mine	20,784	132,060	1
French Drain	Heap Leach Pad and South Cropsy Waste Pile	14,991	28,500	2
WF-3 to WF-5	Beaver Mud Dump and Tailings Pond	7,888	17,460	3
SC-5	Clay Ore Stockpile	3,302	6,270	4
Upgradient of 550-D3 (Interim Treatment)	Portion of South Cropsy Waste Pile	1,154	5,490	5
LPD-6	Heap Leach Pad	1,364	2,510	6
AD-1 (Iowa)	Portions of the Mine Pit and the Underground Mine	1,357	2,240	7
LPD-2	Heap Leach Pad	1,009	1,680	8
SC-7	Ditches from Roads and Crusher Area	75	510	9
AD-5/WR-3 to WF-4	None	483	390	10
WF-1 to WF-2	None	1,228	320	11
CC-2 to CC-3	Roads	120	160	12
Upgradient of WF-1	None	111	14	NR
CC-1 to CC-2	Portion of Upper Cropsy Waste Pile	-28	3	NR
Upgradient of CC-1	None	747	3	NR
550D-3/CC-3 to CC-4	None	-253	-200	NR
ND-5/WF-2 to WF-3	North Dump and Former Land Application Area	3,230	-3,250	NR
CC-4/SC-5 to CC-5	Dike 1	-2,379	-4,790	NR
AD-3/AD-2 to AD-5	Portions of the Mine Pit and the Underground Mine	-1,472	-9,030	NR
CC-5/WF-5 to WF-6	None	6,974	22,370	NR

Note: Negative values may be the result of precipitation and/or sampling error.

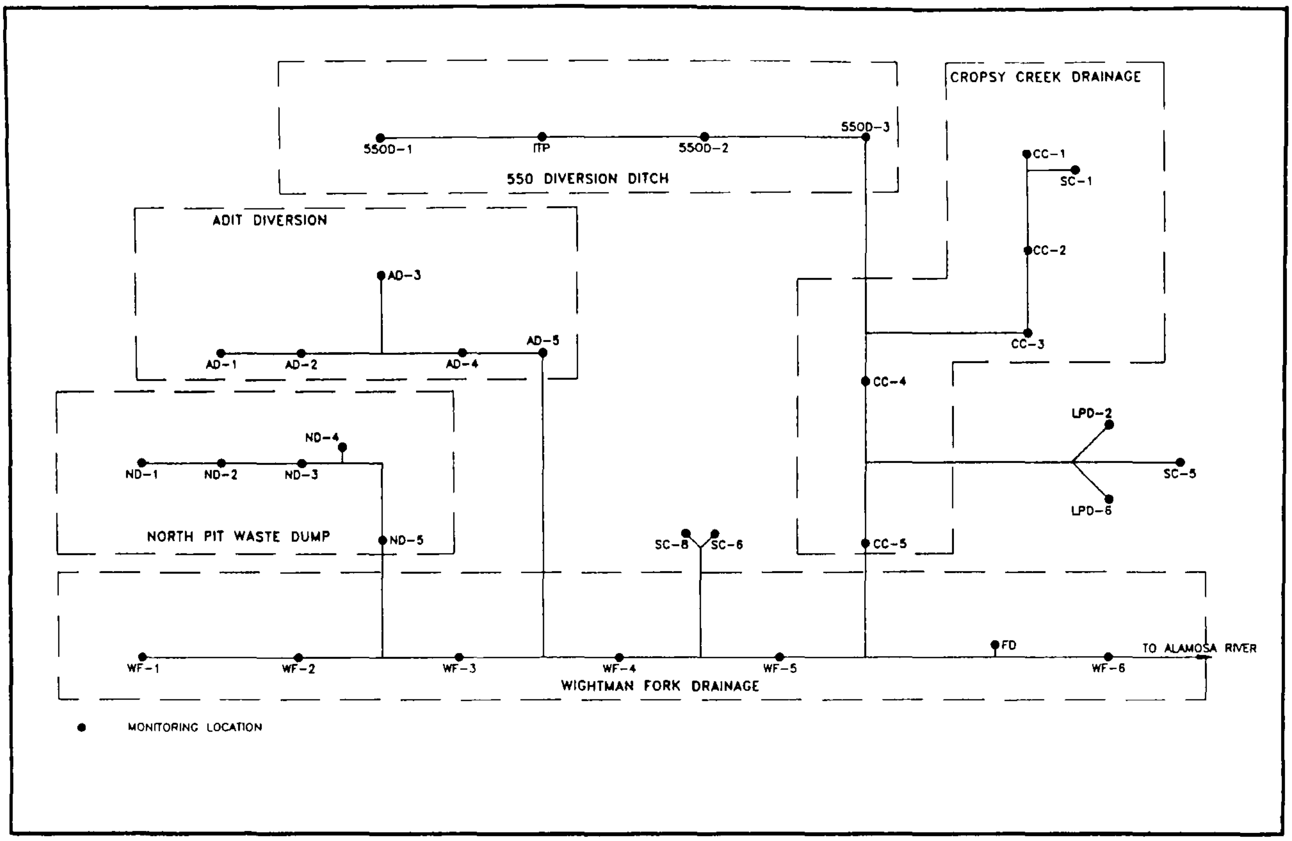

Figure 2. Load Model Schematic.

feasible to achieve. Consequently, as discussed further at the end of this paper, while the selected remedy is expected to result in major reductions in the metal loadings to Wightman Fork at reasonable costs, it may not achieve the NCLs. Therefore, it is recommended that aquatic studies be undertaken to determine what habitat utilization would be achieved with the metal reductions that are achievable and whether alternative NCLs should be considered.

The following subsections discuss the different stages of remedy selection, as follows:

- Step 1 - Technology and Process Option Identification and Screening
- Step 2 - Development of Alternative Remedial Measures
- Step 3 - Basis for Evaluating Alternative Remedial Measures
- Step 4 - Evaluation of Alternative Remedial Measures

STEP 1 - TECHNOLOGY AND PROCESS OPTION IDENTIFICATION AND SCREENING

Candidate technologies and the associated process options were generally screened based upon their implementability, effectiveness, and cost. The screening was conducted qualitatively, using engineering judgment. As this type of screening has been performed for several mining sites in the past, and because there are only a limited number of technologies and process options applicable to mine sites, a more formalized screening process was not required. The discussion below describes the results of the screening process.

No Action has been included as required by the NCP for comparative purposes. This technology involves the reclamation of the mine site area by topsoiling and revegetation; treatment and discharge of the valley heap leach water; and leaving the pit to form a shallow lake. It also assures that the existing treatment plant at the site,

Table 2. Wightman Fork Gauging Station WF-6 - Actual 1992 Water Quality and Cleanup Criteria, Numeric Criteria Levels (NCLs) (mg/l)[1]

Parameter	**Concentration Range**	**Interim NCL (required by end of 1993)[2]**	**Final NCL (required by September 1995)[3]**
Zinc	2.5-6.56	2.9	0.70
Copper	7.27-30.0	3.0	1.6
Lead	0.014-0.087	N/R	0.12*
Silver	<0.0025	N/R	0.0015*
Mercury	<0.0005	N/R	0.001*
Cadmium	0.018-0.062	N/R	0.019
Manganese	5.7-18.0	N/R	5.6
Iron	30.0-88.0	N/R	50
Weak Acid Dissociable (WAD) Cyanide	0.002-0.075	N/R	0.05
pH	3.1-4.7	N/R	2.5-9.0*

Note: 1. Total recoverable concentrations except for WAD cyanide and pH.
2. Based upon grab samples for the period July 1991 to September 1992.
3. 30-day average
N/R = Not Required.
*Constituents already meet the interim and final NCLs.

which treated Reynolds Adit flow and other seepages, would be turned off.

Source Control Measures that were considered included isolation of the sulfide rock responsible for ARD, in order to avoid the formation of acidic conditions and the transport of the products of acid generation, i.e., low pH, high metals total dissolved solids (TDS) and sulfate concentrations. These technologies include permanently flooding the ARD material in order to limit or prevent oxidation, and were retained for further evaluation. Another source control technology involves air sealing the waste rock to prevent the formation of acidic conditions. This technology was eliminated from further analysis due to the likely ineffectiveness of completely sealing large waste piles in a harsh alpine climate. Furthermore, the piles are underlain by fractured bedrock and, in some areas, by a large number of historic mine openings and workings which would provide for continuous air access.

Another source control technology involves removal of sulfide rock and redisposal of the rock in an offsite or onsite facility. Widespread application of this technology was eliminated from further consideration because it is infeasible to remove all the widely-distributed sulfide mineralization in the area without causing very significant environmental impacts. Also, the cost of implementation would be prohibitive. However, removal and onsite relocation of a portion of the mine waste into the open pit or in another onsite facility is retained for further analysis. Final source control technologies considered included the treatment of sulfide rock by physical or chemical processes to separate or destroy the sulfides. These technologies were eliminated because of the infeasibility of removing and treating the large volumes of widely-distributed sulfide mineralization in the area.

Isolation of Sulfide Rock includes several potential remedial technologies, such as: vertical barriers to prevent ground water inflow, capping, and surface and subsurface drainage to prevent infiltration and surface water run-on. Vertical barriers such as slurry walls, sheet piling and vibrating beam were eliminated from further consideration because of construction difficulties in the rugged terrain, the large areal extent of materials and the near-surface, and fractured bedrock which is not amenable to the construction of effective vertical barriers. However, grout curtains, which have been proven to be effective for diverting bedrock fracture ground water flow at other sites, are retained for further analysis.

The capping and surface drainage technologies were retained for further evaluation. Diversion of ground water upgradient of sulfide rock includes the construction of ground water drainage trenches, and tunnels or extraction wells. Installation of extraction wells was eliminated due to the uncertain effectiveness and the large scale of the site. Trenches or tunnels would likely perform better at this site and were, therefore, retained.

Collection of ARD includes gravity drainage, pumping, conveying and storage in an impoundment. The collection of gravity flow from tunnels, seeps or springs is a process which must be performed in combination with other technologies, and was retained for further analysis. The construction of impoundments to temporarily store ARD spring runoff surges and equalize the flow to a treatment system was also retained.

Treatment of ARD includes physical, chemical, and biological process options. The physical treatment options of spray evaporation and mechanical evaporation were eliminated from further analysis because of the relatively cool site climate which results in these process options being very inefficient. The chemical treatment processes of precipitation and neutralization are widely used for inorganic compounds, and were retained for further analysis. This is the same technology used in the onsite treatment plant that had been installed to treat the Reynolds Adit flow and several other ARD seeps. Biological treatment by artificial or natural wetlands, and by land application as well, are potentially viable as a polishing step or treatment of small discharges, and, consequently, were retained.

Institutional Controls include land use limitations such as deed restrictions and site fencing. This technology has not been retained for further analysis as it does not influence water quality in Wightman Fork Creek.

STEP 2 - DEVELOPMENT OF ALTERNATIVE REMEDIAL MEASURES

The types of remedial measures that were developed are identified in Table 3 and include partial (P), short-term (T), combination (C), and envelope (E) measures. Partial measures included those targeted at individual facilities or features at the mine site; e.g., Reynolds Adit plugging or capping and isolation of the South Cropsy Waste Pile. These were selected in order to evaluate the relative costs and benefits of these different measures, and to utilize this information to develop more comprehensive combination alternatives which include a number of the partial measures and provide for increased reduction in metal loads to Wightman Fork Creek.

The short-term measure was developed to allow for early construction of key remediation elements which would provide immediate reduction in metal loads and also allow for the performance of the measures to be monitored and evaluated in the field prior to committing to the final remedial alternative.

The C.1 combination alternative involves: plugging Reynolds Adit; redisposal of the clay ore stockpile in the mine pit; providing drainage around the waste piles; and collecting and treating residual seepages in a modified treatment plant. The C.2 combination adds diversions around the upgradient end of South Cropsy Waste Pile, to reduce treatment plant flow, and the redisposal of the Beaver Mud Dump in the mine pit.

The envelope measures were included to explore the possible maximum level of metal load reduction that could be potentially achieved if costs were not an issue. These include E.1, which involves collection, storage and treatment of ARD flows and seeps, and E.2, which involves consolidation of the ARD material, except the leached residue in the pit (17.1 million tons), and treatment of the residual ARD flows which are substantially less than those in the E.1 alternative.

STEP 3 - BASIS FOR EVALUATING ALTERNATIVE REMEDIAL MEASURES

The approach used to evaluate the alternatives listed in Table 3 is based upon the metal load model discussed in "Summitville Site Water Quality Characterization and Modeling." It includes the following basic steps:

- Map the drainage segments reporting to each surface water sampling point.
- Prepare a flow and metal load model for the site incorporating the 1991 and 1992 measured monthly flows, and copper and zinc concentrations at each sampling point.
- Using the model, determine the delta (increase or decrease) metal load derived from each drainage segment.
- For each remedial alternative, estimate metal load reduction factors for each drainage segment. (Examples include: 99 percent for collection and treatment of acid drainage, 90 percent for removal of a surface solid waste, etc.)
- Estimate the total load reduction for each remedial alternative using the model and the reduction

Table 3. Description of Alternative Remedial Measures

Type of Alternative	Measure		Engineering Elements
	Number	Description	
Partial (P) Measures	P.1	Plug Adits and Treat	-Plug Reynolds Adit and associated adits and store water in mine. Release water at a constant rate (approx. 200 gpm) and treat in the existing water treatment plant (WTP).
	P.2	Plug Adits	-Plug Reynolds Adit and associated adits and backup water to reduce oxidation of sulfides.
	P.3	Relocate South Cropsy Waste Pile to the Pit	-Remove and relocate 6,300,000 tons to the mine pit.
	P.4	Cap and Isolate the South Cropsy Waste and Leach Piles	-Isolation using groundwater drain and diversion system as well as grout curtains.
	P.5	Dam and Flood South Cropsy Waste Pile and Leach Pad	-Construct a water retaining embankment and spillway immediately downgradient from Dike 1 which contains the leach pile. -Level wastes contained in South Cropsy Waste and Leach Piles. -Submerge the leveled material in water stored behind the embankment.
	P.6	Relocate the Clay Ore Stockpile to the Mine Pit ar the Heap Leach Pile	-Move the material to the heap leach pad or the mine pit.
	P.7	Relocate the Beaver Mud Dump to the Pit	-Move the 1,350,000 tons of material to the mine pit.
	P.8	Cap and Isolate Beaver Mud Dump	-Provide isolation using a groundwater drain and diversion system as well as grout curtains.
Short-Term (T) Measures	T.1	Plug Adits, Construct Temporary Seepage Collection Drains, Collect and Treat Major Sources	-Plug Reynolds Adit. Residual discharge is not assumed to develop in the short-term. -Construct a temporary drainage cut-off ditch along downgradient perimeter of Beaver Mud Dump and SC-7 area. -Collect drainage at French Drain, ITP, LPD-2 and 6 seeps, SC-5, a Beaver Dump cut-off ditch, and an SC-7 cut-off ditch and routing to WTP. -Provide for emergency pumping system for wet conditions in order to return excess flow to heap leach in lieu of enlarging WTP capacity and/or building storage reservoir. -Utilize modified WTP with 500-gpm capacity.

Table 3. Description of Alternative Remedial Measures (Continued)

Type of Alternative	Measure		Engineering Elements
	Number	Description	
Combination (C) Measures	C.1	Plug Adits, Drain Around Piles, and Treat	-Plug Reynolds Adit and allow water level buildup in mine. Residual discharge will amount to 125 gpm from the pit and 75 gpm via seepage (P.1). The residual discharge will be collected and treated. -Install downgradient collection system for South Cropsy Waste Pile. -Install downgradient collection system for Beaver Mud Dump. -Remove/relocate clay ore stockpile (130,000 yd^3) to mine pit or heap leach pad (P.6). -Utilize modified WTP with 500 gpm capacity. -Install downgradient collection system for North Dump at ND-5. -Remove and relocate residue in tailings pond. -Construct water storage impoundment for 400 acre-feet capacity.
	C.2	Improve Drainage to Reduce the Treatment Requirements of C.1	Same as C. 1 except includes: -Upgradient diversion of groundwater at south Cropsy Waste Pile. -Relocation of Beaver Mud Dump to mine pit. (This alternative is assumed not to require WTP capacity expansion.)
Envelope (E) Measures	E.1	Collect ARD Flows Using Dams, Treat and Discharge	-Construct South Cropsy and beaver dams and interconnecting ditch and spillway. -Construct a permanent treatment plant with 1,500-gpm capacity. -Excavate and relocate tailings pond residue and dike. -Excavate and relocate Beaver mud Dump in the mine pit.
	E.2.A and E.2.B	Consolidate Material in the Pit with the Exception of the Heap Leach Material. Collect and Treat Pit Seepage as part of the Reynolds Adit Flow.	-remove all on-site waste material except heap leach pile and relocate in the mine pit. This will involve movement of 17.1 million tons. -Mine pit estimated to hold 22 million yd^3 at a 3:1 fill slope. -Two basic options are available: -E.2.A. Placement of waste in the pit and use the Reynolds Adit to collect and treat residual infiltration estimated to average 200 gpm. -E.2.B. Placement of waste in the pit and plugging of the Reynolds Adit in order to restore "natural", near-surface ground water table and inundate sulfide materials. Residual seepage from the pit is estimated at 125 gpm.

factors.

- As appropriate, prepare working sketches of remedial alternatives to facilitate assessment of technical feasibility and to develop construction material quantities.
- Prepare conceptual level cost estimates for each of the remedial alternatives, including capital cost for construction, annual operation and maintenance (O&M) costs and total present worth.

In order to evaluate the relative merits of the various alternatives, the following additional activities were conducted:

- Compute the equivalent metal loads for Wightman Fork corresponding to the current flow conditions and the required final NCLs. These "loads" represent the current regulatory targets at gauging station WF-6.
- Compare the residual Wightman Fork metal loads for the various remedial measures to the final NCLs in order to determine the degree to which the measure could potentially meet the regulatory requirements.
- Compute relative cost per pound of copper load reduction over a 10-year period for each measure in order to allow ranking of the alternatives.
- Draw conclusions on the types of measures that should be considered for the site and the associated changes in water quality standards in the receiving waters that may have to be contemplated if full compliance with either the interim NCLs or the final NCLs is not feasible.
- Assess the data needs or items requiring further verification to support the selection and to allow engineering design of those measures selected for further consideration.

STEP 4 - EVALUATION OF ALTERNATIVE REMEDIAL MEASURES

Table 4 presents a listing of the total present worth (PW) cost associated with each alternative measure, an indication of the benefits in terms of the ratio of the residual annual average copper load to the load calculated using final NCLs, and the PW cost per pound of copper reduction over a ten year period. The total PW costs presented in this table do not include the normal mine closure and reclamation costs which are estimated at approximately $11 million.

The various alternatives are evaluated by plotting each on the average annual residual copper load versus PW cost curve presented in Figure 3. This figure clearly points out the more cost-effective measures as well as those which are economically infeasible. It also provides a basis for selecting a cost- effective phased approach involving the sequential installation of a series of partial and/or short-term alternatives. For example, it is evident that partial measure P.2 (the plugging of Reynolds Adit), followed by temporary measure T.1 (the installation of temporary drains for the collection of residual ARD flow and treatment in the existing treatment plant), is the most cost effective approach in the short term. The 10 year PW cost is under $10 million. However, as the Reynolds Adit plugging would ultimately result in increased ARD seepage via the subsurface, and because the temporary drains are very high maintenance items, one of the combined alternatives (C.1 or C.2) would present the next logical step and possibly the permanent remedial plan. The 10 year PW cost of the two combined alternatives is in the $20 to $25 million range.

The above (P), (T), and (C) measures are not predicted to reach the interim NCLs or final NCLs, but should provide a substantial reduction in copper loading, approaching approximately 75 percent. The significantly more costly (PW ranges from $35 to $45 million) envelope measure E.2 (relocate onsite wastes) may get close to the interim NCLs and possibly reach the final NCLs. The collect-and-treat envelope measure (E.1) appears to provide the best opportunity for meeting the final NCLs but costs substantially more than the other measures (i.e., over $70 million).

REMEDIAL MEASURES PLAN

There is uncertainty associated with how effective any of the remedial measures considered will be. For example, there is a possibility that ground and surface water diversions will be subjected to leakage. Additionally, adit plugging could generate unexpected seepage pathways, and removal of ARD waste from an area may not completely remove the source of ARD. Therefore, it was decided that implementation of the most cost-effective measures should proceed on a phased basis. This approach is also referred to as observational approach, and allows experience gained with the early phases to be used to refine the design and implementation procedures associated with later phases. It also minimizes the amount of data that has to be collected for design purposes, as the early-phase construction activities will provide data for the designs of later phases.

The following four-phased remedial measures plan (RMP) was selected for implementation over a six-year period. It integrated the completion of the site's normal reclamation activities with ongoing modification and refinements to the onsite treatment plant, the removal of the heap leach liquids, and the installation of the remedial measures.

Phase 1

- Plugging of Reynolds Adit (measure P.2, and part of measure C.1).
- Heap leach pad decommissioning, including water

Table 4. Summary of Alternative Remedial Measures, Costs and Benefits

Category of Alternative or Measure	**Alternative**	**Description**[1]	**Total Present Worth Cost ($ million)**[2]	**Average Annual Residual Copper Load as a Ratio of Final NCLs Load**[3]	**PW Cost per Pound of Copper Reduction over 10 years ($/lb)**[4]
Partial (P) Remedial Measures	P.1	Plug Reynolds Adit for water storage purposes; release and treat the collected water.	10.0	7.2	6.6
	P.2	Plug Reynolds Adit. (Allow residual seepage to flow to Wightman Fork Creek).	0.7	7.9	0.5
	P.3	Relocate South Cropsy Waste Pile to the pit.	13.2	14.2	25.8
	P.4	Cap and isolate South Cropsy Waste Pile.	5.2	13.2	8.3
	P.5	Dam and flood South Cropsy Waste Pile and leach pad.	20.8	13.2	31.2
	P.6	Relocate clay ore stockpile to the mine pit or heap leach pile.	0.5	16.8	3.4
	P.7	Relocate Beaver Mud Dump to pit.	3.4	15.3	9.0
	P.8	Cap and isolate Beaver Mud Dump.	4.6	15.5	13.3
Short-term (T) Measures	T.1	Plug adits, construct temporary seepage drains, collect and treat major sources.	3.7	3.0	1.7
Combination Measures (C)	C.1	Plug adits, drain around piles, and treat residual seepage.	22.4	3.6	11.1
	C.2	Improve drainage to reduce the treatment requirements of C.1.	24.9	3.2	11.9
Envelope (E) Measures	E.1	Collect ARD flows using dams; treat and discharge.	72.2	0.4	29.1
	E.2.A	Consolidate material in the pit with the exception of the heap leach material. Collect and treat pit seepage as part of the Reynolds Adit flow.	44.3	1.1	18.5
	E.2.B	As for E.2.A, with the exception that the adits are plugged to reduce seepage requiring treatment.	43.4	1.1	18.2
	E.2.C	As for E.2.B except that no WTP is provided.	36.5	1.9	16.0
No Action	-	-	0.0	17.9	0.0

Note:
1. For further description, see Table 3.
2. These costs do not include ongoing interim treatment activities and the reclamation of the property that has already been committed. This amounts to an additional $11 million in present worth costs.
3. Final NCLs expressed as an annual copper load. Alternative P.1, for example, produces 7.2 times the copper load allowed by the final NCLs.

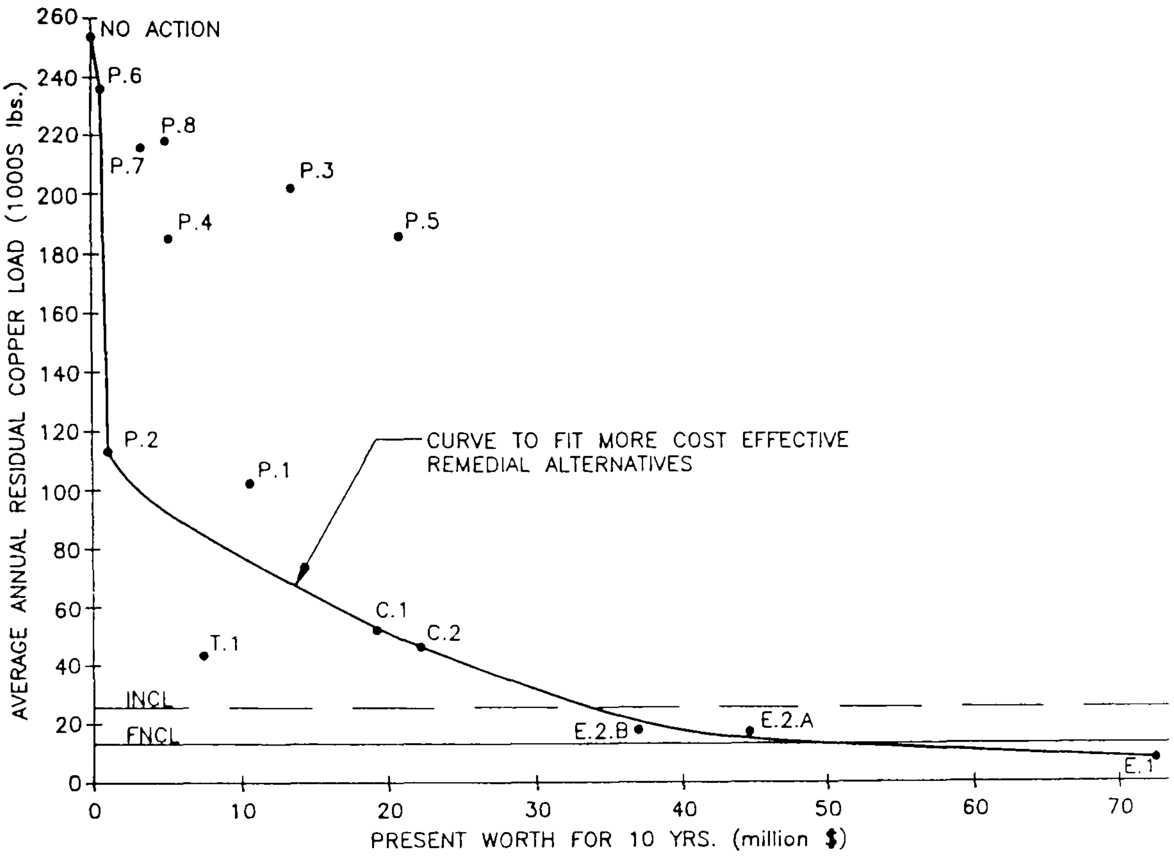

Figure 3. Present Worth of Alternatives Versus Residual Copper Load

treatment and sludge disposal (removal of the heap leach liquids).

- Construction of South Cropsy Waste Pile surface and ground water diversions (part of measure C.1).
- Construction of Beaver Mud Dump ground water diversions.
- Completion of reclamation (part of measure C.1).
- Construction of a portable interim water treatment and sludge disposal system to augment the existing plant's capacity and to handle the heap leach pad liquids (part of measure C.1).
- Monitoring and evaluation of the Phase 1 activities (a key element of the observational approach).

Phase 2

- Collection and treatment of any new seeps that develop as a result of plugging Reynolds Adit (an observation approach required retrofit).
- Treatment or land application of the french drain solution (part of measure C.1).
- Retrofitting of corrective measures for the Phase 1 South Cropsy Waste Pile and Beaver Mud Dump diversion systems (observational approach retrofit).
- Continued operation and possible expansion of the portable interim treatment system (part of measure C.1).
- Establishment of an experimental passive (wetlands) treatment system (an attempt to reduce the treatment cost associated with measure C.1).
- Ongoing monitoring and evaluation.

Phase 3

- Implementation of site-wide passive (wetlands) treatment systems (part of measure C.1).
- Evaluation of the removal (and disposal in the pit) or the isolation of Beaver Mud Dump (part of measure C.2 to further reduce the metal loads. As shown in Figure 3, this is an average cost partial alternative, measure P.7).
- Evaluation of the potential for relocating (and disposal in the pit) of the South Cropsy Waste Pile. (Part of E.2 in an attempt to further reduce metal

loading and reliance on treatment. It is recognized, however, that the initial Figure 3 analyses indicates this alternative, measure P.3, may not be cost-effective.)

- Evaluation of future requirements for the portable interim treatment system (refinement of the treatment part of measure C.2).

Phase 4 - Closure Activities

- During this phase, the finally-selected waste reconsolidation measures will be implemented, the passive treatment system finalized, and, if necessary, the final mechanical/chemical treatment plant capacity will be established and the plant upgraded to facilitate long-term operation.

CONCLUSIONS

The lessons learned at Summitville have been significant and extremely costly. The final costs, in fact, are not likely to be known for several years. As with all environmental incidents, the result is a clearer understanding of the risks one assumes, but also more insight into the opportunities we have for advancing the state of the art of environmental management. The key risks and opportunities that emerged from the Summitville project are as follows:

- Risks Identified
  - It is clear that unless special procedures are implemented for the safe disposal of materials with ARD potential in wetter climates, the environmental and economic consequences are likely to be very significant.
  - Unless the overall project water balance and the associated water management measures have been established prior to the initiation of mining, there is a high risk, particularly in wet climates, that very costly retrofits will be necessary to avoid the buildup and potential spillage of water containing elevated constituent concentrations.
  - The cost of mining and safe waste management in acid rock conditions in an alpine climate can be prohibitive and should be carefully evaluated before the decision is made to mine these areas. Unless the ore body is sufficiently rich to financially support the required environmental controls, the property likely cannot be profitably developed.
- Opportunities
  - The costs of retrofitting measures to control ARD are substantial and increase exponentially as shown in Figure 3 where achievement of very low receiving water standards is required. For example, the PW cost of reducing the metal load by 50 percent is less than 1 million (or \$0.5/lb of copper, Table 4, alternative P.2). The cost of reducing the load by 75 percent increases to 22 million (or \$11.1/lb of copper, alternative C.1). The cost to achieve the final NCLs, which represents an approximately 95 percent reduction, is over \$70 million (or \$29.1/lb of copper, alternative E.1).
  - Practical solutions can, in fact, be developed for complex environmental problems, provided the environmental impacts are systematically analyzed and alternative solutions are carefully selected and evaluated.
  - Phasing of the installation of selected measures on a prioritized basis assures that the remedial effort remains both focused and cost-effective. Current government regulatory programs aimed at remediating impaired mining sites, including the Superfund program, could be improved by incorporating the observational approach.
  - There is a need for combining the technical remedial evaluations with the aspects of cleanup goals. Due to the exponential rise in remediation costs with increasing metals removed, it is important to consider the type of biologic habitat that can be reestablished for a range of metals removed. This will allow selection of the remedial measure that provides the best balance between expenditure and environmental restoration. It is particularly important to back these types of evaluations with site-specific field biological studies as the published standards may be totally inappropriate for the particular site being remediated.

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CROPSY WASTE PILE, BEAVER MUD DUMP, CLEVELAND CLIFFS AND MINE PITS RESPONSE ACTION

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ABSTRACT

The Summitville Mine Superfund Site (the Site) is located about 25 miles south of Del Norte, Colorado in the San Juan Mountain Range. The Site is located in the Rio Grande Drainage Basin near the headwaters of the Alamosa River. The Site was most recently operated by Summitville Consolidated Mining Company, Inc. (SCMCI) as an open pit gold mine with extraction by means of a cyanide leaching process. In December of 1992, SCMCI declared bankruptcy and vacated the Site. At that time, EPA took over operations of the water treatment facilities. Due to the high operation costs of water treatment, EPA established a goal to reduce or eliminate the sources of acid mine drainage (AMD) generation. All of the sources of AMD generation were evaluated and prioritized. Of the twelve areas identified as sources of AMD, the Cropsy Waste Pile, the Cleveland Cliffs Tailings Pond, the Beaver Mud Dump, and the Mine Pits were considered to be the most significant contributors to the generation of metal-laden acidic (low pH) water. EPA developed a strategy to address these source areas, which included three phases of construction. Phase I, completed during the 1993 construction season, included lining of the mine pits with pH neutralizing material and moving 1 million cubic yards of waste to the mine pits. Phase II, completed during the 1994 construction season, included moving 3.5 million cubic yards of waste to the mine pits and contouring of the mine pits so that they are free draining. Phase III, planned for the 1995 construction season, will include the placement of a vegetative cap on the mine pits and revegetation of the footprints of the Cropsy Waste Pile, Beaver Mud Dump and Cleveland Cliffs Tailings Pond.

INTRODUCTION

During December 1992, EPA took over operations of the water treatment facilities at the Summitville Mine after SCMCI declared bankruptcy. To operate and maintain the water treatment facilities, EPA was expending approximately $1.0 million per month. To reduce cost of water treatment and expedite Site remediation, EPA initiated investigations and response actions to reduce or eliminate the generation of AMD. The objectives of these response actions were: 1) To be compatible with the Site-wide remedial action; 2) To reduce or eliminate the need for continued expenditures in water treatment; 3) to reduce or eliminate deleterious quality water flow from the Summitville Mine Site; 4) To reduce or eliminate the acid mine drainage from manmade sources on the Summitville Mine Site; 5) To reduce or eliminate human health or adverse environmental effects from mining operations downstream from the Site; 6) Encourage early action and acceleration of the Superfund process.

This paper describes the evaluation, prioritization, and response actions taken to reduce or eliminate acid mine drainage generated from the Cropsy Waste Pile, Beaver Mud Dump, Cleveland Cliffs Tailings Pond, and the Mine Pits.

SITE LOCATION AND DESCRIPTION

The Summitville Mine Superfund Site is located about 25 miles south of Del Norte, Colorado, in Rio Grande County. It is located within the San Juan Mountain Range of the Rocky Mountains, approximately two miles east of the Continental Divide, at an average altitude of 11,500 feet. The mine is positioned on the northeastern flank of South Mountain (Pendleton and others, this volume). The disturbed area at the Site covers approximately 550 acres. On the north, the Site is bounded by the deserted town of Summitville, and by Wightman Fork Creek. It is bounded by Cropsy Creek to the east, and the peak of South Mountain to the southwest. The Site is located in the Rio Grande Drainage Basin near the headwaters of the Alamosa River. Two tributaries drain the Site - Wightman Fork Creek and Cropsy Creek. The confluence of Cropsy Creek and Wightman Fork is located on the northeastern perimeter downstream of the Site. Wightman Fork Creek drains into the Alamosa River approximately 4.5 miles below the Cropsy Creek confluence.

Topography

Approximately 550 acres of the Site is comprised of heavily altered terrain due to mining operations. The Site's pre-1870 topography consisted of upland surfaces, wetlands, and South Mountain peak. The predominant Site ground cover was alpine tundra at the higher elevations with coniferous forest and subalpine meadow in the lower elevations. The mountains which surround the Site, including Cropsy Mountain to the south, are between 12,300 feet and 12,700 feet in elevation.

The Wightman Fork drainage covers approximately 3.0 square miles upstream from the Wightman Fork diversion. Catchment elevations range from 11,225 feet to 12,754 feet. The Cropsy Creek drainage area includes 0.85 square miles on the northeast slopes of the Cropsy Mountain and the southern slopes of South Mountain. Elevations within this drainage range from 12,578 feet to 11,200 feet at the Cropsy Creek confluence with Wightman Fork (Klohn Leonhoff, 1984). Wightman Fork drains into the Alamosa River approximately 4.5 miles from the Cropsy Creek confluence.

Disruption of the topography began, on a limited scale, in 1870 with placer gold mining in stream-formed alluvial deposits. This placer mining was followed by open cut mining on gold-bearing quartz veins. Underground mining followed. As mining production depths increased, several processing mills were constructed to handle the increased capacity and produce a concentrate suitable for transit. This initial mining phase (through 1890) and additional underground mining from 1925 to 1940 resulted in surface deposition of waste rock near the adit entrances. Additionally, piles of mill tailings were placed downgradient from the stamp mills and the 1934 flotation-cyanidation mill.

Further surface disruption of the topography resulted from work in the late 1960's when Wightman Fork was diverted north to allow construction of a tailings pond. With this new impoundment, mill tailings were put on the Beaver Mud Dump down to the Cleveland Cliffs Tailings Pond.

The most dramatic surface alterations started in 1984, as a result of SCMCI's open pit heap leach gold mining operations. During this time, the Cropsy and North Waste Piles, the Mine Pits, and Heap Leach Pad were constructed.

Hydrogeology

Groundwater at the Site is present as a series of intermittent, shallow, perched aquifers. Shallow groundwater occurs in surficial deposits consisting of colluvium, "slope wash" alluvium and/or glacial ground moraine; and weathered parts of the Summitville Andesite. These shallow systems eventually discharge to surface water. The upper perched aquifer system also contributes to the ground water recharge of the fractured bedrock system. Numerous springs and seeps cover the entire Site, with the greatest number at the locus of the distal edge of the dome. Many springs and seeps are buried beneath mine waste dumps. Most of the springs and seeps flow in direct response to precipitation, with high and low flows corresponding to high and low flow of the surface water system in the area.

A natural surface water drainage system exists along the southern portion of the Site. The surface water drainage system includes Cropsy Creek and Wightman Fork. The Wightman Fork and Cropsy Creek have been diverted around the mining operations.

CONTAMINANTS OF CONCERN

The USEPA identified Contaminants of Concern (COC) based on elevated concentration and potential toxicity of mobilized chemicals. These concentrations were compared to site-specific background levels, which were determined by standard statistical analysis (MK, 1994). Potential adverse effects on human health and the welfare of wildlife were preliminarily assessed (USEPA, 1992). COC identified for the Site are copper, iron, cadmium, lead, silver, zinc, arsenic, aluminum, mercury and cyanide.

All of these contaminants, except cyanide, are found at the Site in naturally occurring minerals and compounds. They are made soluble during the AMD generating chemical process. The AMD process is accelerated by the mining activities which took place at the Site.

ACID MINE DRAINAGE

The chemical ingredients needed to produced AMD are oxygen, water, and sulfide minerals. Sulfide mineral oxidation by water derived from snowmelt and rainfall is a normal geologic process; however, it is markedly accelerated by increased exposure of sulfide minerals to water and oxygen which results of man-made excavations in sulfide-bearing, rock formations. Catalyzation of reactions by indigenous bacteria, Thiobacillas ferroxidans, often accompanies and significantly accelerates the reactions. Primary metallic sulfides and secondary sulfate minerals found at the Site are pyrite (FeS_2) and marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), covellite (CuS), enargite (Cu_3AsS_4), alunite (hydrous potassium aluminum sulfate - $KAl_3(SO_4)_2(OH)_6$), and jarosite (hydrous potassium iron sulfate- $KFe_3(SO_4)_2(OH)_6$).

Pyrite and other sulfide minerals undergo weathering and produce acid solutions containing sulfate ions along with iron, copper, and other dissolved metals. These acid solutions usually have a pH of less than 4.0 and are responsible for degradation of water quality (Siwik and others, 1989).

At Summitville, mining activities resulted in additional sulfidic material surface area available for contact with oxygen and water. Air and water contact additional surface area provided by broken rock accelerates oxidation of minerals and creation of low pH drainage. This drainage water is high in acidity, sulfate (SO_4) ions and dissolved metals.

AMD contributes metal loading to Wightman Fork and Alamosa River. This creates adverse conditions preventing the growth and maintenance of a healthy aquatic ecosystem. These adverse effects have been noted in various studies of water quality of Wightman Fork and the Alamosa River (SCMCI Remedial Measures Plan, 1992).

Of the twelve areas identified on the Site as sources of AMD, the Cropsy Waste Pile, the Cleveland Cliffs Tailings Pond, the Beaver Mud Dump, the Mine Pits, and the underground workings that are below the Mine Pits, are considered to be the most significant contributors to the generation of metal-laden acidic (low pH) water (Ecology & Environment, 1993; Bureau of Reclamation, August, 1993; Morrison Knudsen Corp., January, 1994). General descriptions of these four sources of AMD are given below.

Cropsy Waste Pile Drainage

The water source is comprised of ground water flow from seeps and upgradient drainage through colluvium and alluvium (Geraghty & Miller, 1992) and precipitation infiltrating through mine waste materials. Seasonal release of water to the surface occurs at the toe of the Cropsy Waste Pile and a year round contribution to the Valley Center Drain (VCD). A high flow of 364 gallons per minute (gpm) was recorded in May 1993 at the toe of the Cropsy Waste Pile. Surface flow was not observed at the toe of the Cropsy Waste Pile between January - April 1994. Based on copper as the indicator, water surfacing at the toe of the Cropsy Waste Pile is the second highest peak carrier of metals. 23,305 lbs. of copper dissolved in solution were transported by drainage from July 1993 through June 1994. The estimated annual cost associated to treat this flow is $3.2 Million.

Drainage from Underground Workings

The water source is comprised of groundwater and precipitation infiltrating the mine pit area. These infiltrating waters draining through mineralized rock into the remaining underground workings have historically surfaced as flow from the Reynolds and Chandler Adits. The Reynolds and the Chandler adits have been plugged. The long-term effects of plugging the Reynolds Adit in February 1994 and Chandler Adit in March 1994, and the consequent rise in the South Mountain water table have not been determined. In May 1994, water began discharging from the Chandler Adit from an a leak flowing between the top of the plug and the roof of the adit (Abel, 1994). Peak flow from the Chandler Adit leak in June 1994 was 661 gpm with a copper concentration of 409.40 mg/l and a pH of 2.16 (determined by sampling the stream just outside the adit entrance). By the end of July 1994, the flow of the AMD stream decreased to 130 gpm with a copper content of 268 mg/l and a pH of 2.30. The Reynolds adit had significant flow throughout the year prior to plugging. High flow from the Reynolds Adit (763 gpm) was recorded in June 1993; low flow from the Reynolds Adit (6 gpm) was recorded in April 1994.

Based on copper as the indicator, the underground workings are the highest peak flow carrier of metals. 198,221 pounds of copper dissolved in solution were transported by drainage from July 1993 through June 1994. Peak flow of AMD from the Chandler and Reynolds Adits in June 1994 was 14% less than flow in June 1993. Copper load from underground workings in June 1994 was approximately 23% less than the load in June 1993. In July 1994 volume from the underground workings was 25% less than in July 1993. Copper load was 15% less than in July 1993. The estimated annual cost for treatment of this stream is $4.3 million.

Cleveland Cliffs Tailing Pond and Beaver Mud Dump

The source of water contacting AMD producing materials is comprised of surface drainage into the tailings pond and surrounding area, and the groundwater migration through the Beaver Mud

Dump as well as precipitation infiltrating through Beaver Mud Dump materials. A high flow of 202 gpm was recorded in May 1993; a low flow of 33 gpm was recorded in November 1993. Monitoring was not possible from January 1994 through April 1994, due to snowpack.

Based on copper as the indicator, this flow is the third highest peak flow carrier of metals. 12,294 lbs. of copper dissolved in solution were transported by drainage from July 1993 through June 1994. The estimated annual cost for treatment of this stream is $2.2 million.

DESCRIPTION OF ALTERNATIVES

Five alternatives were developed for the reduction or elimination of AMD from the Cropsy Waste Pile, Cleveland Cliffs Tailings Pond, Beaver Mud Dump, and Mine Pits. The five alternatives are: (1) No Action; (2) Water Treatment; (3) Removal of Waste Materials to the Mine Pits; (4) Cropsy Valley Adit Drain; and (5) Development of a Cropsy Drainage Channel. The following is a discussion of each of these alternatives

No Action

The purpose of considering the no action alternative is to provide a baseline against which other alternatives can be compared. The no action alternative is the cessation of current water treatment activity and sediment control on the Site. Acceptance of this alternative means that existing treatment infrastructure would be mothballed (mothballing is done to ensure reactivation without excessive expense for replacement of equipment damaged by severe weather or other consequences of inactivity). Ditches and ponds used to control surface runoff and sediment would not be maintained. Access to the Site would not be restricted. Monitoring to record and evaluate contaminant transport effects on human health and the environment would continue. The estimated present value cost associated with this alternative is $270,000.

Water Treatment

Alternative 2 is to provide interim treatment of AMD from the Cropsy Waste Pile, the Beaver Mud Dump, and Cleveland Cliffs Tailings Pond using the existing water treatment facilities. It is anticipated that the existing treatment plants will be minimally functional or require replacement within a ten-year timeframe. It is estimated that an average of 161.4 million gallons per year (MGY) of water would require treatment.

Part of the water treatment Alternative is already in place. Overflow water from the Cropsy Waste Pile flows directly into the Heap Leach Pad. Additionally, French Drain water (Cropsy Waste Pile underflow) is being pumped into the Heap Leach Pad. There is no treatment system for the Beaver Mud Dump/Cleveland Cliffs Tailings Pond at this time. Treatment would entail construction of the lower trench drain for the Beaver Mud Dump and treatment of the estimated 50 gpm intercepted flow rate. All waters are eventually pumped to and treated at the existing water treatment facilities. The estimated present value cost associated with this alternative is $85,980,000.

Removal to Mine Pits

Under Alternative 4 the Cropsy Waste Pile would be excavated to uncover naturally occurring surface water seeps that were covered during construction of the Cropsy Waste Pile, and a surface channel to route the seepage water into the Cropsy Creek Diversion via the 550 Diversion Ditch would be provided. Also, the Cleveland Cliffs would be dredged and the Beaver Mud Dump material would be excavated. All excavated material would be placed in the Mine Pits. The estimated quantity of material to be excavated is 4.5 million cubic yards. Foot prints of the waste piles would be revegetated.

Lime, fly ash, cement kiln dust or similar 'treatment' material would line the bottom of the Mine Pits. The final surface contour in the Mine Pits would be self draining and capped to reduce the volume of water percolating through the waste material placed in the Pit. Water that percolates through the cap and the waste material may become acidic. This water would be neutralized as it passes through the high pH material lining the Pit. The estimated present value cost associated with this alternative is $40,840,000.

Cropsy Valley Adit

Alternative 4 involves designing and driving a drainage adit under the Heap Leach Pad and Cropsy Waste Pile to segregate and control contaminated and uncontaminated water discharges. The adit would extend approximately 1 mile in length under the Cropsy Waste Pile and the Heap Leach Pad at an inclined grade of 8% or greater from the portal entrance. Side cuts and drain holes would be placed based on coring ahead of and to the side of the main tunnel. The Cleveland Cliffs Tailings Pond would be dredged and the Beaver Mud Dump material would be excavated and placed in the Mine Pits. Lime, fly ash, cement kiln dust or similar 'treatment' material would line the bottom of the Mine Pits. The final surface contour in the Pits would be self draining to reduce the volume of water percolating through the material placed in the Pit. Water that percolates through the cap and the waste material may become acidic. This water would be neutralized as it passes through the high pH material lining the Pit. The estimated present value cost associated with this alternative is $56,360,000.

Cropsy Channel Drainage

Alternative 5 consists of re-channeling approximately 4,500 linear feet of Cropsy Creek starting at the existing Cropsy Creek Diversion. The horizontal location of the starting point is approximately 1100 feet southwest of the interface between the Heap Leach Pad and the Cropsy Waste Pile. The channel will traverse a path through Dikes 2 and 3; through the northwestern portion of the Heap Leach Pad, including Dike 1; and continue on to the French Drain Sump immediately downstream at an approximate elevation of 11,280.

The entire channel would be excavated into bedrock to a minimum depth of 5 feet to minimize erosion. The system would be constructed to expose different qualities of waters. Uncontaminated drainage could be released directly to Cropsy Creek; contaminated drainage would be diverted into the French Drain Sump for subsequent treatment before release into Cropsy Creek.

The Cleveland Cliffs Tailings Pond would be dredged and the Beaver Mud Dump material would be excavated and placed in the Mine Pits. Lime, fly ash, cement kiln dust or similar 'treatment' material would line the bottom of the Mine Pits. The final surface contour in the Pits would be self draining to reduce the volume of water percolating through the material placed in the Pit. Water that percolates through the cap and the waste material may become acidic. This water would be neutralized as it passes through the high pH material lining the Pit. The estimated present value cost associated with this alternative is $46,790,000.

THE SELECTED ALTERNATIVE

A two stage comparative analysis was completed to select an alternative for the response action to be taken at the Site. During the first stage, each alternative was screened to determine if was protective of human health and the environment and complied with applicable or relevant and appropriate requirements (ARARs). Applicable requirements are defined as cleanup standards, standards of control, and other substantive environmental protection requirements, criteria, or limitations promulgated under Federal or State law that specifically address a hazardous substance, pollutant, contaminant, remedial action location or other circumstance found at a CERCLA site. Relevant and appropriate requirements address problems or situations sufficiently similar to those encountered at the CERCLA site that their use is well suited to the environmental or technical factors at a particular site. Each of the alternatives except for alternative 1, No Action, met the criteria of the first stage of the comparative analysis.

The following evaluation criteria are used during the second stage of the comparative analysis: long-term effectiveness, reduction of toxicity, mobility, or volume through treatment, short-term effectiveness, implementability, and cost.

Alternative 3 was found have the highest overall long-term effectiveness since the other options may require a long-term presence for operation and maintenance activities on the site. With Alternative 3, it is estimated that eighty percent of the seeps under the Cropsy Waste Pile will be exposed, reducing possibility for the generation of AMD. Waste consolidated on the Site will make control, monitoring, collection and treatment of any residual AMD more effective. The no action alternative in not effective in the long-term. The long-term effectiveness of alternative 4 is uncertain since the drainage from the adit may require treatment. The effectiveness of alternative 5 is dependent of successfully intercepting the french drain under the Cropsy Waste Pile.

None of the alternatives reduce the toxicity, mobility or volume of the sources of contamination through treatment.

All alternatives except for the no action alternative utilize water treatment and other engineering controls to reduce releases from the site in the short-term. The no action alterative is not effective in the short-term. Under the no action alternative, it is anticipated that contaminant loading downstream surface waters would increase.

All of the alternatives are implementable and utilize standard construction practices. Alternatives 1, 2 and 3 could be implemented immediately. A portion of alternative 2 is already implemented on the site. A portion of alternative 3 was implemented during the 1993 construction season. For alternative 4, the methodology of effectively diverting and disposing of the waters in such a manner is still untried and unproven. In alternative 5, the installation of the lining required to control seepage from the bedrock into the channel could be difficult to achieve.

Alternative 3 has the lowest present worth costs with the exception of the No Action alternative. Alternative 5 has the next lowest present worth costs. Alternative 2, has the highest present worth costs.

Based on the comparative analysis, the

recommended alternative for the mitigation of AMD generated by the Cropsy Waste Pile, Cleveland Cliffs Tailings Pond, and Beaver Mud Dump waste piles is Alternative 3 - Removal of the Waste Piles to the Mine Pits. The basis for this recommendation is:

- Effectiveness of this Alternative is estimated at 80 percent, while the remaining two alternatives are rated uncertain as to their overall effectiveness.

- This Alternative is readily implementable with conventional construction equipment and can be readily scheduled within the current year's activities.

- Total cost for this Alternative is estimated at $40.8 million dollars, which is the lowest cost option that is protective of human health and the environment and complies with ARARs.

Construction of the Selected Alternative

EPA developed a strategy to implement the selected response action in three phases. Each phase of construction represents work to be accomplished in one construction season. The following is a description of each phase of construction.

Phase I

Phase I construction was initiated in October 1993 and was completed in February 1994. During this phase, pH neutralizing material was placed in the Mine Pits. Approximately 1 million cubic yards of waste was excavated from the Cropsy Waste Pile. The refilling operation accomplished backfilling the of South Pit. Waste materials were placed higher along the perimeter of the South Pit adjacent to the high wall to promote surface runoff. During construction, finer grained waste was placed on the perimeter of the mine pits and compacted. This was done to reduce the potential of infiltration from the fractured highwall rock into the waste material.

Phase II

Phase II construction was initiated in August 1994 and was completed in November 1994. During this phase, approximately 3.5 million cubic yards of waste was excavated from the Cropsy Waste Pile, Beaver Mud Dump and the Cleveland Cliffs Tailings Pond. The excavation was completed to original ground.

Seeps and Springs uncovered by the excavation were evaluated. Contaminated water was directed to the water treatment plant for treatment prior to discharge. Clean water was directed to the Cropsy Creek Drainage Channel.

All excavated materials were transported and placed within the existing mine pits. The final surface contour in the Mine pits is free draining to reduce infiltration of water into the waste material and existing underground workings.

Phase III

Phase III construction is scheduled to be completed during the 1995 construction season. During Phase III, final contouring and revegetation of the footprints of the Cropsy Waste Pile, Beaver Mud Dump, and Cleveland Cliffs Tailings Pond will be accomplished. The final cap will be constructed on the waste placed in the Mine Pits.

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INTERIM PROJECT REPORT
REYNOLDS ADIT CONTROL PROGRAM

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BACKGROUND

The Summitville Mine Superfund site is located adjacent to the Rio Grande National Forest approximately eighteen miles south of US 160 and at an altitude of around 11,500 feet. The site has been the scene of mining activities since the 1870's. The last operation employed heap-leach treatment of ore with a cyanide solution for gold and silver extraction. The ore also contains minerals enriched in copper among other metals. The mining of the ore for the extraction of the precious metals resulted in the construction of two large waste rock piles, an open pit area, one heap-leach pad, several french drains and surface water impoundments, multiple drainage adits, and three wastewater treatment systems. On December 4, 1992, the former operator of the mine, Summitville Consolidated Mining Co., Inc. (SCMCI), declared bankruptcy. The United States Environmental Protection Agency (USEPA) Region VIII Superfund Emergency Response team mobilized to the site in December 1992.

The primary objective of the USEPA team was to prevent the discharge of pollutants to Wightman Fork Creek, a tributary of the Alamosa River. Although the Heap Leach Pad was the immediate concern due to its potential to release contaminated water, other sources of contamination were also addressed to further reduce toxic metal loadings to the stream.

The Summitville mining district was explored and mined by conventional underground mining techniques for over 90 years prior to the SCMCI open pit mining technique. These early efforts resulted in the creation of numerous adits, drifts, and shafts in South Mountain that are generally interconnected. Since these underground workings had a tendency to fill with groundwater during certain seasons, mine adit facilities were installed to drain the workings.

The Reynolds Adit was a major mine drainage facility constructed to provide this dewatering function for the majority of the underground workings in the area of South Mountain. It was driven at one of the lowest topographic elevations and therefore, provides one of the highest gradients for groundwater flow. It was completed in 1906 and has been releasing metal-contaminated, acidic water to Wightman Fork even prior to the SCMCI operations.

The ground surface above the Reynolds Adit rises steeply up from the portal, such that the ground cover increases as one moves from the portal towards the underground mine workings. The ground cover ranges from shallow at the portal to approximately 450 feet where the Reynolds Adit joins with the major workings, some 2,500 feet from the portal.

The Chandler Adit was also driven to access the workings under South Mountain and was located 2,500 feet west of the Reynolds Adit portal at an elevation of 11,500 feet, 180 feet higher than the Reynolds Adit portal.

SCMCI had installed a treatment system to remove copper from the Reynolds Adit discharge as part of a plan for reduction of copper loading to Wightman Fork. A trailer mounted, portable treatment system was in operation when SCMCI declared bankruptcy, but it had numerous technical limitations associated with operation in an extremely cold climate and with sludge removal capacity.

REYNOLDS ADIT

The Reynolds Adit is the lowest elevation "underground mine working" open to the Summitville ore body. The adit was driven during the early part of the century, and was re-furbished in the mid-1960's by a consortium of mining companies. The elevation of the Reynolds Adit portal is about 11,320 feet.

Most of the information about the geology in the Reynolds Adit comes from geologic mapping performed in 1961. (Mann et al, 1961). The geology shown is consistent with that which has been recently observed within the adit.

The adit is driven through relatively poor quality rock throughout, with a high degree of alteration occurring over almost its entire length. This is consistent with the geological information obtained during drilling of the six monitor wells performed as part of SCMCI's remediation project in 1992. In addition to ABCMW-2 through ABCMW-5, two more monitoring wells were drilled by the U.S. Bureau of Reclamation (USBR) in 1994 to monitor the results of the plugging (BORMW1 and BORMW2).

In addition to the monitoring wells, SCMCI reopened the Reynolds Adit and refurbished it from its portal for a distance of about 1450 feet. This involved the removal of a large amount of iron precipitate and replacement of a significant amount of timber sets in the adit. Inspection of the adit indicated that rock conditions are relatively poor. Volcanic rocks exposed in the wall of the adit are moderately to heavily altered, with a high degree of corrosion by acidic water. In places, severe decomposition of the rock has occurred almost to nearly a clay soil condition. Excavation of rock from the adit wall to evaluate the extent to which the rock was decomposed suggests that the rock-forming minerals have been substantially altered by the earlier intrusive activity and by the flow of meteoric (rainfall and snow melt) water through the rock, rather than as a result of the flow of acidic water in the adit. This is also supported by the geologist's observations of the cuttings during the drilling conducted earlier in 1992.

REGIONAL HYDROLOGY

Surface water flow in the area is a combination of runoff, snow melt, and groundwater base flow. Basin yields are generally high, on the order of 50% of precipitation or greater. Peak flows generally occur in the late spring and early summer, resulting from a combination of snow melt and early summer storms. Base flows in the streams are relatively low, due to the low porosity of the rock masses in the area, and the limited soil and alluvial depth.

The two main drainages of the Summitville Site are Wightman Fork and one of its tributaries, Cropsy Creek. Wightman Fork is a tributary to the Alamosa River. In addition to these two natural drainages, water discharges from the Reynolds Adit at its portal. This flow originates as groundwater from infiltration through the mined area and is generally of poor quality. The amount of flow from the adits varies greatly, and is highest during spring runoff.

Prior to plugging, the peak flows from Reynolds Adit ranged from 900 to 1000 gpm with copper concentrations over 600 ppm. Flow from the Reynolds Adit during winter months was less than 100 gpm with corresponding dissolved copper concentrations as high as 140 ppm.

Groundwater flow in the South Mountain area appears to be northeast towards Wightman Fork. The adit appears to drain the north-east side of South Mountain, by draining the underground workings in the Summitville ore body. These workings were developed in the period from the 1880's to the 1970's using underground vein mining development. The workings themselves constitute an area of about 450 acres, or a little less than a square mile. Flow from the adit has been measured from time to time, and has an annual average of about 200-300 gpm, a range which is greatly influenced by the spring snow melt, which varies considerably.

It is estimated under existing conditions that, over the average year, the flow entering Wightman Fork from the underground mine pool is 55 percent surface water and 45 percent groundwater. With the Reynolds Adit plugged, it was predicted that the surface water component would be substantially reduced to 25 percent, raising the groundwater component to 75 percent of the flow entering Wightman Fork from the underground mine pool.

Groundwater hydrology of the site is characterized by thin colluvial and alluvial materials, relatively low hydraulic conductivity bedrock, high precipitation infiltration, and high water table conditions. The groundwater table was not evaluated prior to the original mining, but was evaluated prior to recent mining (pre-SCMCI) and after the completion of recent mining (post-SCMCI). The groundwater level in wells near the ore body was up to 300 feet below ground surface before SCMCI's mining, and dropped approximately 50 feet further since the start of SCMCI's mining impacts.

In general, the groundwater quality is poor from the underground mine pool. The water is acidic, metal bearing, and non-potable due to acid generation from the extensive sulfide mineral assemblages in the rock where it comes into contact with air and water. Groundwater quality in monitor wells also changed in the period 1985 to 1992. Due to the mining activities, none of the original wells survived, and a new set were drilled in 1992.

The quality of the water which previously discharged from the Reynolds Adit portal was generally poor; typical values were:

Species/Unit	Low	Avg	High	Trend
pH (su)	2.3	3.0	3.6	Unclear
TDS (mg/l)	800	2700	6600	Rising
Sulfate (mg/l)	400	1600	4600	Rising
Copper (mg/l)	10	100	300	Rising

Other metals such as aluminum, iron, manganese, and zinc are also present in significant concentrations in the adit flows.

Outflow from the Reynolds Adit discharged directly into Wightman Fork, and ultimately into the Alamosa River watershed. This was a cause of considerable concern for various water quality control agencies. In particular, the increase in the concentrations of copper and sulfate ions in the adit discharges, and in the Wightman Fork, indicated that the recent large scale open pit mining at Summitville may have caused these changes.

FACILITY ASSESSMENT UNDER USEPA EMERGENCY RESPONSE

Reynolds Adit

SCMCI installed a Portable Interim Treatment System (PITS) at the portal of the Reynolds Adit to satisfy their amended compliance plan. This amended compliance plan required SCMCI to reduce metals loadings to Wightman Fork by operating an active treatment plant capable of treating 100 gpm on a monthly basis with a 30 day average removal performance objective of 102 lbs/day of copper from May 1 through October 30 and 44 lbs/day of copper from November 1 through April 30.

When EPA took control at the site, they directed USBR to continue the PITS operation and to evaluate the capacity expansion potential of the plant to treat the entire Reynolds Adit discharge. The PITS plant was considered to have a maximum treatment capacity of approximately 150-170 gpm at high concentrations of copper > 350 ppm. Flow rates exceeding that level had to be bypassed around the plant and would result in an overtopping of the Reynolds Adit collection pond. It was determined that the PITS could not treat all the discharge, nor could it be modified to do so.

A preliminary risk assessment of the potential of the Reynolds Adit to contribute significant levels of copper loading to Wightman Fork was performed. Prior historical data was reviewed and it was determined that the Reynolds Adit could be expected to exceed the PITS capacity by a substantial amount during the 3-4 months of spring runoff. Flows exceeding 600 gpm were predicted during spring runoff.

Alternatives were evaluated by USEPA to make some modifications to the PITS plant to improve its short-term effectiveness and to install a plug in the Reynolds Adit. A plug is a concrete structure placed in contact with sound rock that effectively inhibits the discharge from the adit and impounds water behind the plug.

In February 1993, Environmental Chemical Corporation (ECC), under USBR's direction, initiated a solicitation for the purpose of plugging the Reynolds Adit. The justification for this action was based on a series of meetings with State of Colorado Division of Minerals and Geology and Department of Health personnel, USEPA personnel, USBR, and USEPA contractors. This is documented in an action memorandum. The action memo's determinations and findings were that plugging the adit was desirable and would have the following benefits:

1. Removal of the acid and metal loading from the Reynolds Adit to Wightman Fork. Total untreated copper loading to Wightman Fork in 1993 from Reynolds Adit only was over 154,000 lbs or 77 tons. This discharge to the Wightman Fork was the result of the lack of treatment capacity of the PITS plant to treat the high flows during spring run off.
2. Inundation of all or part of the remaining sulfide materials in and adjacent to the underground mine pool, with the result that further acid generation would be greatly inhibited.
3. Restricted migration of contaminated water in the groundwater system through the rock mass with potential attenuation of the metal concentrations contained in the water by absorption or precipitation within the bedrock.
4. Plugging the adit would have a major cost reduction benefit.The weekly operating cost for the PITS system was in excess of $40,000. This annualizes to a range of $2 million - 3 million.

Chandler Adit

The Chandler Adit was driven to connect and access some of the underground workings at the North end of the ore deposit. There was not much information available about the adit, prior to October 1993, and the portal was partially caved preventing access to the interior.

Since the adit portal was located 180 feet above the Reynolds Adit, it was postulated that when the Reynolds Adit was plugged, the groundwater level in South Mountain would rise to the 11500' elevation and eventually discharge from the Chandler. Hence, the Chandler Adit was planned for plugging in conjunction with the Reynolds Adit program. Since there was never any discharge observed from the Chandler Adit, no monitoring program had been put in place to measure potential flows until May 1994.

REQUEST FOR PROPOSAL (RFP) PROCESS

An RFP to plug the Reynolds Adit was prepared in

February 1993 and mailed to a list of pre-qualified contractors known to have successful experience with adit plug construction. Successful experience in the field was highly weighted during proposal evaluation. The following pre-qualified contractors responded to the RFP and attended the pre-proposal site inspection:

American Mine Services
ZMK Mine Construction
Intermountain Mine Services
Power Engineering
Harrison Western

A technical project evaluation committee was organized with representatives from the USEPA, USBR and ECC.

Following thorough evaluation of technical approach and cost estimates, Intermountain Mine Service (IMS) was selected to perform the Reynolds Adit work. Their technical proposal closely followed earlier recommendations to SCMCI, i.e. installation of two plugs: one at the 12+65 station location and the other at the 6+25 station location.

Following ECC's selection of the contractor, the awarding of the contract was delayed several months to provide Potentially Responsible Parties an opportunity to assume liability and accept an enforcement order to conduct the work. The award was made on October 4, 1993 and mobilization of the contractor was authorized.

During the time of contractor mobilization, a number of additional requirements were added to the base contract which had been a "firm fixed price" award:

1. The joint intergovernmental technical team determined a need for a contingency piping system to allow for draining the 12+65 station plug if necessary in the future. This required a design and selection of corrosion resistant materials.

2. Clearing the cave-in at the Dexter Crosscut and the design of a plug for the Dexter was requested.

3. Re-establishment of the caved portal to the Chandler Adit and the design of a plug was requested.

CONSTRUCTION HISTORY

11/22/93	IMS initiated work on the Reynolds Adit by excavating loose rock from the area of the 12+65 station plug.
12/06/93	This work continued until a significant ground movement occurred at the 2+30 station location and prevented access to the 12+65 station while this caved material was cleared and a limited segment was re-timbered for support. This work occurred along with excavation through the Dexter Cross-cut caved material.
12/14/93	IMS proceeded to clean the location for the plug and drill the grout holes into the rock. Twenty six (26) holes were drilled at radial angles.
12/17/93	Grouting began with a 5:1 ratio grout. A maximum of 60-65 psi pressure was used to inject grout into the holes drilled 6 feet deep. The performance objective for formation grouting was considered unacceptable by IMS due to excessive leakage through fractures or permeable rock so the decision to drill 16' grout holes was made. A second ring of holes 4 feet in front of the 16-foot ring were drilled to a depth of 10' each. Each ring consisted of 26 radial holes.
12/28/93	The drilling work was completed and grouting work began.
12/30/93	All grouting was completed.
01/06/94	Work on the plug began and was completed.
01/09/94	Installation of the 6" High Density Polyethylene (HDPE) pipe was started and work on the Dexter crosscut continued.
01/11/94	A recommendation to install a stiffer steel-reinforced system in the Dexter was made and approved.
01/13/94	IMS completed construction of the plug design with contact grouting. During this time they also cleared the caved material at the Dexter and found it to be related to a major fault containing a high-clay content gouge material which could not be contained with conventional 3-piece timber set construction.

Unfortunately, the Dexter Cross-cut was found to terminate about 350' from the cave-in area, significantly short of its expected connection with the underground mine workings.

01/13/94 All work on the Dexter was terminated pending review of the changed conditions.

01/13/94 Snow was plowed to open the access road to the Chandler Adit to prepare for work in that area.

Following the contact grouting of the 12+65 station Reynolds Adit Plug, estimations of residual leakage from the Reynolds Adit were performed and reported to USEPA. A small seep was observed around the bulkhead and some flow through fractured rock in the adit was observed. The total flow out of the Reynolds Adit was not more than 5 gpm.

1/20/94 IMS began preparing the 6+20 station in the Reynolds Adit for the second plug.

1/22/94 IMS began clearing the caved area at the Chandler portal and constructing the portal structure.

1/24/94 IMS began drilling the 26 grout holes for the 6+20 station plug. The holes were drilled in the same manner as the 12+65 station plug.

1/24/94 Inspection of the 12+65 station plug showed minor seeps from the adit walls and two wet areas near the interface with the floor but no noticeable water migration. A pressure gauge installed to measure pressure behind the plug showed no accumulation at this time.

1/25/94 USEPA instructed USBR and ECC to discontinue work on the 6+20 station plug based on the low flow in the adit, and performance exceeding expectations at the 12+65 station plug. The requirement for the second plug was found to be unnecessarily redundant and was subsequently deleted from the contract scope.

2/03/94 IMS began work on the Chandler Adit following notice to proceed from ECC. The 3+30 station location was selected as the most feasible area for a plug and a ring of 26 grout holes was drilled to a depth of 6 feet each.

2/06/94 The formation grouting was completed.

2/07/94 Placement of the plug was completed.

2/18/94 IMS returned to drill the contact grout holes.

2/21/94 Contact grouting was completed with eight (8) contact grout holes drilled around the plug with #1 located at the 6 o'clock position and the #5 at the 12 o'clock position. The injected grout volumes were recorded as follows:

Drill Hole No.	Radial Angle	Grout(cf)
1	0 degrees	0.23
2	45	0.24
3	90	4.86
4	135	3.37
5	180	**26.98**
6	225	3.49
7	270	2.33
8	315	0.24

The different amounts of contact grout was evidence that the roof area of the adit above the springline was more permeable or fractured than below the springline.

2/22/94 IMS demobilized based upon USEPA's decision to terminate any further work on the Reynolds Adit which would have been redundant and cost-prohibitive.

REYNOLDS ADIT MONITORING PROGRAM

A proposed supplemental monitoring program was developed and submitted for review on February 8th to collect data on the groundwater changes expected to occur following the plugging of the Reynolds Adit and Chandler Adits.

The proposed supplemental monitoring program was not acceptable and was never implemented. The original monitoring plan was continued as follows:

a) Weekly measurement of the piezometric surface in the 6 monitoring wells.

b) Daily estimation of discharge from the Reynolds Adit Pond. The Reynolds Adit Pond is a lined pond outside the adit portal which collects Reynolds Adit drainage, Iowa adit drainage, and some local surface runoff.

c) Weekly visual inspection of the South Mountain drainage to check for new surface seeps of low water quality.

The Reynolds Adit 12+65 station plug is meeting its performance objectives satisfactorily at this time. Reynolds Pond drainage includes Reynolds Adit and other sources. It is important to understand the surface runoff flows and stormwater management plans used in monitoring the Reynolds Adit flows to interpret the data.

1. The PITS plant was operating and treating all discharge from the Reynolds Adit, Iowa adit, and surface runoff that entered the Reynolds Adit Pond at the time of the installation of the 12+65 station plug.

2. The average flow from all sources, including the Reynolds Adit in January 1994 before the plug was installed, was 78.1 gpm with an average copper concentration of 138 ppm.

3. The plug was installed and the flow from the valved pipe through the plug was shut off on January 21st. The flow from all other sources to the Reynolds Adit pond dropped to approximately 9 gpm at an average copper concentration of 50 ppm. This confirmed the initial estimation at the 12+65 station plug that only about 5-10 gpm was migrating and emerging immediately downstream of the plug. This was an 88% reduction in flow and a 65% decrease in concentration of copper.

4. Flow and water quality measurements directly from the Reynolds Adit intersection with the Dexter Cross-cut were taken during February, March, and April. These readings were taken until April 23 at which time the PITS plant was shut down. After the plant was shut down, the Reynolds Adit Pond was allowed to overflow to the Wightman Fork. During this time, it was not possible to segregate the flow from inside the Reynolds Adit from the surface drainage in the area. This prevented any further direct estimations of adit flow.

Over the three month period, the measured flow from the Reynolds Adit, exclusively, ranged from 2.5 gpm to 11.0 gpm with copper concentrations ranging from 33 ppm to 60 ppm.

The reduction in loading per day from the Reynolds Adit was substantial from a discharge of 80 gpm at 140 ppm copper to an average of 7 gpm at 50 ppm copper. This represents a reduction in copper loading from the Adit of 97%.

5. No new seeps of poor water quality (low pH, high conductivity, high metals concentrations) have been identified since the plug was installed in the Reynolds Adit.

CHANDLER ADIT PLUG EXCURSION

The Chandler Adit Plug began discharging at a high rate of flow on May 25, 1994. The routine monitoring plan was changed to reflect this unexpected occurrence. Observaton frequency was increased to daily flow measurement, sampling, and analysis for copper concentration. Initial inspection revealed that the leakage was coming over the top of the plug through the permeable/fractured rock in the roof of the adit.

USBR was instructed to evaluate the plug condition and identify remedies for the plug leakage.

IMS was called back to the site with their consultant to inspect the plug with USEPA, USBR, and ECC. This inspection was completed and preliminary recommendations presented to USBR and USEPA for consideration. The recommended corrective action was the installation of a longer plug adjacent to the first installation with more intensive formation grouting and removal of the failed roof rock material.

ANTICIPATED WORK FOR FISCAL YEAR 1995

Following review of the monitoring data and the contractor's proposal for a longer plug installation, another inspection of the Chandler was performed by a USBR technical expert on October 5.

A final corrective action design has been developed as a result of technical discussions following the expert's inspection and subsequent contract negotiations.

The expected schedule and scope of work to be performed in the Reynolds Adit and Chandler Adits is:

1. Oct 30 - Dec 25, 1994: The Reynolds Adit will have 50 to 60 timber sets replaced or repaired to maintain safe access for maintenance of the plug and piping.

2. Oct 30 - Dec 25, 1994: The High Density Polyethylene pipeline will be completed from the 12+65 station plug in the Reynolds Adit to the portal. The pipeline will have an automatic valve system at the 12+65 bulkhead that will allow draining of the adit if required.

3. Oct 30 - Nov 30, 1994: Corrective action on the unsatisfactory plug in the Chandler will be taken.

4. The current monitoring program will be continued until a more comprehensive monitoring plan under design by USEPA's contractor Morrison-Knudsen is implemented.

5. The ground water computer model for the South Mountain system developed by the Office of Surface Mining will continue to be verified and refined with the accumulation and evaluation of new data. A report on the conclusions from predictions with this model will also be completed.

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WATER TREATMENT AT SUMMITVILLE

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ABSTRACT

Epithermal acid sulfate deposits such as the mineralized zone found at the Summitville Mine Superfund Site produce high-acid, high-metal waters. Lack of buffering materials in and surrounding the deposit contributes to the most acidic, highest metal-contaminated drainage found in Colorado (Ficklin et al, 1992). Disturbances from mining operations have increased the potential for heavy metal contamination of downstream waters. In addition, precious metal leaching operations resulted in the production of significant quantities of water containing cyanide.

Water treatment facilities on site use treatment technologies selected for the destruction of cyanide and removal of metals from acidic drainage and residual process waters. These processes have been effective in significantly reducing and preventing the migration of cyanide and metals to the Alamosa River Basin.

BACKGROUND AND HISTORICAL INFORMATION

Mine Site Geology

The Summitville Superfund Site is located in the southern part of the San Juan Mountains in southwestern Colorado. The mountains are formed from a large erosional remnant of a major composite volcanic field that covered most of the southern Rocky Mountains in middle Tertiary time. The Superfund Site occupies the same general area as the old Summitville Mining District and is situated on the northeast flank of South Mountain, a partly eroded, intracaldera quartz latite porphyry dome that extruded through a thick sequence of dense andesites. The dome is located inside the smaller and younger of two nested calderas near their common northwestern margin, and just northeast of a deep-seated northwest-trending graben-like fault zone. The graben-like structural zone transects the western and southwestern-third of the nested caldera complex and extends northwestward for 26 kilometers.

The younger and smaller caldera, (the Summitville Caldera) was filled with andesitic lavas, related minor flow breccias and volcaniclastic rocks that were later intruded and overlain locally by rhyodacites, quartz latites and silica-rich quartz latites. The quartz latite porphyry that formed South Mountain pervasively contains up to 2.5 percent pyrite and is the host rock for gold mineralization in the district. Major structures (large cracks) crisscross the domical-shaped mountain haphazardly but are most abundant and of greater intensity in the core (throat) of the dome. As a result of erosion, a portion of the northern side of the mountain is now bounded by the steep-dipping, upwardly flared "throat" contact (upper part of the neck that served as the conduit for the extrusion). Consequently, the mountain does not have a dome-like distal profile in all places. More detailed descriptions of the rock-types discussed and the geology of the area can be found in Lipman, (1974), Lipman, (1975) and Steven and Ratte, (1960).

Productive gold (and silver) deposits occur in the central part of the dome in a zone of intense acid-sulfate alteration that is probably related to a weak porphyry copper system at depth. Pods of vuggy silica (intensely silicified rock with phenocrysts totally leached) and massive silica occur along numerous strong structures in the acid-sulfate zone. These are surrounded by zones of advanced argillic alteration consisting of silica-rich alunite and kaolinitic rock. Alunite-rich rocks are common at the higher levels of the deposit. A very large volume of argillized to weakly argillized quartz latite porphyry surrounds the central core of the dome. Clay minerals (principally kaolinite, illite, montmorillonite and chlorite), grade outward from the silica core and alunite-rich zones. Fresh rock (less than 10 percent of all of the mountain) can occasionally be found outward from the chlorite-rich zone. See Stoffregen, (1987) for more detail.

The ore deposits at the Summitville Superfund Site are an excellent example of epithermal Au-Ag-Cu mineralization associated with advanced argillic alteration. Mixed magmatic and surface water, more reducing than the magmatic water that produced the alteration zones, deposited gold and sulfide minerals at relatively shallow depths (Rye, et al., 1990). Gold (and silver) was introduced into the heavily altered structures and adjacent country rock along with copper sulfide mineralization shortly after alteration occurred. It was introduced again along with barite mineralization shortly after copper sulfide mineralization was complete. Meteoric waters percolating downward through the mineralized structures and adjacent country rock subsequently formed an oxidized "blanket" with a very uneven bottom over the upper part of the ore deposit. The bulk of the gold ore was mined from this zone. Gold ore from the oxidized "blanket" was much more amenable to processing than ore from the sulfide or unoxidized zone. Mineralization is associated mostly with the porous vuggy silica zone, and occurs as covellite, luzonite and native gold, changing with depth to covellite and tennanite. Enargite, chalcopyrite, tetrahedrite, argentite, and pyrite are also common in the sulfide zones. Native sulfur is found in the vuggy silica zones in some places. Gold also occurs in near-surface barite, goethite, and jarosite assemblages that crosscut the vuggy silica zones (Stoffregen, 1987).

Post-volcanic processes have been predominantly erosional. Quaternary colluvium, talus and glacial deposits occur in many places on the site. Two major streams that drain the site, Cropsy Creek and Wightman Fork, tend to follow the quartz latite porphyry/andesite contact. Numerous springs and seeps also occur at this contact.

Site Hydrogeology

Groundwater occurs in South Mountain as a large reservoir of water perched over an aquitard (the andesite) that hosts an extensive regional groundwater reservoir. The upper surface of the regional reservoir is somewhat below the bottom of the perched reservoir. The perched reservoir drains from the interior of the mountain either downward through large cracks in the throat of the dome (into the deep-seated, "spent" magma chamber that spawned the dome), or laterally, through large cracks in the remainder of the dome to its distal edges where it exits as springs and seeps.

Abundant groundwater occurs at the contact between the quartz latite porphyry and the underlying andesite in the interior of the dome, but is especially noticeable at that contact at the distal edges of the dome. The porphyry is inherently porous and highly permeable due to tectonic (and cooling) fracturing and faulting and subsequent petrologic degradation by the highly corrosive acid-sulfate alteration fluids. Consequently, it tends to adsorb and hold water. Because of the plethora of large cracks in the dome, hydraulic conductivity of the porphyry is characterized as porous media flow augmented by a great amount of macropore flow.

Groundwater also occurs in abundance at the distal edges of the dome at the colluvium, talus and glacial deposit contacts with the underlying bedrock. The Quaternary deposits have a moderate to low hydraulic conductivity, high precipitation infiltration and therefore, a relatively high groundwater surface. Because the andesite is much less permeable than either the heavily altered quartz latite porphyry or the Quaternary deposits, springs and seeps emanating from the distal edge of the dome usually form large iron oxide-rich bogs outward from the distal edge and on top of the andesite aquitard. Hydraulic conductivity of the andesite, except for a few feet of weathered surface, can be characterized almost entirely as macropore (fracture and fault) flow.

The original, undisturbed (pre-underground mining) groundwater reservoir surface was clearly higher than current data defines. Recent open pit mining activities have shown that meteoric water-generated oxidation envelopes on individual veins and structures penetrated downward over a wide range of depths in the ore deposit. The same is probably true for those structures in the dome that remain unexposed. The lower parts of many exposed veins and structures contain base metal sulfide mineralization to varying degrees and are clearly unoxidized. This would imply that groundwater had previously existed at least up to those levels, although groundwater was not penetrated or exposed by the open pit activities.

Underground mining activities, conducted on a somewhat discontinuous basis from the 1870s to the 1970s, had a profound effect on the groundwater table in the mountain. Most notable were workings named the Ida shaft, Tewksbury shaft, Thornton raise and the Reynolds adit. These workings, though widespread, were all ultimately connected with various secondary workings. This created an extensive drainage system in the core of the mountain, with the lowermost Reynolds adit effectively working as the drain. Pre-open pit mining information indicates that the groundwater surface in the vicinity of the ore deposits as measured from monitor wells was nearly 300 feet below ground surface (SCMCI Remedial Measures Plan, 1992).

Open pit mining activities, conducted between 1984 and 1991 and designed to extract the low-grade gold mineralization in the wall rock between the veins in the ore zone, developed a huge "funneling" system over the upper part of the maze of underground workings. The open pits enhanced precipitation infiltration by shortening vadose zone retention time (from topographic surface to groundwater reservoir surface). Consequently, the groundwater surface in the mountain dropped an additional 50 feet.

Following open pit mining, plugs were set (early 1994) in two adits (the Reynolds and Chandler) that access large areas replete with underground workings. Both lie below the lowest level of open pit mining. The Reynolds adit was draining an average of about 220 gpm prior to plugging. The Chandler adit had no recent flow.

Profound changes in the groundwater reservoir in South Mountain have begun to manifest themselves as a consequence of the plugging activities. Monitor well data indicate that through spring runoff 1994, the groundwater reservoir surface has risen (after peaking and stabilizing) 70 to 160 feet. Secondly, groundwater has found its way around the Chandler plug. The groundwater rise was greater than anticipated and probably rose high enough to cause the outflow around the Chandler plug. However, this is a post-plug/pre-pit cap condition (the open pits are still funneling meteoric water into the underground workings). It is anticipated that backfilling and capping the pit area will alleviate this problem. In addition, several springs, seeps and bogs around the distal edge of the dome are running water longer into the "dry" season and at a greater volume.

Pre-Mining Water Quality

Chemical quality of the groundwater reservoir in South Mountain and its related distally located springs, seeps and bogs prior to the 1870s is unknown. The quartz latite porphyry pervasively contains up to 2.5 percent pyrite in the rock mass (Steven and Ratte, 1960). This pyrite, coupled with the high sulfur content of the alteration and mineralization phases of the extrusion, indicates that the acid water drainage (AWD) generation potential is high for the entire mountain. It is difficult to surmise that low pH/heavy metals-rich waters were not being generated as meteoric waters percolated deeper into the mountain. Acid water drainage with its related heavy metals content was present, but most likely in a less potent form than the acid mine drainage (AMD) generated in the years following the onset of underground mining. Open pit mining has shown clearly that oxygen-rich meteoric waters percolated downward along and through the plethora of veins, veinlets, cracks, fractures, faults, shatter zones and dikes present in the dome.

The extent to which the barren rocks located toward the distal edges of the dome were able to attenuate (buffer) the low pH/heavy metals-rich groundwater that flowed laterally out of the dome is unknown. Suppositions about the pre-mining water quality in Wightman Fork and Cropsy Creek and the groundwater quality in the mountain can be currently made based on water quality data obtained (by the USGS) from springs, seeps, bogs and streams that drain similarly mineralized areas in this part of the San Juan Mountains. Prospect Creek, Iron Creek, Alum Creek and Bitter Creek drain such areas. All enter the Alamosa River upstream from Wightman Fork's confluence with the river.

DEGRADATION OF WATER QUALITY

Acid Mine Drainage

With the onset of underground mining, oxygen, a key ingredient to rapid AMD generation, entered the deep, sulfide minerals-rich zones of the ore deposits. Indigenous pyrite, base metal sulfides, native sulfur and varying amounts of sulfate-rich altered rock containing alunite and jarosite (hydrous potassium aluminum sulfate and hydrous potassium iron sulfate respectively) generate high levels of sulfuric acid when exposed to air and water. The sulfuric acid, in turn, dissolves large amounts of heavy metals from the ore and rock. Underground mining not only accelerated the flow of meteoric water through the mineralized zone and exposed the zone to oxygen, it also created more surface area in the zone with which the water and oxygen could react.

During open pit mining, the Reynolds adit (started in 1897 and finished in 1915) became the focal point for AMD discussions and studies because it was the lone working (adit) that discharged AMD on a continuous basis. It is the lowermost of the old underground workings in the mountain. Recent investigations (weir installation and flow rate monitoring) have shown that during periods of low or no runoff (therefore a lower groundwater surface) AMD through the adit is less at the portal than further back in the adit. During periods of high runoff (therefore a somewhat higher groundwater surface), flow through the adit is greater at the portal than further back in the adit. This implies that macropore flow is significant near the adit as well as throughout the remainder of the mountain.

Open pit mining increased the rate and volume of precipitation infiltration into the underground workings and surrounding mineralized zone. It also vastly increased the surface area exposed in the upper part of the zone with which water and oxygen can react. Because of this increase in precipitation infiltration rate and increased areal exposure, the pits have served indirectly as a catalyst to site-wide increased copper (and other base metals) loading in the AMD from the underground workings (Reynolds adit).

Underground Workings

AMD from underground workings was principally "funneled" to and drained through the Reynolds adit. Two other adits (the Chandler and Iowa) drain smaller areas of the underground workings. The Reynolds, Chandler and Iowa adit portals are situated at elevations of 11,320, 11,500 and 11,872 feet, respectively. The Iowa adit drains a relatively small area of underground workings occurring mostly in the oxidized zone. It appears that the bulk of the Iowa adit discharge is from an ice-filled 25-foot wide shrink stope that daylights to the surface as a glory hole.

Discharge from the Reynolds, Chandler and Iowa adits display a similar trend in seasonal flow and water quality. High flows and concentrations appear during the end of May and first part of June and decrease through summer and fall. Heavy rainfall during summer results in an increase in flow rates and metals concentrations for short durations. During winter, flow and water quality stabilize at lower levels.

Pre-plug discharge from the Reynolds adit exhibited highly variable flow rates. A peak flow rate of 910 gpm was measured in early June 1993 while a low flow rate of 71 gpm was recorded in December 1993. Post-plug flow rates decreased to 50-60 gpm during high flow periods (spring runoff) and 5-10 gpm in low flow periods (winter).

The first discharge from the Chandler adit occurred in May 1994 (post-plugging) and peaked in June, reaching 661 gpm. By October, 1994 the flow had decreased to 80-90 gpm. The Iowa adit discharged at a rate of 140 gpm in June 1994 and by September 1994, flow had decreased to 14 gpm.

Variations in the water quality of the three adits follow the same trends as the flow rates. Metal concentrations peak during spring and early summer, then taper off through the fall and stabilize during winter. Copper is used as an indicator for heavy metal concentrations in monitoring sample analyses. Other metals including iron, aluminum, zinc, manganese, nickel and cadmium follow the same trends as copper.

Pre-plugging copper concentrations in the Reynolds adit discharge reached a high of 630 mg/l in May 1993 and a low of 142 mg/l in December 1993. Post-plugging concentrations ranged between 48 and 67 mg/l. Chandler adit discharge copper concentrations peaked at 430 mg/l in late May 1994 and decreased to 235 mg/l in October 1994. Iowa adit discharge contained a high concentration in June 1994 of 4.8 mg/l and declined to 3.0 mg/l in late August 1994.

Waste Dumps

From 1870 to 1992, exploration work and subsequent mining activities generated a substantial quantity of waste rock in large and small mine dumps, stockpiles, mill tails and spent ore. Dominant among these are the large dumps resulting from open pit mining activities. These include the Cropsy Waste Pile (CWP), the North Pit Waste Dump (NPWD), the Beaver Mud Dump (BMD), the Dexter Clay Ore Stockpile, the Dike 1 Clay Ore Stock Pile and the Heap Leach Pad (HLP). Subordinate to the dumps, but significant, is a tailings pond built in the late 1960s, (prior to open pit mining) called the Cleveland Cliffs Tailings Pond (CCTP). It has been used as a tailings pond on a very limited basis since its construction, and serves mostly as a down-gradient settling pond.

Except for the Dexter Clay Ore Stockpile and the CCTP, all of the dumps are situated over springs, seeps and bogs at the distal edges of the dome. As a consequence, waste rock in the dumps is subject to surface and groundwater infiltration in varying amounts. These co-mingled waters are, in some cases, partly impounded depending on the footprint of the dump as well as adjacent features. Because waste rock consists mostly of the altered and low-grade sulfide mineral parts of the ore deposit, percolating water, coupled with infiltrated air easily reacts with the secondary sulfate and base metal sulfide minerals, generating large quantities of AMD. Chief among the dump AMD generators are the CWP and the BMD. Both contain saturated zones that vary in depth during periods of high and low runoff. Because of their locations on underlying steep slopes, the NPWD and Dike 1 Clay Ore Stock Pile drain easily and do not contain extensive saturated zones.

Drainage from the Dike 1 Clay Ore Stock Pile and the BMD report to Pond P-3 and Pond P-4, respectively. Pond P-4 drains into Wightman Fork. Discharge from the NPWD also drains into Wightman Fork. Drainage from the CWP overflows into the HLP and drains into the French Drain Sump (FD Sump) through an underdrain system.

Discharges from the NPWD and the CWP display a seasonal variation in flow. Flows peak in late May and June and decrease through summer and fall. During winter, flows cease completely or remain extremely low.

The NPWD discharged at rates as high as 398 gpm in early June 1993 and decreased to less than 1 gpm by September. Discharge from the toe of the CWP peaked at 598 gpm in late May 1993 and decreased until little or no overflow was observed in December 1993. Drainage from the CWP is also suspected to discharge into the FD Sump by way of the drainage system (beneath and around the HLP) and a series of seeps which surface at the Dike northeast of the HLP (Dike 1). These seeps show the same seasonality in flow. FD Sump flow rates increased from 70 gpm in winter, 1993-1994, to more than 430 gpm in June 1994, in part due to the changes in drainage from the CWP.

Discharge metal concentrations from the waste dumps follow the same trend as the flow rates. NPWD copper concentrations peaked at 54 mg/l in June 1993. Concentrations decreased through fall and into winter until flow ceased. CWP overflow copper concentrations decreased from 85 mg/l in May 1993 to 34 mg/l in December. These variations in flow rate and metals concentration follow seasonal trends as well as similar short term trends related to precipitation.

Surface Water

Three naturally occurring streams, Cropsy Creek, Wightman Fork and an unnamed, intermittent tributary to Wightman Fork drain the site. Most of Cropsy Creek has been diverted around the eastern edge of the CWP and the HLP (Figure 1). Cropsy Creek flows into Wightman Fork near the northeast border of the site. From the confluence with Cropsy Creek, Wightman Fork flows east and southeast for approximately 4 miles, where it discharges into the Alamosa River. Variations in flow rates and water quality are observed in surface waters as a result of daily and seasonal variations in precipitation.

The site has four main surface water collection ponds for sediment control. Two of the ponds (P-3 and P-4) are used in series. Sediment pond P-3 collects surface runoff from the higher elevations of the site, the Iowa adit drainage ditch, the Dike 1 Clay Ore Stock Pile and several seeps in the vicinity of the pond. Sediment pond P-4 collects the discharge from pond P-3, surface drainage from the BMD and various seeps in its proximity. Flow rates vary seasonally from 10 to 1000 gpm. These waters are characterized by a pH of approximately 3 and copper concentrations which vary seasonally from 2-10 mg/l.

The third sediment control feature is Pond SC-7. This sediment pond has numerous influent sources including surface runoff from the NPWD, discharge from the Chandler adit and several seeps between the Metals Removal Plant (MRP) and the Chandler adit. The discharge rate varies seasonally from 140 to 1200 gpm. This water is characterized by a pH of 2.75 and copper concentrations which vary from 150 to 300 mg/l.

The fourth major water containment feature on site is the CCTP. This pond collects surface drainage from its surroundings and groundwater from the BMD. Overflow from this pond flows directly into Wightman Fork. Flow rates peaked at 348 gpm in mid-June 1993 and decreased throughout fall and winter, to 20 gpm in late November. Copper concentrations peaked at 95 mg/l in June 1993 and decreased to 41 mg/l by December.

Mineral Processing Residuals

Open pit operations initially removed the upper, oxidized portion of the South Mountain orebody. This weathered material contained free gold, silver and iron oxides. As excavation proceeded deeper into the orebody, minerals associated with sulfide mineralization (unoxidized) were transported to the HLP. Minerals occurring in significant quantities include enargite (Cu_3AsS_4), covellite (CuS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). Other sulfide minerals present in the ore include chalcocite (Cu_2S), tetrahedrite ($[Cu,Fe]Sb_4S_{13}$), sphalerite (ZnS), galena (PbS), argentite (Ag_2S) and pyrrhotite ($Fe_{x-1}S$).

Analyses of core material from the February 1991 HLP drilling program included determination of residual copper amenable to complexation with cyanide. The average concentration of cyanide extractable copper was 164.3 mg/kg. Residual leachable gold averaged 0.375 mg/kg while leachable silver averaged 3.40 mg/kg. Subsequent analyses of HLP ore mineral content focused on constituent potential for acid rock drainage (ARD) generation. X-ray diffraction analysis of six core composites indicated significant quantities of quartz (66-75%), alunite and jarosite (together 21% by weight) and pyrite (2-5%). Characterization of HLP core samples by digestion methods indicated an average pyritic sulfur content of 0.24%. The overwhelming bulk of sulfur is present as sulfate in alunite and jarosite. All detectable iron in these samples is of the oxidized ferric form (SCMCI Remedial Measures Plan, 1992).

The mineral processing techniques used by Summitville Consolidated Mining Company Inc. (SCMCI) involved the extraction of precious metals by percolating a dilute cyanide solution through crushed ore. Commercially manufactured sodium cyanide (NaCN) was transported to the site for use in this process. Approximately 7.8 million pounds of cyanide were added to the HLP during leaching operations. Free cyanide (CN^- and HCN) concentrations of 0.1 to 0.3% were maintained in the leaching solution during gold leaching operations. Quicklime (CaO) was added to the crushed ore (~6.0 lb./ton) before placement in the HLP to maintain the alkaline conditions necessary to prevent cyanide loss through volatilization as hydrogen cyanide (HCN).

Assuming that gold cyanide exists in the form $Au(CN)_2^{-1}$ and silver cyanide exists as $Ag(CN)_2^{-1}$, the recovery of gold and silver would have consumed 5,480 and 13,011 pounds of cyanide respectively. (Project records show 300,966 tr. oz. gold and 391,344 tr. oz. silver were recovered.) The remaining cyanide could exist as non-metal cyanide complexes, thiocyanate (SCN^-), various metal cyanide complexes, or may have degraded naturally. A detailed cyanide complex speciation analysis for water and ore in the HLP has not been performed. Metals concentrations and the preferential order for complexation of each species can be used to estimate the various metal cyanide complexes and their respective concentrations in the HLP solution.

Thiocyanate Formation

Cyanide reactions with pyrite and pyrrhotite are among the highest cyanide consuming reactions in gold ore. Formation of thiocyanate proceeds continuously with both of these minerals and is accelerated under conditions that combine partial or inadequate aeration with high alkalinity. All other sulfide minerals (except galena) also contribute to the generation of thiocyanate (Smith and Mudder, 1991).

Metal Cyanide Complexation

Cyanide forms complexes of varying strength with gold, silver, mercury, zinc, copper, iron, nickel and lead (Smith and Mudder, 1991). It is the strength and solubility of the gold cyanide complex that makes the use of cyanide attractive for hydrometallurgical processing of oxidized gold bearing ores. The extent to which metal cyanide complexation occurs with several sulfide minerals found in ore placed in the HLP is documented. Laboratory tests have resulted in 90.2% extraction of copper from chalcocite, 65.8% extraction of copper from enargite, 21.9% extraction of copper from tetrahedrite, 5.6% extraction of copper from chalcopyrite and 18.4% extraction of zinc from sphalerite (Scott and Engles, 1987).

The metal ion of greatest concentration in the HLP solution is copper. Other metals that typically form metal cyanide complexes occur at low concentrations, including gold, silver, zinc, iron, nickel, lead, cadmium and cobalt. Of the copper complexes formed, CuCN is a neutral insoluble salt, while most other copper cyanide complexes are soluble, moderately strong weak acid dissociable (WAD) cyanide complexes.

Iron Cyanide Complexation

Ferrocyanide ($Fe(CN)_6^{-4}$), a strong, stable cyanide complex with low solubility, is formed relatively rapidly under conditions of low alkalinity and reduced aeration. Conditions for formation of thiocyanate and ferrocyanide from iron sulfide minerals are to some extent mutually restrictive due to the different conditions of alkalinity required for formation (Smith, Mudder, 1991).

Given the alkalinity furnished by addition of CaO to the ore, constant aeration of process solution by circulation and significant thiocyanate concentrations found in the HLP process solution, ferrocyanide formation may not be significant. However, a substantial portion of ore placed in the HLP (~2,600,000 tons) has remained submerged for years. Dissolved oxygen concentrations of solution at this depth ranged between 1.5-6.0 mg/l. Only two of 18 solution samples taken at various depths during the 1991 drilling program had dissolved O_2 content of 1.5 mg/l, which is still considered "oxygenated" (Roeber, 1991). Zones of reduced aeration in this portion of the HLP are, however, possible.

Most of the submerged ore is from the oxidized portion of the orebody and may contain a significant amount of iron previously oxidized to the ferrous state. The oxidized iron coupled with the addition of AMD from the CWP and the FD Sump to the HLP (for containment) may have resulted in zones of reduced alkalinity and increased metal ion concentration. These conditions would facilitate the formation of ferrocyanide.

Volatilization of Hydrogen Cyanide

Solution pH was maintained in the range of 9.3 to 11.5 throughout gold leaching operations. Although the theoretical concentration of free cyanide as HCN is as much as ~35% at pH 9.3, no indication of significant HCN volatilization was detected by HLP and process plant monitoring programs. Complexation of cyanide with copper and other metals (to a much lesser extent) restricts the formation of HCN and subsequent volatilization.

Water Quality of Cyanide-Containing Waste Streams

Cyanide-containing waste streams on site are contained and collected in the HLP and FD Sump. In December 1992, the HLP water was characterized by copper and WAD cyanide concentrations of 220 and 235 mg/l, respectively. By September 1994, detoxification efforts had reduced these concentrations to 20 and 15 mg/l. The average pH of water contained in the HLP has remained in the range of 9.0 to 9.5 for the duration of the detoxification phase.

The FD Sump contains contaminated waters collected by the HLP underdrain system and numerous seeps along Dike 1. This combination of waters is characterized by copper and WAD cyanide concentrations of 20 and 7 mg/l, respectively. The pH of the influent streams ranges from 2 to 3.

WATER TREATMENT

Virtually all metal and cyanide load transported from the Summitville Superfund Site to the Alamosa River reduces the potential for a healthy ecosystem. All targeted waste streams on site require treatment for the removal of metals and/or the destruction of cyanide prior to discharge to minimize their potential downstream effects.

AMD originating from underground workings, waste dumps and surface water runoff is characterized by a low pH and high metal concentration. Each AMD stream contains varying levels of metals (copper, iron, aluminum, manganese, zinc, nickel, cadmium) and as a result, has specific requirements for contaminant removal.

HLP and FD Sump waste streams contain lower concentrations of metals which exist in varying degrees as metal cyanide complexes (predominantly copper). In contrast to the acidic streams (underground workings, waste dumps, surface runoff and FD Sump), residual process waters in the HLP have a pH greater than 9.0.

Total metal concentration in the various waste streams on site ranges from 100 to 3,000 mg/l. The underground workings generate water with copper concentrations which vary by a factor of more than thirty. CWP drainage contains five to ten times the copper in other waste dump drainages. Water draining from the surface water collection ponds varies less in metals concentration.

Variations in water quality must be taken into account when considering cost and efficiency in the application of treatment technologies. Reagent consumption varies with acidity, metal content and oxidation/reduction conditions. In addition, waste products produced by contaminant removal from each waste stream can vary significantly in volume and character. Although metals removal and cyanide destruction are the general treatment requirements, specific waste stream characteristics must be considered in process selection and facility design.

Water Treatment Facilities

There are four water treatment facilities at the Summitville Superfund Site. At present, three of these facilities are active. The Cyanide Destruction Plant (CDP) and the Metals Removal Plant (MRP) treat water pumped from the HLP. The Cropsy Water Treatment Plant (CWTP) treats water draining from or impounded in the CWP. Waters surfacing from beneath the HLP and Dike 1 and collected in the FD Sump are also treated in the CWTP. The Portable Interim Treatment System (PITS) was installed to treat acid mine drainage exiting the Reynolds adit. The facility was placed on standby status after plugging of the adit. Locations of the four facilities are shown in Figure 1.

Cyanide Destruction Plant

The CDP is located approximately 1400 ft. northwest of the HLP and was the gold recovery plant during SCMCI operations. Metal cyanide complexes were removed from solution by adsorption on granular activated carbon (GAC). $Au(CN)_2^-$ and $Ag(CN)_2^-$ were desorbed from the GAC in a separate circuit, which produced a small volume of solution with high concentrations of gold and silver. Zinc cementation and solids filtration were then used to remove the precious metals from the concentrated solution. The filtered solids were smelted to form dore metal, which was shipped from the mine for refining and subsequent sale. Metal adsorption was accomplished in six 831 cu. ft. vessels and five 392 cu. ft. vessels.

The gold recovery plant was converted to a water treatment facility in October 1992. The treatment process targeted cyanide destruction using hydrogen peroxide (H_2O_2). Hydrogen peroxide dosing apparatus, polymer addition equipment, a 3416 cu. ft. lamella design clarifier, and a 130 cu ft. plate and frame filter press were installed in (or near) the recovery plant building.

Metals Removal Plant

The MRP is housed in a building that contained a flotation plant used in a short-lived copper recovery operation in the late 1960s. The building is approximately 500 ft. northwest of the Reynolds adit portal. SCMCI installed an alkaline chlorination water treatment plant in the building in 1988-1989. The process included destruction of cyanide by alkaline chlorination and removal of metals by precipitation. It was designed to process up to 500 gpm, although the constructed plant could not accommodate over 300 gpm and could not produce directly dischargeable water at a rate greater than 175 gpm.

Equipment used in the alkaline chlorination process included six 1583 cu ft. reaction/retention vessels, two 1495 cu. ft. lamella design clarifiers, two 260 cu. ft. clarification and flocculation tanks, holding tanks, a sludge thickener, a four-chamber sand cone filter, and an 80 cu. ft. plate and frame filter press. Reagent addition equipment included two chlorinators and associated addition pumps, a lime slaker, a polymer addition system, and other reagent metering pumps. The treatment sequence consisted of two stages of pH adjustment and chlorine addition separated by a clarification stage. This segment destroyed cyanide and removed residual metal hydroxides. Sulfide precipitation of metals followed the second chlorination step. Final clarification consisted of routing water through a second clarifier and the sand filter.

The MRP was converted to an expanded metal sulfide precipitation plant at the same time that the SCMCI gold recovery plant was converted into the CDP. The MRP incorporated all of the existing equipment into the new treatment process configuration except the chlorinators, the lime slaker and the sand filter . The destruction of cyanide in the CDP is followed by the removal of metals in the MRP.

Cropsy Water Treatment Plant

Most of the equipment for the CWTP was obtained from Homestake Mining Company's Bulldog Mine in Creede, Colorado. It was reconstructed on the northwest edge of the HLP. This treatment facility contains two 502 cu. ft. reaction tanks, one 537 cu. ft. reaction tank, one 1053 cu. ft. clarifier, one 191 cu. ft. clarifier and one 100 cu. ft. plate and frame filter press. Also included are reagent mixing and storage tanks and reagent addition apparatus.

The CWTP uses an alkaline precipitation process to remove the metals from solution and a copper-catalyzed hydrogen peroxide oxidation process for cyanide destruction.

Portable Interim Treatment System

The PITS was installed in July 1992 to remove metals from the Reynolds adit discharge. It is located about 250 ft. southeast of the Reynolds adit portal. The plant is a modular system with four components. The first component contains a reagent addition/reaction unit and is followed in series by two clarification units. A sludge dewatering/removal unit is the final stage of the process. The reaction unit consists of reagent storage and delivery equipment and a 264 cu.ft. reaction tank. Each clarifier unit is 3213 cu. ft. The sludge removal unit contains polymer addition equipment and a rotary dewatering drum. A 283 cu.ft. coagulation and flocculation tank and a 1614 cu.ft. sludge settling tank were added to the original configuration during efforts to increase system capacity. The process configuration consisted of pH adjustment in the first unit followed by coagulation and flocculation in the floc tank and clarification in the second and third units. The final stage involved sludge dewatering. An alkaline precipitation process was used to remove heavy metals. The treatment plant is currently inactive.

METALS REMOVAL

Although each waste stream on site varies in water quality, all streams targeted for treatment require processes for metals removal. AMD generated by underground workings, waste rock dumps and surface water runoff from disturbed areas requires treatment to reduce metal load transported to the Alamosa River Basin. In addition, residual process water pumped from the HLP and collected in the FD Sump require treatment for metals removal before discharge to Wightman Fork.

Many treatment technologies have been developed for the removal of metals from liquid waste streams. They include physical, chemical, thermal and biological processes. The selection of treatment processes for metals removal at the Summitville Superfund Site was based upon several factors. Process effectiveness, practicality of application, equipment availability, cost, and health and safety issues were all considered. In December 1992 the existing treatment process configuration was designed for chemical and physical methodologies for metals removal. It was decided that the most practical solution would be to enhance the existing systems.

Precipitation processes for the removal of metals are used in the CDP, MRP and CWTP. A hydroxide precipitation process is used in the CDP and CWTP and a sulfide precipitation process is used in the MRP. Flocculation and clarification processes are employed to separate the precipitated metal compounds from the liquid phase. The final step in metals removal involves dewatering of the sludge produced by the treatment processes.

All precipitation processes are based upon the same fundamental chemical principle. The ionic equilibrium of a metal compound is altered to produce an insoluble metal compound and a salt (Palmer et al, 1988). Success of these processes is dependent upon several factors. An alkaline pH must be maintained to achieve minimum solubilities of metal compounds. Adequate reagent must be added to ensure the precipitation of all metals (reaction completion can be affected by complexing agents that compete with the reagent for the metal ion). Separation of the insoluble metal compound is the final step essential to low total metal concentration in the process effluent stream. The success of this system is often enhanced by coprecipitation of metals in solution. The plurality of metallic species in solution can reduce final concentrations to values lower than those that could normally be achieved by precipitating each metal at its optimum pH.

Hydroxide Precipitation Process

The hydroxide precipitation process converts soluble metal ions into insoluble metal hydroxide compounds. Metal ions that are successfully removed from solution as hydroxide compounds include aluminum, arsenic, cadmium, trivalent chromium, copper, iron, lead, manganese, nickel and zinc (Palmer et al, 1988).

The most common precipitation agents used in this process are caustic soda (NaOH) and lime (CaO). Although both are equally effective in the alkaline precipitation process, caustic soda (as a liquid) is easier to store, handle and pump than a lime slurry. Comparatively, it does not clog valves, form insoluble reaction products or cause density control problems (Palmer et al, 1988). Sodium hydroxide (NaOH) dissociates rapidly, requiring less retention time, and produces less sludge than lime. NaOH is used at the CDP and the CWTP. Treatment of AMD from the Reynolds adit also employed this process until the PITS was shut down in April 1994.

The hydroxide precipitation process is highly dependent upon maintaining the solution pH within the range specified for minimum solubility. The minimum solubilities for cupric, manganic and ferric hydroxides are in the pH range of 9.0 - 10.5, 10.5-13.5 and 5.5-11.5 respectively. Waters containing these metals show a minimum solubility between 9.0 and 9.5. Although each species has a different minimum solubility range, an optimum range is determined empirically and attainment of low metal concentrations is enhanced by coprecipitation.

Sulfide Precipitation Process

The sulfide precipitation process converts soluble metal ions into insoluble metal sulfide compounds. The high reactivity of sulfide ions with metals and the insolubility of heavy metal sulfides over a broad pH range result in metal concentrations lower than those normally achieved by the hydroxide precipitation process. The sulfide precipitation process is often used more effectively as a polishing step after hydroxide precipitation. This sequence of processes achieves the low concentrations inherent to the sulfide process while reducing the consumption of the sulfide reagent.

Sulfide precipitation is effective in removing copper, zinc, manganese, iron, aluminum, silver, lead, mercury, nickel, thallium, arsenic, antimony, vanadium and cadmium (Palmer et al, 1988). The reaction demands neutral to alkaline conditions, in a pH range of 7.0 to 9.0. The pH ranges for minimum solubility of metal sulfides vary; however solubilities decrease as pH increases.

The sulfide precipitation process requires the presence of the sulfide ion. A water soluble sulfide compound such as sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS), or a relatively insoluble sulfide slurry such as ferrous sulfide (FeS) is typically used to introduce the sulfide ion into the waste stream. The former of the two methods requires accurate dosing mechanisms or tanks that are enclosed and vacuum evacuated to prevent odor problems and health hazards caused by hydrogen sulfide (H_2S) generation. The latter of the two methods is not affected by these operational problems. It does, however require higher than stoichiometric reagent consumption and produces significantly more sludge (USEPA, 1980).

A slightly soluble sulfide slurry is used in the MRP treatment process, following the hydroxide precipitation process in the CDP. Ferrous sulfate ($FeSO_4$) and sodium sulfide (Na_2S) are mixed to produce a ferrous sulfide (FeS) slurry. Once added to the waste stream, the FeS dissociates (to the extent defined by its solubility product) to yield a dissolved sulfide concentration of 0.02 ppb in the wastewater (USEPA, 1980). The dissolved sulfide concentration is maintained by the inventory of undissolved sulfide. Sulfide ions provided by undissolved FeS replace the dissolved sulfide consumed by the precipitation process. Metals that exist as hydroxide precipitates or which are introduced by the reagent (iron) are also precipitated by this process. Insoluble metal hydroxides present in the waste stream resolubilize as the metal ion concentration decreases. Liberated metal ions then precipitate as insoluble metal sulfide compounds. Excess dissolved iron from the added reagent can be precipitated as a hydroxide by maintaining the pH between 8.5 and 9.0 (USEPA, 1980).

Coagulation Flocculation and Clarification

Once the metals have been precipitated as metal hydroxides or metal sulfides, they must be removed from the liquid stream. The more conventional techniques for liquid-solid separation are coagulation and flocculation (for particle aggregation), gravity separation (flotation, sedimentation), evaporation and filtration through granular media.

The technique selected for water treatment processes on site occurs in two stages and combines chemical and physical methods to separate particulate matter from the treated water. Precipitated metal hydroxide and metal sulfide compounds adsorb onto a chemical coagulant and form large aggregates (flocs) that are removed from solution through gravity settling procedures. Anionic polymers have been used as coagulants in the CDP, MRP, CWTP and PITS. These polymers serve to destabilize the particles, allowing them to form large shear-resistant flocs. Unlike inorganic coagulants (aluminum sulfate and ferric sulfate) these anionic polymers do not typically produce massive sludge volumes or alter the alkalinity of the waste stream by significant measures (Montgomery, 1985).

Once coagulation and flocculation are complete, solids are separated from the waste stream through clarification. Lamella design (parallel plate and tube settler) clarifiers are used in the CDP and MRP, and previously in the PITS. The CWTP uses an upflow or solids contact clarifier. Overflow from the clarifiers is the treatment effluent. Underflow from the clarifiers is pumped directly to a filter press or is temporarily contained for thickening before dewatering.

Sludge Dewatering

The use of a filter press for dewatering sludge has been employed at each of the water treatment facilities except the PITS. Sludge produced by the PITS system was removed from the clarifiers and dewatered using a rotary drum dewatering device. Currently, the CWTP produces the largest amount of sludge, followed by the MRP and the CDP. Much like the CWTP, excessive influent metal concentrations in PITS influent water resulted in the production of massive volumes of sludge.

New Process Options for Metals Removal

Efforts to improve discharge water quality while reducing water treatment costs continue. Treatment technologies have been proposed for the enhancement of metals removal. A Request for Proposals was conducted to allow new technologies to be offered for review for potential use at the site. These proposals included technologies for alternate metals precipitating agents, chelation, ion exchange, activated carbon adsorption with ion specific resins, ligand adsorption, induced ionic reactions, sludge recycling, column flotation and electrochemical separation. Recently, a producer of a metals removal process which uses macrocyclic bonded silica gels conducted treatability tests on site waters. The potential for integration of this process into site water treatment operations is currently being evaluated.

DESTRUCTION OF CYANIDE

Waters contained in the HLP and collected in the FD Sump require treatment for the destruction of cyanide and the removal of metals. Treatment processes selected for these waters require the destruction of cyanide before metals removal, due to the complexation of cyanide with heavy metals (Au, Ag, Hg, Zn, Cu, Fe, Ni, Pb and Cd). However, reduced species (ammonia, sulfide, non-complexed metals, etc.) can exert an excessive reagent demand when oxidation processes are used for the destruction of cyanide. Under these conditions the reduced species must be oxidized and/or removed from solution prior to cyanide destruction. Several treatment technologies exist for cyanide destruction and removal, including physical, chemical and biological processes.

Although physical processes are proven effective in cyanide removal from liquid waste streams, a process that destroys the cyanide was deemed preferential for use at the site. Processes that remove cyanide simply concentrate free and complexed cyanide into smaller volumes of waste and produce a secondary stream requiring treatment or disposal. Chemical and biological treatment technologies have been developed to destroy cyanide, minimizing secondary treatment and disposal costs. Chemical processes involve oxidation and hydrolysis while biological treatment technologies consist of the aerobic and anaerobic digestion of cyanide by microorganisms. Several technologies were considered for use in the cyanide destruction process at the Summitville Superfund Site. These technologies are described in brevity below.

Natural Degradation of Cyanide

Natural degradation of cyanide can be achieved through a variety of processes including hydrolysis, volatilization, photodegradation, dissociation, precipitation and chemical and bacteriological oxidation. The main mechanisms for natural degradation include volatilization of HCN and dissociation of metal complexes (Smith and Mudder, 1991). However, these processes are time dependent and under natural conditions are only effective if the necessary conditions exist (including but not restricted to temperature, pH, ultraviolet light intensity, oxidation/reduction conditions).

Biological Oxidation of Cyanide

Biological processes have recently become more widely used as a treatment technology for cyanide contaminated wastes. Free cyanide (HCN, CN^-) and all forms of metal complexed cyanide are removed, including WAD cyanide and the stable iron-cyanide complexes (Smith and Mudder, 1991). In addition, thiocyanate, metals and most cyanide destruction byproducts such as ammonia can be removed from waste streams by biological processes. Metals are removed with coagulant aids and as an adsorbent on biofilm while ammonia undergoes nitrification (bacteriological oxidation of ammonia to nitrate). Chemical requirements include an inorganic carbon source to aid in nitrification and phosphorus as a trace nutrient.

The biological process involves two oxidation steps. Cyanide and thiocyanate are first oxidized to produce carbonate, ammonia and sulfate. Metals liberated from the metal-cyanide complexes are then adsorbed onto biofilm surfaces and can be precipitated. Ammonia then undergoes nitrification to produce nitrates. This process has been shown to reduce total cyanide, thiocyanate, ammonia and metal concentrations to less than 1 mg/l (Smith and Mudder, 1991).

Advantages of biological treatment include potential destruction of all forms of cyanide, low reagent costs, removal of heavy metals (adsorption and precipitation), removal of thiocyanate and ammonia, and minimal requirements for design and operation. Disadvantages of this process include effects of temperature extremes, potential requirement for additional metal removal processes, potential unavailability of suitable microbial populations and high capital costs (depending on the site specific system requirements). A pilot test program is being developed to explore the potential use of biological processes in the detoxification of the HLP (see Thompson and Others, this volume).

Chemical Oxidation of Cyanide

The oxidation of cyanide can be accomplished by many processes and oxidizing agents. Some of the more conventional oxidizing agents include chlorine, ozone, wet air, sulfur based compounds and hydrogen peroxide. Destruction of cyanide is achieved by all of these except particular sulfur based compounds. The processes using these agents convert the cyanide to less hazardous compounds such as thiocyanate and insoluble ferrocyanides, producing a secondary waste stream requiring treatment or disposal. The chemical treatment processes that were considered for use at the Summitville Superfund Site included alkaline chlorination, oxidation by sulfur dioxide and oxidation by hydrogen peroxide.

Alkaline Chlorination

Alkaline chlorination is suitable for destroying free and WAD cyanide in aqueous media. The two most common oxidizing agents used in this process are elemental chlorine (Cl_2) and a hypochlorite salt such as sodium or calcium hypochlorite ($NaOCl$ and $Ca(OCl)_2$). Under alkaline conditions, one of these two can be used to oxidize cyanide to cyanogen chloride ($CNCl$). This intermediate product then undergoes hydrolysis and is converted to cyanate (CNO^-). Cyanate is then converted to ammonia and carbonate. Under excess reagent conditions, ammonia is converted to nitrogen gas. The process requires controls for pH and oxidation-reduction conditions and can achieve effluent concentrations of less than one mg/l.

Several disadvantages are associated with this process. The presence of organic compounds and reduced metals can increase consumption of the oxidizing agent by 25 to 100%. The presence of cupric cyanide ($Cu(CN)_2$) can cause precipitation during the chlorination process. This can result in cyanide-containing sludge that requires secondary treatment and a physical system that may need batch cleaning. Ammonia present in waste streams can result in the formation of chloramine, a highly toxic gas. Thiocyanate takes preference to other cyanide compounds in the oxidation sequence and can create excessive reagent demands if present. In addition, strongly complexed cyanide (iron and cobalt cyanide complexes) are not effectively destroyed in this process.

Inco Sulfur Dioxide/Air Oxidation

The Inco Sulfur Dioxide /Air oxidation process uses a mixture of sulfur dioxide (SO_2), sodium sulfite (Na_2SO_3) or sodium meta-bisulphite ($Na_2S_2O_5$) and air within a controlled pH range to destroy cyanide (Smith and Mudder, 1991). Both free and complexed cyanide species are oxidized to produce cyanate. Hydrolysis of the cyanate results in the formation of carbon dioxide and ammonia. The metal-cyanide complexes are destroyed in preferential order. Oxidation of zinc cyanide complexes is followed by iron, nickel and copper complex oxidation (Palmer et al, 1988). This process can achieve total cyanide concentrations of less than one mg/l.

Metals which are liberated from metal-cyanide complexes precipitate as hydroxides. Iron-complexed cyanide is reduced to the ferrous state and removed as insoluble copper, nickel and zinc ferrocyanides ($M_2Fe(CN)_6$ where M is copper, nickel or zinc). Thiocyanate can also be destroyed in this process once cyanide has been removed and only with greater retention times and addition of more reagents.

Copper acts as a catalyst in the INCO process. If not present in ionic form, it can be added to the waste stream (as a copper sulfate solution). This can however result in excessive formation of calcium sulfate (gypsum).

Disadvantages to this process include high reagent costs, the formation of undesirable quantities of gypsum, royalty payments for a patented process and the requirement of strict process control measures.

Hydrogen Peroxide

The process selected for cyanide destruction at the Summitville Superfund Site involves chemical oxidation using hydrogen peroxide (H_2O_2). This process is used to treat waste streams from the HLP and the FD Sump.

Hydrogen peroxide is a strong oxidizing agent and capable of reducing free and WAD cyanide to concentrations well below 1 mg/l. In the presence of a metal catalyst (copper, iron, aluminum or nickel) and under alkaline conditions, it rapidly oxidizes free and complexed cyanide to cyanate. The cyanate then undergoes hydrolysis to form carbonate and ammonia. Metals liberated by the destruction of the metal-cyanide complexes are precipitated as metal hydroxides. In addition, up to 15% of the thiocyanate can be oxidized during treatment (Smith and Mudder, 1991).

An initial dissolved copper concentration of 10-20% of the WAD cyanide concentration is obtained through the addition of reagents, when necessary. Waters treated for cyanide destruction at the Summitville Superfund Site are characterized by a dissolved copper concentration well in excess of this percentage and do not require additional reagents.

Normally, 2 to 4.5 times the theoretical stoichiometric dosage of hydrogen peroxide and a retention time between 20 minutes and 4 hours is necessary for the effective oxidation of cyanide. This factor depends upon the WAD cyanide and copper concentrations in the waste stream, the strength of the hydrogen peroxide solution and the rate of mass transfer of hydrogen peroxide (H_2O_2) to the waste stream. The controlling mechanism of the process in the CDP appears to be mass transfer.

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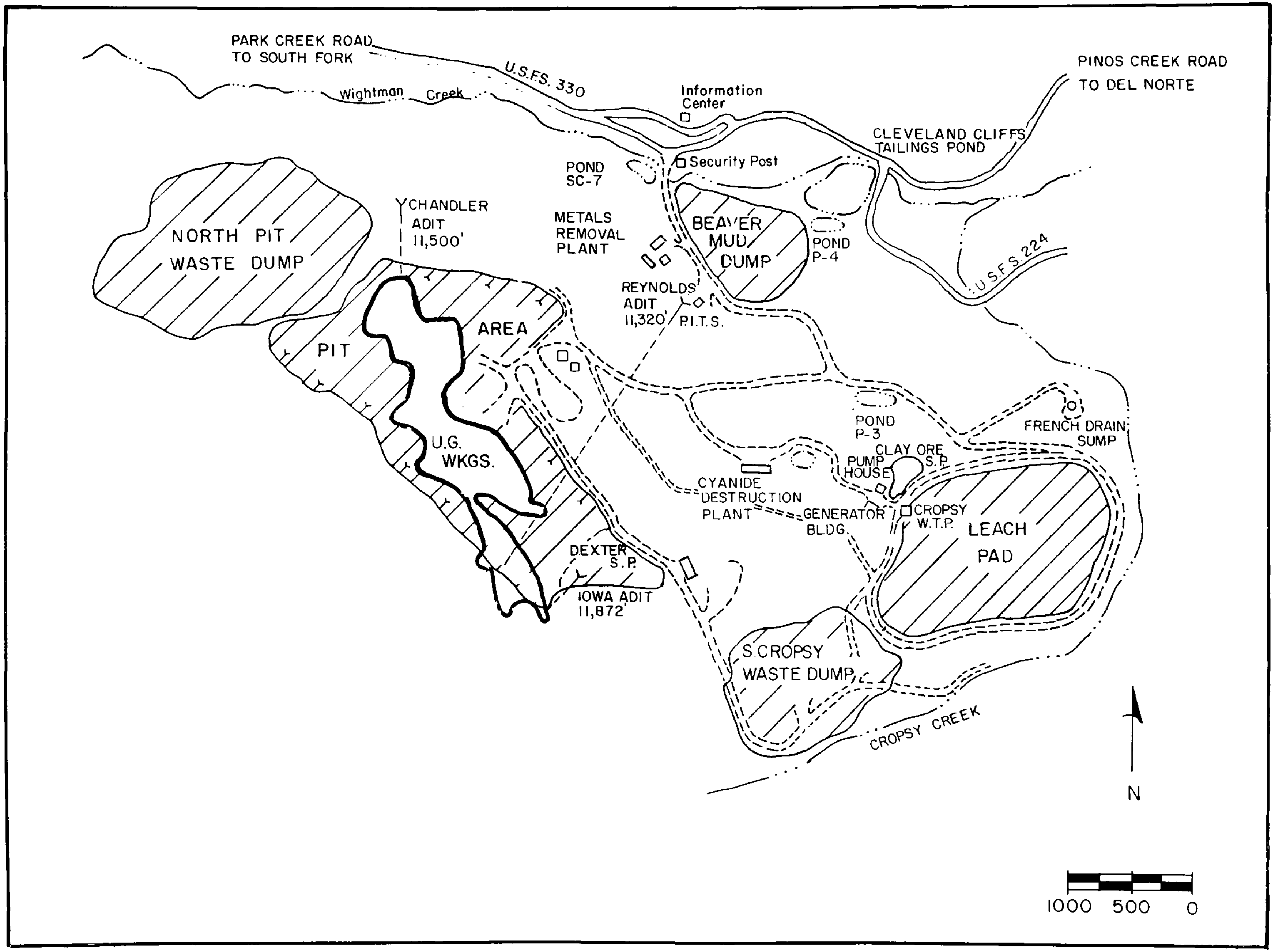

Figure 1. General map of Summitville site.

BIOTREATMENT PROCESSES FOR SPENT ORE DETOX AT THE SUMMITVILLE MINE

Test Results from Focused Feasibility Studies

By
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INTRODUCTION

The Summitville Mine was the site of mining operations that began in 1873 with the discovery and development of gold placer and lode deposits. Located about 25 miles south of Del Norte, Colorado in the San Juan mountains the mine site is at an altitude of 11,500 feet. The site was actively mined for gold, silver and copper between 1873 and 1947. From 1947 to 1986 the mine was inactive until the Summitville Consolidated Mining Corporation, Inc. (SCMCI) a wholly-owned subsidiary of Galactic Resources, Ltd. started an open pit mine and heap leach operation at the site.

SCMCI ran a large tonnage open-pit and cyanide heap leach operation from 1986 to 1992. Gold ore (approximately 10 million tons) was mined, crushed and stacked on a lined leach pad. This leach pad was unique because it was a lined bowl with containment dikes that ponded leach solutions in the ore heap compared to more standard, well-drained percolation-type leach.

Heap leach operations experienced problems with water balance and unplanned solution discharges from the start of the mine life. Solution containment complications and ineffective water treatment contributed to environmental problems. Despite the production of 249,000 troy ounces of gold during the mine operation SCMCI was unable to meet remedial requirements and notified the state of Colorado of its intention to file a Chapter VII bankruptcy in December 1992. The EPA Region VIII Emergency Response Branch took over site operations on December 16, 1992 to prevent a catastrophic release of hazardous substances to the environment. The Summitville Mine site was added to the National Priority List in June 1994.

There are multiple sources of contamination at the site due to historic and SCMCI mining operations. Emergency response operations at the site have prevented releases of severely contaminated solution and studies are underway to define a permanent solution to detoxification or neutralization of the various mine waste units. This report addresses demonstration of an innovative bioremediation technology for treatment of cyanide and soluble leachable metals in the heap and heap solutions.

Heap Leach Remediation Evaluation

The heap leach pad is a bowl-shaped structure located within the Cropsy Creek drainage. A French Drain structure underneath the heap is a network of gravel trenches and perforated pipe designed to intercept groundwater and leakage from the heap. The heap consists of approximately 10 million tons of cyanide-leached ore and 90 to 150 million gallons of process solution. EPA Region VIII commissioned a Focused Feasibility Study (FFS) and Report of Investigation (RI) to evaluate remedial options for the Heap Leach Pad (HLP). The RI/FFS was completed by Morrison Knudsen Corporation and submitted to EPA Region VIII on August 19, 1994.

A Request for Proposal (RFP) was issued by Environmental Chemical Corporation (ECC) in October 1993 at the request of USEPA Region VIII, Department of the Interior and Bureau of Reclamation. The RFP requested interested companies to provide information on their ability to implement innovative treatment technologies to improve treatment efficiency and reduce cost of treatment of the heap leach pad spent ore and leachate solutions. Dames & Moore and Pintail Systems, Inc. (PSI) jointly submitted a proposal suggesting application of biotreatment processes for treatment of the spent ore and process solutions in the HLP. The proposal was accepted for feasibility demonstration under the EPA Superfund Innovative Technology Demonstration Program (SITE) with additional funding from EPA Region VIII. The primary objectives of the Dames & Moore/Pintail Systems proposal were to:

1. Demonstrate the feasibility of spent ore and process solution cyanide bio-detox.

2. Develop site-specific biotreatment processes for spent ore and process solution cyanide detox.
3. Provide treatment data for use in the RI/FS and Record of Decision (ROD) for the Spent Ore and Entrained Solutions operable units at the Summitville Mine.
4. Immobilize potentially leachable metals including zinc, copper, manganese, iron and arsenic within the heap to improve water quality.
5. Define the potential for enhancing precious metal recovery (gold and silver) as a result of spent ore cyanide biotreatment.

Tests and demonstrations outlined in the proposal were conducted in PSI's Aurora, Colorado lab and pilot plant and at the mine site. Spent ore treatability testing included waste characterization, bacteria isolation and bioaugmentation, parallel column treatment tests, data evaluation and reporting.

Biotreatment processes for heap, tailings and process solution detox have been proven at other mine sites in a variety of environments. Biological processes are both site-specific and waste-specific and must be individually engineered and tested for each mine waste. Successfully adapting treatment bacteria to the spent ore environment is a key to developing successful bioremediation potential. Working with a biotreatment population that has been specifically adapted to the ore and augmented to improve cyanide metabolism insures that biotreatment will be effective.

Biological processes for cyanide detoxification in mine waste are receiving attention as an alternative to conventional chemical treatment options. These are some of the advantages of biological treatment:

- Low comparative treatment cost
- Shorter treatment time
- In situ treatment
- Complete detoxification
  - Ends long-term liability
  - Eliminates in-perpetuity monitoring
  - Allows for natural revegetation
- Natural and non-toxic nutrients, by-products and process end-products

Cyanide metabolism is known to occur in several species of bacteria. Bacteria that have the capacity for enzymatic hydrolysis of ionic cyanide or metallo-cyanide compounds use the carbon and/or nitrogen of the cyanide to meet their nutritional needs. The end-products of cyanide metabolism are natural and non-toxic. Some of the reactions involved in microbial cyanide oxidation include:

1) $2Fe(CN)_6^{4-} + 29 \cdot H_2O + 6.5O_2\ 12CO_3^{2-} + \text{----->}\ 12NH_3 + 2Fe(OH)_3(s) + 16H^+$

2) $M_xCN_y + 2 \cdot H_2O + 0.5O_2 \text{ ----> } M/\text{bacteria} + HCO_3 + NH_3$

3) $NH_3 \text{ ----> } NH_2OH \text{ ----> } HNO? \text{ ----> } NO_2 \text{ ----> } NO_3$

4) $NO_3 \text{ ----> } NO_2 \text{ ----> } NO \text{ ----> } N_2O \text{ ----> } N_2$

LABORATORY WORKPLAN

Bacteria Source—Isolation and Development

Cyanide decomposition bacteria have been isolated and augmented in PSI's R&D laboratory for remediation testwork with mine ores, tailings and waste rock. Specific cultures were isolated from spent ore samples collected during the heap drilling program. Preparation for the column tests included:

1. Isolating native bacteria from the spent ore;
2. Adapting the treatment bacteria to the Summitville Mine spent ore in a series of stress and waste infusion media;
3. Characterizing growth and enhancing the new "cyanooxidans" population.
4. Demonstrating bacteria growth and cyanide decomposition in an ore leach flask test.

Test Design

The following workplan was used for the column tests:

1. 75-85 kg of spent ore collected by SAIC and the SITE program was loaded into each of six 6"x10' PVC columns. The columns were fitted with a perforated screen and a tapped end-cap to allow treatment solutions to percolate through the ore and be collected for analysis. The columns were set up as follows:

Column #1:	sulfide zone ore, percolation leach biotreatment;
Column #2:	oxidized ore, 25–90 ft depth, percolation leach biotreatment;
Column #3:	oxidized ore, 90–130 ft depth (saturated zone), saturated with HLP solution, percolation biotreat;
Column #4:	oxidized ore, 0–90 ft depth, rinsed zone (1993 peroxide rinse program), percolation leach biotreatment;
Column #5:	oxidized ore, 0–25 ft depth, percolation leach biotreat;
Column #6:	Control Column, oxidized ore, 90–130 ft depth (saturated zone),

saturated with HLP solution, percolation leach with peroxide-treated HLP solution.

2. The Detox population of bacteria was grown to working strength and transferred to a dilute nutrient solution for application in a percolation leach.
3. Thirty gallons of barren solution supplied by SAIC and ECC were set aside for the saturated column tests.
4. The treatment solutions were applied to each column at a nominal rate of 0.004 gpm/ft^2.
5. Bio-leach or detox barren solutions from the columns were collected and analyzed for total cyanide. Total cyanide, WAD cyanide, gold and select metals were analyzed in column leachate solutions during the course of the test.
6. Cyanide analysis was run as a total or Weak Acid Dissociable cyanide in reflux acid distillation with a colorimetric determination.
7. A material balance was kept to allow calculation of contaminant reduction related to tons of treatment solution applied per ton of ore.
8. Leachate solutions were analyzed for gold and copper to determine metal mobilization due to bacteria processing. Metal analyses were run on an Inductively Coupled Spectrophotometer and an Atomic Absorption Spectrophotometer.
9. Split samples of spent ore and column leachate solutions were collected by SAIC and were submitted to a contract laboratory for confirmation analysis. A diagram of the column test design is shown in Figure 1.

PILOT TEST DATA

The data collected from the pilot column ore treatment program is presented in Figures 2 and 3 and Table 1. Treatment compliance for successful cyanide detoxification was 0.2 mg/L WAD cyanide measured in column leachate solutions. The control peroxide rinse column of saturated zone ore did not achieve compliance with a WAD cyanide standard. All other column treatments reached compliance levels. Total and WAD cyanide were plotted against the tons of solution applied per ton of ore.

Table 1 lists the amount of treatment solution applied per ton of ore for each column to reach compliance. The amount of biotreatment solution required for complete cyanide detoxification is projected to be 25–30% of the amount of solution required by conventional chemical rinse detox treatments.

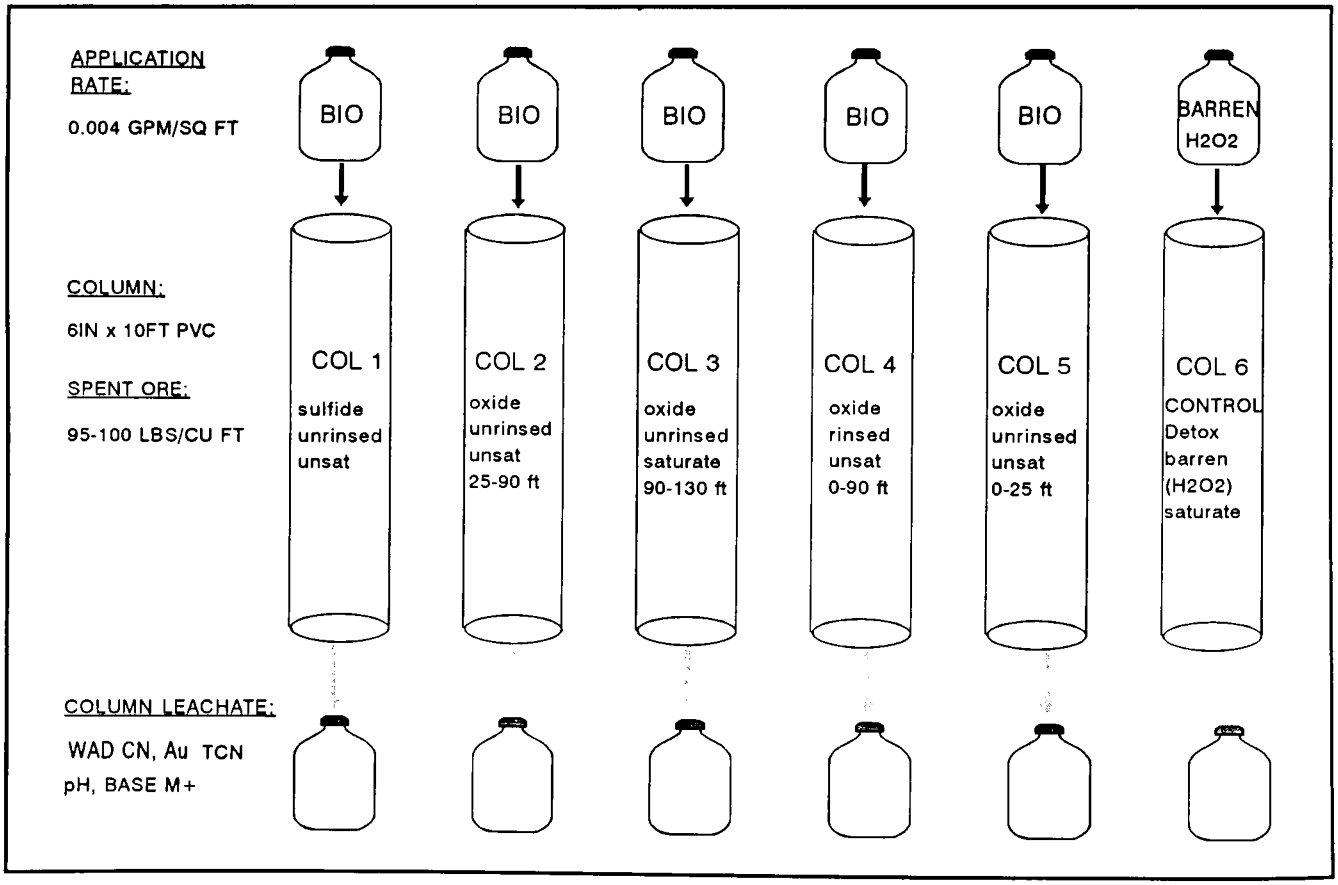

Figure 1. Summitville column test design.

Table 1. Ore effluent solution quality.

Column ID	WAD CN mg/L	$T_{solution}$ per T_{ore}
Col. 1	0.2	0.32
Col. 2	0.1	0.56
Col. 3	0.1	0.28
Col. 4	0.1	0.53
Col. 5	0.1	0.60
Col. 6 Control Peroxide/ Barren	0.4	1.49

A secondary treatment goal in the Focused Feasibility Study was to reduce the amount of leachable or soluble metals in the spent ore and entrained heap leachate solution. Pintail Systems has observed a reduction of soluble metals such as copper in other pilot and field treatment applications. This test was designed to quantify reduction of metals in column leachate solution and to identify any remineralized products in the column tests. A detailed explanation of biomineralization observed in these column tests is discussed in a companion paper to this report. Copper in column leachate solutions is shown in Figure 4 for Column 3 and Column 6. Column 3 was the biotreatment test column run as a saturation zone sample. Column 6 was a control rinse using a barren solution detoxified with hydrogen peroxide in a saturation rinse.

Biomineralization of soluble and leachable metals is a treatment that utilizes natural microbial processes to catalyze formation of new mineral species. Metals in a remineralized form can potentially be re-leached through natural weathering processes but present a greatly reduced threat to the environment.

Bacteria are found in natural and extreme environments and participate in the global cycling of minerals and elements. Through the processes of formation, decomposition and transformation, microbes alter their environment. Biomineralization in this column test program was designed to observe formation of new mineral species on the surface of the host spent ore.

Many of the reactions that catalyze remineralization take place at or close to the surface of the cell membrane. These reactions include complexation, adsorption, chelation and precipitation. The primary mineral precipitates in this study exhibited a wide range of morphologies including crystalline structures and amorphous gel/slime phases. X-ray spectroscopy showed that some of the more abundant minerals formed included calcite, gypsum, bornite and pure metallic ribbons.

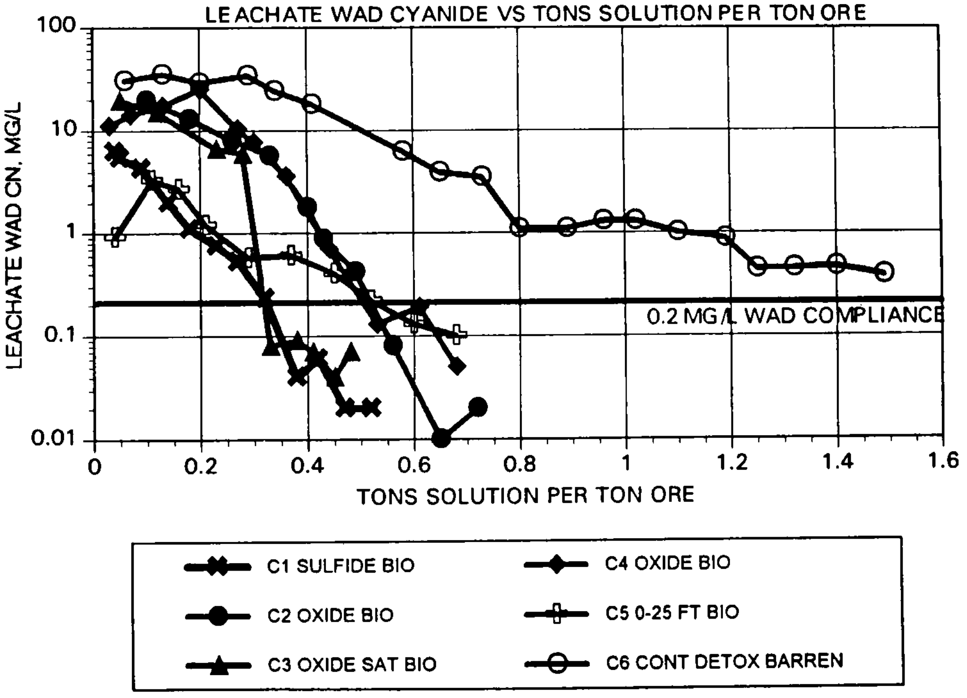

Figure 2. Summitville FFS column tests: leachate WAD cyanide.

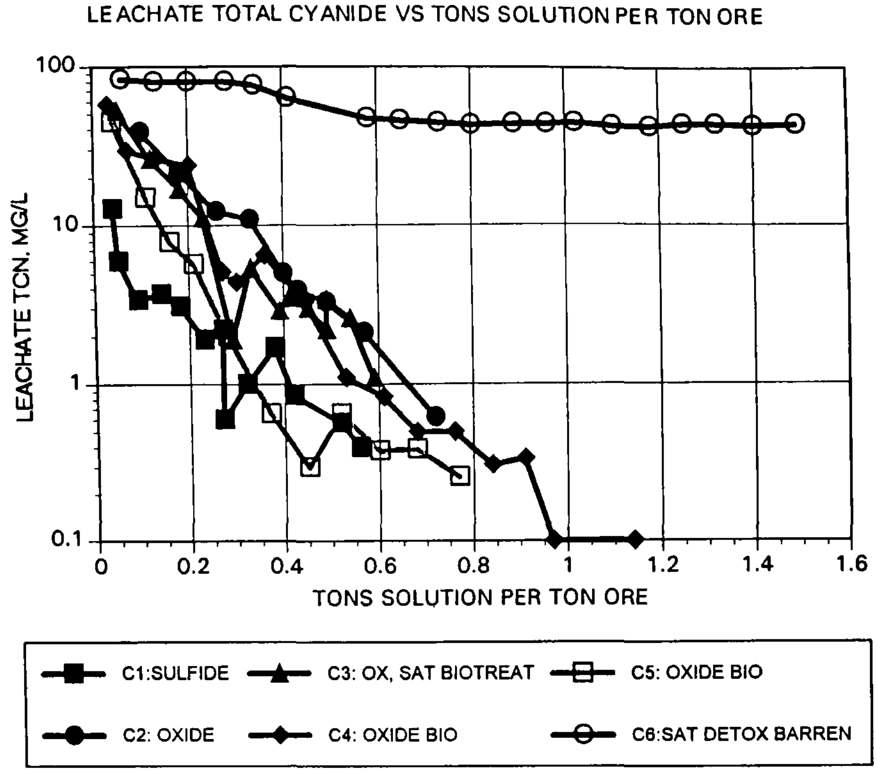

Figure 3. Summitville FFS column tests: leachate total cyanide.

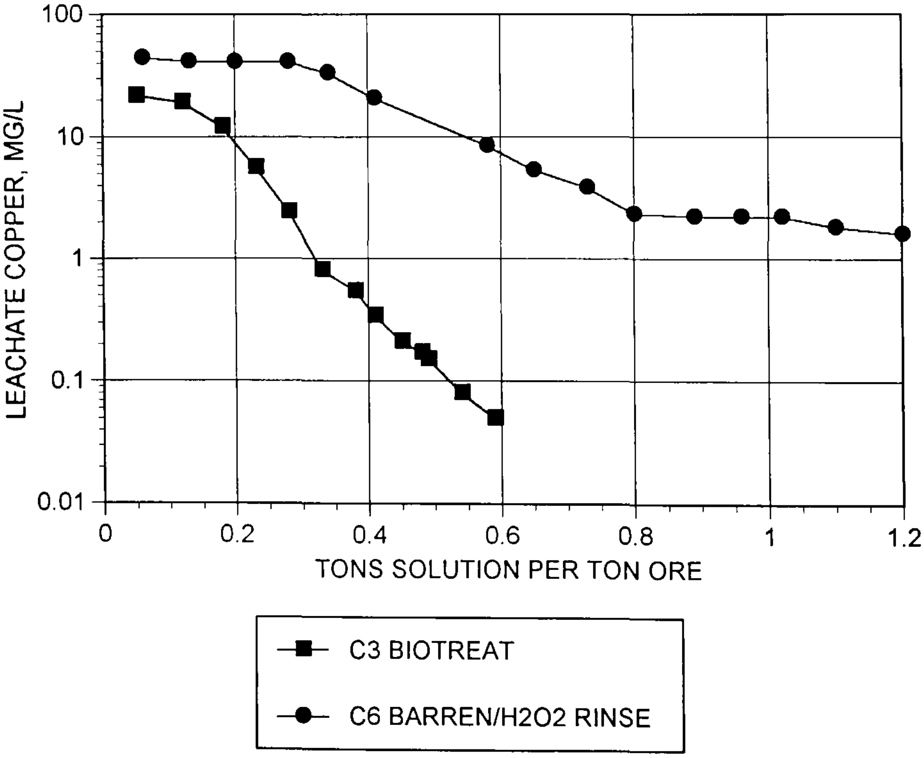

Figure 4. Summitville FFS column tests: leachate solution copper.

CONCLUSIONS

Cyanide detox in spent ore is a function of solution application efficiency and bacterial use of cyanide. The ore biotreatment in this test gave similar results and comparable detox time to prior PSI experiences. The treatment bacteria adapted well to the spent ore environment and effected a rapid detoxification of cyanide in spent ore and ore solutions. The Summitville ore is a suitable candidate for a field biotreatment.

The biological treatment column achieved a >99% removal of weak acid dissociable cyanide with application less than an average of 0.5 tons of solution per ton of ore. Total cyanide in column leachate solutions at the end of the test was <0.5 mg/L indicating that bacterial action in the treatment solution will metabolize strong metal-cyanide compounds. A field treatment of a leach pad cell or other division of spent ore could be planned for a treatment program using less than 0.5 tons of solution per ton of ore.

Biotreatment in this study achieved a greater reduction in total cyanide in a shorter application than competitive treatments can achieve. In Situ biotreatment is the most efficient heap cyanide detox as compared to peroxide rinse treatments. The data generated in this study indicate that the biotreatment processes have the potential to operate as an effective field treatment. Biological treatments are projected to be cost and time competitive with chemical rinse treatments.

The objectives of the pilot column tests were met in this biotreatment demonstration.

1. Existing strains of cyanide-oxidizing bacteria were adapted to grow in the ore environment and to use cyanide as a carbon and/or nitrogen source.
2. The adapted bacteria grew best in a chemically-defined nutrient media of food grade reagents.
3. Flask and column tests of the adapted, augmented treatment population verified that bacteria would grow and metabolize soluble cyanide in the Summitville spent ore.
4. Cyanide was detoxifed in biotreatment tests in spent ore and column leachate solutions with application of less than an average of 0.5 tons of solutions per ton of ore. Cyanide levels did not reach a 0.2 mg/L discharge criteria with the peroxide kill, saturated, barren rinse test column with application of more than 1.5 tons of treatment solution per ton of ore.

BIOMINERALIZATION OF SUMMITVILLE SPENT ORE

SEM Investigation of Biomineralized Metallic Films

By
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J. Steiner (City College of New York), G. Whitney (U.S. Geological Survey)

INTRODUCTION

The Summitville Mine located in southwestern Colorado is an example of the potential impact that natural weathering and mining activities can have on environmental quality. Acid rock drainage and metals leaching from active and historic mine districts are a major environmental problem facing the mining industry today. Sulfide ore exposed naturally or during mining operations has the potential to produce leachates that contain high concentrations of dis solved metals. These leachates can affect the quality of plant and animal health in surface water used for agriculture, recreation and human consumption.

Pintail Systems has developed biological processes for detoxification of cyanide in heap-leached spent ore and process solutions. During application of spent ore cyanide bio-detox processes we have also observed a substantial reduction in many of the leachable metals in biotreatment solutions. These field observations of soluble metal reduc tion led us to propose that metal bio-mineralization should be a secondary treatment goal of spent ore detox in Focused Feasibility Studies (FFS) for the Summitville Mine.

In the FFS (described in a companion paper) for Summitville, spent ore from the heap leach pile (HLP) was loaded into PVC test columns (six inch X ten foot) and was leached with bacteria/nutrient solutions. Two treatment designs were studied: a standard percolation leach (aerobic) and a saturated leach design where the ore was saturated with the heap leach solution to which bacteria and nutrients were applied in a continuous biotreat leach.

The bacteria for all column treatment tests were isolated from the spent ore at depth through the Heap Leach Pile (HLP) in the saturated and unsaturated zones. Bacteria isolated from the heap material were tested for cyanide oxidation capacity and were submitted to a bioaugmentation program to improve reaction kinetics and metals tolerance. The final treatment population consisted of several distinct species including aerobic heterotrophs, facultative anaerobes and sulfate-reducing bacteria.

The remineralization of soluble metals was observed through a decrease in copper in column leachate solutions and the formation of observable mineral products on ore surfaces in the columns. Several of the tests were run in clear PVC columns to facilitate observation of mineral formation. The column ore contents were photographed before, during and after the biotreatment process which ranged from 10 to 20 days for each test column. Ores were collected from each column after the treatment was complete and were submitted for SEM and TEM study at two laboratories—the USGS SEM Laboratory in Denver, Colorado and the City College of New York SEM laboratory.

TREATMENT PROCESS DESCRIPTION

Numerous species of bacteria, fungi and yeasts are capable of accumulating many times their weight in soluble metals. Both living and dead biomass are effective in removing soluble metals from waste streams containing gold, silver, chromium, cadmium, copper, lead, zinc, cobalt and others. Soluble metals may also be immobilized in soils by natural or engineered biomineralization reactions. Several commercial processes using biological reactions are being applied on an industrial scale for metal remediation. Bacteria found in natural and extreme environments have developed a wide variety of metabolic functions to adapt to these environments. These natural microbial functions contribute to global mineral cycling that continuously forms, transforms and degrades minerals and metals in the environment. Biomineralization is described as a surface process associated with microorgan ism cell walls where the remineralization occurs. The biogeochemical activities initiated by microorganisms in ores, soils, surface and groundwater environments can dominate the formation and transformation of those mineral environ ments.

There are two basic mechanisms involved in metal uptake by bacteria:

1. Accumulation by surface binding to the bacterial cell wall or extracellular materials;
2. Uptake into the cell for use in metabolic processes as necessary nutrients.

Surface reactions are accepted as the processes responsible for the majority of the remineralization reactions removing metals from solutions. Intracellular uptake of metals to meet nutritional needs of the cell has a minor role in overall metal removal. Several cell surface reactions contribute to biomineralization:

- complexation with organic compounds produced by the cell;
- precipitation and ion exchange;
- chelation by cell membrane components (pigments, polymers, cellulosic ligands, chitin, etc);
- remineralization from complex interaction with extracellular by-products of cell metabolism.

In addition to direct biological metal accumulation and remineralization reactions, microorganisms may catalyze other chemical and physical processes on micro-and macro-environmental scales which contribute to remineralization reactions. Examples of these reactions include:

1. Production of hydrogen sulfide by sulfate-reducing bacteria which precipitates insoluble metal sulfides from solution;
2. Reduction of available oxygen in the environment thereby limiting bio-oxidation and acid rock generation reactions.

During biomineralization, a complex series of reactions are initiated by microorganisms. In the case of the Summitville spent ore column tests the microorganisms were added with nutrient solutions and also existed in the ore. The metal remineralization process is catalyzed by biological processes alone and by biological processes initiating physical and chemical processes causing an alteration of the micro-environment. During the course of the column tests a series of observations were made on the changing surfaces in the test column. These observations are the basis of the following hypothesis for formation of bio-minerals.

1. Bacteria added to the ore columns attach to the ore surfaces forming a "bio-slime" layer;
2. Soluble metals bind to cell walls and extra-cellular products excreted by the microorganisms (exo-polymers, pigments, waste organics, etc.);
3. Metal hydroxides, oxides and carbonates are formed in the primary "bio-slime" layer as amorphous mineral pre-cursors. Curing or maturation of the amorphous slimes suggests that a molecular rearrangement of the hydroxy-metals to more stable forms occurs;
4. Stabilization of the amorphous precipitates forms a remineralization nucleation crystal template for further mineralization to occur. The micro-environment alteration and bacteria metabolism continue to catalyze the remineralization by ongoing formation of organometallic compounds, precipitates and transformation of metal oxidation states. The biomineralization appears to follow a sequential and "layered" development on many of the surfaces. Some of the minerals formed include calcite, gypsum, bornite, pyrite and covellite.

The first SEM work suggested that calcite spherules, bladed gypsum and layered bornite mineralization occurred as shown in Figures 1–4 with companion EDF scans for remineralized products from test Columns 2 and 5. Column 5 was biotreatment of oxidized ore collected from an unrinsed, unsaturated zone in the HLP between 0–25 foot depths. Column #2 spent oxide ore was collected from an unrinsed, unsaturated zone of the HLP collected between 25–90 foot depths.

The stabilization of microorganisms in soils has been linked to local micro-environmental factors such as clay speciation and the availability of appropriate colloidal surfaces and so forth (Sorenson, L.H. 1975; Stozky, G., 1980; Burns, R., 1990). Microorganisms in macro-scale

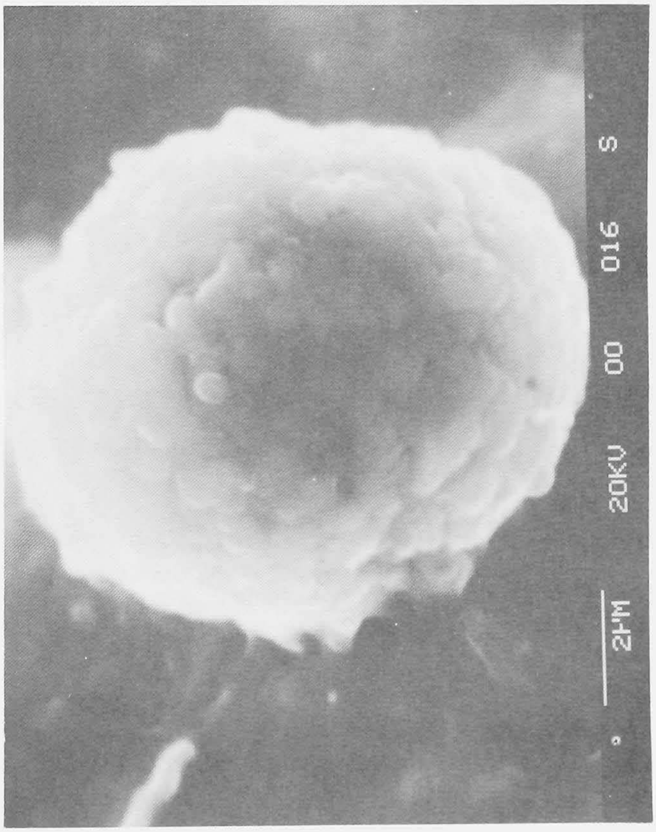

Figure 1a. Calcite sperule

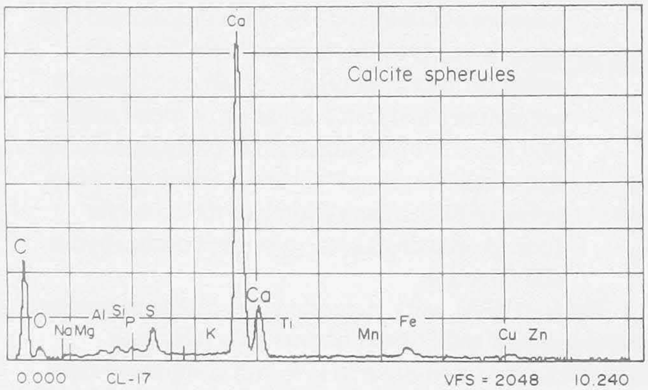

Figure 1b. EDS spectrum for calcite spherule.

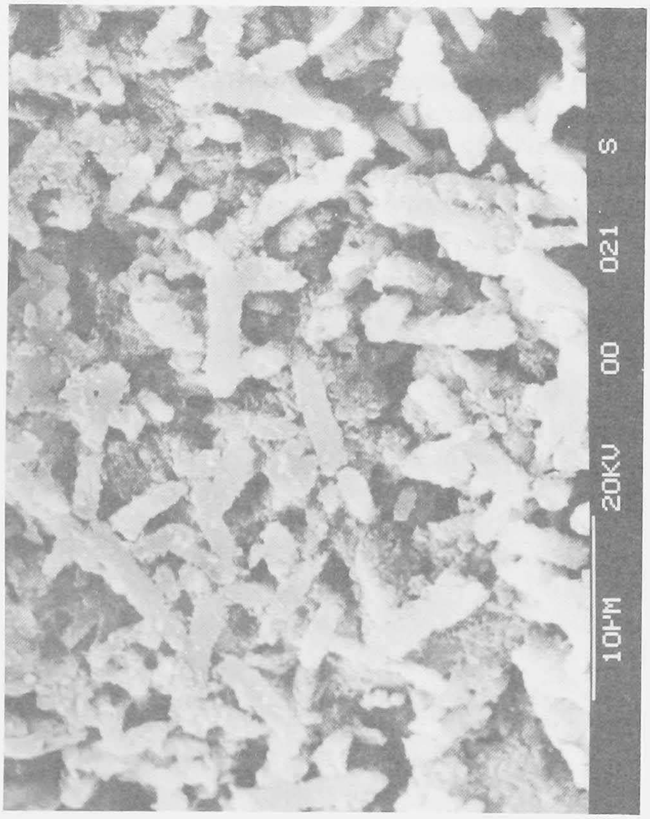

Figure 2a Calcium-rich blades, Column 2.

systems establish population profiles in the near surface environment dependent on mineralogical/organic variations and the availability of oxygen in the environment. In the case of the column treatment tests, the micro-environment was forced by the addition of bacteria and dissolved nutrients.

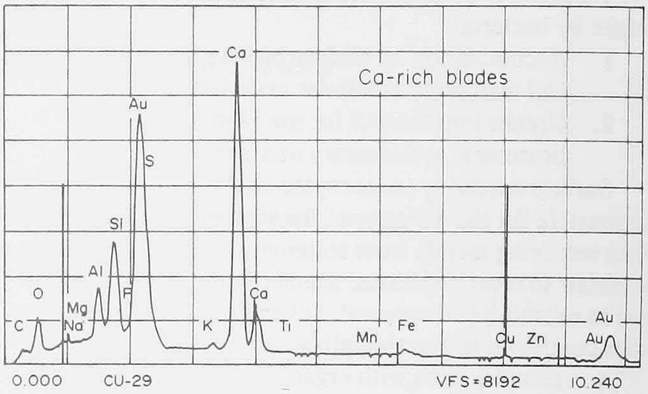

Figure 2b. EDS spectrum of Figure 2a.

Figure 3a. Bio-film layering over groundmass.

The microorganisms injected during the column experiments may be indifferent to such environmental controls given the relatively short life of the experiments, and it might be expected that microbial populations are uniformly distributed in the test column. In these column tests however, SEM investigation revealed that the metal-

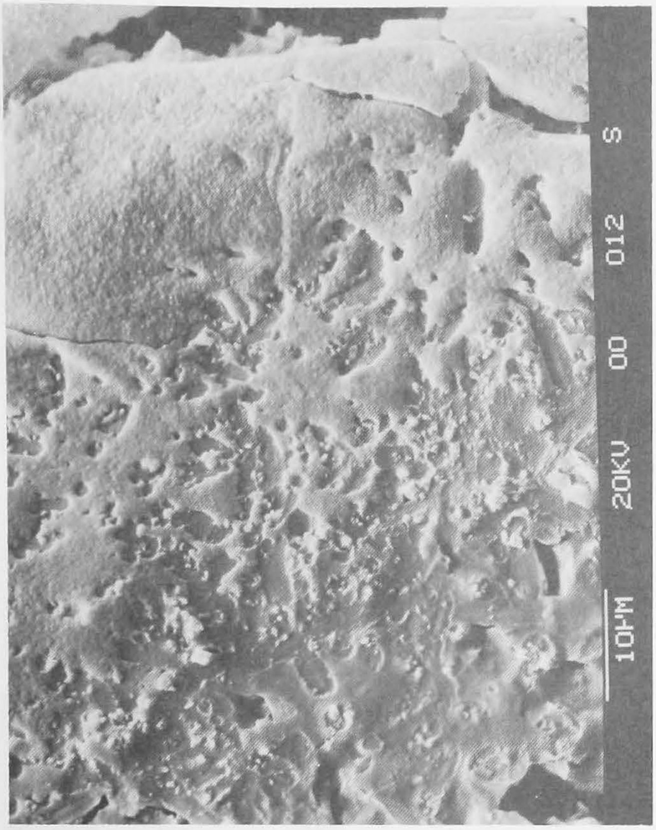

Figure 3b. Figure 3a enlarged area-two layer bornite.

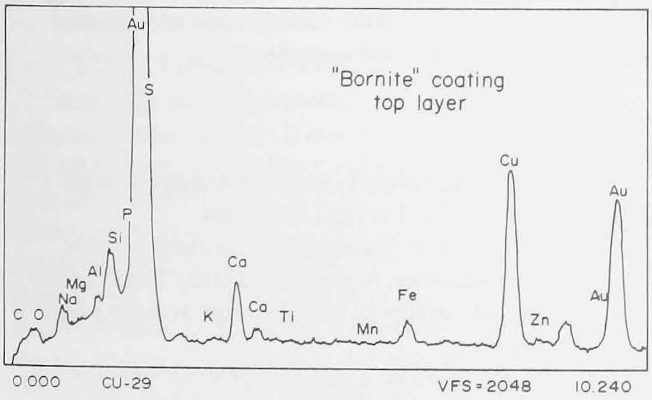

Figure 3c. EDS spectrum of Figure 3a and 3b.

lic-appearing coatings on run products are not uniform in composition, but vary in a complex fashion from point to point within one test column and also from one column to the next. This variability may indicate that the microorganisms are in fact not identically distributed in columns or react differently at different times and places over the course of an experiment. Surface films of remineralized product may thus provide important information concerning the interplay between biological populations and the ambient fluids in bioremediation tests.

To illustrate the variability of the surface film formation of biominerals we compare observations of material in test Column #5 and test Column #2. In both test columns the metal-bearing biomineral sheets coat an aggregate of kaolinite + halloysite + jarosite + alunite. Preliminary Transmission Electron Microscope (TEM) study indicates that the individual substrate minerals are compositionally similar, and exist in about the same proportions in both test columns. The sheets examined to-date tend not to develop on quartz particles as frequently as clay aggregates.

TEST OBSERVATIONS–COLUMN #5

The generally three-part metal-enriched sheets tend to be amorphous at the base (TEM work in progress) and grade upward into breccia-like admixtures of both variably crystallized and fully crystallized minerals ending in outermost layers that are predominantly monomineralic and thin. Outer layers tend to be either Cu, Cu-Fe or Fe-enriched over lower horizons and are markedly thinner, down to 20 Angstroms for copper.

The middle layer(s) is punctuated by seemingly chaotic populations of crystals (primarily sulfides and metals), with metal fragments easily recognized by their high reflectivity in backscatter images. The Cu-Fe-S sequence of the upper layers tends to be stratified upward in a sort of reverse "supergene enrichment" series reflecting an apparent evolution of increasingly neutral pH and reducing conditions as the tests proceed. The progression appears to be made more cryptic by the entrapment of both falling and tumbling particles in addition to those produced by *in Situ* nucleation and growth.

While many embedded crystals of the middle layer(s) follow the inverted supergene sequence (typically precursors to possible chalcopyrite overlain by more covellitic phases) there are numerous exceptions. A flake of tin is shown in Figure 4. The SEM image (top section of Figure 4a) shows that the tin flake is embedded with the copper sulfide materials and is not an artifact. The backscatter image (bottom portion Figure 4a) casts the tin flake as a bright object against a background of copper sulfides, demonstrating that the tin (see energy dispersive X-ray spectroscopy printout Figure 4b) has a greater atomic number than the average for the copper sulfide substrate. This suggests Sn over SnO (cassiterite). An EDS trace (Figure 5) is also given for a middle layer Fe-Cu particle located in the vicinity of the Sn particle.

Whereas the stratigraphic relationship between height and copper and sulfur speciation is yet unclear, it is

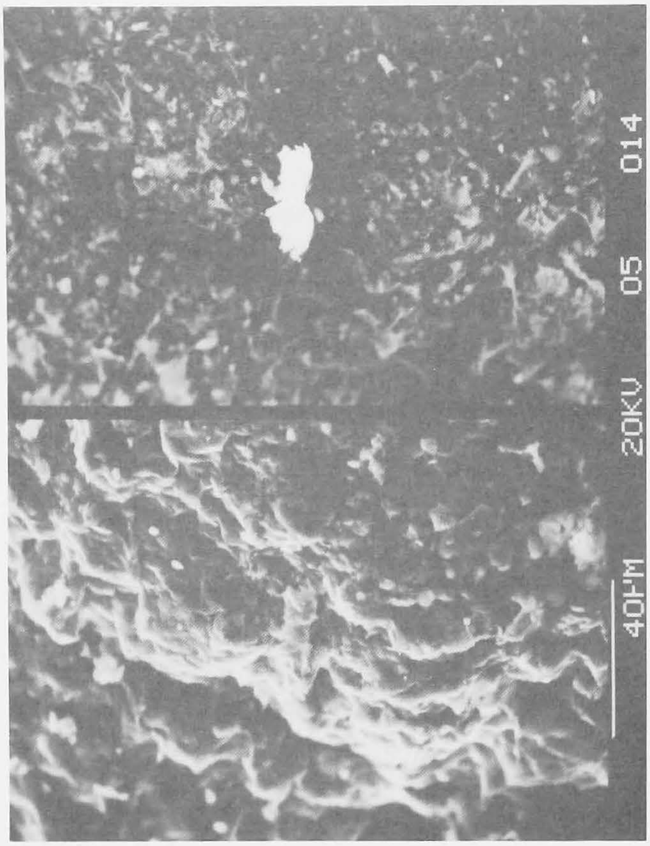

Figure 4a. SEM & backscatter image of Tin particle in Cu-Fe-S film illustrative of chaotic nature of films Top Section: particle in SEM image showing embedded nature Bottom section: particle in backscatter image showing that atomic number of particle exceeds Cu-Fe-S background

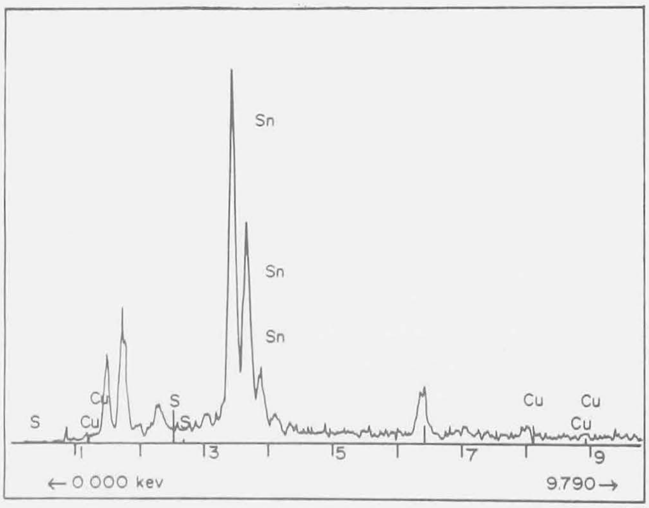

Figure 4b. EDS spectrum for the tin particle showing Sn as predominant element.

apparent that copper and copper sulfide are the probable dominant final crystallization products in microcavities. The intricate patterns formed by copper ribbons (Figures 5 and 6) and copper sulfide ribbons (not illustrated) indicate relatively high structural integrity and high atomic number. Note that much of the background film of Figure 5 is also copper and that the background Cu-films are exceptionally thin comprising a layer of less than approximately 20 Angstroms. Since the underlying material is Cu-Fe-S-Si-Al-bearing, and since the final stage is monomineralic and strongly reduced, there is abundant evidence for precipitation mechanisms that either shift with ambient experimental factors over time or are themselves variable causing different metal populations to precipitate at different times.

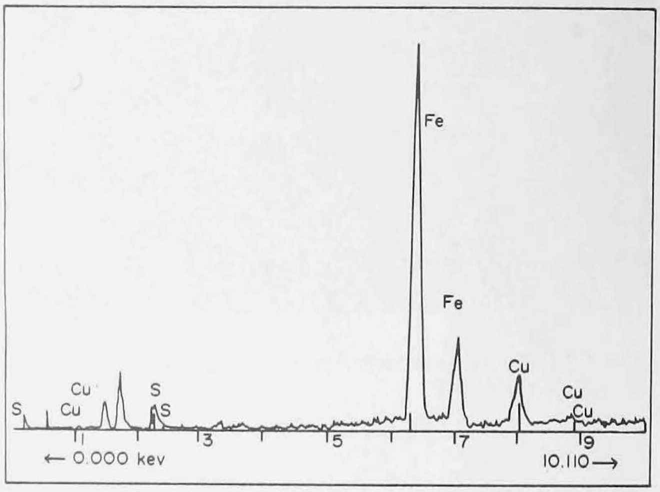

Figure 5. EDS spectrum of Cu-Fe-S interpreted as largely Fe-Cu metal; particle is from chaotic zone and situated close to the Sn particle of Figure 4a.

The geochemical observations are consistent with several models for fluid-crystal evolution:

1. oxidation state variability: a constant process (supersaturation response) whereby fluids in the micro-environment become more reducing over time;
2. ligand depletion: a constant process whereby sulfur and other agents are progressively removed by bacterial action; and
3. bacterial catalysis: a variable process accounting for the plating out of a variable metal film dependent on evolutionary changes taking place in the bacterial colony.

There are thus numerous possible models for film production, several of which may be simultaneously active during the nucleation and growth of films.

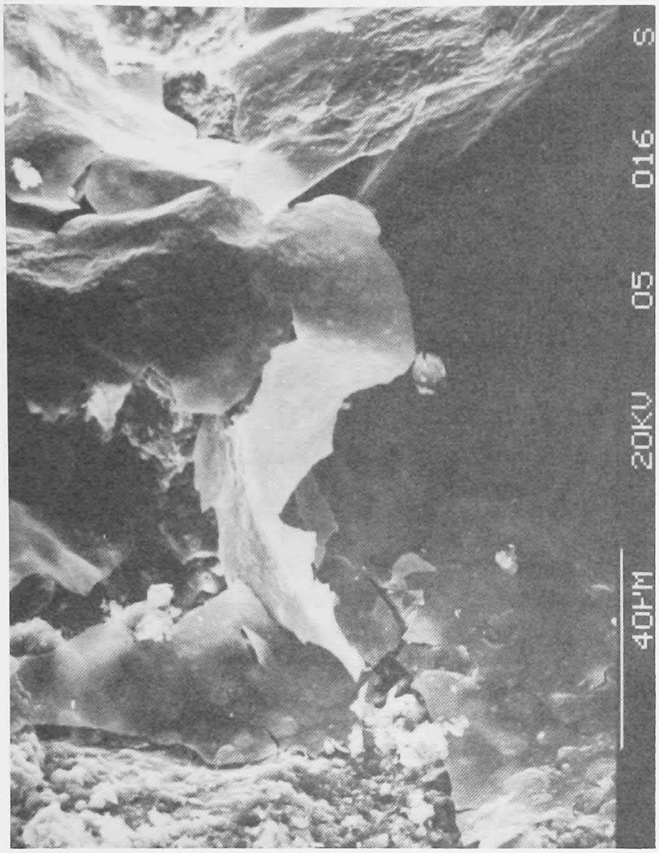

Figure 6. Stereopair of Cu-ribbon against a 20 Angstrom background film of copper. Growth of late-stage film into free cavity.

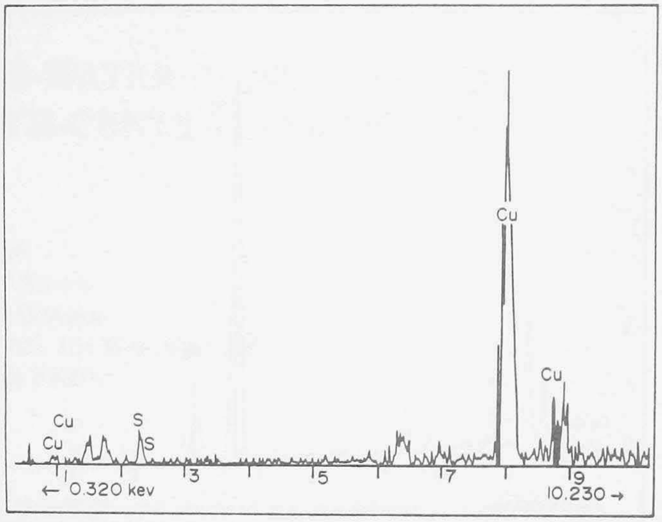

Figure 7. EDS spectrum for Cu-ribbon in Figure 6. Spectrum is consistent with pure native copper admixed with traces of copper sulfide.

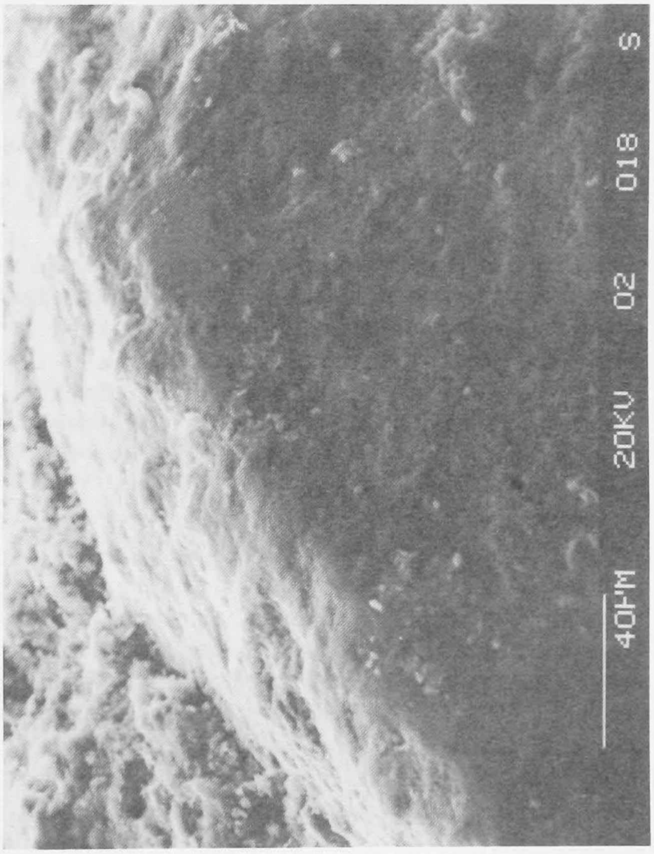

Figure 8. Backscatter image of two-layer Fe sheet. Image shows outermost layer is richer in high atomic number elements than substrate and shows change to simpler mineralogical character.

TEST OBSERVATION–COLUMN #2

Although the bulk material composition of matter recovered from columns 2 and 5 are similar, if not identical, bacterial treatment has resulted in the production of radically different films, at least locally in the column experiments. In Column 2, films have evolved that differ substantially in bulk composition and mineralogy from those in test Column #5. Although the textures are comparable, Figure 8 shows that the deposits tend to be thicker and more hummocky, and that the uppermost stratum is thicker and more frosting-like. The bulk compositional shift, as before, is in the direction of reduced-chemistry phases and mineralogic simplicity. This is apparent in the greater brightness of the surface of the film and the correlative energy dispersive determinations (Figures 9a and 9b). Here both the innermost and outermost layers are iron-enriched and copper-depleted.

This constitutes a marked departure from the overall Cu-Fe-S films forming in samples from the near-surface (Column 5). It is therefore tempting to assign the control to depth of sampling but since there are no major discern-

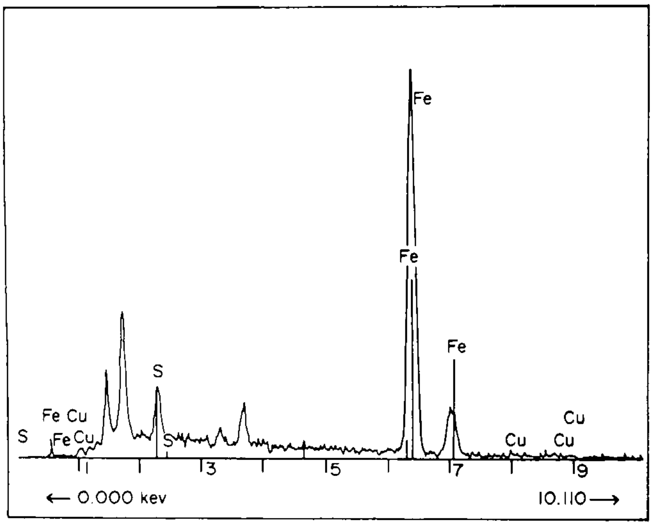

Figure 9a. EDS spectra for Fe-sheet of Figure 8. EDS spectra for lower horizon showing typical metal sulfide-aluminosilicate admixed character of surface films with greatly accentuated percent of Fe.

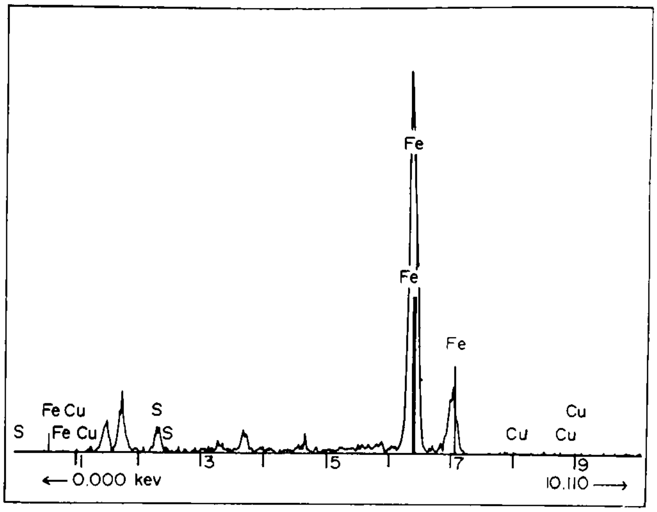

Figure 9b. EDS spectra for upper thin horizon showing Fe-enrichment over the lower horizon.

able differences in substrate character (based on TEM work to be reported elsewhere), it is more probable that the fundamental local cause rests with the microbiological species rather than mineralogy.

CONCLUSIONS

The microscale study clearly defines two distinct microscale films that evolve on generally the same substrate (agglomerations of kaolinite, halloysite, jarosite and alunite) within the confines of highly similar experimental systems. The relative proportions of Cu-versus Fe-enriched film areas have yet to be determined accurately, however, the suggestion clearly arises that the microbial populations have acted locally to produce different film chemistry and endpoints in metal film deposition. The controlling factors are as-yet unrecognized but the suggested possible controls include local production of reducing atmospheres; changing ligand concentration due to bacterial consumption; and varying tendencies to catalyze precipitation reactions linked to changes occurring in bacterial populations. These various localized phenomena appear not to effect the overall release (macroscale release) of dissolved chemicals in the recovered leachate in any pronounced fashion. However, the variability brought out by this study encourages the general concept that a wide range of metal-fixing films are produced by bioremediation that can be engineered to isolate and seal metals in ore waste.

This treatment concept should have application for both *in Situ* treatment of ore and waste rock heaps and for surface passivation of exposed minerals in pit walls. Although biominerals would be subject to natural weathering cycles, the end effect on the environment would be gradual and relatively low impact. Further studies are clearly indicated to define the range of minerals formed, environmental conditions and biomineral stability in standard kinetic leach tests.

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FACTORS AFFECTING SURFACE-WATER QUALITY IN THE ALAMOSA RIVER BASIN, SOUTH-CENTRAL COLORADO

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ABSTRACT

Several studies of the water quality of the Alamosa River, Wightman Fork (which drains the Summitville Mine site), and Terrace Reservoir have been made since 1972. However, the majority of the studies have been carried out since the abandonment of the mine in December 1992. The results of studies done in 1993–94 by the U.S. Geological Survey, in cooperation with the Colorado Division of Minerals and Geology, the Colorado Department of Health, and the U.S. Environmental Protection Agency, and studies made by other agencies, indicate that natural and anthropogenic factors affect water quality of the Alamosa River, its tributaries, and Terrace Reservoir.

Although pre-1985 data are limited, comparisons with post-1985 data indicate that pH has decreased and concentrations of dissolved and total or total-recoverable copper, iron, and possibly zinc have increased in the Alamosa River downstream from its confluence with Wightman Fork. Detailed spatial and temporal sampling and analysis during 1993 indicates that concentrations of dissolved and total-recoverable aluminum, copper, iron, manganese, and zinc generally decreased and pH increased in Wightman Fork downstream from the mine to the confluence with the Alamosa River, probably as a result of dilution by tributary inflows. During and following the peak of snowmelt runoff, Wightman Fork is the primary source of aluminum, copper, iron, manganese, and zinc in the Alamosa River upstream from Terrace Reservoir (about 20 miles downstream from Wightman Fork). Before the peak of snowmelt runoff, water with low pH and elevated concentrations of dissolved and total-recoverable aluminum and iron originating upstream from Wightman Fork affect water quality of the Alamosa River. This water originates in unmined or minimally mined areas that contain hydrothermally altered rock. Additionally, following one summer rainstorm that occurred in the Alamosa River basin downstream from Wightman Fork, water with low pH and elevated concentrations of dissolved and total-recoverable aluminum, copper, iron, lead, manganese, and zinc also entered the Alamosa River from other unmined or minimally mined hydrothermally altered areas, affecting quality of water entering Terrace Reservoir. During 1994, additional studies to further evaluate the effects of the Summitville Mine site and snowmelt and rainfall runoff on the water quality of the Alamosa River were made.

Detailed studies of the water quality, limnology, sediment deposition and geochemistry, and movement of metals into, within, and through Terrace Reservoir were made during 1994. Particular emphasis was placed on evaluation of the potential effects of physical and geochemical processes in the reservoir on downstream water quality of the Alamosa River.

All the natural and anthropogenic factors that affect water quality in the Alamosa River basin need to be considered in making decisions about remediation of the Summitville Mine site. These decisions require a clear understanding of the natural geochemical conditions and processes in the basin, as well as the anthropogenic effects from the mine site, because the former will continue to affect water quality after remediation is completed.

SOURCES OF WATER HAVING LOW pH AND ELEVATED METAL CONCENTRATIONS IN THE UPPER ALAMOSA RIVER FROM THE HEADWATERS TO THE OUTLET OF TERRACE RESERVOIR, SOUTH-CENTRAL COLORADO, APRIL–SEPTEMBER, 1993

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ABSTRACT

A synoptic sampling of water quality and streamflow discharge in the Alamosa River and one of its tributaries, Wightman Fork, from April through September 1993, was used to characterize water quality in the river, to locate sources of water with low pH and elevated metal concentrations, and to evaluate the effect of the Summitville Mine on water quality in the river basin. Wightman Fork is the primary source of aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) during peak flow and the falling limb of the spring runoff hydrograph. However, other areas, both upstream and downstream from Wightman Fork, supply low-pH and elevated concentrations of aluminum and iron to the Alamosa River, particularly during the early weeks of spring runoff (first flush, upstream from Wightman Fork) and during one sampled storm event (downstream from Wightman Fork). Source areas of low-pH water containing elevated metals concentrations are either in areas of intense mining activity (for example, the Summitville Mine) or are in areas of minimal mining activity underlain by highly altered volcanic rocks containing numerous naturally occurring springs of low-pH, metal-rich water.

INTRODUCTION

Summitville Mine, a gold mine operation that used a cyanide heap leach to extract the metal, is located near the headwaters of Wightman Fork, a tributary to the Alamosa River in the San Juan Mountains of south-central Colorado. The mine was abandoned in December 1992. Without site maintenance, low-quality water (low pH, elevated metal and cyanide concentrations) from mine workings and the cyanide heap leach could flow offsite into the Wightman Fork of the Alamosa River. Therefore, the U.S. Environmental Protection Agency (EPA) occupied the site and increased onsite water-treatment capacity in an attempt to minimize offsite flow of low-quality water (Pendleton and Posey, in this volume).

As part of the early remedial investigations, before Summitville Mine received EPA Superfund designation, the U.S. Geological Survey (USGS) in cooperation with the Colorado Division of Minerals and Geology, the Colorado Department of Health, and the U.S. Environmental Protection Agency conducted a synoptic sampling program in the Alamosa River and Wightman Fork. The program included water-quality sampling and measurement of streamflow discharge at eight sites on the Alamosa River and three sites on Wightman Fork or tributaries to Wightman Fork eight times from April through September, 1993 (fig. 1). The objectives of the program were to:

1. Characterize water quality in the Alamosa River from the headwaters to just downstream from Terrace Reservoir,
2. Identify source areas of streamflow that contribute low pH and elevated metals concentrations, and
3. Evaluate the effects of mine-water discharges from historic mining areas and the Summitville Mine on water quality of the Alamosa River and Wightman Fork.

Personnel from the EPA Technical Assistance Team provided invaluable assistance with the sampling and chain-of-custody protocols.

APPROACH

Water-quality samples were collected and streamflow discharge measurements made at eight sites on the Alamosa River and three sites on Wightman Fork and a tributary eight

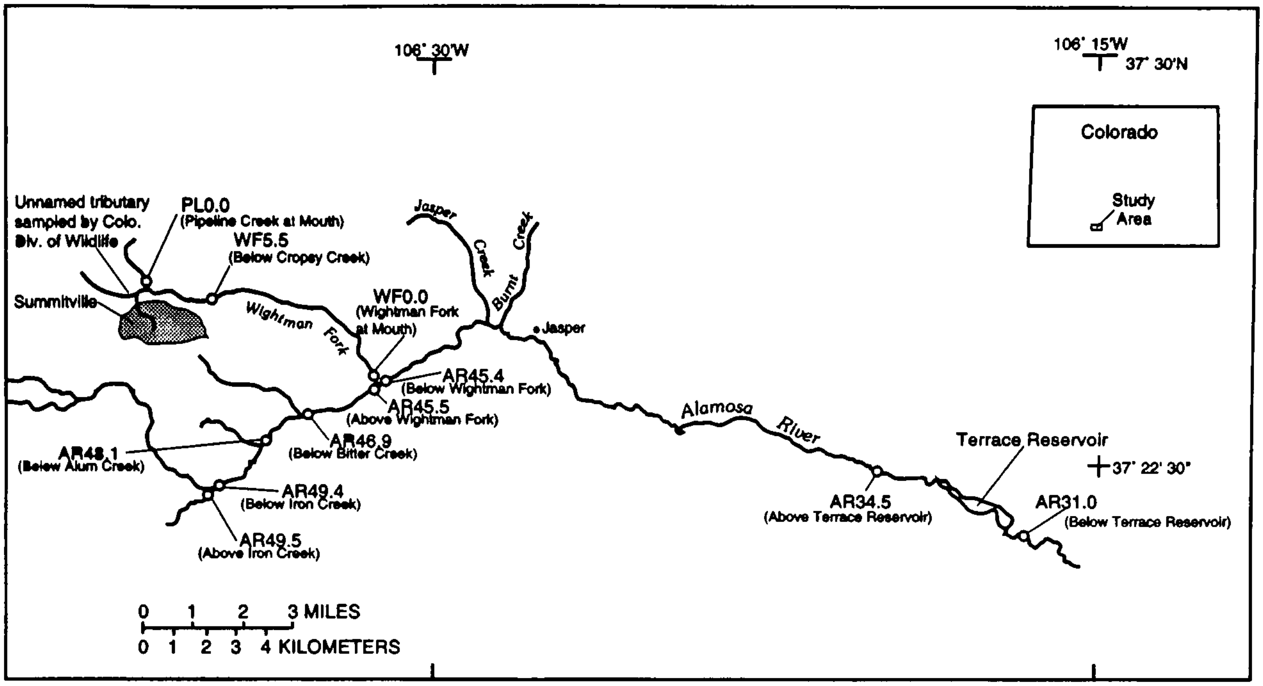

Figure 1. Map showing location of study area and sampling sites. Alpha portion of location is abbreviation for the stream name. Numeric portion of location is miles upstream from the mouth of the river.

times from April through September 1993 (figs. 1 and 2). Sampling dates were scheduled to provide the most reasonable coverage of the seasonal streamflow variation within the basin. Samples were collected during April 21–23; May 4–6; May 18–20; June 2–4; June 21–23; July 12–14; August 9–11; and September 7–9. This coverage included sample collection during critical flow periods such as early runoff (first flush), peak flow, and low-flow conditions. No pre-runoff, base-flow conditions were sampled because of the timeframe of the study. Analysis of streamflow at AR34.5 for 1993 (fig. 2) indicates that samples collected during April and May represent snowmelt conditions on the rising limb of the hydrograph, and the April samples represent first flush from the basin. Peak flow at AR34.5 occurred on May 27 (Craig Cotton, Colorado Division of Water Resources, Division 3, oral commun., 1993). Therefore, samples collected during June and July represent receding snowmelt conditions, and the August and September samples represent late-summer flow during the monsoon season.

Routine water-quality sampling included onsite measurements of streamflow, specific conductance, and pH. Streamflow measurements were made using at least 10 measurements of depth and velocity across the width of the stream. Whenever possible, no more than 5 percent of the flow was included in any measured subsection. Depth- and width-integrated water-quality (cross-section) samples were collected, and streamflow measurements were made across the entire width of the stream except at some sites when snow and ice cover and high flow necessitated collection of point samples and indirect estimates of streamflow discharge. Differences between water-quality samples collected from an integrated cross section compared to those collected at a point are discussed by von Guerard and Ortiz (in this volume). In the field, portions of unfiltered sample were preserved with ultra-pure nitric acid to a pH less than 2 for analysis of total-recoverable (total) concentrations of selected trace metals. Separate aliquots of sample were filtered through a 0.45 µm (micrometer) filter and preserved with ultra-pure nitric acid to a pH less than 2 for analysis of dissolved trace metals. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Arvada, Colorado. Samples were delivered to the NWQL by members of the Environmental Protection Agency Technical Assistance Team using EPA chain-of-custody protocols. Analyses by the NWQL used standard USGS analytical techniques (Fishman and Friedman, 1989; Fishman, 1993). Chain-of-custody protocols were used by the NWQL for all samples associated with this project, and laboratory quality-assurance procedures were used to meet CERCLA (Comprehensive Environmental Response and Compensation Liability Act) guidelines. Sampling protocols for streamflow measurement, sample collection, sample preparation, and sample preservation followed USGS methodology (Rantz and others, 1982; Edwards and Glysson, 1988; Sylvester and others, 1990). Results for some of the major water-quality properties and concentrations of dissolved and total aluminum, copper, iron, manganese, and zinc are discussed herein.

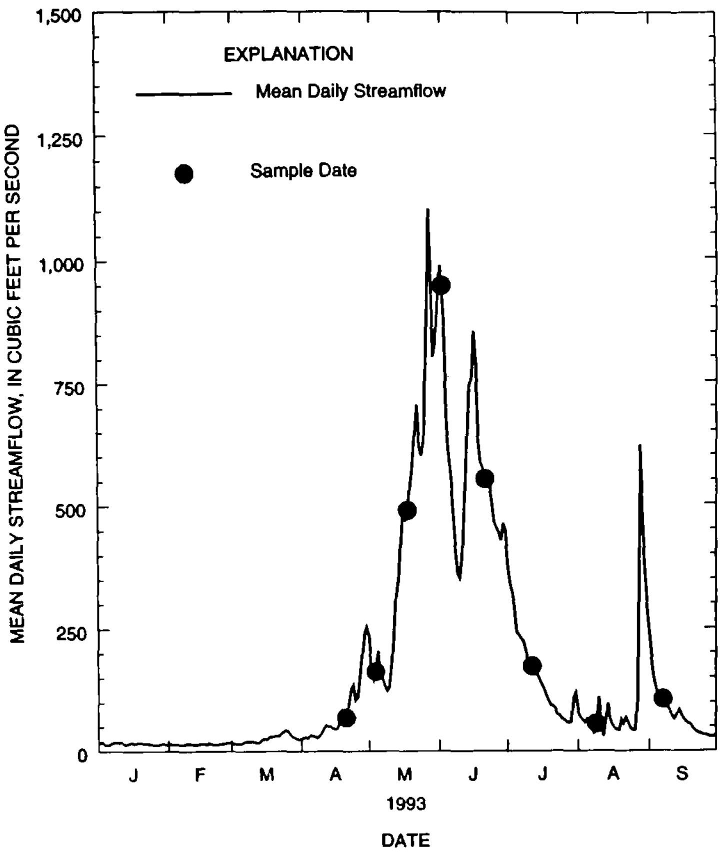

Figure 2. Mean daily streamflow for Alamosa River above Terrace Reservoir (AR34.5), January–September 1993 (data source: Craig Cotton, Colorado Division of Water Resources, Division 3, written commun., 1993).

RESULTS AND DISCUSSION

General Water Quality

Water quality in the basin is variable (table 1), but the water generally is acid, has low specific conductance, moderate hardness, and low alkalinity. Values of pH range from 3.3 at WF5.5 (Wightman Fork below Cropsy Creek) on June 22 to 7.6 at AR49.5 (Alamosa River above Iron Creek) on May 19. Specific conductance ranged from 22 µS/cm (microsiemens per centimeter) at PL0.0 (Pipeline Creek) on July 13 to 2,520 µS/cm at WF5.5 (Wightman Fork below Cropsy Creek) on September 8. Values of hardness ranged from 6 mg/L (milligrams per liter) at PL0.0 on June 22 and July 13 to 560 mg/L at WF5.5 on May 5. Alkalinity ranged from less than 1 mg/L at several sites to 96 mg/L at WF5.5 on April 23. This high value for alkalinity could be the result of alkalinity introduced during the water-treatment process at the Summitville Mine. It remains in the stream water because substantial snowmelt runoff had not yet begun at the site (elevation about 11,000 ft (feet) = about 3,350 m (meters)). Sites having alkalinity less than the detection limit of 1 mg/L as $CaCO_3$ are: AR34.5 (Alamosa River above Terrace Reservoir) on June 2 and August 10; AR45.4 (Alamosa River below Wightman Fork) on June 2, July 13, and August 10; AR45.5 (Alamosa River above Wightman Fork) on April 22 and May 4; AR46.9 (Alamosa River below Bitter Creek) on April 22 and May 5; AR48.1 (Alamosa River below Alum Creek) on May 6; WF0.0 (Wightman Fork at mouth) on May 18, June 2, June 22, and July 13; and WF5.5 on May 20, June 4, June 22, and July 13. These low alkalinity values occurred primarily during periods of higher runoff and indicate that water in the basin is poorly buffered, and that acidity in the basin increases during periods of higher streamflow discharge. The low value of alkalinity measured at AR34.5 on August 10 was the result of a storm

Table 1. Summary statistics for some major water-quality properties and streamflow discharge

[(µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; ft^3/s, cubic feet per second]

Property	Minimum	Maximum	Mean
pH (standard units)	3.3	7.6	5.9
Specific conductance (µS/cm)	22	2,520	318
Hardness (mg/L as $CaCO_3$)	6	560	81
Alkalinity (mg/L as $CaCO_3$)	<1	96	11
Streamflow discharge (ft^3/s)	1.1	858	155

on August 9, which is discussed in more detail in Ortiz and others (paper, in this volume). Values of streamflow discharge range from 1.1 ft^3/s (cubic feet per second) at PL0.0 on September 8 to 858 ft^3/s at AR34.5 on June 2. The Alamosa River and Wightman Fork are gaining streams (increasing streamflow discharge with distance downstream) throughout the reaches studied.

Variations in Metal Concentration and pH

Because streamflow discharge increases downstream on the Alamosa River and Wightman Fork, and evaporation is minimal, higher concentrations of a constituent in downstream relative to upstream sites indicate a source of the constituent exists between the two sites. In this discussion, water-quality data are compared in terms of concentration and instantaneous loads. Instantaneous load is the product of total-recoverable constituent concentration and streamflow discharge and represents the mass rate-of-flow of a constituent. Concentrations are compared to water-quality criteria to assess toxicity of water samples. Relative concentrations and loads are used to identify and prioritize source areas for constituents to the river and to assess whether dilution or reactive geochemistry causes concentration decreases between upstream and downstream locations. For example, dilution, mineral precipitation, and sorption all cause decreases in concentration between two locations. Loads will not decrease if dilution only is causing concentration decreases, because mass is conserved during dilution. Decreases in loads between two locations are caused by a loss of mass of a constituent from the water column that is caused by chemical processes such as mineral precipitation and sorption.

Wightman Fork

The elevated metal concentrations in Wightman Fork (table 2) are caused by metal input from Wightman Fork upstream from Pipeline Creek and/or the Summitville Mine site. PL0.0 had lower levels of all constituents and near neutral pH relative to WF5.5. Maximum values at PL0.0 exceeded aquatic-life criterion only for iron. Samples collected from the primary tributary to Wightman Fork upstream of Pipeline Creek (fig. 1) also indicate low values for metal concentrations (John Woodling, Colorado Division of Wildlife, oral commun., 1994). However, all values for Wightman Fork samples for all constituents in this report except dissolved aluminum and pH at WF0.0 exceeded EPA water-quality criteria (table 2). Water samples collected by the Colorado Division of Wildlife from Wightman Fork downstream from Pipeline Creek contain greater metal concentrations than those from Pipeline Creek but much lower concentrations than samples from WF5.5. These data indicate that the water is affected as is flows from the western end of the Summitville site, but the majority of the effect occurs between Pipeline Creek and WF5.5 (John Woodling, Colo. Div. of Wildlife, oral commun., 1994). Therefore, elevated metal concentrations that occur as Wightman Fork crosses the Summitville Mine site are derived from Summitville. Input from tributaries north of Wightman Fork as represented herein by Pipeline Creek is minimal. Variations in the data for Wightman Fork are discussed in greater detail in Ward and Walton-Day (in this volume).

Alamosa River Upstream from Wightman Fork

A comparison of data at sites AR49.5 (Alamosa River above Iron Creek) and AR45.5 (Alamosa River above Wightman Fork) indicates which constituents are introduced into the Alamosa River above Iron Creek and between Iron Creek and Wightman Fork (table 3). The maximum levels of the metals at AR49.5 indicate that the river contains moderate concentrations of aluminum and iron but only minor amounts of copper, manganese, and zinc. Values for pH are near neutral. Only one water-quality criterion was exceeded; on September 8, pH was 6.4, which is lower than the desired range for aquatic life (pH = 6.5–9.0). Concentrations of metals at AR45.5 were greater than at AR49.5 for all constituents. Greatest increases between maximum values at the two sites were for aluminum (one order of magnitude) and iron

Table 2. Summary statistics for selected constituents for selected sites on Pipeline Creek and Wightman Fork

[Concentrations in micrograms per liter except pH in standard units. Min., minimum concentration; Max., maximum concentration; Med., median concentration; TAl, total-recoverable aluminum; DAl, dissolved aluminum; TCu, total-recoverable copper; DCu, dissolved copper; TFe, total-recoverable iron; DFe, dissolved iron; TMn, total-recoverable manganese; DMn, dissolved manganese; TZn, total-recoverable zinc; DZn, dissolved zinc]

	PL0.0			WF5.5			WF0.0			Aquatic-Life Criteria[a]
	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.	
TAl	60	210	150	9,200	42,000	23,500	2,800	16,000	8,050	-
DAl	25	220	40	1,200	41,000	18,000	<10	15,000	4,700	150
TCu	<1	2	1	1,700	38,000	4,700	430	12,000	2,350	-
DCu	<1	3	2	1,600	37,000	4,700	80	12,000	2,250	4[b]
TFe	80	460	205	15,000	100,000	39,000	4,300	33,000	10,500	1,000
DFe	<10	240	73	1,000	97,000	27,000	5	21,000	3,550	-
TMn	<10	50	20	4,550	7,800	6,600	1,400	3,700	2,150	1,000
DMn	5	29	14	4,600	7,900	6,200	1,200	3,700	2,150	-
TZn	<10	40	<10	1,100	6,700	2,000	330	2,300	815	-
DZn	3	46	7	570	6,500	2,200	180	2,300	795	47
pH	6.8	7.3	7.1	3.3	5.5	3.7	4.0	7.5	4.95	6.5 - 9.0

[a] Included for comparison. Values are most conservative reported by Environmental Protection Agency for various types of freshwater aquatic life unless otherwise noted (U.S. Environmental Protection Agency, 1986).

[b] Chronic toxicity for brook trout.

(two orders of magnitude). Maximum measured values exceeded water-quality criteria for all metals except manganese. In addition, pH values at this site were acidic (pH less than 7) during all sampling periods. These results indicate that there are sources of low-pH water and metals between Iron Creek and Wightman Fork.

Sources of metals and acidity to the Alamosa River upstream from Wightman Fork have the greatest effect on water quality during the first flush of snowmelt. That is, concentrations of some metals and hydrogen ion are greater upstream than downstream from Wightman Fork only during first flush. Elevated concentrations of total and dissolved aluminum in the Alamosa River are diluted by the flow from Wightman Fork during first flush (April sampling, fig. 3a). However, during peak flow (June 2–4 sampling period), the concentrations of aluminum were greater downstream from Wightman Fork than upstream, indicating contribution of most of the metal from Wightman Fork. Load data (fig. 3b) and ratios of instantaneous total loads of metals in Wightman Fork at the mouth to Alamosa River above Wightman Fork (table 4) confirm this conclusion. Iron data show a similar trend. The first-flush data (figs. 3a and 3b) indicate that the source of elevated aluminum and iron concentrations lies between AR49.4 (Alamosa River below Iron Creek) and AR46.9 (Alamosa River below Bitter Creek). AR48.1 (Alamosa River below Alum Creek) was not sampled during the first flush. These sources upstream from the mouth of Wightman Fork supplied greater amounts of aluminum and iron to the Alamosa River than the Wightman Fork supplied during first flush, some parts of the rising limb of the snowmelt hydrograph, and during later summer (table 4).

Sources of acidity to the Alamosa River upstream from Wightman Fork had their greatest effect on water quality and instantaneous hydrogen ion loads during the first two sampling periods. The instantaneous load of hydrogen ions (the product of 10^{-pH} and streamflow discharge; fig. 3c) is greater upstream than downstream from Wightman Fork only during the April and May 4–6 sampling periods indicating that at these times upstream sources provided more acidity to the Alamosa River than Wightman Fork. Additional data collected on May 6 identify specific sources of acidic water to the Alamosa River upstream from Wightman Fork. Values of pH measured at all easily located inflows on the north side of the Alamosa River between Iron Creek and Terrace Reservoir indicate that numerous acidic tributaries were flowing into the Alamosa River upstream from Wightman Fork (fig. 4).

Table 3. Summary statistics for selected constituents for selected sites on the Alamosa River

[Concentrations in micrograms per liter except pH in standard units. Min., minimum concentration; Max., maximum concentration; Med., median concentration; TAl, total-recoverable aluminum; DAl, dissolved aluminum; TCu, total-recoverable copper; DCu, dissolved copper; TFe, total-recoverable iron; DFe, dissolved iron; TMn, total-recoverable manganese; DMn, dissolved manganese; TZn, total-recoverable zinc; DZn, dissolved zinc]

	AR49.5			AR45.5			AR45.4			AR34.5		
	Min.	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**	**Min.**	**Max.**	**Med.**
TAl	<10	520	165	1,100	5,400	1,850	2,600	5,100	2,900	1,800	160,000	2,200
DAl	<10	40	<10	<10	4,800	65	120	3,900	750	<10	1,800	50
TCu	<1	2	<1	4	24	8.5	105	2,800	832	100	1,500	450
DCu	<1	2	<1	<1	26	2.5	39	2,600	732	14	1,100	250
TFe	40	330	195	1,700	22,000	5,200	4,600	12,000	6,800	3,200	770,000	4,900
DFe	5	44	19.5	250	4,800	1,085	1,600	5,300	2,300	30	2,700	1,300
TMn	<10	40	30	90	530	180	470	890	730	390	1,400	570
DMn	2	17	8	54	530	170	450	850	720	360	950	570
TZn	<10	40	<10	<10	90	30	120	500	230	90	1,300	220
DZn	<3	6	<3	4	87	24	130	500	210	70	290	200
pH	6.4	7.6	6.9	3.5	6.8	6.0	4.7	5.4	4.9	4.6	7.0	6.05

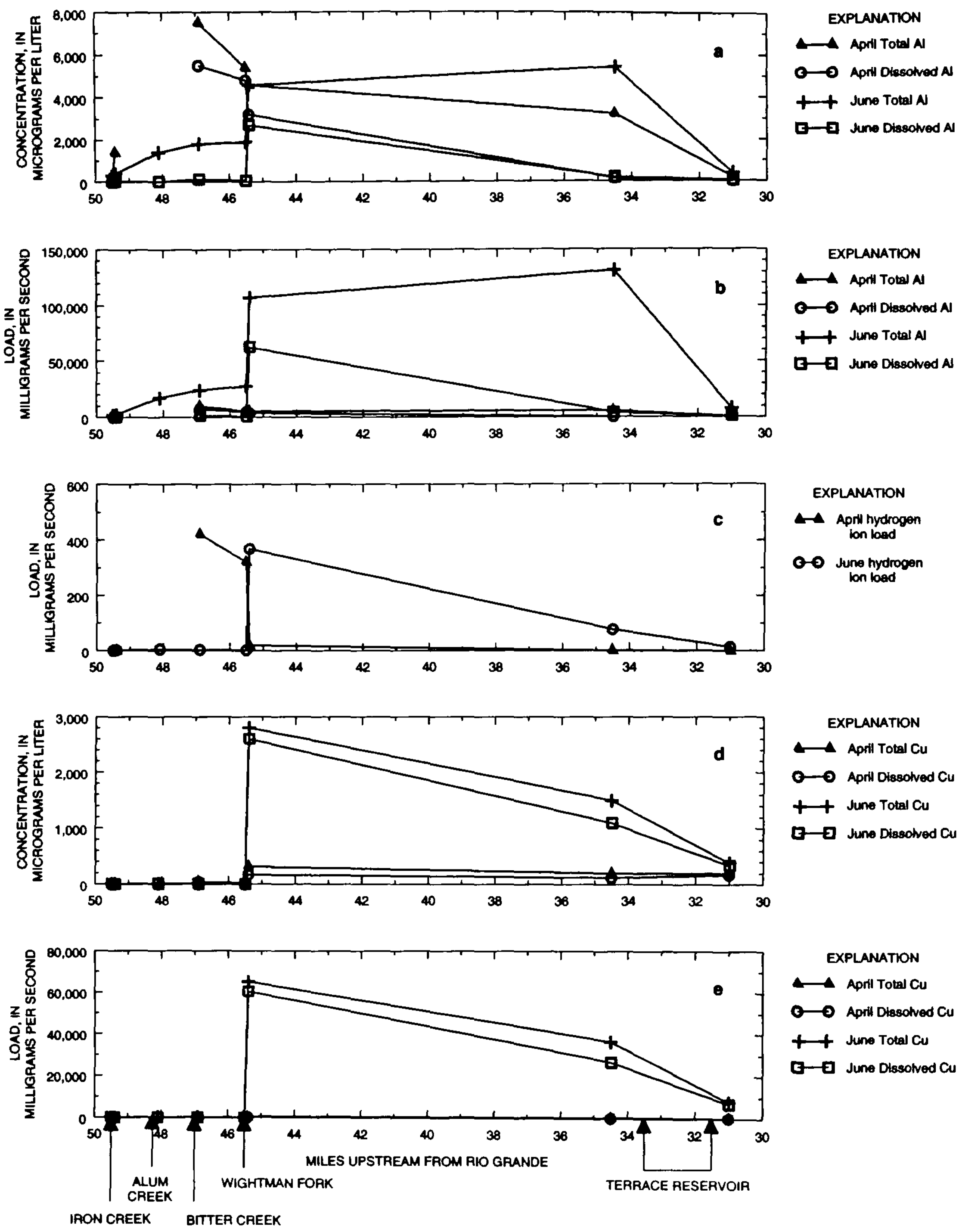

Figure 3. Variation in total and dissolved aluminum concentrations (3a); total and dissolved aluminum loads (3b); hydrogen ion loads (3c); total and dissolved copper concentrations (3d); and total and dissolved copper loads; (3e) among sampling sites on the Alamosa River for the April sampling (first flush) and the June 2–4 sampling (peak flow).

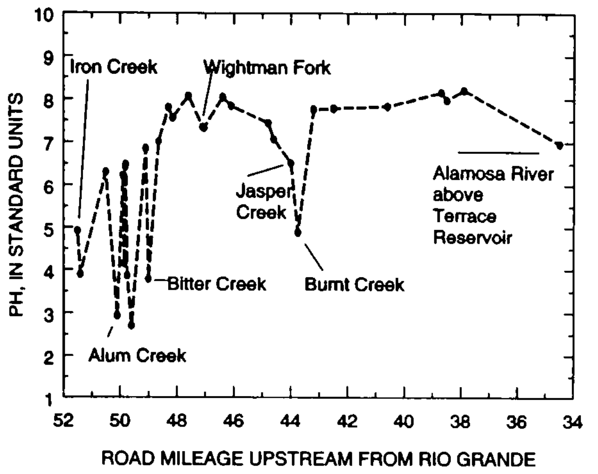

Figure 4. Results of synoptic pH sampling on the Alamosa River, May 6, 1993.

Concentrations and loads of copper, manganese, and zinc were consistently lower upstream than downstream from Wightman Fork indicating that Wightman Fork, and not upstream Alamosa River areas, is the primary source of those metals to the Alamosa River during all sampling periods (figs. 3d and 3e; table 4). Ratios of instantaneous loads in Wightman Fork to the Alamosa River above Wightman Fork indicate that for these metals, Wightman Fork is the most important contributor of copper. It contributed up to 340 times more copper than upstream areas. Trends in the manganese and zinc ratios toward 1 at lower flow indicate that during baseflow (not sampled in this study) upstream areas may supply at least half of the metal mass to the Alamosa River.

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Alamosa River Downstream from Wightman Fork to Terrace Reservoir

There is some input of metals and low-pH water to the Alamosa River downstream from Wightman Fork. During May, acidic tributaries contributed water to the Alamosa River downstream from Wightman Fork (fig. 4). Analysis of samples collected from AR34.5 (Alamosa River above Terrace Reservoir) before and after a storm that occurred the evening of August 9, 1993, confirms that sources of low-pH water and metals exist downstream from Wightman Fork. Rain fell on the region east of, and not including, the Wightman Fork drainage. Pre-storm pH at AR34.5 was 6.1, whereas post-storm pH was 4.6. Concentrations of total and dissolved aluminum, copper, iron, manganese, and zinc were elevated up to more than 2 orders of magnitude after the storm. The effects of the storm are discussed in greater detail in Ortiz and others (paper, in this volume).

Ratios of instantaneous loads of metals in samples collected in the Alamosa River downstream from Wightman Fork to instantaneous loads in the Alamosa River upstream from Terrace Reservoir indicate that sources for the metals possibly exist between the two locations and that reactions are occurring to remove metals from the water column (table 5). During the rising limb of the hydrograph, ratios for all metals are less than one, indicating that some sources for the metals might exist between the two sampling points.

Table 4. Ratio of instantaneous total load of metal in Wightman Fork at mouth to load in Alamosa River above Wightman Fork

[Ratio >1 indicates Wightman Fork supplies most of the metal to the Alamosa River; ratio <1 indicates areas upstream from Wightman Fork supply most of the metal to the Alamosa River]

Date	Aluminum	Iron	Copper	Manganese	Zinc
April 21–23, 1993	0.24	0.10	16	1.1	1.8
May 4–6, 1993	.27	.15	7	1.3	1.5
May 18–20, 1993	1.3	.85	47	4.1	11
June 2–4, 1993	3.0	2.8	230	6.4	15
June 21–23, 1993	1.7	2.4	340	4.6	>26[a]
July 12–14, 1993	2.0	1.9	330	4.6	16
August 8–10, 1993	1.1	.39	62	3.6	9.6
September 7–8, 1993	.71	.36	53	3.2	5.9

[a] Concentration of total-recoverable zinc at Alamosa River above Wightman Fork is less than detection limit of 10 μg/L.

Table 5. Ratio of instantaneous total load of metal in Alamosa River below Wightman Fork to Alamosa River upstream from Terrace Reservoir

[Ratio <1 indicates possible source of metal between Wightman Fork and Terrace Reservoir; ratio >1 indicates possible loss of metal from water column by geochemical reactions]

Date	Aluminum	Iron	Copper	Manganese	Zinc
April 21–23, 1993	0.87	0.80	0.60	0.79	0.09
May 4–6, 1993	.75	.75	.66	.91	.83
May 18–20, 1993	.61	.54	.89	.74	.66
June 2–4, 1993	.81	.68	1.8	1.1	1.5
June 21–23, 1993	1.0	1.0	1.4	1.0	1.1
July 12–14, 1993	1.1	1.0	1.6	1.0	1.1
August 8–10, 1993[a]	2.5	2.6	3.3	2.1	2.2
September 7–8, 1993	1.1	1.1	1.0	1.1	.90

[a] Using prestorm data.

Sources could include tributaries, material stored within the streambed, and ground water. During peak flow, the falling limb, and summer conditions, most ratios are greater than or equal to one. This indicates that under these flow conditions, there was often loss of metal mass from the water column. Such losses are attributed to precipitation of mineral phases from the water column and/or sorption of metals to minerals in the streambed. Evidence of precipitation of aluminum phases (white crusts and coatings on streambed material above the high-water mark) and iron phases (orange crusts and coatings) exist downstream from Wightman Fork.

These conclusions, particularly the existence of nonstorm related sources of metals between the Wightman Fork and Terrace Reservoir, require additional corroboration. The conclusions are based on ratios of instantaneous loads for each point. Samples were not collected from upstream to downstream with sampling times allowing for the same parcel of water to be sampled at upstream and downstream sites. Because the stream hydrology and geochemistry are dynamic, such sampling is necessary to quantitatively compare loads. However, the crusts of aluminum and iron minerals that have been observed in the stream are evidence that some precipitation reactions occur and that sorption surfaces exist. In addition, desorption from, dissolution of, and resuspension of these minerals could provide dissolved and suspended material to the stream during the rising limb of the snowmelt hydrograph and during storms.

Terrace Reservoir Outlet

Concentrations and loads of some constituents on some dates are lower at AR31.0 (below Terrace Reservoir) than at AR34.5 (Alamosa River above Terrace Reservoir; fig. 3). However, the opposite also is true. Because residence times within the reservoir were variable during this study, it is impossible to compare inflow and outflow concentrations and loads with the objective of determining whether the reservoir is a source or sink for any constituent. Ongoing studies are using more appropriate sampling designs to address this question (Balistrieri, abstract in this volume; Ortiz and others, abstract in this volume).

Sources of Low-pH Metal-Rich Water

Sources of low-pH, metal-rich water to the Alamosa River include:

1. Areas that are disturbed by mining, such as the Summitville Mine site, and
2. Areas that have had minimal mining activity and contain rocks that have been highly altered by hydrothermal activity. (For example, the Stunner Altered Area drained by Iron, Alum, and Bitter Creeks upstream from Wightman Fork, the Jasper Altered Area drained by Burnt Creek and Jasper Creek downstream from Wightman Fork and, to some extent, the Summitville Mine site (fig. 5).

Many natural sources of acidic water have been identified in these altered areas (Bob Kirkham, Colorado Division of Minerals and Geology, personal commun., 1993; Miller and McHugh, 1994). In addition, low-pH, metal-rich ground water attributed to natural sources was described by Hamilton (1989).

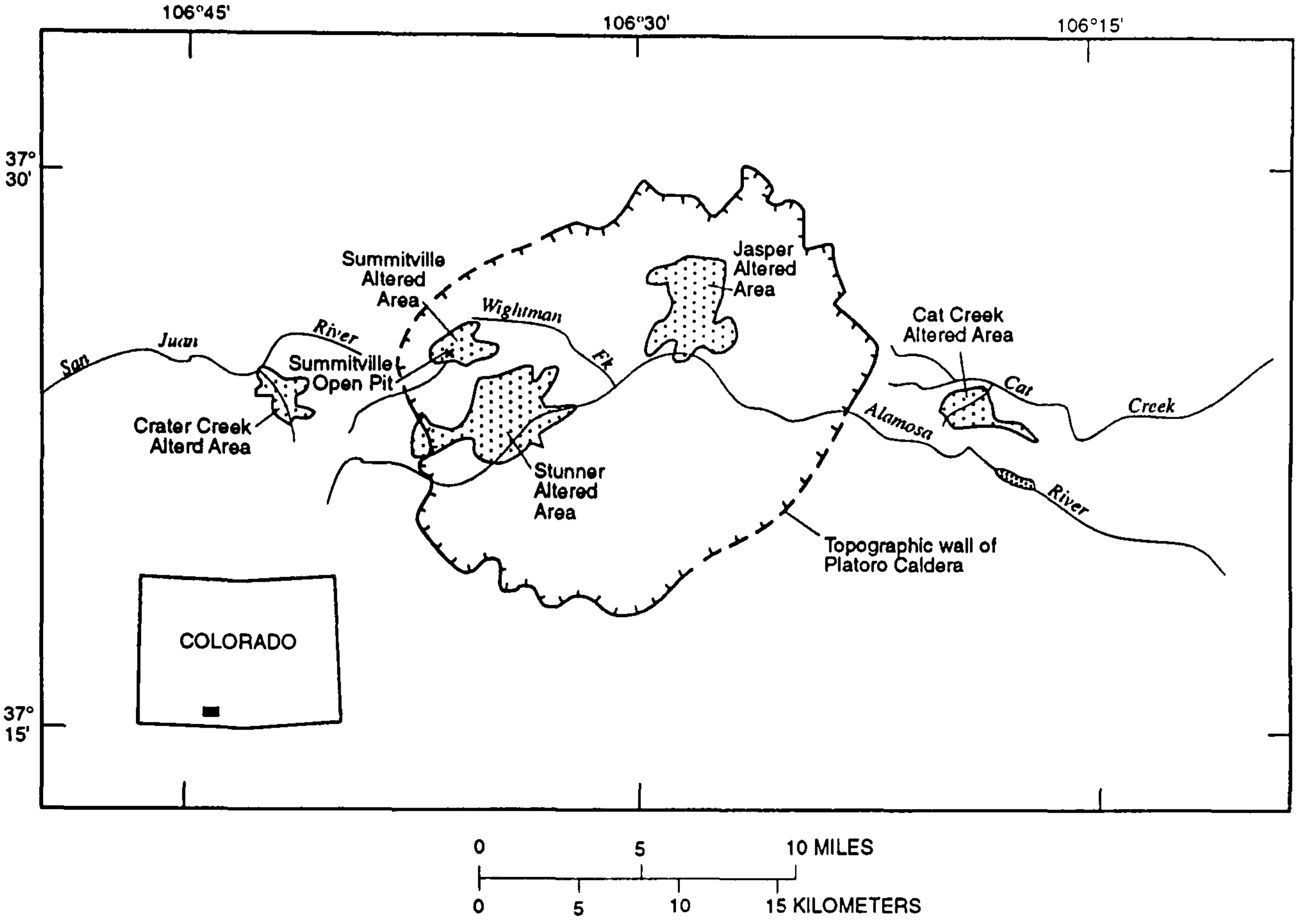

Figure 5. Map showing location of altered areas in and adjacent to the upper Alamosa River Basin (from Miller and McHugh, 1994; after Lipman, 1975).

SUMMARY

1. Some metals and low-pH water enter the Alamosa River upstream from Wightman Fork during the first flush of snowmelt and on the rising limb of the snowmelt hydrograph.

2. Wightman Fork is the source of most of the copper, manganese, and zinc discharged into the Alamosa River during most sampling periods and is the primary source of aluminum, iron, copper, manganese, and zinc during the latter weeks of spring runoff.

3. Some metals and low-pH water enter the Alamosa River downstream from Wightman Fork, as indicated by the pH of tributaries and limited sampling of a storm event.

4. Sources of low-pH, metal-rich water to the Alamosa River are naturally occurring and related to mining activities.

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EFFECTS OF SAMPLING METHODS ON COPPER AND IRON CONCENTRATIONS, ALAMOSA RIVER, SOUTH-CENTRAL COLORADO, 1993

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ABSTRACT

Synoptic samples were collected to characterize the water quality of the Alamosa River and Wightman Fork in 1993. Percent difference was computed for the replicate sample sets and between point samples and cross-section samples for concentrations of total-recoverable and dissolved copper and iron. For total-recoverable and dissolved concentrations, point-sample concentrations generally, but not always, were larger than cross-section-sample concentrations. The variability in the differences between point and cross-section samples does not allow for the application of a generalized coefficient to adjust a point concentration to a cross-section concentration.

INTRODUCTION

In 1993, the U.S. Geological Survey, in cooperation with the Colorado Division of Minerals and Geology, the Colorado Department of Health, and the U.S. Environmental Protection Agency, collected synoptic samples to characterize the water quality of the Alamosa River and the tributary Wightman Fork (fig. 1). The Wightman Fork drains the Summitville superfund site. The Alamosa River is located in a remote, rugged river canyon. Access to the river for water-sample collection is limited during periods of high streamflow. The collection of representative samples is critical to characterize water quality in streams and rivers. Considerable evidence exists to support the need for collecting depth-and-width-integrated samples, hereinafter called cross-section samples, to quantify suspended-sediment and associated trace-element concentrations (Porterfield, 1972; Horowitz and others, 1990). Unfortunately, when access is limited, only point samples can be obtained at the sampling sites.

Cross-section samples are obtained by subdividing a stream cross section into equal widths and collecting a depth-integrated sample at the centroid of each subsection (fig. 2). Water collected at each subsection usually is composited in a single container for processing. Depth integrating a sample is the collection of a sample through the entire vertical of each subsection with the sampler moving at a constant rate (transit rate) down and up through the vertical. The transit rate should not exceed 0.4 times the stream velocity in the slowest subsection of the cross section. Cross-section samples usually are collected using equipment specifically designed for that purpose (Edwards and Glysson, 1988). A point sample is collected at a single depth-integrated vertical in a fast moving portion of the stream or as far from the streambank as possible.

Point samples often cause over or underestimates of trace-element concentrations when compared to cross-section samples (Horowitz and others, 1992). This is especially true at sites where stream mixing is incomplete or where sand constitutes a large portion of the suspended sediment. Because access problems required that point samples be obtained at certain sites and certain times, concentration of selected trace elements were compared between cross-section samples and point samples at four sites to determine whether point-sample concentrations adequately represent cross-section-sample concentrations. This paper describes these comparisons.

DATA-COLLECTION METHODS

Replicate cross-section samples were collected at the Alamosa River below Terrace Reservoir (AR31.0), Alamosa River below Wightman Fork (AR45.4), Alamosa River above Wightman Fork (AR45.5), Wightman Fork below Cropsy Creek (WF5.5), and Pipeline Creek near the Mouth (PL0.0) (fig. 1). Pipeline Creek (PL0.0) is tributary to Wightman Fork and is generally unaffected by mine drainage. Pipeline Creek generally contributes about 13 to 32 percent of the streamflow of the Wightman Fork below Cropsy Creek (WF5.5). Cross-section and point-sample sets were collected at the Alamosa River below Wightman Fork (AR45.4), Alamosa River above Wightman Fork (AR45.5),

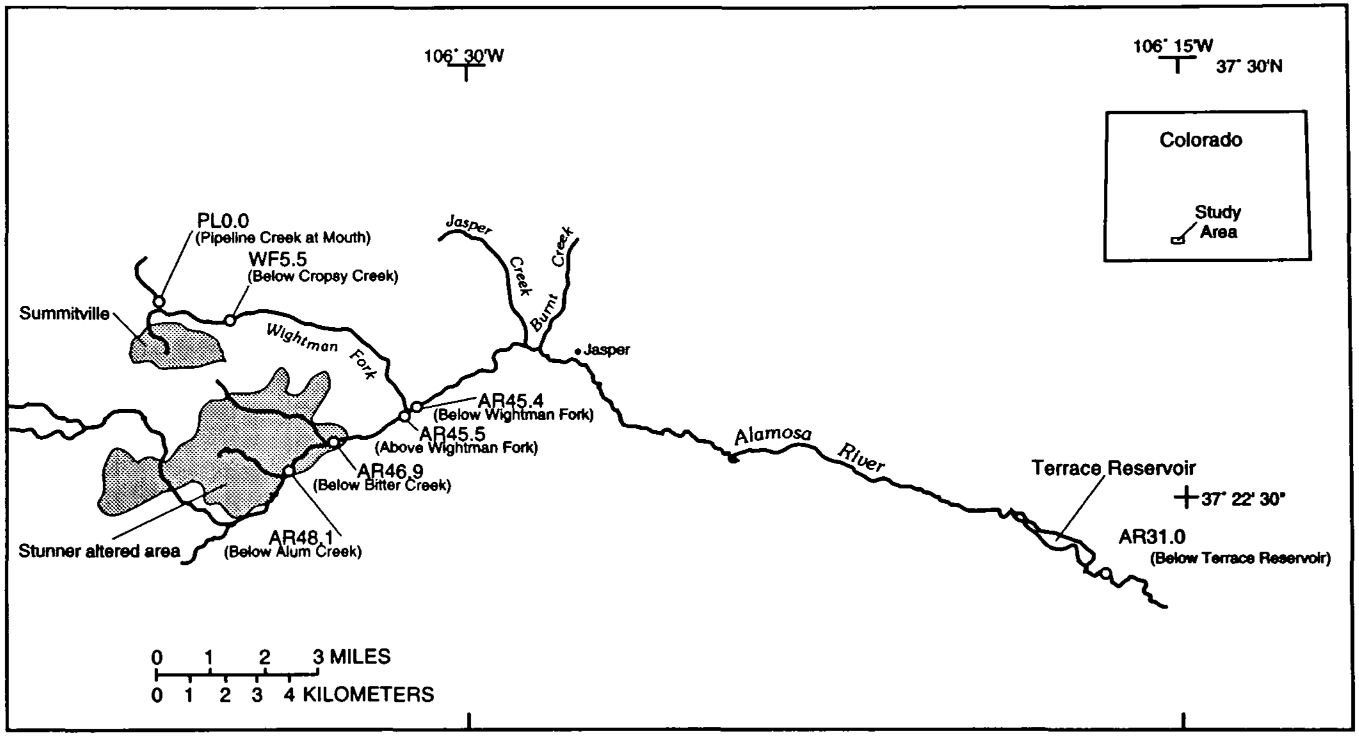

Figure 1. Location of study area (Summitville and Stunner altered area after figure 5 in Walton-Day and others in this volume).

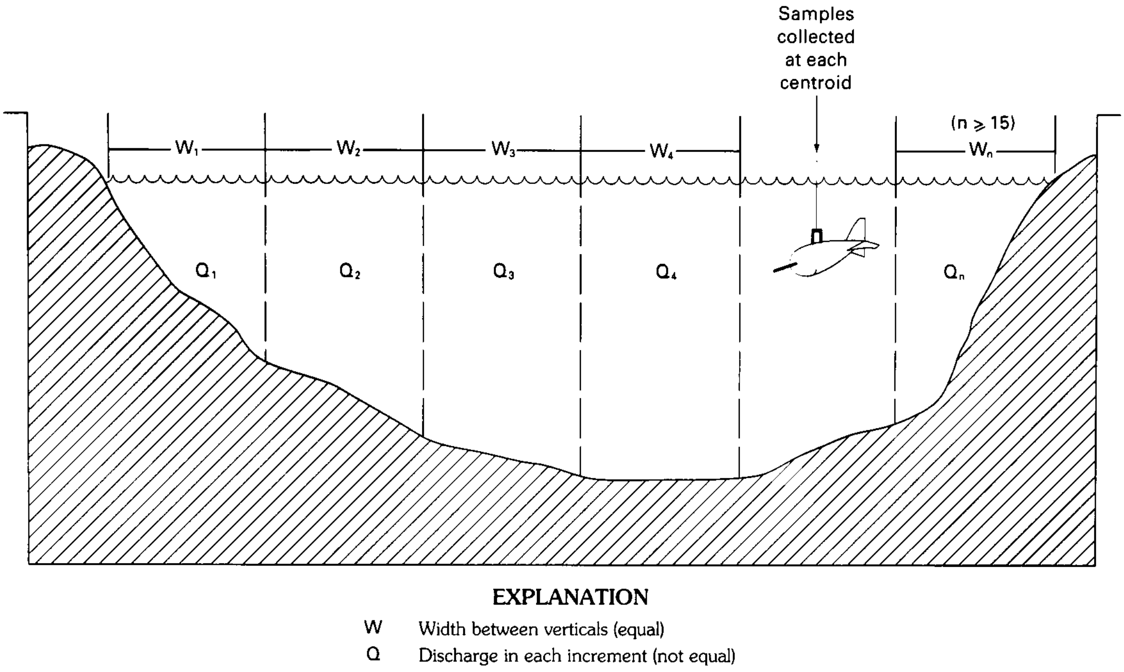

Figure 2. Cross-section-sampling technique.

Alamosa River below Bitter Creek (AR46.9), and Alamosa River below Alum Creek (AR48.1) (fig. 1).

Replicate cross-section samples were collected during each sampling trip at a selected site. Replicate sample sets include the collection of two cross-section samples consecutively. Replicate cross-section samples were obtained by dividing the cross section into at least 15 equally spaced verticals. Replicate 1 is a composite of each vertical and replicate 2 is a composite that was collected consecutively with replicate 1. Each replicate sample was collected using the same method. Thus, each cross-section sample is a composite of at least 15 verticals and the sampling differences in space and time between the two samples are reduced to a minimum. Comparison of the two replicate samples provide an indication of the reproducibility of the sample. These data are summarized in table 1.

At four sites (table 2), when access to the Alamosa River was limited during periods of high streamflow, only depth-integrated point samples were collected. In anticipation of the limited access conditions at these four sites, cross-section samples and point samples were collected consecutively for selected trace elements. These sample sets were collected before and after periods of high streamflow.

Techniques described by Edwards and Glysson (1988) for collection of representative water samples from streams and rivers were used. Point samples were depth integrated using the same equipment used to obtain cross-section samples. All point samples were collected from the north side of the river (left bank). The north side of the Alamosa River is the source of all water from hydrothermally altered areas (Lipman, 1975). The Summitville Mine area affects Wightman Fork, and the Stunner altered area affects Iron Creek, Alum Creek, and Bitter Creek.

DISCUSSION OF RESULTS

Replicate cross-section samples are used to quantify error related to sampling and analysis. Replicate sample sets represent the entire range of streamflow conditions and range of trace-element concentrations encountered during the synoptic sampling. Percent difference between replicate cross-section samples was computed for concentration of total-recoverable and dissolved copper and iron by:

$$\blacktriangle_c = \{(R_2-R_1)/R_1)\} \times 100 \qquad (1)$$

where:

$\blacktriangle_c$ = concentration difference, in percent,

R_1 = replicate 1 cross-section-sample concentration, and

R_2 = replicate 2 cross-section-sample concentration.

A positive percent difference means that the concentration of replicate 2 was larger than the concentration of replicate 1. Because conditions did not change between the two replicate samples, a positive and negative difference are interpreted the same, only the magnitude is significant. Sampling and analytical precision were evaluated by comparing percent difference of concentrations of total-

Table 1. Trace-element concentrations and percent difference for replicate sample sets of cross-section samples for selected sites on the Alamosa River

[Cu_{total}, total-recoverable copper; Cu_{diss}, dissolved copper; Fe_{total}, total-recoverable iron; Fe_{diss}, dissolved iron; --, no data; sample-site numbers (such as AR31.0) correspond to those in fig. 1]

Date	Streamflow, in cubic-feet per second	Constituent	Concentration, in micrograms per liter		Concentration difference, in percent
			Cross-section replicate		
			Replicate 1	Replicate 2	
ALAMOSA RIVER BELOW TERRACE RESERVOIR (AR31.0)					
042193	59	Cu_{total}	190	200	5
042193	59	Cu_{diss}	170	170	0
042193	59	Fe_{total}	450	470	4
042193	59	Fe_{diss}	18	10	–44
ALAMOSA RIVER BELOW WIGHTMAN FORK (AR45.4)					
050493	100	Cu_{total}	110	100	–9
050493	100	Cu_{diss}	38	40	5
050493	100	Fe_{total}	5,800	5,900	2
050493	100	Fe_{diss}	1,800	1,800	0
ALAMOSA RIVER ABOVE WIGHTMAN FORK (AR45.5)					
060293	520	Cu_{total}	7	7	0
060293	520	Cu_{diss}	2	2	0
060293	520	Fe_{total}	6,700	6,900	3
060293	520	Fe_{diss}	420	360	–14
WIGHTMAN FORK BELOW CROPSY CREEK (WF5.5)					
062293	28	Cu_{total}	17,000	16,000	–6
062293	28	Cu_{diss}	17,000	16,000	–6
062293	28	Fe_{total}	50,000	47,000	–6
062293	28	Fe_{diss}	42,000	42,000	0
PIPELINE CREEK NEAR THE MOUTH (PL0.0)					
090893	1.1	Cu_{total}	<1	1	--
090893	1.1	Cu_{diss}	1	1	0
090893	1.1	Fe_{total}	200	210	5
090893	1.1	Fe_{diss}	130	140	–8

Table 2. Trace-element concentrations and percent difference between cross-section samples and point samples for selected sites on the Alamosa River

[Cu_{total}, total-recoverable copper; Cu_{diss}, dissolved copper; Fe_{total}, total-recoverable iron; Fe_{diss}, dissolved iron; --, no data; sample-site numbers (such as AR45.4) correspond to those in fig 1]

Date	Streamflow, in cubic-feet per second	Constituent	Concentration, in micrograms per liter		Concentration difference, in percent
			Cross-section sample	Point sample	
ALAMOSA RIVER BELOW WIGHTMAN FORK (AR45.4)					
051893	319	Cu_{total}	580	800	38
051893	319	Cu_{diss}	470	700	49
051893	319	Fe_{total}	6,800	7,800	15
051893	319	Fe_{diss}	1,800	2,500	39
062293	414	Cu_{total}	1,200	2,100	75
062293	414	Cu_{diss}	1,100	2,000	82
062293	414	Fe_{total}	4,900	6,800	39
062293	414	Fe_{diss}	3,000	4,600	53
ALAMOSA RIVER ABOVE WIGHTMAN FORK (AR45.5)					
051893	235	Cu_{total}	9	8	–11
051893	235	Cu_{diss}	2	2	0
051893	235	Fe_{total}	4,900	4,000	–18
051893	235	Fe_{diss}	870	930	7
071393	109	Cu_{total}	5	4	–20
071393	109	Cu_{diss}	1	<1	--
071393	109	Fe_{total}	2,000	2,000	0
071393	109	Fe_{diss}	600	580	–3
ALAMOSA RIVER BELOW BITTER CREEK (AR46.9)					
050593	70	Cu_{total}	15	17	13
050593	70	Cu_{diss}	14	13	–7
050593	70	Fe_{total}	6,900	6,900	0
050593	70	Fe_{diss}	2,500	2,700	8
071393	133	Cu_{total}	4	4	0
071393	133	Cu_{diss}	2	<1	--
071393	133	Fe_{total}	2,000	2,100	5
071393	133	Fe_{diss}	700	790	13
ALAMOSA RIVER BELOW ALUM CREEK (AR48.1)					
050693	70	Cu_{total}	12	15	25
050693	70	Cu_{diss}	13	15	15
050693	70	Fe_{total}	5,900	6,200	5
050693	70	Fe_{diss}	2,000	1,800	11
071493	133	Cu_{total}	5	5	0
071493	133	Cu_{diss}	2	1	50
071493	133	Fe_{total}	2,200	2,400	9
071493	133	Fe_{diss}	920	1,000	9

recoverable and dissolved copper and iron between replicate-sample concentrations (table 1). The largest percent difference (–44) occurred at concentrations less than 20 micrograms per liter. Percent difference for the replicate data set usually was between –10 and 10 percent (table 1).

Similarly, point-sample and cross-section-sample concentrations from selected sites were compared using percent difference. Percent difference was computed between point and cross-section samples for total-recoverable and dissolved copper and iron by:

$$\blacktriangle_p = \{(P_c - X_c)/X_c)\} \times 100 \tag{2}$$

where:

$\blacktriangle_p$ = concentration difference, in percent,
P_c = point-sample concentration, and
X_c = cross-section-sample concentration.

A positive percent difference indicates that the point-sample concentration was larger than the cross-section concentration. For concentrations of total-recoverable and dissolved copper and iron, point and cross-section sample sets collected at the Alamosa River below Wightman Fork (AR45.5) had the largest percent differences, and point-sample concentrations always were larger than cross-section sample concentrations (table 2). The sampling site for the Alamosa River below Wightman Fork, is located about 200 yards downstream from the confluence with Wightman Fork, and the stream channel makes two sharp bends downstream from the confluence. Based on observations of streamflow conditions at that point on the Alamosa River, stream mixing is incomplete, and point samples are not representative of the stream cross section. For the two sample sets, streamflow from Wightman Fork was about 26 (May 18) and 15 (June 22) percent of the Alamosa River streamflow. During sampling trips in August, a white precipitate was noticed on substrate of the Alamosa River downstream from Wightman Fork. The white color was isolated along the north bank of the Alamosa River for about 0.25 mile downstream. Stream mixing was noticeable at this point with the white staining of the substrate detected on both sides of the stream channel. Complete mixing of the Alamosa River and Wightman Fork was thought to be at some point more than 0.25 mile and possibly about 1 mile or more downstream from the confluence of Wightman Fork.

For concentrations of total-recoverable and dissolved copper and iron, percent difference for cross-section and point samples computed at the Alamosa River above Wightman Fork (AR45.5) generally is within the range of the replicate sample set (tables 1 and 2). For total-recoverable copper and iron, point samples tended to underestimate cross-section-sample concentrations by as much as –20 and –18 percent, respectively. This may be a result of lower concentrations of suspended sediment sampled due to the heterogenous distribution of suspended sediment in the stream cross section (Edwards and Glysson, 1988). This sample site is considered to be well mixed with the nearest major tributary about 1.4 miles upstream.

Percent difference computed for cross-section and point samples for concentrations of total-recoverable and dissolved constituents at the Alamosa River below Bitter Creek (AR46.9) and the Alamosa River below Alum Creek (AR48.1) generally was within the range of the replicate sample set (tables 1 and 2). The sampling site below Bitter Creek was located about 150 yards downstream from the confluence with Bitter Creek. The sampling site below Alum Creek was located about 0.3 mile downstream from the confluence with Alum Creek. During the sampling period, streamflow from Bitter Creek and Alum Creek was about 4 percent of the flow of the Alamosa River downstream from each tributary. Percent difference computed for concentration of total-recoverable and dissolved constituents indicate that point-sample concentrations tended to be larger than cross-section-sample concentrations. Percent difference percent for concentration of total-recoverable and dissolved copper ranged from 0 to 25 and –7 to 50 percent, respectively, and for concentrations of total-recoverable and dissolved-iron percent different ranged from 0 to 9 percent and 5 to 13 percent, respectively. This positive bias indicates that the mixing of tributary inflows might not be complete at these sampling sites.

CONCLUSIONS

For total-recoverable and dissolved concentrations point-sample concentrations generally, but not always, were larger than cross-section-sample concentrations. Higher concentrations of point samples could result from the contribution of copper and iron from the north side of the river which drains hydrothermally altered areas. The variability in the difference between point- and cross-section-sample concentrations seems to be dependent on the length of stream mixing between the upstream tributaries and the sampling site and the contribution of streamflow from the upstream tributary. The variability in the differences between point- and cross-section samples does not allow for the application of a generalized coefficient to adjust a point-sample concentration to a cross-section-sample concentration. However, point samples could be useful if coefficients were developed at individual sites for a range of hydrologic conditions. Data presented in the report are not adequate to develop reliable relations. Based on this analysis, the use of point samples could lead to considerable overestimation of trace-element concentrations and loads.

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EFFECT OF A LOCALIZED RAINSTORM ON THE WATER QUALITY OF THE ALAMOSA RIVER UPSTREAM FROM TERRACE RESERVOIR, SOUTH-CENTRAL COLORADO, AUGUST 9–10, 1993

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ABSTRACT

The quality of the Alamosa River upstream from Terrace Reservoir is known to be affected by acid mine drainage originating from historically mined areas, such as the Summitville Mine, and hydrothermally altered areas upstream from Wightman Fork. During August 1993, water-quality samples collected at the Alamosa River upstream from Terrace Reservoir included low-flow (August 9) and post-storm rainfall-runoff (August 10) conditions. The rainfall-runoff sample was collected after a localized rainstorm that was confined to areas downstream from Wightman Fork. The data indicate that source areas downstream from Wightman Fork can substantially affect the water quality of the Alamosa River flowing into Terrace Reservoir. The pH on the Alamosa River upstream from Terrace Reservoir was 6.1 in the pre-storm sample and 4.6 in the post-storm sample. With the exception of dissolved lead, concentrations of total-recoverable and dissolved aluminum, copper, iron, lead, manganese, and zinc were larger in the post-storm runoff sample. Dissolved aluminum concentrations were elevated by as much as two orders of magnitude. Aquatic-life standards were exceeded for most analyzed constituents. Concentrations of total-suspended sediment were more than 50 times larger in the post-storm sample than in the pre-storm sample.

INTRODUCTION

About 26 miles of the Alamosa River and Wightman Fork were identified, as early as 1974, as stream reaches affected by metal-mine drainage (Wentz, 1974). In 1993, the U.S. Geological Survey in cooperation with the Colorado Division of Minerals and Geology, the Colorado Department of Health, and the U.S. Environmental Protection Agency collected water-quality samples to characterize the quality of water in the Alamosa River and Wightman Fork (fig. 1). The quality of water at site AR34.5 (Alamosa River above Terrace Reservoir) is characterized by neutral to low-pH water and elevated concentrations of trace metals (Walton-Day and others, in this volume). Sources of acid water and trace metals in the basin include the abandoned Summitville gold mine and areas of hydrothermally altered rock upstream and downstream from Wightman Fork. To date (1994), the focus of water-quality investigations in the basin has been concentrated on substantially affected areas, such as the Summitville gold mine and areas upstream from Wightman Fork. However, water-quality data collected on August 10, 1993, in response to a localized rainstorm, indicate that metals and low pH water from tributaries downstream from Wightman Fork can be important during certain periods. This paper will use these data to demonstrate the existence of potential source areas downstream from Wightman Fork and to describe the effect of storm runoff on the water quality of the Alamosa River entering Terrace Reservoir.

DATA-COLLECTION METHODS

During early August 1993, water-quality samples were collected at several sites in the Alamosa River Basin as part of a basin-wide synoptic sampling program. Samples collected on August 9 included a sample at site AR34.5 (fig. 1). The site is directly upstream from Terrace Reservoir and represents the quality of water entering the reservoir. Streamflow at the time of sample collection at 5:30 p.m. was 53 cubic feet per second (ft^3/s) and represented low-flow conditions. No water-quality samples were collected upstream near the mouth of Wightman Fork on August 9, 1993 (site AR45.4). On the morning of August 10, streamflow in the Alamosa River upstream from Terrace Reservoir had substantially increased and the river was turbid. Inspection of the continuous streamflow record at AR34.5 indicated runoff from an earlier rainstorm had substantially increased streamflow. Peak streamflow was 194 ft^3/s at approximately 7:00 a.m. on August 10. An additional water-quality sample was collected at the site in an attempt to characterize the effect of post-storm runoff on water quality at the site. Streamflow had receded to 169 ft^3/s

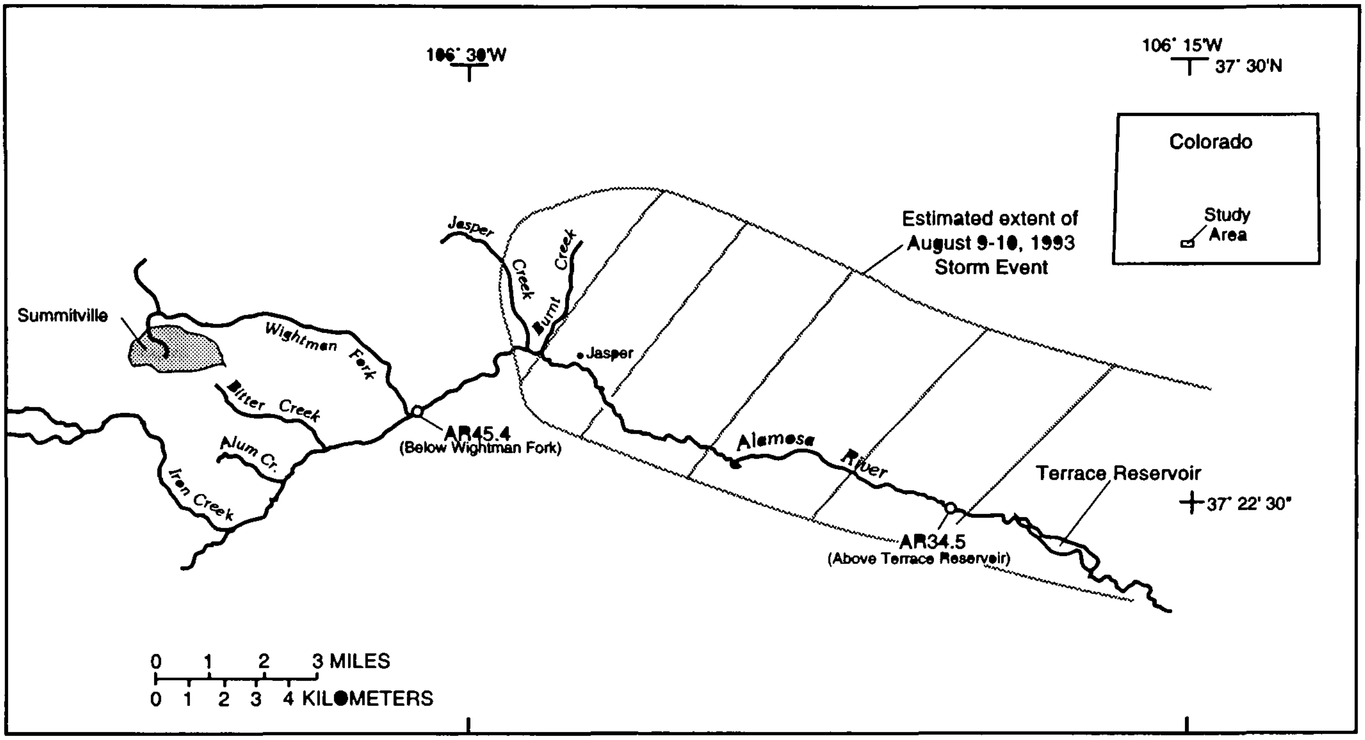


Figure 1. Map showing location of study area, sampling sites, and estimated extent of rainstorm on August 9–10, 1993.

when the sample was collected at 8:30 a.m. A reconnaissance of the areal extent of the storm indicated the storm was localized and runoff was limited to an area downstream from Wightman Fork. The areal extent of the rainstorm was determined by an inspection of tributaries upstream from AR34.5 for evidence of runoff (high-water marks and unusually turbid water), puddles in the roadway, and turbidity in the Alamosa River. This reconnaissance was mostly limited to the north side of the river. Thus, water quality of the post-storm sample (August 10) represented contribution from a source area downstream from the Summitville Mine and hydrothermally altered areas upstream from Wightman Fork. The extent of the storm did not include site AR45.4 (Alamosa River below Wightman Fork) and, as such, data collected at the site on August 10 can be considered representative of low-flow conditions. All samples were collected utilizing depth- and width-integrated sampling techniques as described by Ward and Harr (1990). Sample processing, streamflow measurement, and analytical techniques utilized U.S. Geological Survey techniques as described by Guy and Norman (1970), Rantz and others (1982), Edwards and Glysson (1988), Fishman and Friedman (1989), Sylvester and others (1990), and Fishman (1993). U.S. Environmental Protection Agency guidelines for sample chain-of-custody were followed as described by Keen (1993).

DISCUSSION OF RESULTS

Walton-Day and others (in this volume) indicated potential source areas of metals might be between Terrace Reservoir and Wightman Fork. Instantaneous total loads for selected metals during low-flow conditions were 2.1 to 3.3 times greater at AR45.4 (August 10) than at AR34.5 (August 9) (table 1). This would indicate that source areas upstream from AR45.4 contributed the majority of these metals measured entering Terrace Reservoir. In contrast, during the storm runoff on August 10, contributions from areas upstream from AR45.4 accounted for 4 to 38 percent of the total metal loads at Alamosa River above Terrace Reservoir. Given steady-state conditions at AR45.4 and the areal extent of the rainstorm, the data indicate the existence of metal sources downstream from Wightman Fork. Potential sources include acidic tributary inputs and materials deposited and stored within the streambed. Although areas upstream from Wightman Fork are the focal points of ongoing investigations in the basin, source areas downstream from Wightman Fork have the potential to substantially affect the water quality of the Alamosa River entering Terrace Reservoir.

Table 1. Ratio of instantaneous total-recoverable metal loads in Alamosa River below Wightman Fork (AR45.4) sample to Alamosa River above Terrace Reservoir (AR34.5) samples, August 9–10, 1993

Selected total-recoverable metal	Ratio of instantaneous total-recoverable metal loads for AR45.4 (August 10) and AR34.5 (August 9 and August 10)	
	Pre-storm sample at AR34.5 August 9[1]	Post-storm sample at AR34.5 August 10
Aluminum	2.5	0.10
Copper	3.3	0.22
Iron	2.6	0.04
Manganese	2.1	0.26
Zinc	2.2	0.38

[1] From Walton-Day and others (in this volume).

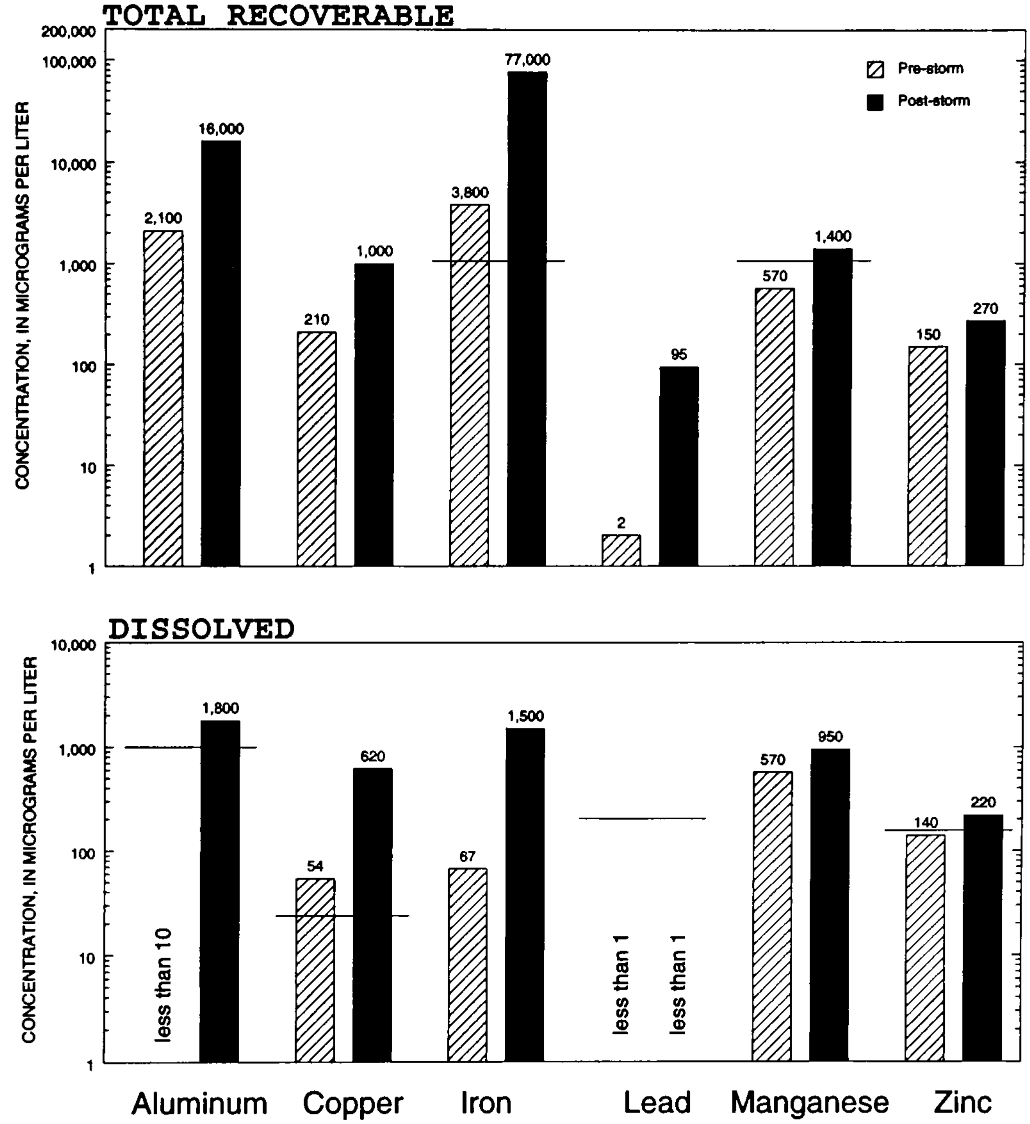
A comparison of the pre-storm and post-storm water-quality data for site AR34.5 indicates a substantial change in water quality at the site. As discussed previously, streamflow was 53 and 169 ft^3/s at the times samples were collected. Specific conductance was 396 and 509 microsiemens per centimeter; hardness was 110 to 140 milligrams per liter (mg/L). The pH was 6.1 and 4.6, which equates to a thirty-fold increase in the hydrogen ion concentration of the river. Alkalinity was 5.9 and less than 1 mg/L. Total suspended-sediment concentrations were 39 and 2,170 mg/L. The fifty-fold change in the concentration of suspended sediment is an indication that erosional processes can play a substantial role in the concentration of metals in the river. All trace metals, with the exception of dissolved lead, had larger concentrations in the post-storm sample (August 10) than in the pre-storm sample (August 9) (fig. 2). Dissolved lead was undetected in both samples.

The effect a rainstorm can have on water quality of the Alamosa River upstream from Terrace Reservoir is illustrated by the variability of the aluminum and pH data. Although aluminum is a common element in the Earth's outer crust, it is seldom found in solution in natural waters, with the exception of low pH waters (Hem, 1985). Pre-storm concentrations of dissolved aluminum at AR34.5 (pH 6.1) did not exceed the detection limit of 10 micrograms per liter (μg/L). In contrast, the concentration of dissolved aluminum reported in the post-storm runoff sample (pH 4.6) was 1,800 μg/L, nearly twice the acute aquatic-life standard set by the State of Colorado (Colorado Department of Health, 1990). The decrease in pH, due to storm runoff, was the primary cause for the increased concentration of dissolved aluminum in the river.

Aquatic-life standards associated with several metals were exceeded at AR34.5 during post-storm runoff (fig. 2). Acute metal concentrations can be detrimental to aquatic life within a relatively short time period. Acute standards for dissolved aluminum, copper, and zinc were exceeded in the runoff. Dissolved zinc concentrations exceeded the acute standard set for trout. Pre-storm concentrations for dissolved copper also exceeded the acute standard. Chronic aquatic-life standards for total-recoverable iron and manganese were exceeded in the post-storm sample. Iron concentrations at AR34.5 routinely exceeded the chronic standard of 1,000 μg/L.

SUMMARY

Water quality of the Alamosa River upstream from Terrace Reservoir is affected by sources downstream from Wightman Fork and areas of hydrothermally altered rock upstream from Wightman Fork. During a localized rainstorm in August 1993, the majority of the total-recoverable loads for aluminum, copper, iron, manganese, and zinc entering Terrace Reservoir were contributed by source areas downstream from Wightman Fork. A comparison of the water-quality data for pre- and post-stormflows indicated a substantial change in the chemical composition of water upstream from Terrace Reservoir. Increased flow, specific conductance, hardness, and total-suspended-sediment concentrations occurred as a result of the storm. Suspended sediments can provide an important transport mechanism for trace elements entering the reservoir as well as posing a threat to potential fisheries. Concentrations of selected trace metals, with the exception of dissolved lead, were larger in post-storm samples than in pre-storm samples. Post-storm concentrations of dissolved aluminum at AR34.5 were nearly 200 times the pre-storm concentrations at the site. The increased solubility of selected trace metals at lower pH values increase the potential that aquatic-life standards will be exceeded during storm runoff. The storm data, collected as part of a cooperative sampling program, have provided a better understanding of the effects of a rainstorm on water quality of the Alamosa River upstream from Terrace Reservoir but are by no means exhaustive.



Note: Horizontal lines denote aquatic-life standards. Total-recoverable standards denote CHRONIC levels. Dissolved standards denote ACUTE levels. Dissolved Zinc level denotes ACUTE TROUT standard. (Colorado Department of Health, 1990)

Figure 2. Concentrations of selected trace metals for pre-storm and post-storm runoff on the Alamosa River at site AR34.5, August 9–10, 1993.

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SEASONAL VARIATIONS IN WATER QUALITY ON WIGHTMAN FORK OF THE ALAMOSA RIVER, 1993

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ABSTRACT

Water-quality sampling and analyses were done in order to understand the effects of the Summitville Mine on Wightman Fork of the Alamosa River and to assess seasonal variations in water quality. Comparison of data from the background site at Pipeline Creek with Wightman Fork data indicated that water entering Wightman Fork from the Summitville Mine site upstream from its confluence with Pipeline Creek and between Pipeline Creek and Cropsy Creek contributed most of the solute mass present in Wightman Fork. On Wightman Fork, values of hardness and specific conductance and concentrations of calcium and all metals decreased from the upstream (Wightman Fork below Cropsy Creek) to downstream (Wightman Fork at mouth) sites. Values of pH increased from the upstream to downstream sites on Wightman Fork. Metal loads generally decreased or showed no difference from the upstream to downstream sites. Reactions that might be removing dissolved metals from the water column probably were occurring, but could not be quantified using this data set. Strong inverse correlations between concentrations of metals and pH indicate that pH controlled the solubility and supply of metals to Wightman Fork in 1993.

INTRODUCTION

The Summitville Mine, located near the headwaters of Wightman Fork, a tributary to the Alamosa River, was abandoned in December 1992. At that time, the U.S. Environmental Protection Agency (EPA) assumed operation of, and expanded water treatment facilities at the mine site to minimize offsite migration of low-quality water (Pendleton and Posey, in this volume). The U.S. Geological Survey (USGS) in cooperation with the Colorado Division of Minerals and Geology, the Colorado Department of Health, and the EPA conducted a synoptic sampling of the Alamosa River and Wightman Fork from snowmelt through the summer of 1993. The objectives of this study were to characterize water quality in the Alamosa River from the headwaters to just downstream from Terrace Reservoir, to identify source areas of streamflow that contribute low pH and elevated metals concentrations, and to evaluate the effects of mine-water discharges from historic mining areas and the Summitville Mine on water quality of the Alamosa River and Wightman Fork. Water quality on the Alamosa River, and sources of metals to the Alamosa River system are discussed in Walton-Day and others (in this volume). This paper reports sources of metals to Wightman Fork and seasonal variations in concentrations and loads of several major water-quality parameters and aluminum, copper, iron, manganese, and zinc at two sites on Wightman Fork and from a background site on Pipeline Creek (fig. 1).

METHODS

Water-quality samples were collected and streamflow-discharge measurements were made at two sites on Wightman Fork and at one background site on Pipeline Creek (PL0.0), a tributary to Wightman Fork. The upstream site on Wightman Fork (WF5.5) is directly downstream from Cropsy Creek and the Summitville Mine. The downstream site on Wightman Fork (WF0.0) is at the mouth of Wightman Fork directly upstream from its confluence with the Alamosa River. The sites were sampled eight times from April through September 1993, except that WF5.5 and PL0.0 were not sampled in August. Sampling dates were scheduled to provide the most accurate coverage of the seasonal streamflow variation within the basin. Samples were collected during April 21–23, May 4–6, May 18–20, June 2–4, June 21–23, July 12–14, August 9–11, and September 7–9. This coverage included sample collection during critical flow periods such as early runoff, peak flow, and low-flow conditions. Analysis of streamflow at AR34.5 (Alamosa River above Terrace Reservoir) for 1993, indicates that samples collected during April and May represent snowmelt conditions on the rising limb of the hydrograph. The April sample is first flush (the first large streamflow from snowmelt) of the Alamosa River basin (fig. 2). Peak flow at AR34.5 occurred on May 27 (Craig Cotton, Colorado Division of Water Resources, Division 3, oral commun., 1993); samples collected during June and July represent receding snowmelt conditions. The August and September samples represent late-summer flow during the thunderstorm season.

Water-quality sampling included onsite measurements of streamflow, specific conductance, and pH. Streamflow measurements were made using at least 10 vertical depth and velocity measurements across the width of the stream.

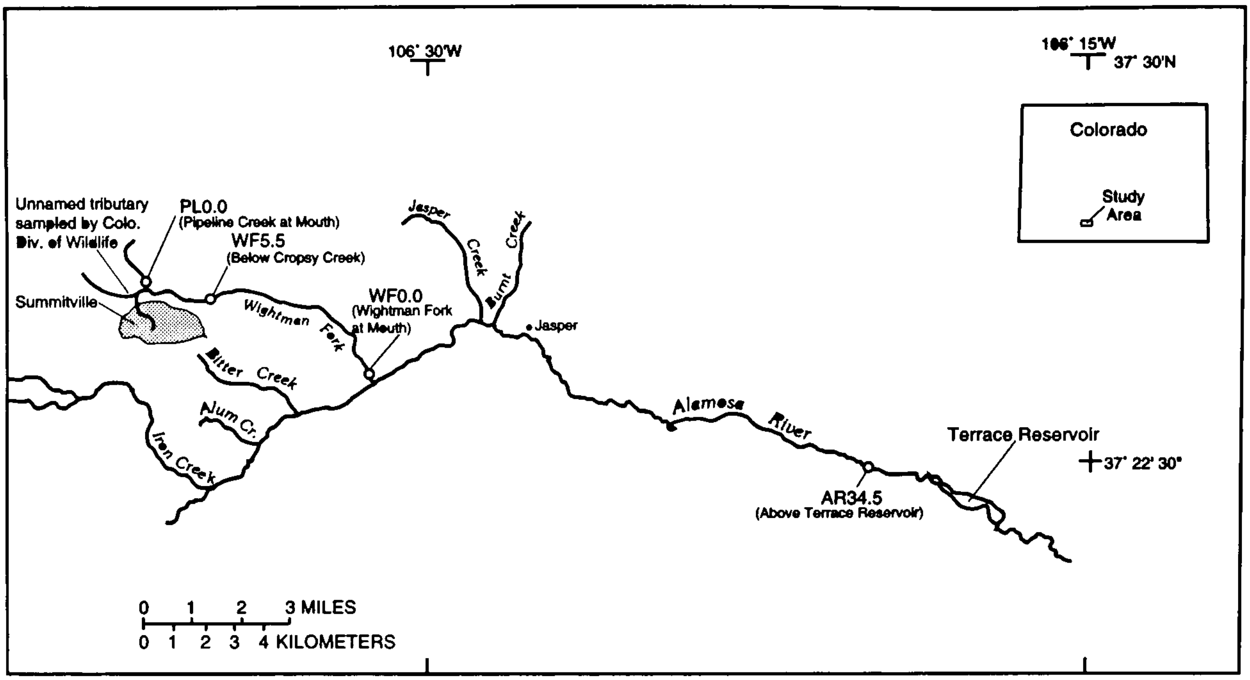

Figure 1. Map showing location of study area and sampling sites.

Wherever possible, no more than 5% of streamflow discharge was included in any measured subsection. Depth- and width-integrated (cross section) water-quality samples were collected at all times and at each site except during the April sampling at WF5.5 when a depth-integrated point sample was collected. At that time, extensive snow and ice cover precluded integration across the width of the stream. In the field, portions of unfiltered sample were preserved with ultra-pure nitric acid to pH less than 2 for analysis of total-recoverable (total) concentrations of selected trace metals. Separate aliquots of sample were filtered through a 0.45-μm (micrometer) filter and preserved with ultra-pure nitric acid to pH less than 2 for analysis of dissolved trace metals and major cations. Water-quality samples were analyzed for major ions and selected trace elements by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado. Samples were delivered to the NWQL by members of the EPA Technical Assistance Team using EPA chain-of-custody protocols. Analyses by the NWQL used standard USGS methodology (Fishman and Friedman, 1989; Fishman, 1993). Chain-of-custody protocols also were used by the NWQL for all samples associated with this project and laboratory quality-assurance procedures were used to meet CERCLA (Comprehensive Environmental Response and Compensation Liability Act) guidelines. Sampling protocols for streamflow measurement, sample collection, sample preparation, and sample preservation followed USGS methodology (Rantz and others, 1982; Edwards and Glysson, 1988; Sylvester and others, 1990).

RESULTS AND DISCUSSION

Data are reported in μg/L (micrograms per liter) or mg/L (milligrams per liter) for concentration and mg/s (milligrams per second) for instantaneous load. Instantaneous load is the product of metal concentration and streamflow discharge and represents the mass rate-of-flow of a constituent. Maximum, minimum, and median concentrations for selected constituents are listed in table 1. Correlation coefficients of selected total and dissolved constituent concentrations and instantaneous loads with streamflow discharge and pH for Wightman Fork sample sites are listed in table 2. For WF5.5 (n=6), the correlation coefficient is significantly different from zero at the 90% level or greater if the absolute value of the correlation coefficient is greater than 0.61. For WF0.0 (n=8), the correlation coefficient is significantly different from zero at the 90% level or greater if the absolute value of the correlation coefficient is greater than 0.50.

Site Comparisons

Comparisons of concentrations and loads between upstream and downstream sites reveal the fate of the constituents in the water column between the sites. If concentrations or loads increase, constituents might be entering the stream from a source between the two sites. If concentrations decrease but loads remain unchanged, relatively clean

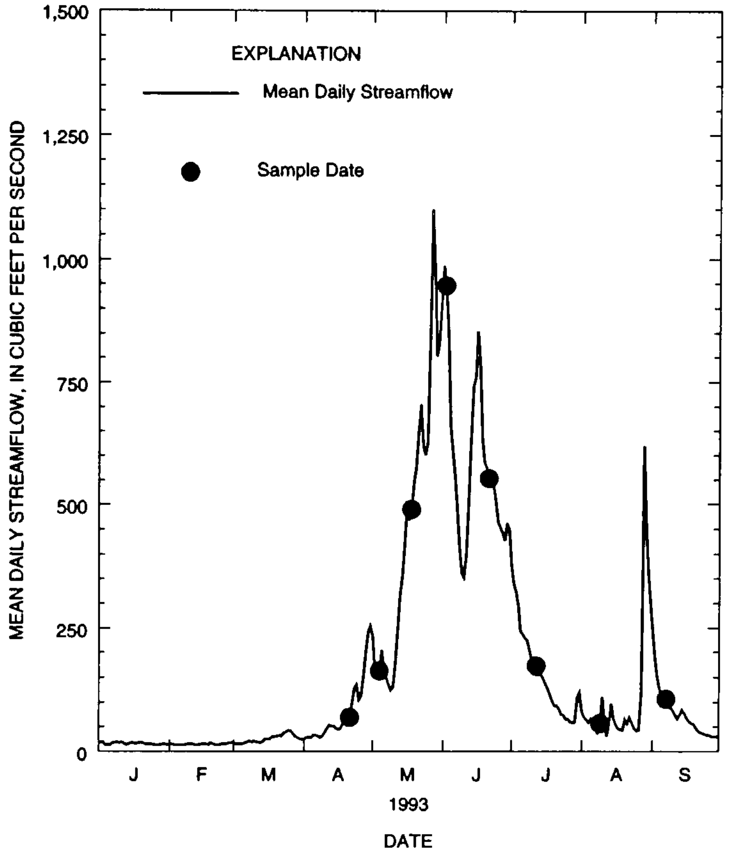

Figure 2. Mean daily streamflow for Alamosa River above Terrace Reservoir (AR34.5), January–September 1993 (data source: Craig Cotton, Colorado Division of Water Resources, Division 3, written commun., 1993).

water from a source between the sites probably is diluting the constituents. If concentrations and loads decrease, the constituents probably are being removed from the water column by chemical reactions.

Comparison of data between sites PL0.0 and WF5.5 indicates that concentrations of solutes increase by as much as four orders of magnitude between the two sites (table 1). This increase indicates that there is a solute source in Wightman Fork upstream from its confluence with Pipeline Creek and/or between the mouth of Pipeline Creek and site WF5.5. Samples collected by the Colorado Division of Wildlife (DOW) from the Wightman Fork just downstream from Pipeline Creek have metals concentrations greater than those at Pipeline Creek, but less than those at site WF5.5. Samples collected by (DOW) from the primary tributary to Wightman Fork upstream from Pipeline Creek (fig. 1) have concentrations similar to those in Pipeline Creek (John Woodling, Colorado Division of Wildlife, oral communication, 1994). These data indicate that the Summitville area provides metals to Wightman Fork upstream and downstream from the confluence with Pipeline Creek. Other tributaries entering Wightman Fork from the north are draining areas with geology similar to that in the Pipeline Creek basin, and probably have similar water chemistry.

Concentrations of all the metals, hardness, specific conductance, and calcium decreased between the upstream (WF5.5) and downstream (WF0.0) sites on Wightman Fork (table 1 and fig. 3). Values of pH increased from the upstream to the downstream sites. Instantaneous loads of metals either decreased by up to 45%, showed no significant difference, or on the June 2–4 sampling trip, increased between the upstream and downstream Wightman Fork sites. The June 2–4 increase in loads at the downstream site was caused by very high flow at the time that site was sampled (fig. 3). It is difficult to use these data to assess whether there are sources for the metals between the two sites, or whether geochemical reactions are occurring along the stream that remove metals from the water column. All sites were sam-

Table 1. Summary statistics for concentrations of selected constituents

[Concentrations in micrograms per liter except Hardness in milligrams per liter $CaCO_3$ and pH in standard units. Min. = minimum concentration; Max. = maximum concentration; Med. = median concentration; TAl = total-recoverable aluminum; DAl = dissolved aluminum; TCu = total-recoverable copper; DCu = dissolved copper; TFe = total-recoverable iron; DFe = dissolved iron; TMn = total-recoverable manganese; DMn = dissolved manganese; TZn = total-recoverable zinc; DZn = dissolved zinc]

	PL0.0			WF5.5			WF0.0		
	Min.	Max.	Med.	Min.	Max.	Med.	Min.	Max.	Med.
TAl	60	210	150	9,200	42,000	23,500	2,800	16,000	8,050
DAl	25	220	40	1,200	41,000	18,000	<10	15,000	4,700
TCu	<1	2	1	1,700	38,000	4,700	430	12,000	2,350
DCu	<1	3	2	1,600	37,000	4,700	80	12,000	2,250
TFe	80	460	205	15,000	100,000	39,000	4,300	33,000	10,500
DFe	<10	240	73	1,000	97,000	27,000	5	21,000	3,550
TMn	<10	50	20	4,550	7,800	6,600	1,400	3,700	2,150
DMn	5	29	14	4,600	7,900	6,200	1,200	3,700	2,150
TZn	<10	40	<10	1,100	6,700	2,000	330	2,300	815
DZn	3	46	7	570	6,500	2,200	180	2,300	795
pH	6.8	7.3	7.1	3.3	5.5	3.7	4.0	7.5	4.95
Hardness	6	20	11	170	560	220	58	290	150

Table 2. Correlation coefficients of concentrations and loads of selected constituents with streamflow discharge and pH at sample sites on Wightman Fork

[All data except pH log (base 10) transformed. Q = streamflow discharge; TAl = total-recoverable aluminum; DAl = dissolved aluminum; TCu = total-recoverable copper; DCu = dissolved copper; TFe = total-recoverable iron; DFe = dissolved iron; TMn = total-recoverable manganese; DMn = dissolved manganese; TZn = total recoverable zinc; DZn = dissolved zinc; Ca = calcium. Correlations that are significantly different from zero at the 90% level or greater are underlined]

	WF5.5		WF0.0	
	Q	pH	Q	pH
TAl	0.47	-0.83	0.22	-0.95
TAl load	.92	-.86	.85	-.63
DAl	.43	-.85	.25	-.99
DAl load	.89	-.89	.48	-.95
TCu	.37	-.80	.08	-.85
TCu load	.76	-.91	.70	-.75
DCu	.37	-.81	.16	-.96
DCu load	.76	-.91	.60	-.69
TFe	.49	-.79	.59	-.81
TFe load	.88	-.86	.87	-.53
DFe	.49	-.84	.27	-.99
DFe load	.83	-.90	.51	-.94
TMn	-.44	.44	-.37	-.71
TMn load	.98	-.67	.88	-.55
DMn	-.45	.29	-.44	-.69
DMn load	.99	-.71	.84	-.60
TZn	.21	-.68	-.06	-.88
TZn load	.86	-.88	.79	-.69
DZn	.25	-.70	-.03	-.93
DZn load	.86	-.89	.72	-.78
pH	-.66	1	-.27	1
Hardness	-.56	.79	-.83	.36
Ca	-.51	.77	-.82	.40
Specific conductance	-.77	.60	-.96	.16

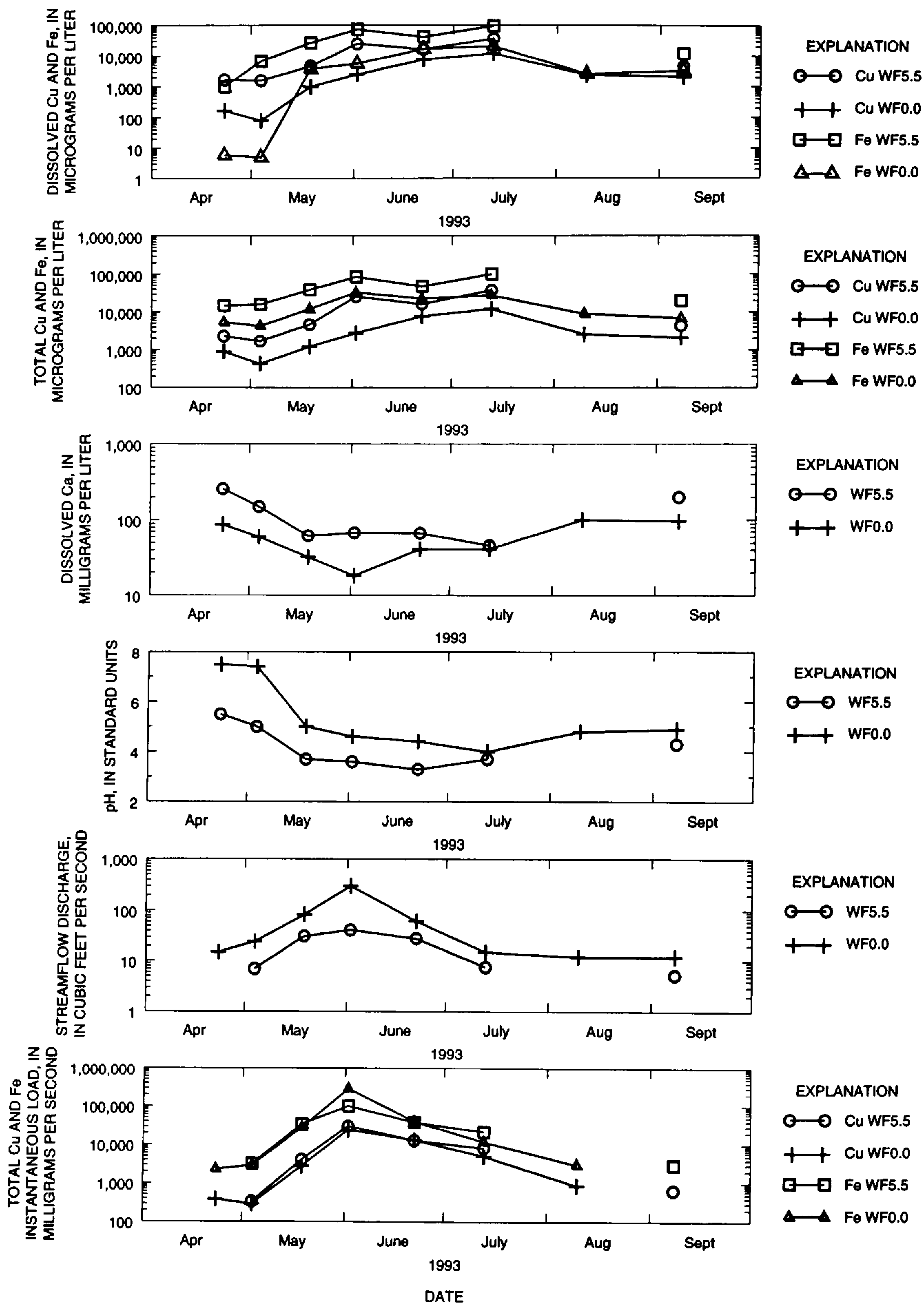

Figure 3. Graphs showing variations in total and dissolved copper concentrations, instantaneous loads of total and dissolved copper, dissolved calcium, streamflow discharge and pH at WF0.0 and WF5.5.

pled from downstream to upstream to help minimize contamination. Samples were not collected from upstream to downstream with sampling times allowing for the same parcel of water to be sampled at upstream and downstream sites. Because stream hydrology and geochemistry are dynamic, such sampling is necessary to quantitatively compare loads. However, the data can be used qualitatively. Therefore, the decrease in concentration of constituents and, with one exception, the decrease or unchanging loads between upstream to downstream sites indicate that (1) additional amounts of these constituents are probably not entering the water column from any sources between the upstream and downstream site, and that (2) dilution between upstream and downstream sites or removal of metals from the water column by chemical reactions such as mineral precipitation or adsorption possibly is occurring. More appropriate sampling design or independent evidence is required to verify these statements.

Seasonal Variation and Relations to pH

Relations between streamflow discharge and constituent concentration indicate seasonal variation in the source and supply of the constituent in the drainage basin. For example, an inverse relation between streamflow discharge and constituent concentration indicates that the supply of the constituent is limited or constant. A positive relation between streamflow discharge and constituent concentration or load indicates that more constituent is produced with increasing discharge. Relations between pH and constituent concentration could indicate that pH controls the solubility of the constituent.

For both Wightman Fork sites, correlations of most metal loads and specific conductance are significantly related to streamflow discharge (table 2). There is a significant inverse relation between pH and streamflow discharge at WF5.5, and between hardness and calcium concentrations and streamflow discharge at WF0.0. All metal concentrations and loads (except total and dissolved manganese concentrations at WF5.5) have a strong inverse relation to pH (table 2, fig. 3).

The inverse relation of streamflow discharge to specific conductance indicates that the supply of major cations to Wightman Fork was limited. With increasing discharge, dilution decreased the concentration of the constituent (for example, calcium at WF0.0, fig. 3). The inverse relation between pH and streamflow discharge at WF5.5 (table 2, fig. 3) indicates an increase in the production of acidic waters during high flow and a decrease in the volume of acidic waters during low flow.

The positive relation between most metal loads and streamflow discharge indicates that more constituent was produced with increasing runoff. Constituents were either flushed from the drainage basin at high discharge or more mass of the constituent was produced during high discharge. One cause of increased release or production of the constituents with high discharge may be the dissolution of easily soluble salts during snowmelt (Plumlee and others, in this volume). This dissolution would only show a surge increase and not a sustained increase over time. Metals and acidity may be intermittently discharged from sources such as acidic springs, seeps, and mine-drainage tunnels during higher flows. These discharge sources could be diminished or eliminated during lower flows.

Strong inverse relations between pH and the concentrations and loads of most metals (table 2) indicates the supply and solubility of the metals were dependent on pH; the concentrations of metals were greater under acidic conditions. This relation conforms with accepted solubility controls for these metals. The failure of manganese concentrations to conform to these relations at WF5.5 (table 2) might indicate that there were non-acidic sources of manganese (for instance, soluble manganese generated by normal rock weathering) that contributed significant amounts of manganese to streamflow.

Stronger correlations between concentrations of metals and pH than between the concentrations of metals and streamflow discharge indicates that pH was more important in determining metal concentrations than was streamflow discharge. In addition, for some metals (for instance, copper at both sites and iron and zinc at WF5.5), correlation coefficients between metal load and pH are more significant than those between metal load and streamflow discharge indicating that pH was a more important determinant to the load than was streamflow.

SUMMARY

The Summitville area provides metals to Wightman Fork upstream and downstream from the confluence with Pipeline Creek. On Wightman Fork, most constituents show a decrease in concentration from upstream to downstream. With one exception, instantaneous metal loads decreased between the upstream and downstream sites or showed no difference. Dilution from clean water entering the stream between the two sites or natural reactions that can remove metals from the water column (such as mineral precipitation and sorption) are probably causing the observed concentration (and load) decreases, but additional data are needed to verify this statement. Most metal loads are positively related to streamflow discharge whereas specific conductance is inversely related to streamflow discharge. Concentrations and loads of most metals are inversely related to pH indicating the strong control of pH on solubility and supply of metals to Wightman Fork.

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TRANSPORT OF METALS INTO AND THROUGH TERRACE RESERVOIR, SOUTH-CENTRAL COLORADO, APRIL-SEPTEMBER 1994

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ABSTRACT

The Alamosa River drains the Summitville Mine and other mineralized areas. The acidic- and metal-enriched drainage is subsequently discharged into Terrace Reservoir. A study was begun in April 1994, by the U.S. Geological Survey, in cooperation with the U.S. Environmental Protection Agency, to evaluate the seasonal, episodic, and annual transport of metals into and through Terrace Reservoir.

To evaluate metal transport into Terrace Reservoir, about 80 water samples were collected for chemical analyses from the Alamosa River upstream from Terrace Reservoir. Weekly cross-sectional integrated samples were collected between late-April through September, additional samples will be collected in October and November 1994, and January, February, and March 1995. About 20 point samples were collected concurrently with the cross-sectional samples to evaluate river mixing. Between August through September, several storm-runoff samples were collected at a single point in the river using an automatic sampler. Several discrete samples were collected during the runoff event. The discrete samples were flow-weighted and composited into a single sample to determine the event-mean constituent concentration. Selected discrete samples also were analyzed to provide information on constituent concentrations that occur throughout the runoff event. The storm-runoff peak generally occurred between 11 p.m. and 4 a.m.

Continuous field measurements of streamflow, pH, and specific conductance were made on the Alamosa River upstream from Terrace Reservoir. These data were evaluated as potential predictor variables for filtrable and non-filtrable metal concentrations and loads. Preliminary analyses indicated that these field parameters may be significantly correlated with copper, iron, manganese, and zinc concentrations and, therefore, might be useful in quantifying concentrations and loads of selected metals transported into Terrace Reservoir.

To evaluate metal transport through Terrace Reservoir, about 20 water samples were collected for chemical analyses from the Alamosa River below Terrace Reservoir from late-April through September. Additional samples will be collected in October and November 1994, and January, February, and March 1995.

SURFACE WATER QUALITY OF THE ALAMOSA RIVER AND SELECTED TRIBUTARIES, 1972 to 1994

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ABSTRACT

Data from a number of studies were compiled to evaluate the possible historical changes of 13 selected parameters at 8 selected stations. The parameters selected were alkalinity, Al, Cd, Ca, specific conductance, Cu, Fe, Mn, Ni, Pb, pH, Na, and Zn. The sites evaluated were Iron Creek, Alamosa River at Stunner Pass Bridge, Alum Creek, Alamosa River above Wightman Fork, Wightman Fork, Burnt Creek, Alamosa River below Jasper, and Alamosa River above Terrace Reservoir. Four flow periods were established to compensate for limited flow data and data variabilities associated with flow changes. These flow periods included: (a) Wintertime, (b) Pre-runoff, (c) Runoff, and (d) Post-runoff.

During the wintertime flow period there existed a dearth of historical data on the upper Alamosa River sites. Sufficient data, however, were available at the lower Alamosa River sites to distinguish significant historical differences occurring for alkalinity, specific conductance, Cu, pH, Na, and Zn at the AR bl. Jas. site and for specific conductance, Cu, Fe, pH, Na, and Zn at the AR ab. Terrace Reservoir site. All of these changes were for increased total recoverable metals and specific conductances and decreased pHs and alkalinities.

During the pre-runoff period historically significant differences occurred for Fe, pH, and Zn at AR ab. WF; for specific conductance, Fe, Na, and Zn at WF; for pH at Burnt Creek; for Cu,Fe,pH, Na and Zn at AR bl. Jas.; and for Cu, Fe, pH, Na, and Zn at AR ab. TR. All of these changes were for increased metals and specific conductances and decreased pHs and alkalinities.

There were a number of historically significant changes that occurred during the runoff flow period. These included changes in Fe and Zn at AR at SPB; changes in Cd and Cu at Alum Creek; changes in Fe at AR ab. WF; changes in alkalinity, Ca, specific conductance, Cu, Fe, Ni, pH, Na, and Zn at the WF at bridge site; changes in alkalinity, specific conductance, Cu, Fe, pH, Na, and Zn at AR bl. Jas; and changes in alkalinity, specific conductance, Cu, Fe, pH, Na, and Zn at AR ab. TR. Decreases occurred in Zn at AR at SPB and Cu and Cd at Alum Creek. All other changes during this flow period involved increased metals and specific conductances and decreased pHs and alkalinities.

There was limited data for performing the Wilcoxson rank sum test for the post-runoff flow period. Data that were available revealed historically significant differences for pH and Zn at AR at SPB; Cu at Alum Creek; alkalinity at AR ab. WR; alkalinity, Al, Cd, specific conductance, Cu, pH, Na, and Zn at WF; alkalinity, specific conductance, and pH at AR bl. Jas; and for alkalinity, specific conductance, Cu, pH, Na, and Zn at AR ab. TR. Decreases occurred in Zn concentrations at AR at SPB and copper at Alum Creek. An increased pH was noted at AR at SPB. All of the other changes involved increased metals and specific conductances and decreased pHs and alkalinities.

A number of possible causal factors for these historical differences were addressed. These possibilities included plugging of the tunnels above the Stunner Pass bridge for improved water quality noted at the AR at SPB site. Possible causal factors for declining water quality noted on the WF and downstream sites included Summitville site activities, possible input from the Jasper area, and possible flow differences between the two test periods. Data analysis indicated that Summitville site activities were primarily responsible for the declining water quality that was noted on Wightman Fork and downstream sites at least for some of the parameters.

INTRODUCTION

A compilation of several studies was used to evaluate changes in water quality of the Alamosa River and its tributaries since 1972. This evaluation is limited by the low number of reports and the limited numbers of common parameters analyzed at common sites. Thirteen parameters at eight stations were selected for evaluation. Because most of the data did not include flow measurements, we elected to describe it in terms of four flow periods in an attempt to minimize concentration variations caused by flow differences. The flow periods selected were:

Wintertime flow period. Time period between mid-November until the end of March. This is a low flow period with groundwater contributions predominating.

Pre-runoff flow period. Time period starting the first of April and extending to mid-May. During this flow period there is increasing flow resulting from snow melt in the lower canyon and ice melt from the river.

Runoff flow period. Time period from mid-May to mid July. This period is characterized by snow melt at ever increasing elevations until the flows start returning to low flow conditions.

Post-runoff flow period. Time period from mid-July through mid-November. The end of runoff and the beginning of summer thunderstorms sometimes overlap during this time period.

Where there were multiple data points, standard deviations were used to indicate variability that can be expected overall from rainstorm events and flow variability. Since the data are not gaussian distributed, statistical deviations do not have the usual statistical interpretations.

With these limitations in mind the following 8 stations were selected: (a) Alamosa River above Terrace Reservoir (Ala R above Ter); (b) Alamosa River below Jasper (Ala R. below Jas); (c) Burnt Creek at road (Burnt Creek); (d) Wightman Fork at bridge just above mouth (WF @ bridge); (e) Alamosa River above Wightman Fork (Ala R. above WF); (f) Alum Creek at bridge (Alum Creek); (g) Alamosa River at Stunner Pass bridge (Ala R @ SPB); (h) Iron Creek at road crossing (Iron Creek). The Alamosa River site below Terrace Reservoir was not selected for evaluation since the reservoir had varying opening and closing times.

Those parameters that were evaluated included alkalinity, aluminum, cadmium, calcium, specific conductance, copper, iron, manganese, nickel, lead, pH, sodium, and zinc. Sulfate and arsenic were of concern but only limited historical data were available. Mean values, standard deviations, and the number of data points for the flow periods at the selected stations are presented in appendix tables 1 through 13.

DATA INTERPRETATION

Observations of the appendix tables were used to make up the summary tables that are presented in the appendix for each of the four flow periods for the 13 parameters and 8 stations selected for evaluation.

The Wilcoxson rank sum statistic W was applied to the Mueller & Mueller 1986 and 1994 raw data where sufficient data existed. Since detection limits were not the same in the 1986 and 1994 data, all values less than the highest detection limit were given the value of zero for the statistical calculation Tables were used to obtain the two tailed p values for small sample sizes and are indicated by less than or greater than signs before the p values indicated. Otherwise the two tailed p values were calculated. The p values obtained from this test statistic W are presented in numerical form in Summary tables 1 through 4. The p values that were less than 0.05 are presented in stippled format and are generally considered as significant.

Alkalinity was not amenable to the Wilcoxson test procedure and was, therefore, evaluated in a different format using the following four notations that were also applied to other data that could not be evaluated using the Wilcoxson test. These four notations are explained below.

NSHD. No significant historical difference. Data were placed in this category if there was overlap of standard deviations of the means of data being compared.

PSHD. Possible significant historical difference. The majority of data put into this category had an inadequate number of samples to use for statistical evaluation but what data were available indicated a possible difference.

IHD. Insufficient historical data to draw a conclusion. A number of data sets did not have any historical data available and, therefore, fell into this category.

SHD. Significant historical difference. Data in this category did not have overlaping standard deviations of the means of data being compared. Data put into this category is stippled in the tables.

The parameters which showed significance are discussed below for the four flow periods. The numbers in parentheses following each stated parameter represents the means for the 1986 and 1994 data, respectively.

Winter Flow Period

There was little wintertime water quality data available prior to the 1994 studies due to the inaccessibility of the upper Alamosa River canyon above Jasper. At the Stunner Pass bridge site on the Alamosa River there was a possible 1.9 pH unit decrease when the 1986 data was compared to the 1994 data. There was a possible 40% decrease in alkalinity that would tend to support this possibility.However, the number of data points is limited and caution is needed in this interpretation.

For the Alamosa River below Jasper site during this flow period significant statistical differences between the 1986 and 1994 data were noted for alkalinity (20 mg/l to 2 mg/l), specific conductance (312 umho/cm to 462 umho/cm), copper (<2 ug/l to 188 ug/l), pH (6.7 to 5.0), sodium (6.4 mg/l to 20.4 mg/l), and zinc (20 ug/l to 129 ug/l). Statistically significant differences were also noted for specific conductance (264 umho/cm to 380 umho/cm), copper (10 ug/l to 117 ug/l), iron (0.9 mg/l to 2.4 mg/l), pH (6.7 to 6.2), sodium (5.6 mg/l to 14.5 mg/l), and zinc (33 ug/l to 95 ug/l) at the Alamosa River above Terrace Reservoir site. Other possible signficant historical differences were difficult to evaluate because of insufficient data or the presence of a large standard deviation.

Pre-runoff Flow Period

Sufficient data was available during this flow period to determine statistically significant differences for the parameters given at the following sites: Alamosa River above Wightman Fork confluence: iron (<1 mg/l to 7.2 mg/l), pH (6.5 to 5.5), zinc (17 ug/l to 35 ug/l); Wightman Fork at bridge: specific conductance (123 umho/cm to 238 umho/cm), iron (<1 mg/l to 4 mg/l), sodium (2 mg/l to 7.2 mg/l), and zinc (25 ug/l to 232 ug/l); Alamosa River below Jasper: alkalinity (33 mg/l to 4.6 mg/l), copper (<2 ug/l to 128 ug/l), iron (<1 mg/l to 5.4 mg/l), pH (7.3 to 5.7), sodium (3 mg/l to 5.5 mg/l), and zinc (25 ug/l to 79 ug/l); Alamosa River above Terrace Reservoir: copper (<2 ug/l to 120 ug/l), iron (<1 mg/l to 4.2 mg/l), pH (6.9 to 6.4), sodium (2.5 mg/l to 6.6 mg/l, and zinc (<2 ug/l to 72 ug/l).

Insignificant historical data prevailed at Iron Creek for all parameters. Only alkalinity, aluminum, and manganese had IHD notations and other parameters did not show significant historical differences for Alum Creek or Alamosa River at Stunner Pass bridge for the pre-runoff flow period.

Runoff Flow Period

More historical data was available for this flow period than for the previous two flow periods discussed and, therefore, a number of statistically significant historical differences became apparent in the data for this period. These are summarized below: Alamosa River at Stunner Pass Bridge: iron (0.2 mg/l to 1.3 mg/l), and zinc (15 ug/l to 8.8 ug/l); Alum Creek: cadmium (13 ug/l to 2.8 ug/l), and copper (480 ug/l to 210 ug/l); Alamosa River above Wightman Fork: iron (0.9 mg/l to 2.1 mg/l); Wightman Fork at bridge: alkalinity (16 mg/l to 2.8 mg/l), calcium (4.1 mg/l to 11 mg/l), specific conductance (99 umho/cm to 497 umho/cm), copper (38 ug/l to 5430 ug/l), iron (1.2 mg/l to 18 mg/l), nickel (<1 ug/l to 53 ug/l), pH (7.0 to 4.4), sodium (1.6 mg/l to 17.8 mg/l), and zinc (25 ug/l to 890 ug/l); Alamosa River below Jasper: alkalinity (32 mg/l to 4.1 mg/l), specific conductance (105 umho/cm to 162 umho/cm), copper (<2 ug/l to 828 ug/l), iron (0.6 mg/l to 5.9 mg/l), pH (7.3 to 5.5), sodium (3.1 mg/l to 4.7 mg/l), and zinc (6 ug/l to 186 ug/l); Alamosa River above Terrace Reservoir: alkalinity (15.7 mg/l to 4.3 mg/l), specific conductance (113 umho/cm to 162 umho/cm), copper (<2 ug/l to 706 ug/l), iron (0.5 mg/l to 5 mg/l), pH (7.1 to 6.0), sodium (1.9 mg/l to 4.7 mg/l), and zinc (10 ug/l to 149 ug/l).

No historically significant changes occurred on Burnt Creek during this flow period. It should be noted that the zinc changes on the Alamosa River at the Stunner Pass Bridge and the cadmium and copper changes on Alum Creek during this flow period were **reductions.** The reductions at the Stunner Pass Bridge site might be associated with the plugging of some of the old mine tunnels that existed directly upstream from this particular site.

Post-runoff Flow Period

A sufficient amount of 1994 data existed for this flow period but the amount of 1986 data was limited and, therefore, there are a number of "IDH" notations in summary table 4. Those parameters that showed significant historical differences for the affected stations are summarized below. Some historical data other than the 1986 data were available for this flow period and have been entered at the proper location in the data below for comparison purposes to the 1986 data.

Alamosa River at Stunner Pass Bridge: pH(6.4,1986 to 7.4,1994) and zinc (19 ug/l,1986 to 9 ug/l, 1994); Alum Creek: copper (450 ug/l,1986 to 253 ug/l, 1994); Alamosa River above Wightman Fork: alkalinity (8 mg/l,1974 and 11 mg/l,1986 to 1.3 mg/l,1994); Wightman Fork at bridge: alkalinity (20 mg/l,1986 to 0 mg/l,1994), aluminum (6 mg/l,1989 to 23 mg/l,1994), cadmium (3 ug/l,1974 and 1986 to 15.4 ug/l,1994), specific conductance (260 umho/cm,1974 and 120 umho/cm,1986 to 1120 umho/cm,1994), copper (1300 ug/l,1974 and 83 ug/l,1986 to 12800 ug/l,1994) pH(5.3,1974 and 7.0 to 1986 to 4.0,1994), sodium (2.0 mg/l,1986 to 62.2 mg/l,1994),and zinc (540 ug/l,1974 and 46 ug/l,1986 to 2040 ug/l, 1994); Alamosa River below Jasper: alkalinity (2.5 mg/l,1974 and 39 mg/l,1986 to 0.9 mg/l,1994), specific conductance (270 umho/cm,1974 and 147 umho/cm,1986 to 373 umho/cm,1994), and pH (5.7,1974 and 7.7,1986 to 4.7,1994); Alamosa River above Terrace Reservoir: alkalinity (18 mg/l,1974 and 17.6 mg/l,1986 to 1.2 mg/l,1994), specific conductance (125 umho/cm,1986 to 342 umho/cm,1994),copper (<2 ug/l,1986 to 1410 ug/l,1994), pH (7.2,1974 and 7.2,1986 to 4.8,1994), sodium (1.9 mg/l,1986 to 14.2 mg/l,1994), and zinc (60 ug/l,1974 and <2 ug/l,1986 to 310 ug/l,1994).

Just as during the runoff flow period it should be noted that the changes at the Stunner Pass Bridge site involved an historical **increase** in pH and a **decrease** in zinc. A reduction in copper occurred at Alum Creek.

DISCUSSION

A number of parameters were shown to have frequent historically statistically significant differences when 1986 data was compared to 1994 data. Data for those parameters in this category were taken from Appendix Tables 1,5,6,7,11,12,and 13 and were plotted and presented in the Appendix as Figures 1 through 7 for the four flow periods at the Alamosa River above Wightman Fork, Wightman Fork at bridge, Alamosa River below Jasper, and Alamosa River above Terrace Reservoir sites. These parameters included alkalinity, specific conductance, copper, iron, pH, sodium and zinc and were selected because they showed more frequent historically significant differences as indicated from the data interpretation section.

The historically signficant differences noted in the data interpretation section became readily apparent when the parameter means were plotted. Alkalinity (Fig.1) at the WF site during the wintertime and pre-runoff flow periods for 1994 were nearly comparable to those for 1986 for the same flow periods. During the most recent mining activities at the Summitville site, Reynold's adit became a problem source of acid mine drainage and high copper concentrations for Wightman Fork. This adit was plugged towards the end of January, 1994, but in the early part of spring runoff the Reynold's adit began leaking in front of the plug and leakage of the plug placed in the Chandler adit also occurred during the same time period resulting in an eventual depletion of alkalinity at the WF site as well as an average two pH unit decline (Fig.5) and increased levels of copper (Fig.3) and zinc (Fig.7). The impacts of Wightman Fork also are apparent at the two downstream sites for copper, iron, sodium, and zinc.

During the course of these studies data was also obtained at a site above Jasper to determine whether or not there was any metal/acid impact from the mineralized areas in the Jasper locale. Observation of Summary Table 5 (in the appendix) that compares the data collected at the site above Jasper with that collected at the site below Jasper indicated a generally poorer water quality at the site above Jasper. There was a difference in calcium with higher levels occurring below Jasper than above Jasper. Burnt and Jasper Creeks produced elevated levels of calcium.

Since 1994 was a dry year for the region, the question of whether differences between the two sets of data could be associated with flow conditions on the river had been raised. 1986 was also a dry year and a statistical evaluation of flow data for the two time periods indicated that there was not a significant difference for the flow periods that were compared except for the wintertime flow period for the Alamosa River above Terrace Reservoir site (see Summary Table 6 in the appendix).

Observations of the 1992 and 1993 TREC data from USGS, Stern, and USF&WS sources revealed no noticeable differences when compared to the 1994 M&M data for Al,Cu (first three flow periods), Mn, Ni, or pH. There were some apparent differences for Cd, Ca, specific conductance, Cu (post-runoff on WF and downstream sites), Fe (WF site for post-runoff), Na, and Zn especially at the WF site and downstream sites for some flow periods.

Comparison of the 1986 M&M data with the Moran & Wentz data from the early part of the 1970s indicated some differences. For the Moran & Wentz data, alkalinity was lower at the WF and AR below Jas sites, Ca was higher at the same sites and at Alum Creek; specific conductances, Cu, and Zn were higher at the WF and AR below Jas sites, and the pH was lower at the WF and AR below Jas sites. Data were generally comparable at sites above WF indicating that water quality differences that were noted on WF and at downstream sites were possibly associated with mining activities that occurred at the Summitville site from May 1971 to June 1972.

SUMMARY

A number of data sets were compiled to compare historical water quality for 13 parameters at 8 stations on the Alamosa River and some of its tributaries for four flow periods. Data interpretation indicated probable and possible historical changes to have occurred for a number of metals, pH and alkalinity at a number of sites for flow periods where there was sufficient data available.

ACKNOWLEDGEMENTS

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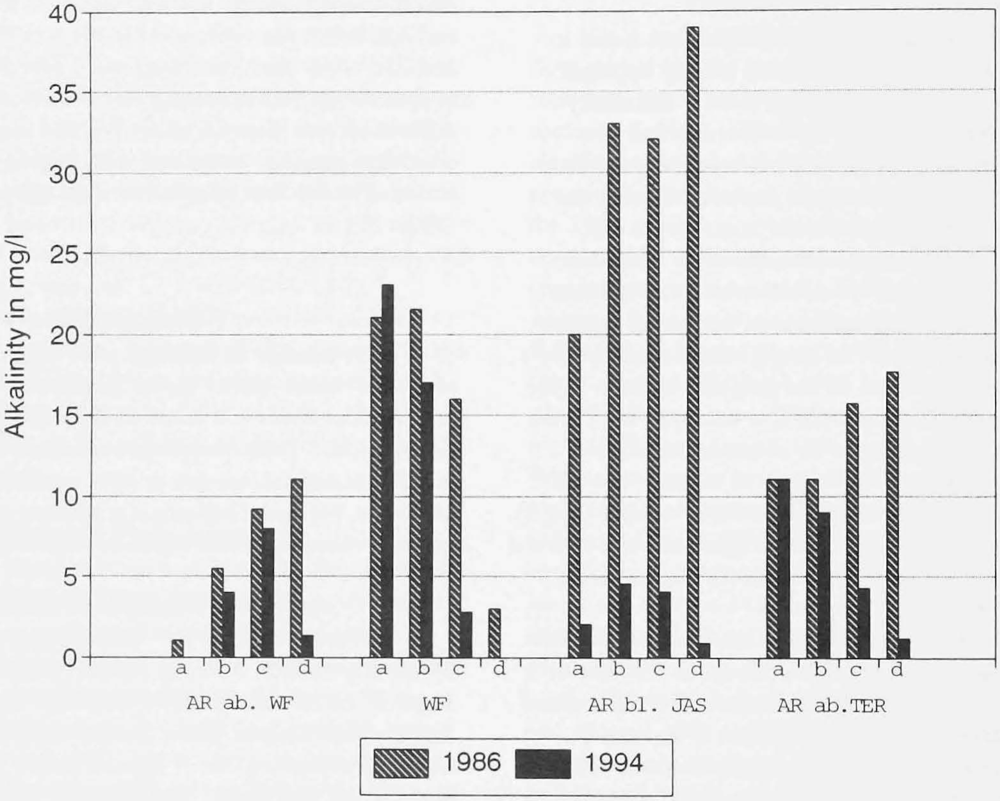

Figure 1. Mean alkalinity concentrations (mg/L) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system.

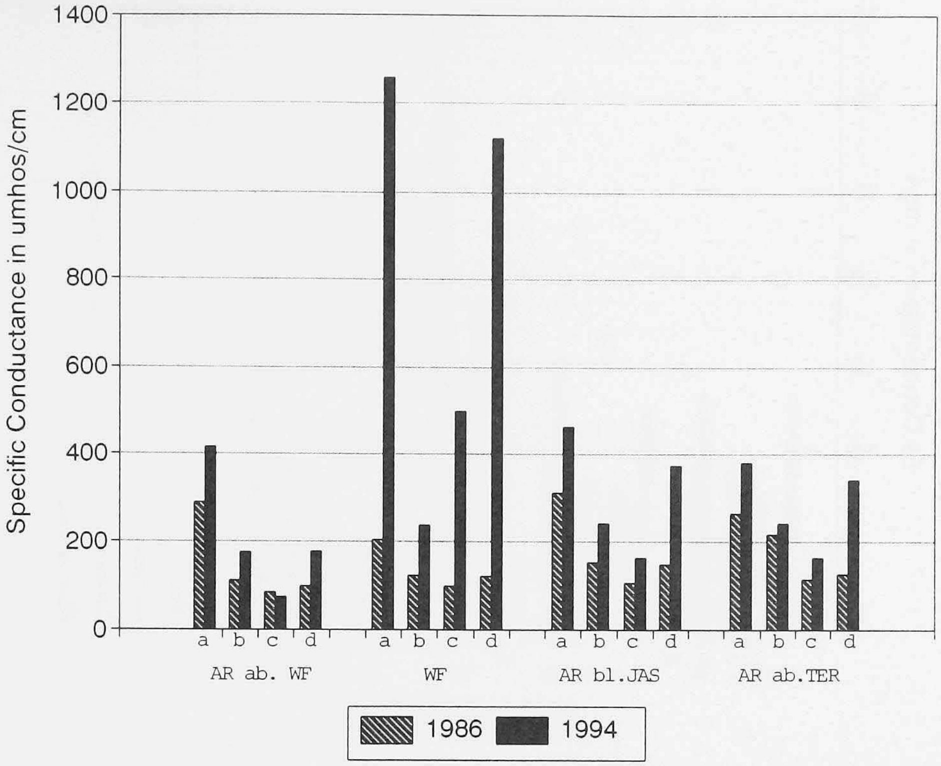

Figure 2. Mean specific conductance values (µmho/cm) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system.

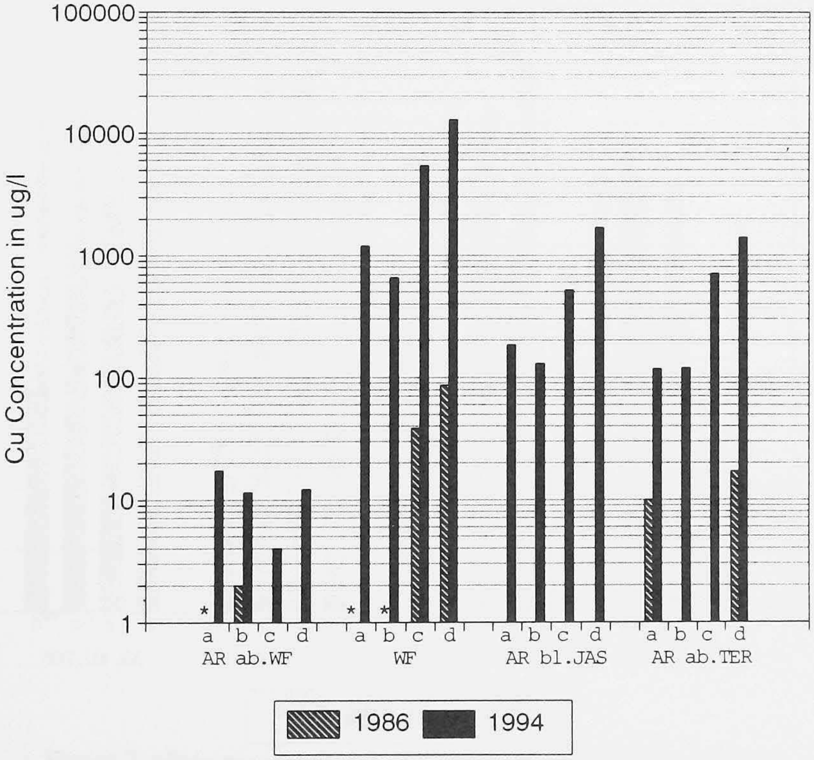

Figure 3. Mean concentrations of copper (µg/L) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system. Asterisks indicate no data for those particular stations and flow periods.

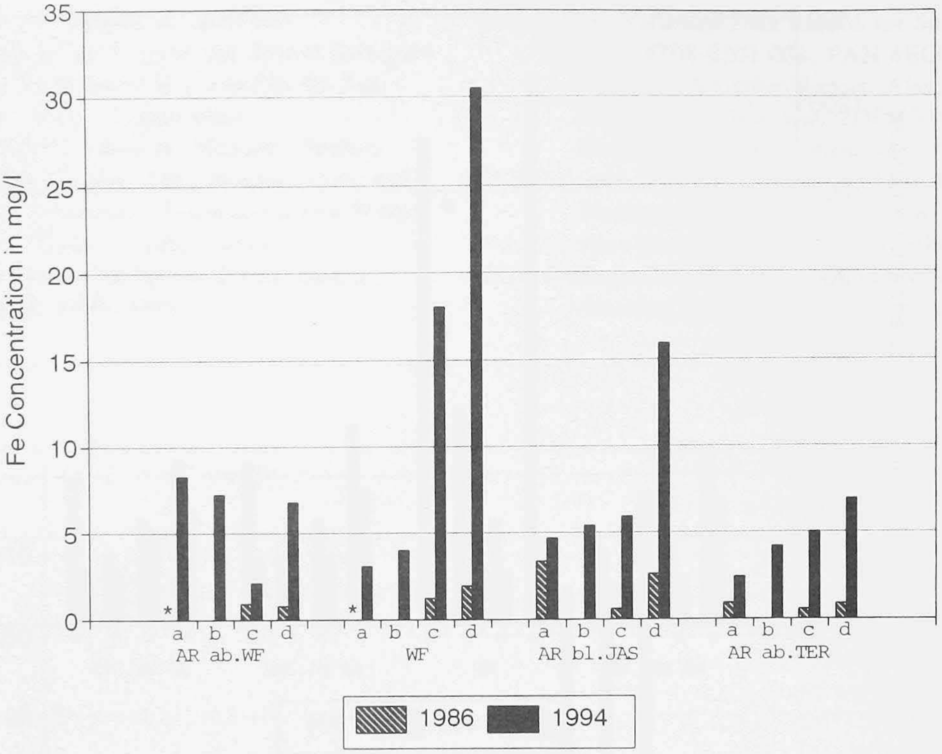

Figure 4. Mean concentrations of iron (µg/L) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system. Asterisks indicate no data for those particular stations and flow periods.

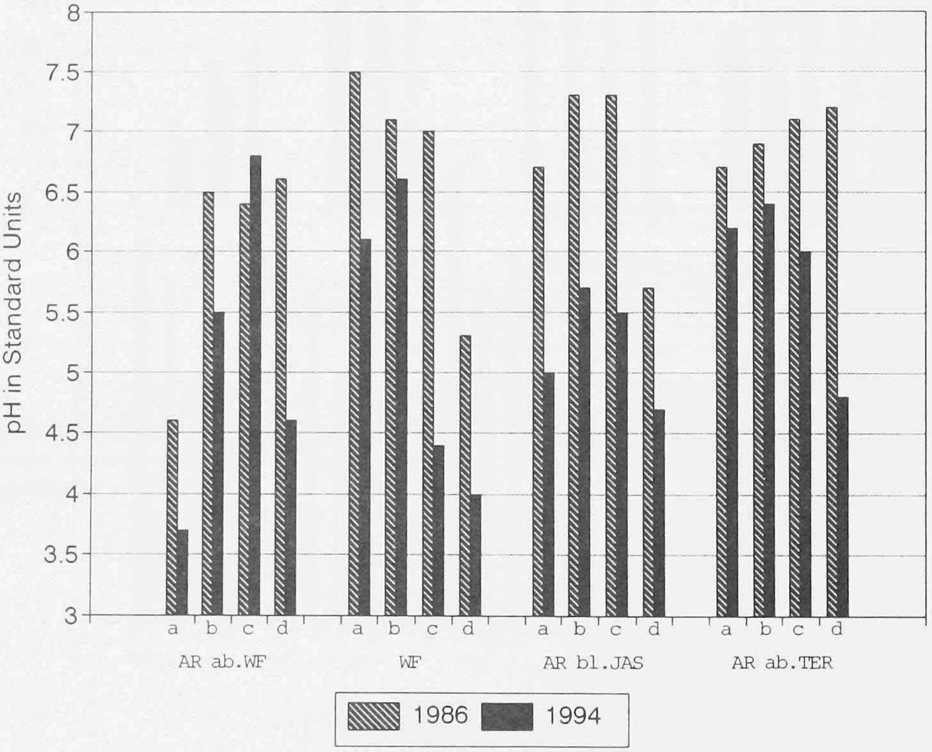

Figure 5. Mean pH values (std. units) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system.

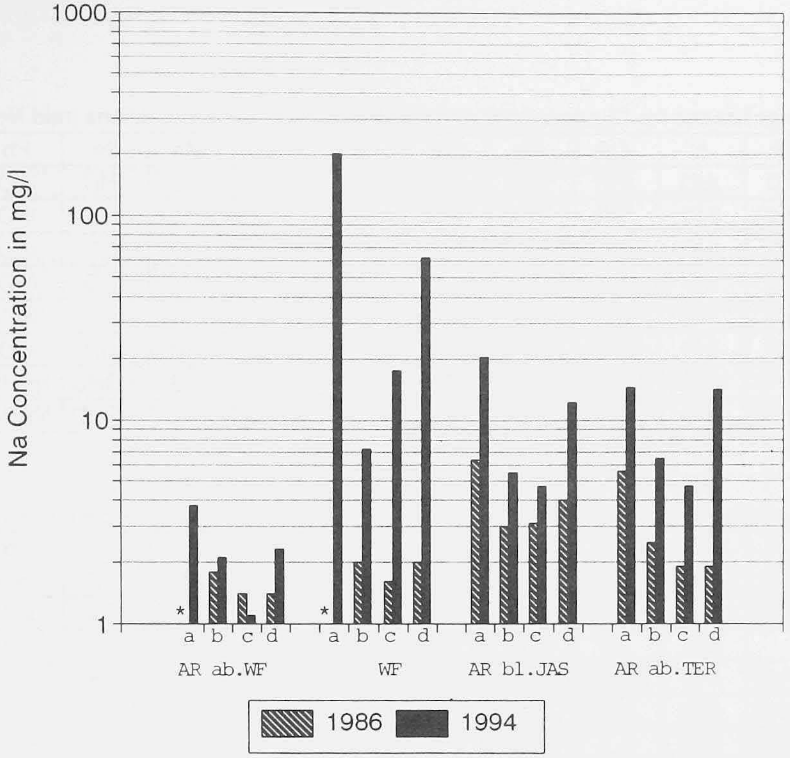

Figure 6. Mean concentrations of sodium (mg/L) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system. Asterisks indicate no data for those particular stations and flow periods.

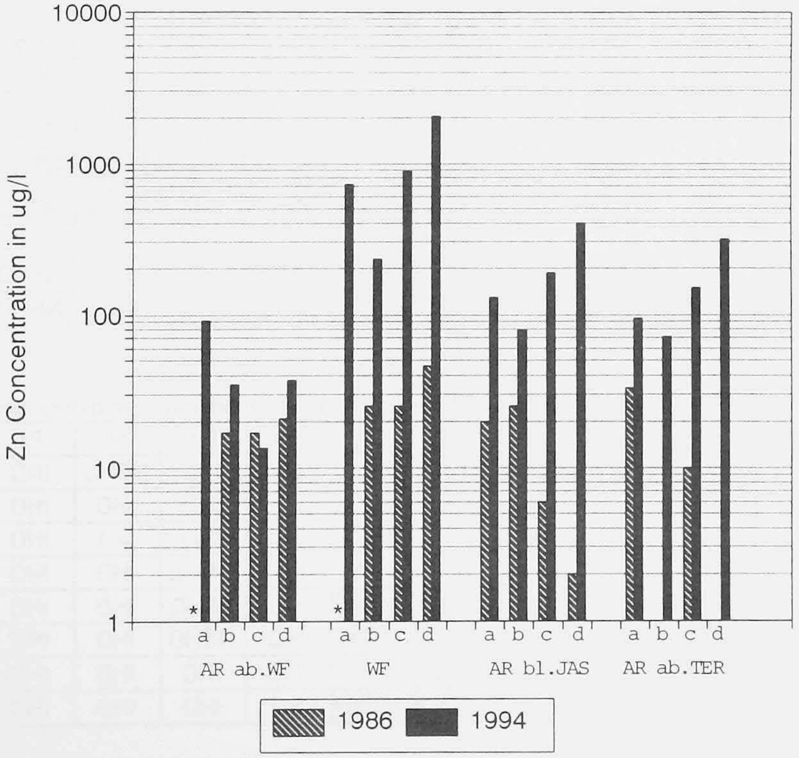

Figure 7. Mean concentrations of zinc (µg/L) during wintertime (a), Pre-runoff (b), Runoff (c), and Post-runoff (d) flow periods for 1986 and 1994 at noted sites on the Alamosa River system. Asterisks indicate no data for those particular stations and flow periods.

Summary Table 1.

Interpretation of historical significance for 13 parameters at 8 stations for winter flow conditions.(mid Nov. through March)

Site/parameter	Alk	Al	Cd	Ca	SC	Cu	Fe	Mn	Ni	Pb	pH	Na	Zn
Iron Creek	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Ala R. @ SPB	PSHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Alum Creek		IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Ala R. above WF	PSHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
WF @ bridge	NSHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Burnt Creek	IHD	IHD	IHD	IHD	>.1	IHD	IHD	IHD	IHD	IHD	>.1	IHD	IHD
Ala R. below Jas.	PSHD	IHD	NSHD	.0656	.0015	.0010	.2228	IHD	NSHD	NSHD	.0191	.0010	.0021
Ala R above Ter	NSHD	IHD	NSHD	.1284	.0003	.0041	.0189	IHD	NSHD	NSHD	.0077	.0039	.0039

Summary Table 2.

Interpretation of historical significance for 13 parameters at 8 stations for pre-runoff flows. (April through mid-May)

Site/parameter	Alk	Al	Cd	Ca	SC	Cu	Fe	Mn	Ni	Pb	pH	Na	Zn
Iron Creek	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Ala R. @ SPB	NSHD	IHD	>.1	>.1	>.1	>.1	>.1	IHD	>.1	>.1	>.1	>.1	>.1
Alum Creek		IHD	>.1	>.1	>.1	>.1	>.1	IHD	>.1	>.1	>.1	>.1	>.1
Ala R. above WF	NSHD	IHD	NSHD	.4477	.0736	NSHD	.0253	IHD	NSHD	NSHD	.0526	NSHD	.0369
WF @ bridge	NSHD	IHD	.2636	.1585	.0253	IHD	.01797	IHD	NSHD	NSHD	.1360	.0253	.0253
Burnt Creek	NSHD	IHD	>.1	IHD	>.1	>.1	>.1	IHD	>.1	>.1	<.05	>.1	>.1
Ala R. below Jas.	SHD	IHD	NSHD	.3613	.3070	.0233	.0438	IHD	NSHD	NSHD	.0455	.0322	.0233
Ala R above Ter	NSHD	IHD	NSHD	.2120	.1310	.0209	.0209	IHD	NSHD	NSHD	.0039	.0209	.0209

Summary Table 3.

Interpretation of historical significance for 13 parameters at 8 stations for runoff flows. (mid-May through mid-July)

Site/parameter	Alk	Al	Cd	Ca	SC	Cu	Fe	Mn	Ni	Pb	pH	Na	Zn
Iron Creek	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD	IHD
Ala R. @ SPB	NSHD	IHD	NSHD	.3960	NSHD	.2611	.0149	IHD	NSHD	NSHD	.3525	.2417	.0277
Alum Creek		IHD	<.05	>.1	>.1	<.05	>.1	IHD	>.1	>.1	>.1	>.1	>.1
Ala R. above WF	NSHD	IHD	NSHD	.1195	NSHD	>.1	.0149	IHD	NSHD	NSHD	.1604	.4817	NSHD
WF @ bridge	SHD	IHD	NSHD	.0290	.0004	.0007	.0010	IHD	.0172	NSHD	.0004	.0020	.0007
Burnt Creek	NSHD	IHD	>.1	>.1	>.1	>.1	>.1	IHD	>.1	>.1	>.1	>.1	>.1
Ala R. below Jas.	SHD	IHD	NSHD	NSHD	.0007	.0009	.0013	IHD	.3502	NSHD	.0003	.0090	.0009
Ala R above Ter	SHD	IHD	NSHD	.3865	.0004	.0007	.0007	IHD	NSHD	NSHD	.0031	.0007	.0010

Summary Table 4.

Interpretation of historical significance for 13 parameters at 8 stations for post-runoff flows. (mid-July through mid-Nov.)

Site/parameter	Alk	Al	Cd	Ca	SC	Cu	Fe	Mn	Ni	Pb	pH	Na	Zn
Iron Creek	IHD	IHD	PSHD	PSHD	PSHD	IHD	IHD	IHD	NSHD	IHD	PSHD	IHD	NSHD
Ala R. @ SPB	NSHD	IHD	>.1	NSHD	>.1	>.1	>.1	IHD	IHD	IHD	<.05	>.1	<.05
Alum Creek		IHD	>.1	IHD	>.1	<.05	>.1	IHD	>.1	IHD	>.1	>.1	>.1
Ala R. above WF	SHD	NSHD	>.1	IHD	>.1	>.1	IHD	NSHD	IHD	IHD	>.1	>.1	>.1
WF @ bridge	SHD	SHD	<.05	IHD	<.05	<.05	>.1	PSHD	IHD	IHD	<.05	<.05	<.05
Burnt Creek	NSHD	NSHD	IHD	IHD	IHD	IHD	IHD	NSHD	IHD	IHD	IHD	IHD	IHD
Ala R. below Jas.	SHD	PSHD	>.1	IHD	<.05	>.1	IHD	IHD	IHD	IHD	<.05	>.1	>.1
Ala R above Ter	SHD	PSHD	>.1	NSHD	<.05	<.05	>.1	IHD	IHD	IHD	<.05	<.05	<.05

IHD = Insufficient historical data

NSHD = No significant historical difference or p>0.5 for the Wilcoxson test

PSHD = Possible significant historical difference

SHD = Significant historical difference

Stippled cells are those which would usually be accepted as statistically different.

Summary Table 5.

Comparison of water quality during 1994 for sites above Jasper with the site below Jasper for the four flow periods for alkalinity, aluminum, cadmium, calcium,specific conductance, copper, iron, manganese,nickel, lead, pH, sodium, and zinc.

Period	Winter Flow						Pre-runoff Flow						Runnoff Flow						Post-runoff Flow					
Site	AR above Jas			AR below Jas			AR above Jas			AR below Jas			AR above Jas			AR below Jas			AR above Jas			AR below Jas		
Parameters	Mean	SD	#	Mean	SD	#	Mean	SD	#	Mean	SD	#	Mean	SD	#	Mean	SD	#	Mean	SD	#	Mean	SD	#
Alk mg/l	2.4	1.8	12	2	1	45	4.6	2.6	17	4.6	3.2	17	2.9	2	6	4.1	4.6	8			0	39	9	5
Al ug/l	3085	531	18	2290	590	45	2094	727	18	1970	806	17	2951	955	10	2370	500	11	5518	903	4	7960	9100	8
Cd ug/l	1	0.5	18	0.8	0.6	48	0.4	0.3	18	0.4	0.4	17	1	1.1	10	0.8	0.8	11	3.8	0.2	4	2.3	0.8	8
Ca mg/l	19.8	6.7	18	28	123	48	6.3	2.1	18	8.5	3.2	17	8.2	10.8	10	5.1	3.6	11	14.7	14.3	4	16.7	15.5	8
SC umho/cm	456	141	18	462	93	47	205	67	18	242	80	17	179	72	10	162	62	11	393	105	4	373	103	8
Cu ug/l	192	74	18	188	69	48	173	73	18	128	40	17	1029	842	10	828	550	11	2903	73	4	1690	539	8
Fe mg/l	4.9	1.1	18	4.7	2	48	6.2	3.3	18	5.4	3	17	6.2	2.8	10	5.9	1.9	17	11.5	0.8	4	15.9	18	8
Mn ug/l	879	164	18	640	98	48	422	199	18	400	160	17	768	807	10	380	110	11	1173	171	4	1370	1370	8
Ni ug/l	13.9	6.7	18	16.5	5	48	7.8	2.4	18	6.8	1.8	17	11.3	7.2	10	11.4	6	11	27.1	3.9	4	31.7	20.2	8
Pb ug/l	6.6	8.7	18	7.8	21	48	2.1	4.6	18	1.5	3.7	17	2.3	4.6	10	0.23	6	11	2.2	3.7	4	31	56	8
pH	4.8	0.3	18	5	0.3	47	5.8	0.8	18	5.7	0.6	17	5.3	0.7	10	5.5	0.6	11	4.5	0.1	4	4.7	0.1	5
Na mg/l	29.2	35.8	18	20.4	19.5	48	4.3	1.6	18	5.5	2	17	5.2	3.6	10	4.7	2.9	11	13.8	12.6	4	12.2	7	8
Zn ug/l	174	31	18	129	27	48	82	24	18	79	22	17	318	244	10	186	103	11	599	48	4	395	74	8

Summary Table 6.

Two-Tailed p values of the Wilcoxson rank sum statistic W for Flow

	Flow Period			
Site	Winter	Pre-runoff	Runoff	Post-runoff
Alum	IHD	>.10	>.10	IHD
WF@bridge	IHD	.1264	>.10	IHD
AR above Ter	.0049	.1151	.8209	IHD

Appendix Table 1.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF ALKALINITY FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER AND ITS TRIBUTARIES. CONCENTRATION GIVEN IN MG/L (+\- one standard deviation and (x) number of data points)
M&M = Mueller & Mueller; M&W = Moran & Wertz

YEAR DATA COLLECTED	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
1986		8 (1)		1.0 (1)	21 (1)	0.2 (1)	20+\-5(4)	11+\-3(5)	M&M, 1986
1994		5 (1)		0.0+\-0(11)	23+\-32(11)		2+\-1(45)	11+\-3(50)	M&M, 1994
Pre-runoff Flows (April through mid-May)									
1986		15+\-0(1)		5.5 (1)	21.5 (1)	6.8+\-8.6(3)	33+\-6(4)	11+\-5(4)	M&M, 1986
1993				<1+\-?(2)	43+\-14(2)			5.2+\-.1(2)	USGS, 1993
1994		15+\-2(3)		4+\-3(11)	17+\-4.2(14)		4.6+\-3.2(17)	9+\-2.7(23)	M&M, 1994
Runoff Flows (mid-May through mid-July)									
1986		14+\-1(9)		9.2+\-3(9)	16+\-4(9)	1.3+\-.5(8)	32+\-7(10)	15.7+\-3.1(10)	M&M, 1986
1993				7+\-3(5)	<1+\-?(4)			2.2+\-1.4(4)	USGS, 1993
1994	1.7+\-.5(3)	13+\-4(12)		8+\-1.7(11)	2.8+\-2.5(4)	3 (1)	4.1+\-4.6(8)	4.3+\-3.7(12)	M&M, 1994
Post-runoff Flows (mid-July through mid-November)									
1972	0 (1)		0 (1)	8 (1)	3 (1)		2.5+\-.5(2)	18 (1)	M&W,1974
1986		13+\-2(5)	0+\-0(5)	11+\-6(5)	20+\-11(5)	0+\-0(5)	39+\-9(5)	17.6+\-5(5)	M&M, 1986
1993				31+\-43(2)	3.2+\-2.6(2)			4.5+\-3.5(4)	USGS, 1993
1993				0 (1)	0 (1)			0 (1)	USF&WS, 1993
1994		8.2+\-4.1(7)		1.3+\-2(10)	0 (10)	0 (2)	0.9+\-0.9(8)	1.2+\-1.2(9)	M&M, 1994

Appendix Table 2.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF ALUMINUM FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)

TREC = total recoverable; DM = dissolved metal

M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1993								900 (1)	Stern,1993
TREC-1994								823 (1)	Stern,1994
TREC-1994	2970 (1)	2470+\-580(2)	41400+\-25400(2)	4580+\-960(11)	3811+\-1150(11)	4470 (1)	2290+\-590(48)	1140+\-540(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TREC-1993								1600 (1)	Stern,1993
TREC-1993				4150+\-1770(2)	2950+\-212(2)			2700+\-707(2)	USGS,1993
DM-1993				3350+\-2050(2)	<10+\-0(2)			150+\-?(2)	USGS,1993
TREC-1993				5220 (1)	3070+\-0(1)			3280 (1)	USF&WS,1993
TREC-1994								2230 (1)	Stern,1994
TREC-1994		755+\-385(3)	29400+\-7800(3)	2170+\-990(14)	2580+\-1390(14)	4770+\-2500(7)	1970+\-806(17)	1460+\-513(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1993		673 (1)		1110 (1)				1910 (1)	Stern,1993
TREC-1993				1450+\-409(6)	10900+\-4190(4)			3230+\-1560(4)	USGS-1993
DM-1993				35+\-31(7)	9100+\-5230(4)			80+\-76(4)	USGS-1993
TREC-1993			40900 (1)	928 (1)	18000 (1)			1980 (1)	USF&WS,1993
DM-1993			41400 (1)	<20 (1)	17900 (1)			93.8 (1)	USF&WS,1993
TREC-1994								1430 (1)	Stern,1994
TREC-1994	1180+\-318(3)	965+\-911(12)	33900+\-5250(7)	1020+\-276(12)	8600+\-5500(12)	3500+\-1200(4)	2370+\-500(11)	2100+\-738(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
TREC-1987				4500 (1)	6000 (1)	7000 (1)	1500 (1)		Kirkham,1989
TREC-1993		912+\-385(2)		21 (1)				1670+\-210(2)	Stern,1993
TREC-1993				2000+\-283(3)	8100+\-1960(2)			6630+\-8110(4)	USGS,1993
DM-1993				200+\-283(2)	4400+\-2690(2)			600+\-1040(3)	USGS,1993
TREC-1993			65900 (1)	2900 (1)	7150 (1)			2030 (1)	USF&WS,1993
DM-1993			65200 (1)	2140 (1)	3490 (1)			<40 (1)	USF&WS,1993
TREC-1994	5290+\-2070(3)	1240+\-1220(7)	56300+\-14700(9)	2480+\-1390(10)	23000+\-5200(6)	5570 (1)	7960+\-9100(8)	3200+\-1900(9)	M&M,1994

Appendix Table 3.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF CADMIUM FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)

TREC = total recoverable; DM = dissolved metal; TM = total metal

M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1986								<10 (1)	M&M,1986
TREC-1992		<.3 (1)		<.3 (1)			2.1+\-.5(2)	1.1+\-.5(2)	Stern,1992
TREC-1993								.3 (1)	Stern,1993
TREC-1993				<6 (1)	13 (1)			<6 (1)	EPA,1993
DM-1993				<6 (1)	11 (1)			<6 (1)	EPA,1993
TREC-1994								<.3 (1)	Stern,1994
TREC-1994	< (1)	0.2+\-.2(2)	5.3+\-.3(2)	0.26+\-.3(11)	4.2+\-.7(11)	1.9 (1)	0.8+\-.6(48)	0.57+\-.6(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TREC-1986		< (1)	40 (1)	< (1)	40+\-0(1)	<10+\-0(2)	<10+\-0(1)	<10+\-0(2)	M&M.1986
TREC-1993								1.0 (1)	Stern,1993
TREC-1993				<1+\-0(2)	3+\-1.4(2)			0.5+\-.7(2)	USGS,1993
DM-1993				<1+\-0(2)	2.5+\-.7(2)			0.5+\-.7(2)	USGS,1993
TREC-1993				<.5 (1)	3.1 (1)			0.7 (1)	USF&WS,1993
TREC-1994								<.3 (1)	Stern,1993
TREC-1994		< (3)	3.7+\-1.1(3)	2.9+\-1.0(14)	1.2+\-.6(14)	0.04+\-.1(7)	0.4+\-.4(17)	0.3+\-.3(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1986		1+\-3(8)	13+\-11(8)	2+\-5(8)	11+\-19(8)	4+\-10(8)	<10 (7)	<10+\-<(6)	M&M,1986
TREC-1992		0.8 (1)					3.2+\-0(1)	3.2 (1)	Stern.1992
TREC-1993		<.3 (1)		<0.3 (1)				1.3 (1)	Stern,1993
TREC-1993				<1 (7)	10.3+\-8(4)			1.3+\-.6(4)	USGS,1993
DM-1993				<1 (7)	9.5+\-8(4)			1.3+\-.6(4)	USGS,1993
TREC-1993			6.0 (1)	<0.5 (1)	22 (1)			2.8 (1)	USF&WS,1993
DM-1993			6.3 (1)	<0.5 (1)	23 (1)			2.8 (1)	USF&WS,1993
TREC-1994								<0.3 (1)	Stern,1994
TREC-1994	<.3 (3)	0.16+\-.32(12)	2.8+\-1.4(4)	<0.3 (12)	5.6+\-5.2(12)	0.2+\-.35(4)	0.8+\-0.8(11)	0.54+\-.51(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	10 (1)				3 (1)		10 (1)		M&W,1974
TM-1972								30 (1)	M&W,1974
TREC-1986		3+\-4(3)	5+\-4(3)	<10 (3)	3+\-4(3)	<10 (3)	<10 (3)	<10 (3)	M&M,1986
TREC-1987				<10 (1)	10 (1)		<10 (1)		Kirkham,1989
TREC-1992		0.35+\-0.35(2)		<0.3 (1)			2+\-.5(2)	1.7+\-.4(2)	Stern,1992
TREC-1993		<0.6 (2)		1.6 (1)				0.8+\-.2(2)	Stern,1993
TREC-1993				<1 (7)	7.5+\-.7(2)			1+\-.6(3)	USGS,1993
DM-1993				<1 (7)	7.0+\-0(2)			1+\-.6(3)	USGS,1993
TREC-1993			7.5 (1)	.5 (1)	6.5 (1)			1.2 (1)	USF&WS,1993
DM-1993			8.2 (1)	.5 (1)	6.9 (1)			1.2 (1)	USF&WS,1993
TREC-1994	<.3 (3)	<.3 (7)	4.4+\-1.9(9)	<0.4 (7)	15.4+\-3.4(10)	<0.3 (1)	2.3+\-0.8(8)	1.6+\-0.5(9)	M&M,1994

Appendix Table 4.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF CALCIUM FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN MG/L (+\- one standard deviation and (x) number of data points)

DM = dissolved metals; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
DM-1986							26+\-7(3)	20+\-1(3)	M&M,1986
DM-1994	1.9 (1)	4.3+\-.7(2)	2.0+\-.4(2)	6.4+\-2.2(11)	55+\-23(11)	70 (1)	28+\-12(48)	27+\-11(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
DM-1986		3 (1)	1.7 (1)	4.3 (1)	6 (1)	8.2 (1)	2.9 (1)	5.4 (1)	M&M,1986
DM-1993				20+\-4(2)	74+\-19(2)			24+\-7(2)	USGS,1993
DM-1994		2.0+\-.1(3)	0.8+\-.2(3)	11.8+\-31(14)	11+\-4(14)	16+\-5(7)	8.5+\-3.2(17)	11.5+\-5(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
DM-1986		2.5+\-.8(5)	1.2+\-.3(5)	3.1+\-.8(4)	4.1+\-1.5(5)	10+\-2(5)	2.0+\-.5(5)	4.1+\-1(4)	M&M,1986
DM-1993				8.2+\-1.8(7)	33+\-11(4)			17+\-3(4)	USGS,1993
DM-1993			25.0 (1)	8.1 (1)	79.4 (1)			18.8 (1)	USF&WS,1993
DM-1994	1.2+\-.1(3)	2.0+\-.7(12)	1.7+\-1.3(7)	2.2+\-.6(11)	11+\-11(12)	8.9+\-2.9(4)	5.1+\-3.6(11)	5.5+\-3.7(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	12 (1)		63 (1)	12 (1)	30 (1)		44 (1)	38 (1)	M&W,1974
DM-1986		1.1+\-0(2)	0.9 (1)		1.7 (1)	9.2 (1)	1.9 (1)		M&M,1986
DM-1993				13.5+\-.5(2)	98.5+\-2(2)			37+\-9(3)	USGS,1993
DM-1993			49.6 (1)	29.9 (1)	71 (1)			43 (1)	USF&WS,1993
DM-1994	1.4+\-.2(2)	3.4+\-2.2(7)	2.9+\-2.4(9)	7.7+\-13(10)	36.8+\-48(10)	116 (1)	16.7+\-15.5(8)	16.9+\-13(9)	M&M,1994

Appendix Table 5.

A SUMMARY OF THE HISTORICAL MEAN SPECIFIC CONDUCTANCE FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. VALUES GIVEN IN umohs/cm at 25 C (+\- one standard deviation and (x) number of data points)
M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA COLLECTED	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
1986		155 (1)	2000 (1)	290 (1)	205 (1)	1040 (1)	312+\-117(4)	264+\-24(5)	M&M, 1986
1994	205 (1)	220+\-15(2)	1635+\-28(2)	417+\-47(11)	1258+\-597(11)	736 (1)	462+\-93(47)	380+\-37(50)	M&M, 1994
Pre-runoff Flows (April through mid-May)									
1986		80 (1)	1860 (1)	110 (1)	123 (1)	500+\-224(4)	153+\-39(4)	217+\-58(4)	M&M, 1986
1993				223+\-93(4)	769+\-219(2)			351+\-123(2)	USGS.1993
1994		98+\-10(3)	1386+\-218(3)	174+\-63(14)	238+\-61(14)	470+\-124(7)	242+\-80(17)	243+\-70(23)	M&M, 1994
Runoff Flows (mid-May through mid-July)									
1986		64+\-11(9)	1423+\-262(9)	82+\-16(4)	99+\-17(9)	391+\-192(10)	105+\-21(10)	113+\-34(10)	M&M. 1986
1993			1023 (1)	72+\-19(4)	492+\-232(4)			182+\-35(4)	USGS. 1993
1993				56 (1)	874 (1)			136 (1)	USF&WS. 1993
1994	59+\-6(3)	56+\-9(12)	1281+\-143(7)	72+\-13(11)	497+\-370(12)	398+\-215(4)	162+\-62(11)	162+\-45(12)	M&M, 1994
Post-runoff Flows (mid-July through mid-November)									
1972	180 (1)		2000 (1)	140 (1)	260 (1)		270+\-110 (1)	320 (1)	M&W,74
1986		73+\-14(5)	1449+\-108(5)	97+\-28(5)	120+\-17(5)	861+\-170(5)	147+\-14(5)	125+\-22(5)	M&M, 1986
1993				128+\-1(2)	1190+\-14(2)			384+\-95(4)	USGS, 1993
1993			1010 (1)	140 (1)	462 (1)			186 (1)	USF&WS, 1993
1994	288+\-1(3)	98+\-31(7)	1604+\-217(9)	178+\-60(10)	1120+\-421(10)	962 (1)	373+\-103(8)	342+\-97(9)	M&M, 1994

Appendix Table 6.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF COPPER FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)
TREC = total recoverable; DM = dissolved metal; TM = total metal

YEAR DATA COLLECTED	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TM-1986							<2 (3)	10+\-14(3)	M&M,1986
TREC-1992		15.7 (1)		25 (1)			538+\-98(2)	256+\-25(2)	Stern,1992
TREC-1993								106 (1)	Stern,1993
TREC-1993				<20 (1)	2100 (1)			310 (1)	EPA,1993
DM-1993				<20 (1)	2000 (1)			190 (1)	EPA,1993
TREC-1994								107 (1)	Stern,1994
TREC-1994	7 (1)	5.2+\-2.6(2)	142+\-116(2)	17.3+\-5.1(11)	1206+\-435(11)	34 (1)	188+\-69(48)	117+\-36(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TM-1986		<2 (1)	320 (1)	2 (1)		<2 (1)	<2 (1)	<2 (1)	M&M,1986
TREC-1983								140 (1)	Stern,1993
TREC-1993				20.5+\-4.9(2)	665+\-332(2)			150+\-71(2)	USGS,1993
DM-1993				21+\-7.1(2)	395+\-368(2)			67+\-67(2)	USGS,1993
TREC-1993				32 (1)	918 (1)			231 (1)	USF&WS,1993
TREC-1994								122(1)	Stern,1994
TREC-1994		2.3+\-2.3(3)	276+\-67(3)	11.4+\-4.7(14)	650+\-295(14)	40+\-22(7)	128+\-40(17)	120+\-42(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TM-1986		13+\-21(8)	480+\-250(8)	<2 (8)	38+\-49(8)	6+\-2(8)	<2 (8)	<2 (8)	M&M,1986
TREC-1990		14+\-0(1)	220+\-0(1)		16900 (1)			1270 (1)	M&M,1990
TREC-1992		61+\-0(1)					1170 (1)	1000 (1)	Stern,1992
TREC-1993		1.7+\-0(1)		4.6 (1)				896 (1)	Stern,1993
TREC-1993				5.8+\-1.7(7)	5950+\-4920(4)			843+\-455(4)	USGS,1993
DM-1993				1.8+\-.4(6)	5800+\-5000(4)			568+\-396(4)	USGS,1993
TREC-1993			231+\-0(1)	6.3 (1)	13600 (1)			1220 (1)	USF&WS,1993
DM-1993			228+\-0(1)	5.6 (1)	13600 (1)			1130 (1)	USF&WS,1993
TREC-1994								107 (1)	Stern,1994
TREC-1994	3.8+\-1.9(3)	1.5+\-1.6(12)	210+\-50(7)	4.0+\-2(12)	5430+\-5780(12)	416+\-678(4)	828+\-550(11)	706+\-648(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	10 (1)		270 (1)	14 (1)	1300 (1)		200 (1)	17 (1)	M&W,1974
TM-1972							180 (1)	40 (1)	M&W,1974
TM-1986		17+\-24(3)	450+\-110(3)	<2 (3)	83+\-41(3)	17+\-2(3)	<2 (3)	<2 (3)	M&M,1986
TREC-1987				10 (1)	2500 (1)	50 (1)	150 (1)		Kirkham,1989
TREC-1992		8.2+\-0(10)					1015 (1)	886 (1)	Stern,1992
TREC-1993		4.7+\-1(2)		119 (1)				236+\-98(2)	Stern,1993
TREC-1993				9+\-1.4(2)	2350+\-354(2)			490+\-442(3)	USGS,1993
DM-1993				5.5+\-3.5(2)	2250+\-212(2)			243+\-326(3)	USGS,1993
TREC-1993			281 (1)	9.4 (1)	2230 (1)			214 (1)	USF&W,1993
DM-1993			292 (1)	7.5 (1)	2080 (1)			124 (1)	USF&W,1993
TREC-1994		<.3+\-<(7)	253+\-80(9)	12.3+\-7(10)	12800+\-5100(10)	36 (1)	1690+\-539(8)	1410+\-502(9)	M&M,1994

Appendix Table 7.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF IRON FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN MG/L (+\- one standard deviation and (x) number of data points)

TREC = total recoverable; DM = dissolved metal; TM = total metal; M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1986							3.3+\-2.4(3)	0.9+\-.6(3)	M&M,1986
TREC-1992		5.4 (1)		5.8 (1)			3.0+\-1.5(2)	1.6+\-.2(2)	Stern,1992
TREC-1994								0.8 (1)	Stern,1994
TREC-1994	1.2 (1)	2.2+\-0.8(2)	21.9+\-2.1(2)	8.3+\-1.5(11)	3.1+\-1.1(11)	1.5 (1)	4.7+\-2(48)	2.4+\-1.1(50)	M&M.1994
Pre-runoff Flows (April through mid-May)									
TREC-1986		<1 (1)	118 (1)	<1 (1)	<1 (1)	<1 (1)	<1 (1)	<1 (1)	M&M,1986
TREC-1993								5.4 (1)	Stern,1993
TREC-1993				15+\-9.8(2)	4.8+\-.8(2)			6.6+\-2.3(2)	USGS,1993
DM-1993				3.5+\-2(2)	.006+\-.0007(2)			1.1+\-.9(2)	USGS,1993
TREC-1993				22 (1)	5.4+\-0(1)			8.0 (1)	USF&WS,1993
TREC-1994								3.2 (1)	Stern,1994
TREC-1994		1.5+\-.5(3)	83+\-49(3)	7.2+\-3.5(14)	4+\-2.8(14)	6.5+\-6.7(4)	5.4+\-3(17)	4.2+\-2(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1986		0.2+\-.5(8)	79+\-25(8)	0.9+\-1.3(7)	1.2+\-1.4(8)	6.0+\-5.6(8)	0.6+\-1.1(8)	0.5+\-.8(8)	M&M,1986
TREC-1992		1.2 (1)					5.8 (1)	5.8 (1)	Stern,1992
TREC-1993		0.9 (1)		1.7 (1)				6.3 (1)	Stern,1993
TREC-1993				4.0+\-2.2(7)	24+\-9(4)			8.4+\-6.2(4)	USGS,1993
DM-1993				0.6+\-.3(7)	11.9+\-8.4(4)			1.7+\-.8(4)	USGS,1993
TREC-1993	2.7 (1)		106 (1)	1.9 (1)	34.7 (1)			4.3 (1)	USF&WS,1993
DM-1993	1.9(1)		107 (1)	0.6 (1)	26.8 (1)			2.8 (1)	USF&WS,1993
TREC-1994								2.2 (1)	Stern,1994
TREC-1994	2.6+\-.8(3)	1.3+\-.9(12)	82.4+\-40(7)	2.1+\-1(11)	18+\-14(12)	6.5+\-5.5(4)	5.9+\-1.9(17)	5.0+\-1.7(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	1.2 (1)		170 (1)	0.6 (1)	0.3 (1)		3.2 (1)	0.02 (1)	M&W,1974
TM-1972							1.7 (1)	0.24 (1)	M&W,1974
TREC-1986		0.8+\-.8(2)	59+\-3.5(2)	0.8 (1)	1.9+\-1.9(2)	11.5+\-8(2)	2.6+\-2.5(2)	0.85+\-.85(2)	M&M,1986
TREC-1987				8 (1)	4.5 (1)		4.5 (1)		Kirkham,1989
TREC-1992		0.9 (1)					4.4 (1)	4.5 (1)	Stern,1992
TREC-1993		1.0+\-.2(2)		2.2 (1)				3.7+\-0.8(2)	Stern,1993
TREC-1993				4.7+\-1.1(2)	8.0+\-1.4(2)			28+\-42(3)	USGS,1993
DM-1993				1.5+\-.2(2)	3.0+\-.5(2)			0.6+\-.8(3)	USGS,1993
TREC-1993	20.4 (1)		174 (1)	5.9 (1)	5.3 (1)			4.8 (1)	USF&WS,1993
DM-1993	7.7 (1)		178 (1)	2.5 (1)	2.4 (1)			4.9 (1)	USF&WS,1993
TREC-1994	7.3+\-6.3(5)	0.9+\-0.4(7)	90.5+\-58(9)	6.8+\-4.4(10)	30.5+\-21(10)	0.3 (1)	15.9+\-18(8)	6.9+\-4.4(9)	M&M,1994

Appendix Table 8.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF MANGANESE FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)
TREC = total recoverable; DM = dissolved metal; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1992		370 (1)		580 (1)			760+\-41(2)	450+\-13(2)	Stern,1992
TREC-1993								270 (1)	Stern,1993
TREC-1994								240 (1)	Stern,1994
TREC-1994	290 (1)	230+\-17(2)	2500+\-1400(2)	530+\-180(11)	2600+\-400(11)	1600 (1)	640+\-98(48)	330+\-91(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TREC-1993								480 (1)	Stern,1993
TREC-1993				440+\-130(2)	1500+\-140(2)			520+\-85(2)	USGS,1993
DM-1993				420+\-160(2)	1400+\-210(2)			490+\-120(2)	USGS,1993
TREC-1993				500 (1)	1200 (1)			560 (1)	USF&WS,1993
TREC-1994								350 (1)	Stern,1994
TREC-1994		80+\-29(3)	1900+\-770(3)	220+\-100(14)	840+\-210(14)	620+\-190(7)	400+\-160(17)	320+\-110(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1992		57 (1)					590 (1)	550 (1)	Stern,1992
TREC-1993		34 (1)		62 (1)				400 (1)	Stern,1993
TREC-1993				130+\-29(7)	2000+\-1300(4)			560+\-180(4)	USGS,1993
DM-1993				92+\-35(7)	2400+\-990(4)			490+\-130(4)	USGS,1993
TREC-1993	240 (1)		2400 (1)	90 (1)	3500 (1)			420 (1)	USF&WS,1993
DM-1993	250 (1)		2500 (1)	92 (1)	3700 (1)			430 (1)	USF&WS,1993
TREC-1994								190 (1)	Stern,1994
TREC-1994	110+\-19(3)	54+\-33(12)	2100+\-520(7)	76+\-10(12)	1800+\-1200(12)	370+\-170(4)	360+\-110(11)	330+\-110(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
TREC-1987				500 (1)	3000 (1)	2000 (1)	300 (1)		Kirkham,1989
TREC-1992		44 (1)					440 (1)	370 (1)	Stern,1992
TREC-1993		110+\-67(2)		590 (1)				550+\-95(2)	Stern,1993
TREC-1993				220+\-28(2)	3400+\-280(2)			810+\-500(3)	USGS,1993
DM-1993				220+\-7(2)	3500+\-350(2)			670+\-250(3)	USGS,1993
TREC-1993	460 (1)		4500 (1)	380 (1)	3500 (1)			580 (1)	USF&WS,1993
DM-1993	500 (1)		4800 (1)	400 (1)	3700 (1)			640 (1)	USF&WS,1993
TREC-1994	370+\-240(2)	74+\-48(7)	3330+\-728(9)	248+\-122(10)	4580+\-776(10)	1700 (1)	1370+/-1370(8)	566+\-213(9)	M&M,1994

Appendix Table 9.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF NICKEL FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)

TREC = total recoverable; DM = dissolved metal; TM = total metal; M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1986							0.03+\-0.05(3)	<1 (3)	M&M,1986
TREC-1992		9+\-0(1)		11 (1)			14+\-0(2)	9.5+\-2.1(2)	Stern,1992
TREC-1993				11 (1)				9.5 (1)	Stern,1993
TREC-1993				20 (1)	140 (1)			20 (1)	EPA,1993
DM-1993				20 (1)	120 (1)			30 (1)	EPA,1993
TREC-1993								5.3 (1)	Stern,1994
TERC-1994	9.6 (1)	10.5+\-.9(2)	112+\-1.5(2)	11+\-4(11)	51.8+\-26(11)	4.2 (1)	11.5+\-5(48)	8.4+\-5.3(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TREC-1986		<1+\-0(1)	<1 (1)	<1 (1)	<1 (1)	<1 (1)	<1 (1)	<1 (1)	M&M,1986
TREC-1993								19 (1)	Stern,1993
TREC-1993				10 (1)	61 (1)			18 (1)	USGS,1993
DM-1993				9 (1)	60 (1)			18 (1)	USGS,1993
TREC-1993				<15 (1)	69 (1)			23 (1)	USF&WS,1993
TREC-1994								8.5 (1)	Stern,1994
TREC-1994		1.5+\-2.1(3)	72+\-20(3)	4.6+\-2.3(14)	13+\-3.4(14)	11+\-3.9(7)	6.8+\-1.8(17)	6.4+\-1.9(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1986		<1 (4)	0.1+\-.08(3)	<1+\-<(4)	<1 (4)	<1 (4)	<1 (4)	<1 (4)	M&M,1986
TREC-1992		<2.5 (1)					18 (1)	15 (1)	Stern,1992
TREC-1993		<1 (1)		2.3 (1)				11 (1)	Stern,1993
TREC-1993	<15 (1)			<15 (1)	122 (1)			<15 (1)	USF&WS,1993
DM-1993	<15 (1)			<15 (1)	129 (1)			<15 (1)	USF&WS,1993
TREC-1994								3.6 (1)	Stern,1994
TREC-1994	2.9+\-2.5(3)	1.8+\-2.2(12)	73+\-21(7)	1.7+\-2.6(11)	53+\-43(12)	9.3+\-7.1(4)	11.4+\-6(11)	8.7+\-5.0(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	8 (1)		100 (1)	3 (1)	50 (1)		150 (1)	13 (1)	M&W,1974
TM-1972								100 (1)	M&W,1974
TREC-1987				10 (1)	60 (1)		25 (1)		Kirkham,1989
TREC-1992		<3 (1)					15 (1)	12 (1)	Stern,1992
TREC-1993		3.6+\-.5(2)		17 (1)				13+\-.7(2)	Stern,1993
TREC-1993	<15 (1)		103 (1)	<15 (1)	35 (1)			<15 (1)	USF&WS,1993
DM-1993	<15 (1)		116 (1)	<15 (1)	53 (1)			<15 (1)	USF&WS,1993
TREC-1994	7.6+\-4(2)	2.6+\-2.2(7)	95+\-14(9)	4.5+\-4.1(10)	124+\-21(10)	9.5 (1)	31.7+\-20.2(8)	18.5+\-6.9(9)	M&M,1994

Appendix Table 10.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF LEAD FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)
TREC = total recoverable; DM = dissolved metal; TM = total metal; M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
TREC-1986							<4 (3)	<4 (3)	M&M,1986
TREC-1992		6 (1)		10 (1)			5+\-5(2)	3+\-3(2)	Stren,1992
TREC1993								21 (1)	Stern,1993
TREC1993				<2.5 (1)	12 (1)			3.5 (1)	EPA,1993
DM-1993				<2.5 (1)	<2.5 (1)			2.5 (1)	EPA,1993
TREC-1994								<3 (1)	Stern,1994
TREC-1994		38+\-38(2)	40+\-40(2)	13+\-21(11)	17+\-23(11)	<4 (1)	7.8+\-21(48)	8.5+\-20(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
TREC-1986		<4 (1)	<4 (1)	<4 (1)	<4 (1)	<4 (1)	<4 (1)	<4 (1)	M&M,1986
TREC-1993								15 (1)	Stern,1993
TREC-1993				1+\-1.4(2)	3+\-2.8(2)			2 (1)	USGS,1993
DM-1993				<1+\-<(2)	<1+\-<(2)			<1 (1)	USGS,1993
TREC-1993				1.7 (1)	4.5 (1)			1.7 (1)	USF&WS,1993
TREC-1994								<3 (1)	Stern,1994
TREC-1994		<4+\-<(3)	46+\-65(3)	1.7+\-3.9(14)	6.7+\-7(14)	7+\-9(7)	1.5+\-3.7(17)	3.2+\-12(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1986		<4+\-<(4)	<4+\-<(3)	<4+\-<(4)	<4+\-<(4)	<4+\-<(4)	<4+\-<(4)	<4+\-<(4)	M&M,1986
TREC-1992		<10 (1)					<10 (1)	<10 (1)	Stern,1992
TREC-1993		<2 (1)		<2 (1)				<2 (1)	Stern,1993
TREC-1993				2+\-2.8(7)	12+\-7.9(3)			4.3+\-3.9(4)	USGS,1993
DM-1993				<1+\-<(7)	4.3+\-5.7(4)			<1+\-<(4)	USGS,1993
TREC-1993	<1 (1)		5.2 (1)	<1 (1)	18 (1)			1.2 (1)	USF&WS,1993
DM-1993	<1 (1)		6.8 (1)	<1 (1)	13 (1)			2.8 (1)	USF&WS,1993
TREC-1994								<3 (1)	Stern,1994
TREC-1994	<4+\-<(3)	1.2+\-3.9(12)	6.3+\-6.8(7)	1+\-3.2(11)	5.6+\-7.5(12)	2.3+\-4(4)	0.2+\-.6(11)	0.8+\-1.2(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	6 (1)		1 (1)	1 (1)	2 (1)		4 (1)	2 (1)	M&W,1994
TM-1972							200 (1)	200 (1)	M&W,1994
TREC-1987				<50 (1)	70 (1)		<50 (1)		Kerkham,1987
TREC-1992		<3 (1)					<3 (1)	<3 (1)	Stern,1992
TREC-1993		<5 (2)		<2 (1)				<5 (2)	Stern,1993
TREC-1993				1+\-1.4(2)	5+\-4.2(2)			33+\-54(3)	USGS,1993
DM-1993				<1 (2)	<1 (2)			<1 (3)	USGS,1993
TREC-1993	<1.4 (1)		5.8 (1)	2.9 (1)	2.5 (1)			<1.4 (1)	USF&WS,1993
DM-1993	<1.4 (1)		5.8 (1)	<1.4 (1)	<1.4 (1)			<1.4 (1)	USF&WS,1993
TREC-1994	11+\-13(5)	<3 (3)	129+\-387(9)	3+\-8(10)	13.6+\-22(10)	<3 (1)	31+\-56(8)	6.8+\-11(9)	M&M,1994

Appendix Table 11.

A SUMMARY OF HISTORICAL MEANS OF pH VALUES FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN STANDARD UNITS (+\- one standard deviation and (x) number of data points)
M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA COLLECTED	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
1986		6.7 (1)	3.0 (1)	4.6 (1)	7.5 (1)		6.7+\-.6(4)	6.7+\-.3(5)	M&M, 1986
1994	4.1 (1)	4.6+\-.02(2)	2.92+\-.07(2)	3.7+\-.2(11)	6.1+\-.7(11)	4.3 (1)	5.0+\-.3(47)	6.2+\-.5(50)	M&M, 1994
Pre-runoff Flows (April through mid-May)									
1986		6.8 (1)	2.8 (1)	6.5 (1)	7.1 (1)	4.5+\-.4(4)	7.3+\-.3(10)	6.9+\-.3(4)	M&M, 1986
1993				4.2+\-.8(3)	7.4 (2)			6.4+\-.4(2)	USGS, 1993
1994		6.8+\-.1(3)	2.8+\-.02(3)	5.5+\-.9(14)	6.6+\-.2(14)	4.3+\-.2(7)	5.7+\-.6(17)	6.4+\-.3(25)	M&M, 1994
Runoff Flows (mid-May through mid-July)									
1986		6.7+\-.3(9)	2.8+\-.04(9)	6.4+\-.1(10)	7.0+\-.1(9)	4.8+\-.4(10)	7.3+\-.3(10)	7.1+\-.1(10)	M&M, 1986
1990		6.0 (1)	2.5 (1)		3.0 (1)			4.6 (1)	M&M, 1990
1993				6.4+\-.3(4)	4.5+\-.4(4)			5.9+\-.4(4)	USGS, 1993
1993			3.1 (1)	7.0 (1)	4.7 (1)			6.0 (1)	USF&WS, 1993
1994	5.8+\-.4(3)	6.9+\-.6(12)	2.8+\-.1(7)	6.8+\-.4(11)	4.4+\-.9(12)	4.6+\-.6(4)	5.5+\-.6(11)	6.0+\-.7(12)	M&M, 1994
Post-runoff Flows (mid-July through mid-November)									
1972	4.4 (1)		2.7 (1)	6.6 (1)	5.3 (1)		5.7+\-.5(2)	7.2	M&W,1974
1986		6.4+\-.1(5)	2.9+\-.03(5)	6.1+\-.6(5)	7.0+\-.2(5)	3.9+\-.2(5)	7.7+\-.05(5)	7.2+\-.1(5)	M&M, 1986
1993				5.6+\-.6(2)	4.8+\-?(2)			5.9+\-1(4)	USGS, 1993
1993			2.9 (1)	5.2 (1)	5.2 (1)			6.5 (1)	USF&WS, 1993
1994	3.6+\-.1(2)	7.4+\-0.3(4)	2.8+\-0.1(6)	4.6+\-0.2(7)	4.0+\-0.3(5)	4.2 (1)	4.7+\-0.1(5)	4.8+\-0.3(7)	M&M, 1994

Means are the mean of the pH values and not the pH of the mean Hydrogen ion concentration.

Appendix Table 12.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF SODIUM FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN MG/L (+\- one standard deviation and (x) number of data points).

DM = dissolved metals; M&M = Mueller & Mueller

YEAR DATA COLLECTED & TYPE	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE OF DATA
	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	
Wintertime Flows (mid-November through March)									
DM-1986							6.4+\-.8(3)	5.6+\-3(3)	M&M, 1986
DM-1994	3.1 (1)	2.9+\-.3(2)	3.3+\-.2(2)	3.8+\-.9(11)	203+\-219(11)	7.8 (1)	20.4+\-19.5(48)	14.5+\-.9(50)	M&M,1994
Pre-runoff Flows (April through mid-May)									
DM-1986		1.5 (1)	2.5 (1)	1.8 (1)	2 (1)	4 (1)	3 (1)	2.5 (1)	M&M,1986
DM-1993				2.1+\-.4(2)	63.5+\-25(2)			14.8+\-7(2)	USGS, 1993
DM-1994		1.6+\-.05(3)	1.8+\-.5(3)	2.1+\-.5(14)	7.2+\-3.6(14)	6+\-1(7)	5.5+\-2(17)	6.5+\-2.1(23)	M&M, 1994
Runoff Flows (mid-May through mid-July)									
DM-1986		1.3+\-.3(8)	2.3+\-.5(8)	1.4+\-.4(8)	1.6+\-.5(8)	5.9+\-2.3(8)	3.1+\-.6(8)	1.9+\-.4(8)	M&M,1986
DM-1993				1.4+\-.2(7)	23.9+\-17(4)			7+\-3(4)	USGS,1993
DM-1993			1.8 (1)	1.5 (1)	80.7 (1)			8.2 (1)	USF&WS,1993
DM-1994	1.0+\-.5(3)	1.0+\-.2(12)	1.8+\-.4(7)	1.1+\-.2(11)	17.8+\-19(12)	5.1+\-1.8(4)	4.7+\-2.9(11)	4.7+\-2.4(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1986		1.2+\-.1(3)	2.5+\-.3(3)	1.4+\-.4(3)	2.0+\-.4(3)	10+\-.8(3)	4.0\-.8(3)	1.9+\-.3(3)	M&M,1986
DM-1993				2.0+\-.2(2)	115+\-7(2)			26+\-9(3)	USGS,1993
DM-1993			2.4 (1)	2.8 (1)	68.7 (1)			12.6 (1)	USF&WS,1993
DM-1994	3.1+\-.3(5)	1.8+\-0.6(7)	3.6+\-2(9)	2.3+\-0.7(10)	62.2+\-73(10)	12.4 (1)	12.2+\-7(8)	14.2+\-6.3(9)	M&M,1994

Appendix Table 13.

A SUMMARY OF HISTORICAL MEAN CONCENTRATIONS OF ZINC FOR THE FLOW PERIODS GIVEN AT THE DESIGNATED STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES. CONCENTRATION GIVEN IN ug/l (+\- one standard deviation and (x) number of data points)
TREC = total recoverable; DM = dissolved metal; TM = total metal; M&W = Moran & Wertz; M&M = Mueller & Mueller

YEAR DATA	STATIONS ON THE ALAMOSA RIVER OR ITS TRIBUTARIES								SOURCE
COLLECTED & TYPE	Iron Creek	Ala R. @ SPB	Alum Creek	Ala R. above WF	W.F. @ bridge	Burnt Creek	Ala R. below Jas.	Ala R. above Ter	OF DATA
Wintertime Flows (mid-November through March)									
TREC-1986							20+\-16(3)	33+\-4(3)	M&M,1986
TREC-1992		60 (1)		89 (1)			219+\-62(2)	139+\-21(2)	Stern.1992
TREC-1993								140 (1)	Stern,1993
TREC-1993				100 (1)	1300 (1)			240 (1)	EPA,1993
DM-1993				110 (1)	1300 (1)			190 (1)	EPA,1993
TREC-1994								98 (1)	Stern,1994
TREC-1994	58 (1)	35+\-4(2)	908+\-28(2)	92+\-66(11)	728+\-207(11)	106 (1)	129+\-27(48)	95+\-13(50)	M&M-1994
Pre-runoff Flows (April through mid-May)									
TREC-1986		17 (1)	540 (1)	17 (1)	25 (1)	33 (1)	25 (1)	<2 (1)	M&M,1986
TREC-1993								98 (1)	Stern,1993
TREC-1993				75+\-21(2)	360+\-42(2)			8056+\-695(2)	USGS,1993
DM-1993				64+\-33(2)	205+\-35(2)			110+\-57(2)	USGS,1993
TREC-1994								97 (1)	Stern,1994
TREC-1994		13+\-3(3)	464+\-120(3)	35+\-19(14)	232+\-56(14)	70+\-27(7)	79+\-22(17)	72+\-21(23)	M&M,1994
Runoff Flows (mid-May through mid-July)									
TREC-1986		15+\-10(8)	714+\-335(8)	17+\-13(8)	25+\-14(8)	68+\-42(8)	6+\-11(8)	10+\-20(8)	M&M,1986
TREC-1990		3 (1)	660 (1)		5100 (1)			390 (1)	M&M,1990
TERC-1992		3 (1)					273 (1)	239 (1)	Stern,1992
TERC-1993		5.4 (1)		9.1 (1)				177 (1)	Stern,1993
TERC-1993				23+\-8(6)	1320+\-790(4)			248+\-57(4)	USGS,1993
DM-1993				11+\-4.8(7)	1310+\-840(4)			230+\-42(4)	USGS,1993
TERC-1993			924 (1)	16.6 (1)	2630 (1)			270 (1)	USF&WS,1993
DM-1993			1020 (1)	16.3 (1)	2870 (1)			290 (1)	USF&WS,1993
TERC-1994								46 (1)	Stern,1994
TERC-1994	16+\-1(3)	8.8+\-3.4(12)	471+\-78(7)	13.6+\-5.6(12)	890+\-681(12)	108+\-123(4)	186+\-103(11)	149+\-82(12)	M&M,1994
Post-runoff Flows (mid-July through mid-November)									
DM-1972	50 (1)		940 (1)	20 (1)	540 (1)		140 (1)	50 (1)	M&W.1974
TM-1974							100 (1)	70 (1)	M&W.1974
TREC-1986		19+\-14(3)	660+\-101(3)	21+\-10(3)	46+\-18(3)	137+\-17(3)	2+\-3(3)	<2 (3)	M&M-1986
TREC-1987				10 (1)	900 (1)	200 (1)	60 (1)		Kirkham,1989
TREC-1992		17 (1)					312 (1)	261 (1)	Stern,1992
TREC-1993		24+\-17(2)		248 (1)				138+\-22(2)	Stern,1993
TREC-1993				30 (2)	1040+\-226(2)			193+\-67(3)	USGS,1993
DM-1993				32+\-1.4(2)	1025+\-106(2)			167+\-46(3)	USGS,1993
TREC-1993			544 (1)	52 (1)	1040 (1)			165 (1)	USF&WS,1993
DM-1993			580 (1)	60 (1)	1110 (1)			221 (1)	USF&WS,1993
TREC-1994	41+\-4.6(5)	9+\-4(7)	721+\-114(9)	37+\-18(10)	2040+\-1060(10)	136 (1)	395+\-74(8)	310+\-64(9)	M&M,1994

EVENTS AND TRENDS MONITORING OF WATER QUALITY ON THE ALAMOSA RIVER AND SELECTED TRIBUTARIES: 1994

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ABSTRACT

The purpose of this study was to quanitify the variability that existed on the Alamosa River as a result of spring runoff, storm events, drainage from naturally mineralized areas and mining activities.

Monitoring of water quality was performed at twelve stations on the Alamosa River and its tributaries during the last six weeks of 1993 and the first ten months of 1994 for a total of twenty-seven parameters which included temperature, alkalinity or acidity, pH, specific conductance, sulfate, chloride, fluoride, sodium, calcium, iron, potassium, cobalt, strontium, lithium, cadmium, zinc, copper, lead, manganese, chromium, nickel, aluminum, silica, arsenic, molybdenum, silver, and flow. The sampling frequencies varied from 3 to 14 day intervals depending upon the flow conditions and the accessibility/inaccessibilityof the sampling sites. Wintertime sampling of sites in the upper canyon were at a frequency of 4-6 week intervals.

In general, waters draining from non-mineralized areas showed decreased total recoverable metal concentrations and increased pHs during spring runoff. Changes noted on the Alamosa River at the Stunner Pass Bridge site, for example, included decreased total recoverable zinc (39 to 5.9 ug/l), copper (5.4 to < 1 ug/l), manganese (244 to 24 ug/l), and dissolved sulfate (95 to l6 mg/l) and decreased specific conductance (167 to 67 umho/cm) and increased pH (4.6 to 7.6). All stated values given in parentheses above, as well as for Wightman Fork below, reflect changes that occurred between pre-runoff and runoff flow conditions.

Water draining from mineralized areas, in contrast, showed increased total recoverable metal concentrations and decreased pHs during spring runoff. Changes noted on Wightman Fork, for example, included increased total recoverable Mn (600 to 6000 ug/l), Cd (0.2 to 20 ug/l), Zn (150 to 4000 ug/l), iron (2 to 60 mg/l), Cu (3 to 20 mg/l), and Al (1 to 30 mg/l). These changes occurred at a time when the pH decreased from 7.7 to 3.3.

Alum Creek is a small tributary that drains a naturally mineralized area. Water quality parameters studied on this source indicated the following values and ranges obtained during the course of the study. Some of the values (marked with an asterisk) are associated with runoff from a rainstorm that occurred on 7/29/94: pH (2.66* - 2.99), specific conductance (1083 - 2090* umho/cm), acidity (465 - 1400 mg/l), Cd (2.4 - 6.7 ug/l), Zn (333 - 936 ug/l), Cu (150 - 433* ug/l), Al (16 - 83* mg/l), Mn (1063 - 4350 ug/l), Ni (48 - 124* ug/l), Fe (18 - 188* mg/l), Pb (<3 - 1161* ug/l), Cr (<2 - 22* ug/l), Sr (<6 - 564 ug/l), Li (17 - 39 ug/l), Si (13 - 39 mg/l), Na (0.9 - 8.4 mg/l), K (0.6* - 2.9 mg/l), Ca (0.5 - 8.8 mg/l), sulfate (352* - 1056 mg/l), F (0.6 - 1.3 mg/l), Co (17 - 323 ug/l), and Mo (<9 - 421* ug/l).

Data from Jasper Creek, a tributary that drains a partially mineralized area, showed the following range of values obtained during the course of the study for the stated parameters: pH (4.1 - 7.7), specific conductance (62-323 umho/cm), acidity (30-68 mg/l), Cd (<0.2-1 ug/l), Cu (<0.8-60 ug/l), Zn (4.8-49 ug/l), Al (357-10588 ug/l), Mn (17-857 ug/l), Ni (0.8-13.2 ug/l), Fe (208-21800 ug/l), Pb (<3-21 ug/l), Sr (<4-225 ug/l), Si (4-14 ug/l), Ca 1.5-22 mg/l), sulfate (33-157 mg/l), F (0.14-1.6 mg/l), and Co (<2-17.5 ug/l). Variability obtained was a function of the snowmelt elevation and source of runoff for storm events.

Downstream impacts, underlying causal factors, as well as data from other tributaries and the upper Alamosa River will be presented. Some data comparing dissolved with total recoverable metal values will also be presented.

METAL FLUXES ACROSS THE SEDIMENT-WATER INTERFACE IN TERRACE RESERVOIR, COLORADO

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Acidic and metal enriched drainage from the Summitville Mine flows into the Wightman Fork in the San Juan Mountains of Colorado. This stream and other tributaries draining mineralized areas then flow into the Alamosa River. Terrace Reservoir is located along the Alamosa River approximately 20 kilometers downstream of the confluence of the Wightman Fork and Alamosa River, and is a likely repository for metal enriched sediments carried by the Alamosa River.

This study is designed to assess whether the sediments of Terrace Reservoir are a significant sink or source for dissolved metals (e.g., Cu and Zn) and what geochemical processes may be controlling the mobility of these metals. Two methods are used to determine the flux of metals into or from the sediments. First, concentrations of dissolved elements in the water at the bottom of the reservoir and porewater from the upper 3 centimeters of sediment are used to calculate diffusive fluxes using Fick's First Law. And second, fluxes are directly determined from concentrations of dissolved metals in four samples collected at five hour intervals from a benthic flux chamber.

Fluxes were measured at three sites in the reservoir at monthly intervals between June and September 1994. Results from this study, in conjunction with the basic limnological characteristics (e.g., pH, dissolved oxygen, and nutrients) of the reservoir, dissolved metal concentrations in the water column, and sediment geochemistry, will be used to evaluate the significance of Terrace Reservoir as a secondary source of metals to the environment and provide information for the development of remediation plans for this area.

SEDIMENT-TRACE ELEMENT GEOCHEMISTRY OF TERRACE RESERVOIR

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During July and August 1994, surface and subsurface bed sediments were sampled in Terrace Reservoir to determine trace element concentrations, partitioning, and distribution patterns, and to attempt to relate the sediment chemistry to mining and mine processing activities at Summitville, Colorado. Surface-sampling sites were randomly selected based on a 5-second (about 150 m) square grid; 30 surface sediment samples were collected using a stainless steel Ekmann grab. Although the grab collected material from depths to 20 cm, the actual samples were taken from the upper 2 to 3 cm. Subsurface bed samples were obtained using a stainless steel plastic-lined gravity core and a vibrocoring system. Analyses of these samples are intended to establish a recent trace-element geochemical history of the reservoir, and as an aid in understanding the geochemical precesses ongoing in the sediment column. A total of four gravity cores (67 to 94 cm) and four vibrocores (46 to 137 cm) were collected.

Based on the surface bed sediment grab samples, the bottom of the reservoir was covered by a thin (3 to 5 cm thick), soupy, red-orange floc. Much of this material washed out of the sampler during collection. Based on sample color, it was inferred that this material contained substantial quantities of Fe oxide. The subsurface sediments were markedly more indurated. Color varied with depth in the sediment column; the material nearest the surface generally was light brown to tan, followed by a lighter grayish material having some thin black layers or inclusions. The majority of the sediments were in the silt/clay size (<63-µm) range; little or no sand-size (>63-µm) material was present.

Initial chemical analyses of the surface sediments, a mixture of indurated sediment and floc residue, indicate an enrichment in Cu, Pb, Zn, As, Hg, Fe, and Al relative to unaffected (background level) fine-grained sediments collected in a variety of environments throughout the U.S. The Cu concentrations are about 100 times, and the As and Hg concentrations are about 10 times higher than typical background levels (Table 1). The Zn, Pb, Fe, and Al concentrations also are elevated; however, enrichment factors are only on the order of 1.5 to 2.0 times background levels. On the other hand, the concentrations of Cr, Ni, Co, Ti, and Mn fall within the range of normal background concentrations (Table 1).

Table 1: Chemical Concentrations in Surface Sediments from Terrace Reservoir and in Background Samples from Around the U.S.

Element	Minimum	Maximum	Mean	Median	Mean Background and Range
Cu (mg/kg)	730	2300	1500	1500	20 (4-43)
Pb (mg/kg)	31	83	62	64	23 (9-47)
Zn (mg/kg)	100	440	185	150	88 (23-200)
Co (mg/kg)	7	58	23	15	17 (6-39)
Cr (mg/kg)	17	27	21	21	51 (20-90)
Ni (mg/kg)	8	28	13	11	25 (4-66)
As (mg/kg)	28	215	74	65	7.0 (1.5-15)
Sb (mg/kg)	1.1	3.0	2.0	2.0	0.6 (0.1-1.2)
Se (mg/kg)	0.9	1.4	1.1	1.1	0.4 (0.1-0.9)
Hg (mg/kg)	0.20	0.54	0.31	0.30	0.05 (0.02-0.13)
Fe (wt. %)	5.9	14.6	8.3	7.5	2.8 (1.1-6.1)
Mn (mg/kg)	310	2900	690	490	600 (200-1000)
Al (wt. %)	8.3	11.0	9.6	9.6	5.5 (2.1-8.1)
Ti (wt. %)	0.20	0.38	0.32	0.34	0.41 (0.19-0.66)

LIMNOLOGICAL CHARACTERISTICS OF TERRACE RESERVOIR, SOUTH-CENTRAL COLORADO, 1994

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ABSTRACT

Terrace Reservoir has received drainage of metal-enriched water from the Summitville Mine and from other mineralized areas within the Alamosa River Basin. A study was begun in May 1994, by the U.S. Geological Survey, in cooperation with the U.S. Environmental Protection Agency, to evaluate the effect of hydraulic residence times, thermal-stratification patterns, pH, and dissolved-oxygen concentrations on the transport and mobility of metals in the reservoir water column and bottom sediments.

Onsite profile measurements of water temperature, pH, dissolved oxygen, and specific conductance were made biweekly at seven reservoir sites between May 20th and August 1994 and once in late September. Additional reservoir profile measurements are planned for October 1994, November 1994, January 1995, February 1995, and March 1995. In addition to the profile measurements, the reservoir water column was sampled at multiple depths at three sites once in June, July, August, and September. An additional, sampling of the reservoir water column is planned for early Spring. The samples were analyzed for concentrations of suspended solids, major ions, nutrients, and metals. Concurrent with reservoir water-column sampling, two sediment cores were collected at the same three reservoir sites. The upper 5 centimeters of the sediment cores were subsequently subsampled at about 0.5 centimeter intervals; the pore water was then extruded from each interval, filtered, and analyzed for concentrations of metals. The remaining dewatered sediment samples also were analyzed for metals. In addition to the sediment cores, a benthic flux chamber was deployed to collect reservoir samples at the sediment-water interface over an 18-hour period.

Hydraulic residence times for Terrace Reservoir are shortest during the late spring when streamflows are largest due to snowmelt runoff. Preliminary data indicate the reservoir is thermally stratified from late spring through the summer, and underflow is prevalent during this period. During periods when underflow occurs, metal-enriched water entering the reservoir from the Alamosa River may be routed through the deeper parts of the reservoir. Depending on residence times, and the physical and chemical processes that occur in the reservoir, dissolved metals in the reservoir may precipitate and settle from the water column, and suspended metals entering the reservoir may settle from the water column.

The pH of the reservoir water generally has ranged between about 4.5 and 6.0. Preliminary data indicate the pH decreased between spring and summer of 1994 and that pH tended to decrease with increasing depth. Although the pH of the reservoir water is similar to the pH of the Alamosa River upstream from Terrace Reservoir, there is some indication that the pH in the reservoir might be decreasing as the result of physical and/or chemical processes that occur in the reservoir.

The reservoir is well oxygenated, dissolved-oxygen concentrations are larger than 6.0 milligrams per liter and the percent saturation of dissolved oxygen generally is greater than 80 percent. The percent saturation of dissolved oxygen is relatively constant throughout the water column indicating that either (1) decomposition within the water column may not be substantial, or (2) the rate of decomposition is less than the rate of reaeration. Large dissolved-oxygen concentrations throughout the reservoir water column probably affect the magnitude of metal flux from the reservoir sediments to the water column.

THE BIOGEOCHEMISTRY OF WETLANDS IN THE SAN LUIS VALLEY, COLORADO: THE EFFECTS OF ACID DRAINAGE FROM NATURAL AND MINE SOURCES

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ABSTRACT

The chemical composition of sediment, water, and rooted aquatic vegetation from wetlands in the San Luis Valley, Colorado is used to assess whether acidic, metal-bearing waters carried by the Alamosa River have influenced the biogeochemistry of wetlands near or within the Alamosa National Wildlife Refuge. Acid drainage from mineralized areas and mines, including the Summitville Mine, is characterized by low pH values, elevated concentrations of sulfate, Al, Fe, Mn, Co, Cu, Ni, and Zn in the water, and high concentrations of As, Cr, Cu, Pb, and Zn in the stream sediments. The behavior of two of these elements, Cu and Zn, are examined in the wetlands. Water in all of the studied wetlands has basic pH values and is very low in dissolved metal concentrations. Sediments and aquatic plants in wetlands receiving Alamosa River water have higher concentrations of Cu and Zn than wetlands receiving water from other sources. Accumulation rates of Cu and Zn in a wetland receiving Alamosa River water are between two and four times greater than in one receiving Rio Grande River water.

INTRODUCTION

The exposure of pyrite and other metal sulfides to air and water during open pit mining activities at Summitville, Colorado has resulted in the addition of acidic waters enriched in sulfate and metals into the Wightman Fork. This stream and other tributaries draining mineralized areas south and southeast of Summitville in the San Juan Mountains flow into the Alamosa River and downstream to the San Luis Valley. The U.S. Fish and Wildlife Service is concerned about the potential impact of this acid drainage on the productivity and stability of wetland ecosystems in the valley, particularly those located in the Alamosa National Wildlife Refuge. These wetland ecosystems provide sanctuary and food for migratory birds, including endangered species such as the whooping crane.

This work assesses whether natural and mine drainage is transported throughout the Alamosa River system and, if so, what influence it has on the biogeochemistry of wetlands near and within the Alamosa National Wildlife Refuge. Information about the biogeochemistry of these wetlands will be used by Refuge personnel to manage wildlife within this area.

METHODS

Sampling

In June 1993 bed sediment and water were collected from the Wightman Fork and nine locations along the Alamosa River (Fig. 1). Site 1 was located above the confluence of the Wightman Fork and Alamosa River. Site 2 was in the Wightman Fork. Jasper, Burnt, and Silver Creeks enter the Alamosa River between sites 4 and 5. Site 6 was just upstream of the Alamosa campground. Terrace Reservoir is located between sites 6 and 7. Water from the

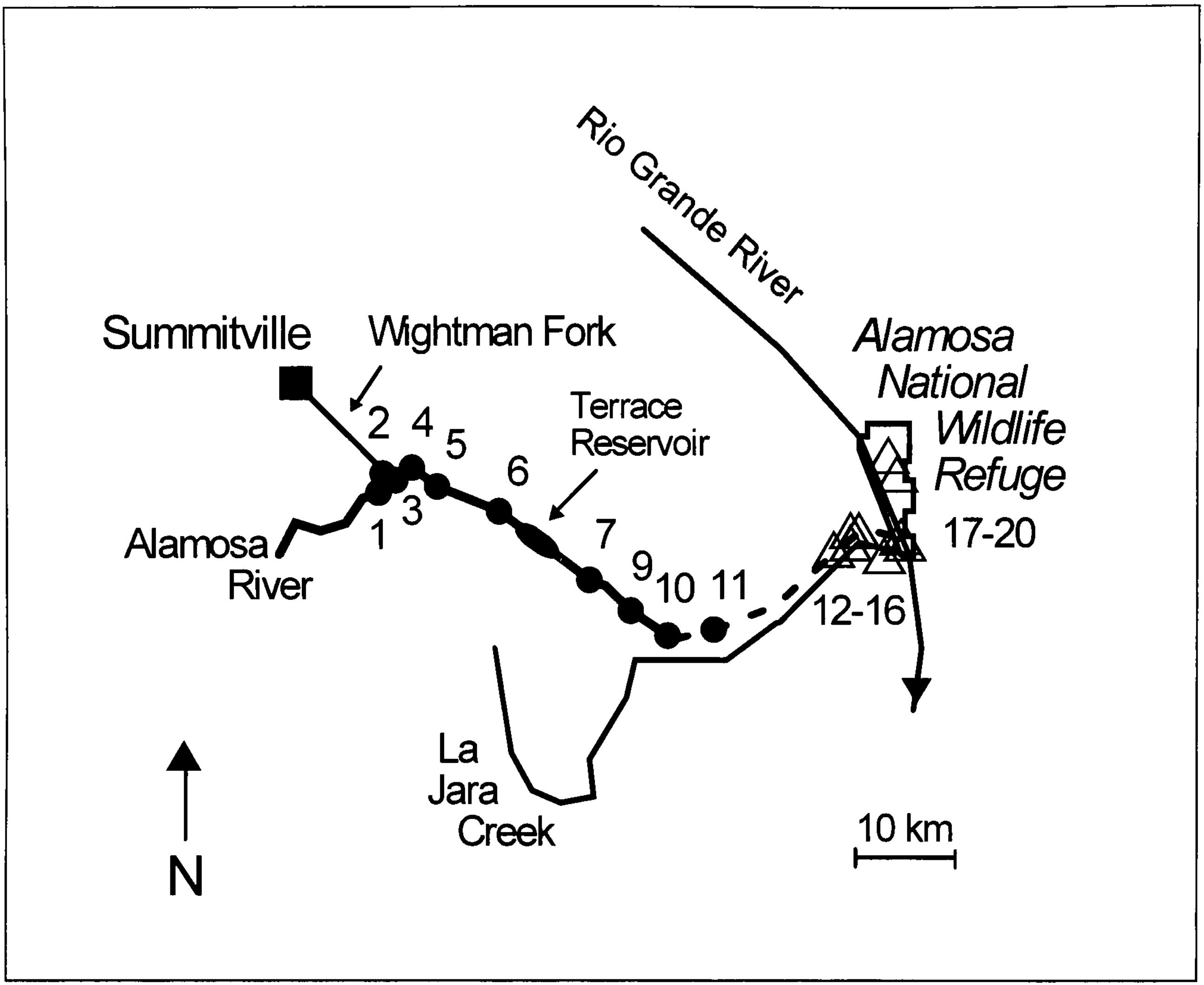

Figure 1. Sampling sites in Alamosa River (sites 1, 3-11) and Wightman Fork (site 2), and within wetlands in the San Luis Valley (sites 12-20).

Alamosa River begins to be diverted into canals below site 7. The Alamosa River does not flow through a defined channel between site 10 and the Alamosa National Wildlife Refuge. Instead, the flow is diffuse within this area.

Water, surface sediment or 30 cm long cores, and aquatic wetland plants also were collected from nine areas within wetlands just west of (sites 12-16) or within (sites 17-20) the Alamosa National Wildlife Refuge (Fig. 1). These wetlands receive surface water from either the Alamosa River, Rio Grande River, or a mixture of La Jara Creek and Alamosa River waters.

Water was collected in acid cleaned and well rinsed polyethylene bottles. Measurements of pH and conductivity as well as filtering of water through 0.22 μm Nuclepore filters were done in the field. A subsample of filtered water was taken for chloride and sulfate determinations and the remaining portion was acidified to pH 2 using ultra-clean, concentrated nitric acid.

Stream sediments and surface sediments in some wetlands were collected by scooping the upper two centimeters into polyethylene specimen containers. Wetland cores were collected by pushing a 10.2 cm diameter, acrylic butyrate core liner into the sediments. These cores were extruded into 2 or 5 cm sections and placed into polyethylene specimen containers.

The stems, leaves, and flowers of the wetland plant species, Persicaria amphibia L. (S. Gray) or commonly known as water smartweed, were collected and rinsed by hand.

Table 1. Chemical characteristics of water in the Wightman Fork (June 1993).

	Site 2a[a]	Site 2b[a]
pH	4.54	4.55
SO_4 (ppm)	380	390
Fe (ppm)[b]	17	17
Mn (ppb)[b]	2400	2400
Al (ppm)[b]	12	12
Co (ppb)[b]	97	92
Cu (ppb)[b]	8500	8600
Ni (ppb)[b]	100	95
Zn (ppb)[b]	1700	1700

[a] replicate samples
[b] dissolved (<0.22 μm)

Analytical

Measurements of pH were made with an Orion pH meter and glass electrode standardized daily with pH buffers of 4, 7, and 10. Conductivity was measured with an Orion conductivity meter and electrode that was standardized daily with solutions of 1000 and 10,000 μmhos/cm. Dissolved chloride concentrations were determined by silver nitrate titrations using an automated chloridometer (Grasshoff, 1976). Dissolved sulfate concentrations were determined using a barium sulfate precipitation method similar to the one presented in the work of Grasshoff (1976). Instead of gravimetrically measuring the precipitate, excess dissolved barium was measured by atomic absorption spectrophotometry.

River and wetland sediments were dried and ground. Plant samples were washed with distilled, deionized water, dried, and then ashed. Plant samples were composed of five to ten individual plants. Total concentrations of major, minor, and trace elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on acid digested sediment and plant samples (Briggs, 1990). Blanks, replicate samples, and reference materials were included in the analyses. The moisture content of selected wetland cores was determined by the difference between wet and dried (100°C) sediment weights. Sedimentation rates of selected wetland cores were determined by lead-210 (^{210}Pb) dating techniques (Flynn, 1968).

RESULTS AND DISCUSSION

Our approach for assessing the impact of acid drainage on the wetlands is to first examine the influence of the Wightman Fork on the Alamosa River and identify elements that are indicative of the mine drainage. We then evaluate the spatial extent of the indicator elements within the Alamosa River system. Finally, we compare the concentration of selected indicator elements in sediments and plants in wetlands that receive Alamosa River water with those that receive water from other sources as well as calculate accumulation rates of those metals in the wetland sediments.

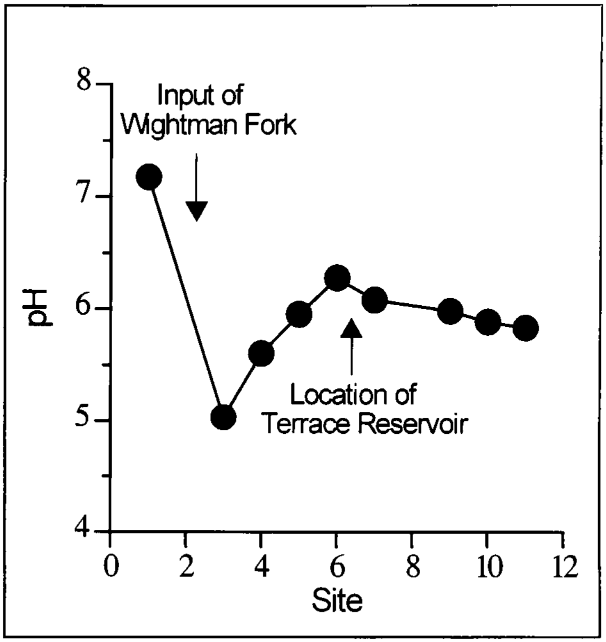

Figure 2. Values of pH in water from sites in the Alamosa River during June 1993.

Wightman Fork and Alamosa River

Water

The Wightman Fork (site 2) was characterized by low pH values, high sulfate concentrations, and metal enrichments during June 1993 (Table 1). These characteristics indicate that metal sulfide ores were being oxidized in areas with little buffering capacity. A comparison of the geochemistry of the Alamosa River above and below the confluence with the Wightman Fork indicates that drainage from the Summitville Mine significantly impacted the Alamosa River during June 1993 (Figs. 1-3). At this time the pH of the Alamosa River was neutral (7.18) above the confluence (site 1, Fig. 2), and decreased just below the confluence (site 3) due to input from the acidic waters of the Wightman Fork. Waters farther downstream of the confluence (sites 4-11) were also acidic. Sulfate and certain dissolved metals (e.g., Fe, Mn, Cu, and Zn) were enriched in the water immediately below (site 3) as compared to above (site

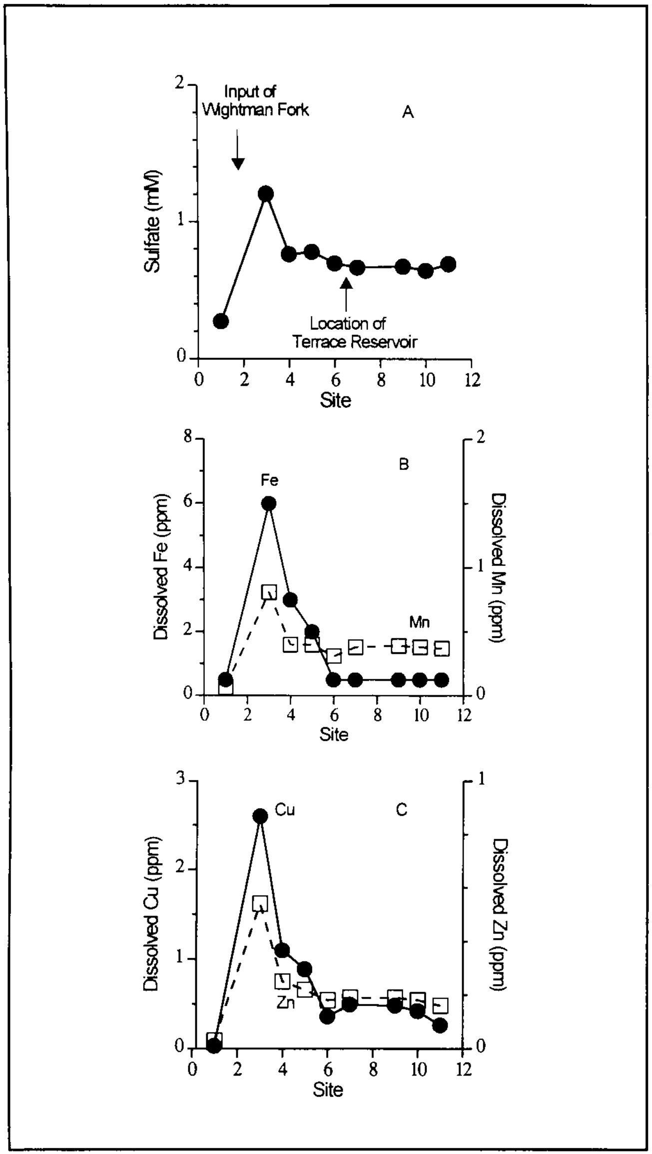

Figure 3. Dissolved concentrations of a) sulfate, b) Fe, Mn, c) Cu, and Zn in the Alamosa River during June 1993.

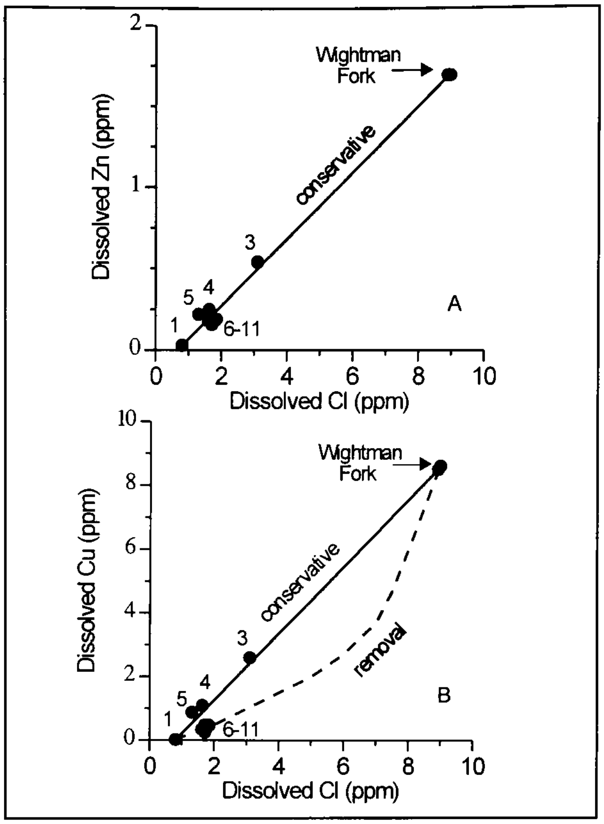

Figure 4. Dissolved concentrations of a) Zn and b) Cu versus dissolved chloride concentrations in samples from the Wightman Fork and Alamosa River.

1) the confluence (Fig. 3). The concentrations of these species decreased farther downstream of the confluence (Fig. 3). Concentrations of dissolved Al, Co, and Ni were measurable in the Wightman Fork (Table 1), but were below detection limits above and below the confluence. The chemical characteristics of the Wightman Fork and Alamosa River are variable with time and, therefore, these data only provide a snapshot of their conditions during our sampling time.

Decreases in sulfate and metal concentrations downstream can be due either to dilution or chemical reactions such as sorption or precipitation. The relative importance of these two processes can be evaluated by comparing dissolved concentrations of sulfate and metals to concentrations of a conservative element such as chloride (Boyle and others, 1974). Conservative elements are affected only by dilution and evaporation, and do not undergo significant chemical reactions during the timescales of these physical processes. If two solutions with different concentrations of a conservative element, such as chloride, are mixed in various ratios, then the concentration of the element in the mixtures should lie along a straight line that connects the two endmember element concentrations. If a dissolved concentration plot of a conservative element (e.g., chloride) versus another element is linear, then that other element is also conservative. If such a plot shows curvature downward, then dissolved concentrations of the given element in the mixtures have been influenced by chemical removal processes. A plot showing curvature upward indicates a source or production of the element during mixing.

We have chosen the Wightman Fork (site 2) and the Alamosa River upstream of the confluence (site 1)

Table 2. Metal concentrations in sediment from the Alamosa River (site 1) and Wightman Fork (site 2).

Element	Site 1[a]	Site 2a[b]	Site 2b[b]
Fe (%)	4.5	6.5	6.3
Mn (ppm)	660	600	580
As (ppm)	4.5	50	70
Co (ppm)	13	13	13
Cr (ppm)	7.5	13	15
Cu (ppm)	22	330	310
Ni (ppm)	6	7	8
Pb (ppm)	24	70	66
V (ppm)	110	110	110
Zn (ppm)	76	110	110

[a] sample located in Alamosa River upstream of confluence with Wightman Fork

[b] replicate samples located in Wightman Fork

as the two endmembers in our study as these are the primary solutions that are mixed downstream of the confluence. In reality, the Alamosa River system is not so simple as there are other tributaries (e.g., Jasper and Burnt Creeks) that enter the Alamosa River below the confluence.

A comparison of dissolved Zn and chloride concentrations indicates that decreases in Zn concentrations downstream of the confluence primarily are due to dilution (Fig. 4a); i.e., the points from sites downstream of the confluence tend to fall on a linear line that connects the points of the two endmembers. In fact, all points, except site 5, fall within 25% of their predicted concentrations based on two endmember mixing. Zn concentrations at site 5 are 65% higher than predicted from the mixing curve and, most likely, represent inputs of Zn from other tributaries such as Jasper or Burnt Creeks. Plots of sulfate and Mn versus chloride concentrations indicate that decreases in their concentrations downstream of the confluence are also due to dilution. Concentrations of dissolved Cu at the first three sites below the confluence decrease due to dilution (Fig. 4b). As with Zn, Cu concentrations at site 5 are elevated (65%) relative to that predicted from mixing of the two endmembers, again suggesting a source of metals between sites 4 and 5. In contrast to Zn, Cu concentrations farther downstream (sites 6-11) fall between 50 and 73% below the line that connects the two endmembers. These observations suggest that decreases in dissolved Cu concentrations at these sites include removal by some chemical process (Fig. 4b).

Stream sediment

Certain elements (e.g., Fe, As, Cr, Cu, Pb, and Zn) are enriched in stream sediments of the Wightman Fork relative to sediments in the Alamosa River above the confluence (site 1) (Table 2). The influence of the Wightman Fork on the sediment composition of the Alamosa River is assessed by examining the ratio of the metal content of the sediment at sites downstream of the confluence (sites 3-11) to the metal content in the Alamosa River at the site above the confluence (site 1). These ratios indicate that the enrichment of elements in sediments below the confluence is very significant for Cu (9-19 times) and moderately significant for As (1.8-3.4

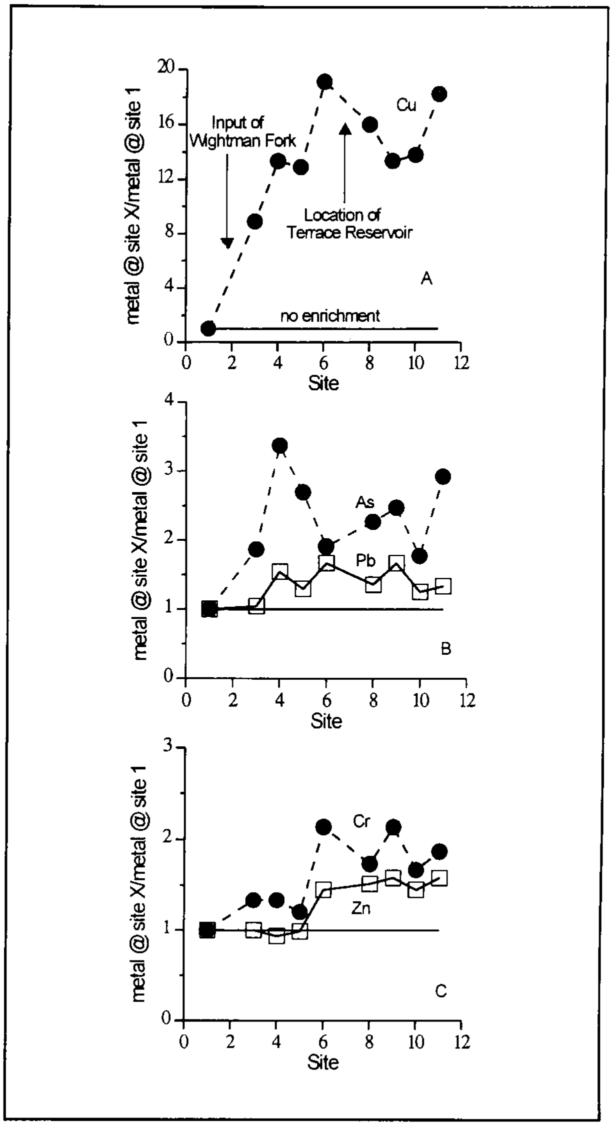

Figure 5. Ratios of a) Cu, b) As, Pb, c) Cr, and Zn concentrations in Alamosa River sediments to metal concentrations in sediments from above the confluence (site 1). Values > 1 indicate enrichment relative to site 1.

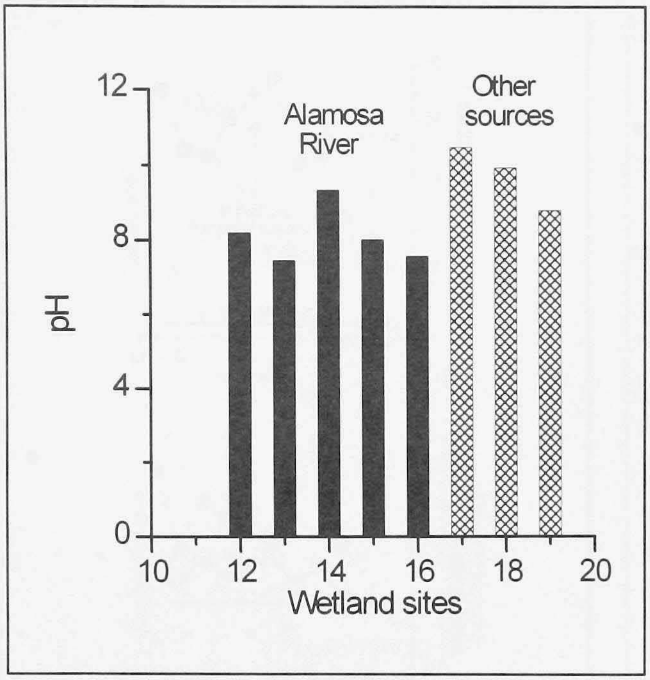

Figure 6. Values of pH in waters of wetlands in the San Luis Valley during June 1993.

times), Cr (1.2-2.1 times), Pb (1.3-1.7 times), and Zn (1-1.6 times) (Fig. 5). Cr and Zn, in contrast to As, Cu, and Pb, are not significantly enriched directly below the confluence but rather much farther downstream.

Several processes may be responsible for the enrichment of certain elements in the sediments of the Alamosa River downstream of the confluence. The presence of red-brown flocs in the river water and reddish stains on the riverbed rocks indicate the precipitation of iron oxyhydroxides. These solid phases have a strong affinity or sorption capacity for dissolved metals (Davis and Leckie, 1978). Thus, metal enrichments in sediments can occur by adsorption of dissolved metals onto or co-precipitation with iron oxyhydroxide phases. In addition, the iron oxide flocs with adsorbed metals can be transported downstream and settle out as the velocity of the river decreases. Little chemical removal of dissolved Zn below the confluence (Fig. 4a) and enrichments of Zn in the sediments farther downstream (Fig. 5b) suggest that transport in the solid phase may be important for this element.

Indicator Elements

The water and stream sediment data from the Wightman Fork and Alamosa River suggest that As, Cr, Cu, Pb, and Zn are the most likely indicators of drainage from mineralized areas in the Alamosa River basin of the San Juan Mountains. We will now focus on Cu and Zn as we examine the biogeochemistry of the wetlands in the San Luis Valley because 1) both elements have the potential of being transported to the wetlands in dissolved and particulate phases, 2) the chemical signal for Cu is very large (Figs. 3c and 5a), and 3) both Cu and Zn are of interest to wetland managers because of their potential toxicity to aquatic biota (Gough et al., 1979).

Wetlands

Water

The wetlands west and outside of the Alamosa National Wildlife Refuge primarily receive Alamosa River water (sites 12-15) or a combination of La Jara Creek and Alamosa River water (site 16). The wetlands within the Refuge tend to receive surface waters from the Rio Grande River (sites 17-20). Contributions from groundwater at sites within the Refuge are not known, but are possible.

The pH values of water in the wetlands in June 1993 were basic and much higher than water in the Alamosa River (Figs. 2 and 6). In addition, conductivity, Na, and chloride were elevated in the wetlands. Conductivity of the Alamosa River at sites 4 to 11 ranged from 138 to 158 µmhos/cm, Na concentrations were 5-8 ppm, and chloride concentrations ranged from 1.3-1.8 ppm. The wetlands that receive Alamosa River water had conductivities of 369 to 1930 µmhos/cm, Na concentrations of 45-190 ppm, and chloride concentrations of 2.6-49 ppm. Evaporation is most likely responsible for the pH and conductivity differences between the river and wetlands (Stumm and Morgan, 1981).

Dissolved Cu and Zn concentrations in the wetland waters were below detection (< 40 ppb). This observation is consistent with decreases in solubility and increases in sorption of these elements at high pH.

Sediment

Concentrations of Cu and Zn in the sediments of the wetlands indicate that those wetlands receiving surface water from the Alamosa River (sites 12-16) are enriched in these elements relative to wetlands that receive surface water from other sources (sites 17-19) (Fig. 7). These observations suggest that the metal enriched waters of the Alamosa River are contributing to the enrichment of certain metals in wetlands receiving that water.

The accumulation rates of Cu and Zn in two wetlands, one receiving Alamosa River water (site 16) and one receiving primarily Rio Grande River water (site 17), can be determined using the following

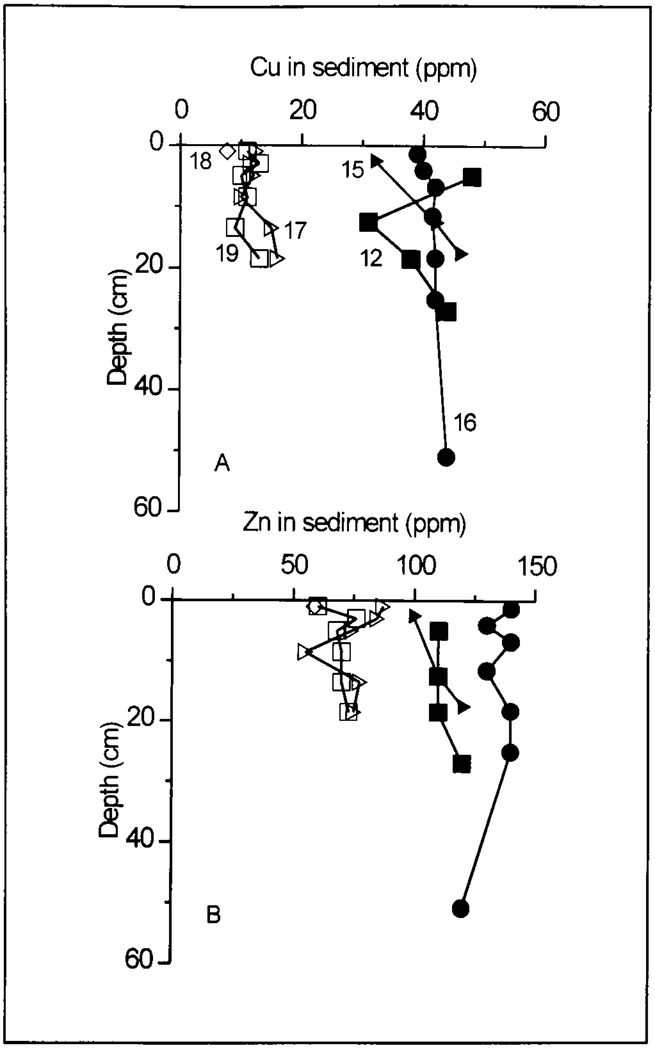

Figure 7. Profiles of a) Cu and b) Zn concentrations in sediments of wetlands in the San Luis Valley. Solid symbols denote sites that receive Alamosa River water. Open symbols denote sites that primarily receive Rio Grande River water.

equation:

$$R_{Me} = [Me]_{sed} * S * \rho * (1-X_W)$$

where:

R_{Me}= metal accumulation rate ($\mu g/cm^2/y$)

$[Me]_{sed}$ = sediment metal concentration (ppm or $\mu g/g$)

S = sedimentation rate (cm/y)

ρ = wet bulk density (g/cm^3)

X_W = weight fraction of water (dimensionless).

Sedimentation rates for the wetlands were determined from profiles of ^{210}Pb. The basic equation is:

$$A_t = A_0 * e^{-\lambda t}$$

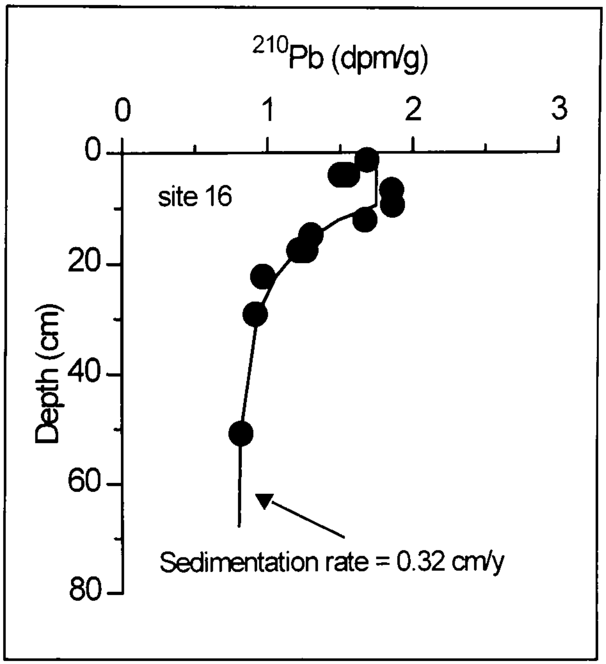

Figure 8. Profile of ^{210}Pb at wetland site 16 in the San Luis Valley. There is a mixed layer in the upper 10 cm and the solid line below this depth is the model fit for the sedimentation rate.

where:

A_t = activity of ^{210}Pb in sediment at time = t (dpm/g)

A_0 = activity of ^{210}Pb in sediment at time = 0 (dpm/g)

λ = decay constant for ^{210}Pb (1/y).

An exponential curve was fit to the data and the equation was solved for the condition when A_t = 1/2 * A_0, i.e., when one half life (i.e., 22.3 y for ^{210}Pb) has elapsed. The sedimentation rates were calculated using the depths for this condition and are equal to 0.32 and 0.35 cm/y, respectively, for sites 16 and 17. The data and model fit for site 16 are illustrated in figure 8.

Wet bulk densities were determined from the moisture contents of the cores and are between 1.43 to 1.66 g/cm^3 for the two sites.

The average accumulation rates of Cu and Zn during the past 30 years (i.e., approximately the upper 10 cm) in the wetland receiving Alamosa River water are 8(±1) and 25(±3) $\mu g/cm^2/y$, respectively. These values are significantly larger than the average accumulation rates of 2.0(±0.3) μg $Cu/cm^2/y$ and 14(±2) μg $Zn/cm^2/y$ in the wetland primarily receiving Rio Grande River water.

Aquatic wetland plants

The Cu and Zn contents of the aquatic wetland

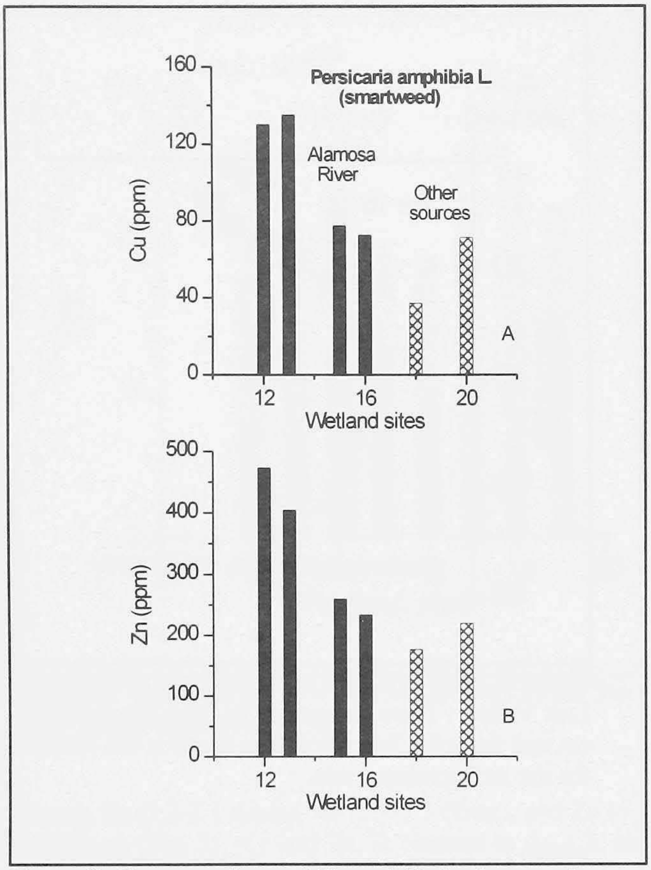

Figure 9. Concentrations of Cu and Zn in the aquatic wetland plant, Persicaria amphibia L. (S. Gray) or smartweed, in the San Luis Valley.

species, Persicaria amphibia L. (S. Gray) or smartweed, tend to be higher in wetlands that receive Alamosa River water (sites 12, 13, 15, and 16) than in those that do not receive water containing acid drainage from mineralized areas (sites 18 and 20) (Fig. 9). Although rooted aquatic macrophytes like smartweed can assimilate dissolved metals from the water through their leaves, most uptake is through their roots. Therefore, differences in the biogeochemistry of smartweed in the wetlands is assumed to reflect differences in the geochemistry of the sediments.

CONCLUSIONS

1.) Cu and Zn appear to be excellent tracers of acid drainage from natural and mine sources in the Alamosa River basin of the San Juan Mountains.

2.) Cu and Zn from acid drainage are transported throughout the Alamosa River system and into surrounding wetlands in the San Luis Valley.

3.) The chemical composition of sediments and rooted aquatic vegetation in wetlands in the San Luis Valley depends on the source of water. Wetlands receiving Alamosa River water are enriched in Cu and Zn compared to those receiving water from other sources.

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EVALUATION OF THE CHEMICAL, PHYSICAL AND BIOLOGICAL CONDITIONS OF THE SUMMITVILLE MINE SUPERFUND SITE, AND ALAMOSA RIVER AND ASSOCIATED TRIBUTARIES

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The Summitville Mine Superfund Site, including the abandoned cyanide heap-leach facilities, and associated mine workings and mine adit drainages, discharge to the upper Alamosa River by way of the Wightman Fork, some 5 miles upstream from its confluence with the Alamosa River. To date, environmental data have been collected in May and August 1991, April, July and October 1993, and July and September 1994. Environmental data from all of these indicate what changes in water quality have occurred since 1992. Water column and sediment chemistry, flow estimates and toxicity test data, used in conjunction with other environmental data including in-stream biological data and physical habitat, determine what impact, if any, the Summitville Superfund Site is having on the aquatic life resources within the Alamosa River drainage.

The U.S. Environmental Protection Agency (EPA) is participating with other agencies, including the U.S. Fish and Wildlife Service (USFWS) and Colorado Department of Natural Resources and their representatives, in the collection of environmental data necessary to support the interim remedial investigation and record of decision for EPA's Superfund program at the Summitville Mine Superfund Site, Summitville, Colorado. The primary focus of this environmental sampling effort is on aquatic life resources of the Alamosa River, and associated tributaries and wetlands. The potential environmental risks to the aquatic life resources of the Alamosa River drainage will be incorporated into the Superfund Ecological Risk Assessment for the site.

The USFWS is concerned about the potential short- and long-term effects that the treated and untreated water may have on federal trust resources downstream from the Summitville Mine Superfund Site. EPA is providing the USFWS with an evaluation of the potential harm to aquatic resources and potential threat from bioaccumulation downstream from the site.

The State of Colorado's Division of Minerals and Geology and Division of Wildlife are conducting an aquatic life Use Attainability Analysis (UAA) of selected streams within the Alamosa River drainage in accordance with the requirements of the federal Clean Water Act and the Colorado Water Quality Standards. The purpose of the UAA is to assign the highest potential aquatic life use and corresponding ambient water quality criteria recommendations to Wightman Fork and the Alamosa River consistent with the requirements of the Clean Water Act. The UAA will consider and incorporate any additional sources of contamination not specifically associated with the Summitville Mine, but suspected of contributing significant "background" loadings of heavy metals to the Alamosa River. EPA will provide the State with the chemical, physical and biological data necessary to frame the basis for their recommendations.

HISTORIC FISHERIES RECORDS: ALAMOSA RIVER

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ABSTRACT

Interest in the historic fish distribution of the Alamosa River developed following operation of a heap leach cyanide extraction process in the basin in the late 1980s and subsequent disappearance of fish from the lower reaches of the river and Terrace Reservoir by 1990. In 1889 the Alamosa River was known as a trout stream that contained Rio Grande cutthroat (Oncorhynchus clarki virginalis). By 1985 the Rio Grande cutthroat had disappeared, although reproducing brook trout (Salvelinus fontinalis) were reported in a Alamosa River headwater reach. Although fish were absent in 1985 in the Alamosa River reach immediately upstream of Wightman Fork, fish were present in Terrace Reservoir, in an Alamosa River reach just upstream of the impoundment and on the floor of the San Luis Valley. The Colorado Division of Wildlife maintained a rainbow trout (Oncorhynchus mykiss) fishery in Terrace Reservoir by stocking fingerling fish that overwintered and grew to catchable size. Following closure of the Galactic Summitville operation in 1990, fish were absent in the mainstem Alamosa River from a point near the Alum Creek confluence through Terrace Reservoir to the floor of the San Luis Valley. Acidity and metal levels in the Alamosa River tributaries of Alum, Bitter, Jasper and the lower portions of Iron Creek and Wightman Fork alone and in combination, precluded fish survival in these tributaries and the mainstem Alamosa segment described in the previous sentence. Reproducing brook trout and low numbers of non-reproducing Snake River cutthroat (Oncorhynchus clarki sp) remained in some Alamosa River headwater reaches. Rio Grande cutthroat were present only in one Alamosa tributary, Rough Canyon Basin, the result of a fish stocking program. Warmwater fish species were present in an Alamosa River stream reach on the floor of the San Luis Valley near the mainstem Rio Grande. Unlike most Colorado mountain streams, much of the Alamosa River and many tributaries were devoid of fish.

INTRODUCTION

In 1986 Galactic Resources opened an open pit cyanide heap leach operation at Summitville, Colorado. Discharges from the facility increased the metal concentrations, principally copper, in Wightman Fork and the Alamosa River downstream of the confluence of the two waters. In June, 1990 a fish kill was confirmed by the Colorado Division of Wildlife (DOW) in a private pond supplied with irrigation water from the Alamosa River. Copper concentrations in the Alamosa River upstream of Terrace Reservoir were 1,270 ug/l on June 23, 1990, compared to a level of less than 30 ug/l in 1986 (Mueller, written commun., 1990). The rainbow trout (Oncorhynchus mykiss) 96-hour LC50 copper concentration was 52 ug/l (Davies and Goettle, 1976). A 96-hour LC50 is the level which will kill 50 percent of the test organisms in four days. A copper concentration of 1,270 ug/l would be acutely lethal to rainbow trout. DOW field collections on July 12, 1990, demonstrated that there were no fish in Terrace Reservoir. Terrace Reservoir had been stocked with fingerling rainbow trout in 21 of the 31 years between 1960 and 1990. These fish grew to catchable size over time and were harvested by anglers. To define the extent of environmental damage to the Alamosa River, it is necessary to describe the fish community of the Alamosa River Basin prior to the Galactic Summitville operation. Restoration objectives for the Alamosa River may be based on either reestablishing historic populations or developing other options.

HISTORIC RECORDS OF FISH POPULATIONS IN THE SAN LUIS VALLEY

Few records exist regarding the native fish populations of the Rio Grande Basin in Colorado (the San Luis Valley) prior to introduction of exotic species that started in the late 1800s. The earliest report available describing fisheries in

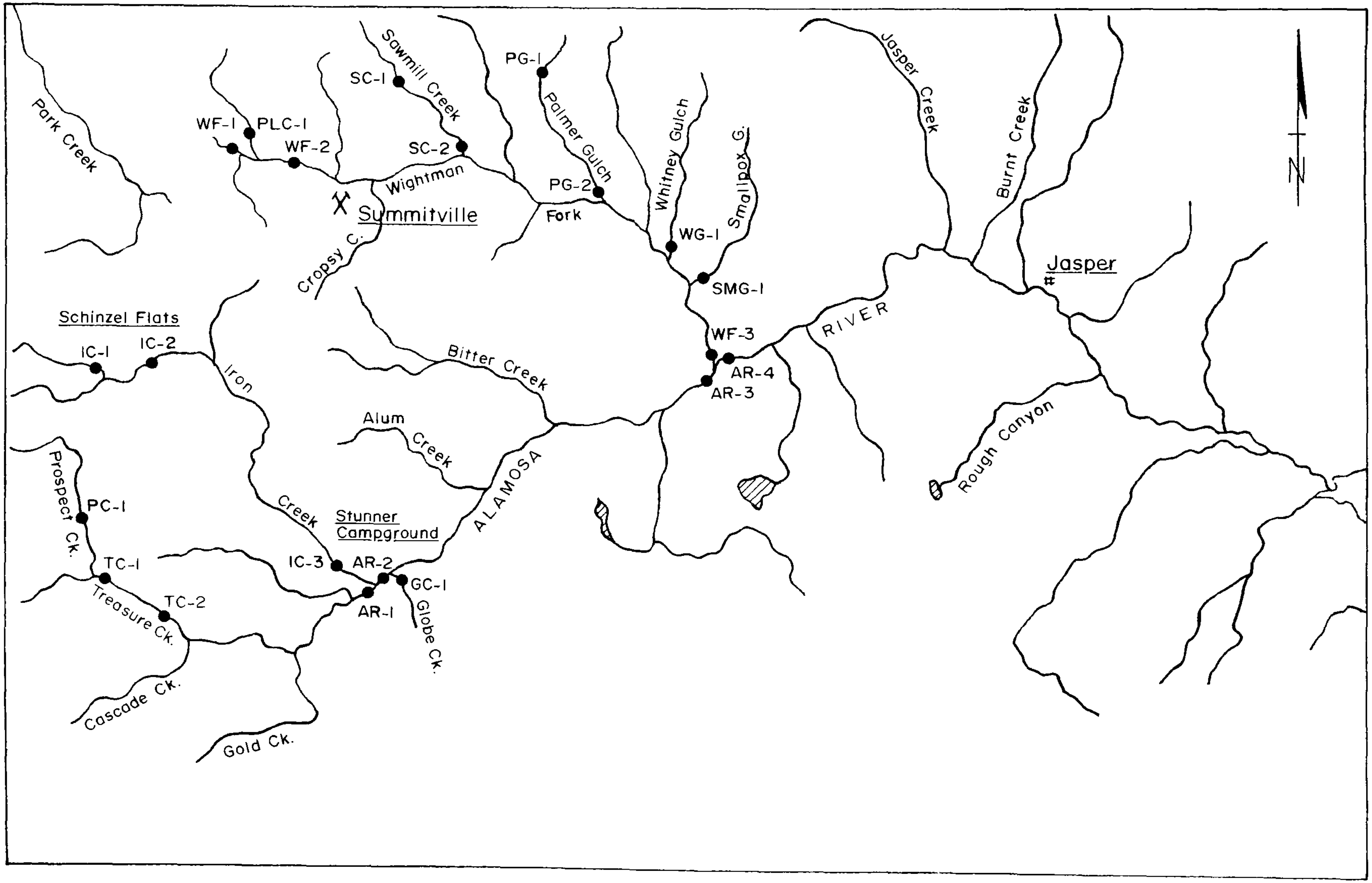

Figure 1. Alamosa River basin fish sampling sites.

the Rio Grande Basin dates to 1779 (Thomas, 1969). Fray Juan Agustin de Morfi, a priest who accompanied the governor of New Mexico, Don Juan Bautista de Anza, on a punitive expedition against the Comanche Indians in eastern Colorado, described four fish species in the Rio Grande near the confluence of this river with the Conejos River.

The first scientific study of fish distributions in the Colorado portion of the Rio Grande Basin was conducted in 1889 (Jordan 1891). Four species of fish were found at several sampling locations in the San Luis Valley (Table 1), two minnow species, one sucker and the Rio Grande cutthroat (Oncorhynchus clarki virginalis). The Rio Grande cutthroat is listed by the DOW as a "species of special concern." The Rio Grande sucker (Catostomus plebeius) may currently be extirpated from Colorado and is listed by Colorado as an endangered species. The only collections of Rio Grande sucker in the 1990s have been in Hot Creek, a tributary of the Conejos River. (Alves, oral commun., 1994)

The American eel (Anguilla rostrata) also was considered to be native to the Rio Grande (Ellis 1914). The American eel is unusual in that adults migrate to the Atlantic Ocean to spawn with individuals returning to freshwater to mature. Construction of dams has restricted the migration of this species, and natural eel populations may be extirpated in Colorado. Recent collections of adult eels in Colorado (Zuckerman 1985) may be the result of fish escaping from commercial hatcheries in the San Luis Valley.

Total number of species considered to be potentially native to the Rio Grande in Colorado ranged from four to ten (Table 1). Compared to river basins throughout the United States, this represents a depauperate fish community. Extirpation of native species, or significant loss of fish habitat in the basin, increases the difficulty of maintaining the natural aquatic ecosystems of the San Luis Valley.

HISTORIC RECORDS OF FISH POPULATIONS IN THE ALAMOSA RIVER

The Alamosa River is a smaller tributary of the Rio Grande and did not merit the attention of the good priest and naturalist, Fray Juan Agustin de Morfi. Jordan (1891) stated that the Alamosa River among other Rio Grande tributaries in Colorado were "all noted as trout streams, although the lower waters of all are consumed by irrigating ditches." The Rio Grande cutthroat was probably the only trout present in the Alamosa River at the close of the 19th century. Although non-native trout species had been introduced to Colorado by 1889, none were found in the Rio Grande Basin at that time (Jordan 1891).

Table 1. Fish species potentially native to Rio Grande basin.

Species	Jordan 1891	Ellis 1914	Zuckerman 1984
American eel Anguilla rostrata		X	X
Black bullhead Ictalurus melas			X
Green sunfish Lepomis cyanellus			X
Rio Grande cutthroat Oncorhynchus clarki virginalis	X	X	X
Rio Grande sucker Catostomus plebius	X	X	X
Rio Grande chub Gila pandora	X	X	X
Longnose dace Rhinichthys cataractae	X	X	X
Red shiner Notropis lutrensis			X
Fathead minnow Pimephales promelas			X
Bullhead minnow P. vigilax			X

Documentation of trout in the Alamosa River prior to mining in the late 19th and the 20th centuries indicated that naturally occurring metal concentrations did not prohibit colonization of the entire Alamosa River by fish. Sulfide ore bodies are found in various tributary drainages of the Alamosa River, including Wightman Fork, Iron, Alum, Bitter, Burnt and Jasper Creeks. When these ores are exposed to water and air, sulfuric acid is produced. Sulfuric acid mobilizes metals from the ore, which enters streams, such as the Wightman Fork. Jordan (1891) did note that headwater areas of the Animas River in southwest Colorado were devoid of fish due to "salts of iron." Such an observation was not made for the Alamosa River where the principal cause of fish mortality was "irrigation ditches." If naturally occurring metals had prohibited fish colonization from most areas of the Alamosa drainage, Jordan would probably have documented the problem.

ALAMOSA RIVER PRE-GALACTIC FISH POPULATIONS

The DOW samples fish populations throughout the state as a portion of wildlife management programs.

Terrace Reservoir was sampled by the DOW on one occasion prior to development of the Galactic Summitville operation. In July, 1975 four species of fish were collected in the reservoir (Table 2), including rainbow trout and the Rio Grande chub (Gila pandora), a DOW "species of special concern." The Rio Grande chub is native to the basin and is not intentionally stocked by the DOW. Prior to modern aquaculture sorting methods, some species were accidentally reared and stocked in small numbers by various hatchery systems. The presence of this chub in Terrace Reservoir is a reasonable indication that native, reproducing fish populations were found in this portion of the mainstem Alamosa River prior to the Galactic Summitville operation.

The rainbow trout collected from Terrace Reservoir in 1975 ranged in length from seven to ten inches. Rainbow trout are not native to any river in Colorado, including the Alamosa. The rainbow trout population in the reservoir was developed and maintained through a DOW stocking program using fingerlings generally ranging from two to four inches in length. DOW records indicate rainbow trout fingerlings were not stocked in Terrace Reservoir in 1973, 1974 or 1975 (Kroekel, written commun., 1993). It is probable that the two- to four-inch fingerlings stocked in 1972 would have grown larger than seven inches by July 1975. Angler interviews by the DOW demonstrate stocked rainbow overwintered in the reservoir at that time and often reached a length of 16 inches (Apker, oral commun., 1992).

Table 2. Alamosa River drainage fish sampling summary.

Station	Site	Year	Length feet	Width feet	Species	Number
Treasure Cr	TC1	1994	200	8	Snake R. cutthroat	1
Treasure Cr	TC2	1994	—	—	Snake R. cutthroat	8
Prospect Cr.	PC1	1994	600	8	Snake R. cutthroat	12
Iron Cr.	IC1	1994	178	2	—	0
	IC2	1994	200	8	Snake R. cutthroat	2
	IC3	1993	200	12	—	0
Globe Cr.	GC1	1994	83	3	—	0
Alamosa R. Above Iron Cr.	AR1	1993	376	25	Brook trout	5
					Snake R. cutthroat	5
Stunner Campground	AR2	1978	500	20	Brook trout	38
		1993	165	37	Brook trout	2
					Snake R. cutthroat	2
Above Wightman Fork	AR3	1978	500	10	—	0
		1993	250		—	0
Below Wightman Fork	AR4	1993	250	—	—	
Above Terrace Reservoir	AR5	1978	750	30	Fathead minnow	1
					Rainbow trout	51
					Rio Grande chub	2
Terrace Reservoir	TR1	1975	—	—	Rainbow trout	4
					Cutthroat trout	3
					White sucker	4
					Rio Grande chub	17
		1990	—	—	—	0
		1993	—	—	—	0
Alamosa River Below Terrace Reservoir	AR6	1993	250	—		0
US Highway 85	AR7	1984-85	250	—	Fathead minnow	?
					White sucker	?
					Carp	?
		1993	150	33	Fathead minnow	13
					White sucker	16
					Brook stickleback	2

It is possible that the seven-inch rainbow trout collected in 1975 was the result of some natural reproduction within or upstream of the reservoir.

Rainbow trout, cutthroat trout and fathead minnows (Pimephales promelas) were collected in the Alamosa River just upstream of Terrace Reservoir in 1978, (Table 2). The rainbow trout ranged in length from three to six inches in length. Rainbow trout stocked in Terrace Reservoir that year averaged 2.4 inches. It is possible the rainbow trout collected in 1978 in the Alamosa River upstream of Terrace were fish from the stocking program that year. The DOW does not stock fathead minnows, and there are no records of cutthroat trout being stocked in 1978. Both species may be an indication of some natural reproduction in Terrace Reservoir or upstream of the impoundment.

Fish were not present in the Alamosa River Reach between Wightman Fork and Bitter Creek in 1978, an indication of toxic metal concentrations in that stream reach. Thirty-eight brook trout (Salvelinus fontinalis) ranging from one to five inches were collected upstream of Bitter Creek at the Stunner campground in 1978. One fish was five inches in length whereas the rest ranged from one to three inches, an indication of successful reproduction in this stream reach in 1977. The brook trout, a fall spawning species, is not native to the Rio Grande and was stocked in the basin following the 1859 Colorado gold rush. There is no record of the DOW ever stocking brook trout in the Alamosa River upstream of Terrace Reservoir. DOW records indicate brook trout were planted in Terrace Reservoir once in 1953 (Kroekel, written commun., 1993). No conclusion can be reached as to the origin of the brook trout population in the Stunner campground portion of the Alamosa River.

In 1984 fathead minnows, carp (Cyprinus carpio L.) and white suckers were collected from the Alamosa River on the floor of the San Luis Valley where US highway 285 crosses the stream, at that point little more than an irrigation ditch. Of these species only the fathead may be native at this site. This fish community was maintained by natural reproduction.

ALAMOSA RIVER POST-GALACTIC FISH POPULATIONS

Wightman Fork

Brook trout were known to be in Wightman Fork upstream of Summitville prior to the Galactic operation, although there are no sampling data. Brook trout were present in 1987 in the Wightman Fork segment upstream of Summitville (Figure 1). Between 1987 and 1990, Galactic personnel placed waste material in an area drained by a tributary of Wightman Fork known as the South Fork of Wightman Fork. By 1993 most brook trout had disappeared from Wightman Fork between the South Fork of Wightman Fork and Summitville, where only one fish was collected in 1993 compared to 26 in 1987 (Table 2). By 1993 reproducing populations of brook trout remained only in Pipeline Creek and Wightman Fork upstream of the South Fork of Wightman Fork. Evidently elevated metal concentrations associated with the waste material placed in the South Fork were of sufficient magnitude that brook trout no longer maintain a reproducing population in Wightman Fork downstream of the South Fork of Wightman Fork. DOW sampling in 1987 demonstrated that no fish were in the Wightman Fork downstream of the Galactic Summitville operation (Table 3).

Tributaries to Wightman Fork downstream of Summitville were sampled in 1993 and 1994 (Woodling, 1993; Martin, 1994). No fish were found in Sawmill Creek, Palmer, Whitney and Smallpox Gulches. Metal concentrations were at, or less than, detection limits in all these Wightman Fork tributaries. Absence of fish in these small, steep waters was attributed to physical habitat and size rather than issues connected to metals and/or mining.

Alamosa River

Prospect and Treasure Creeks are two headwater streams of the Alamosa River. Metal concentrations in 1994 were at or near detection limits when low numbers of adult Snake River cutthroat trout were collected in both streams (Martin, 1994). Fingerling trout (two to four inches in length) were not collected. Presence of small fish would indicate these fish maintained a population through natural reproduction. The DOW stocked fingerling Snake River cutthroat in these waters in 1992 and 1993 but not 1994, and not in subsequent years (DOW, unpublished data, 1992). Trout populations in the uppermost reaches of these two headwater streams may be maintained by artificial stocking since natural reproduction does not appear to be viable.

The possible cause of the reproductive failure in Treasure and Prospect Creeks was not readily apparent. The physical habitat of both waters was typical of any high-elevation Colorado trout stream and thus not a cause of reproductive failure. Water quality may be involved. Alkalinity and hardness of these waters were low, 8 to 12 mg/l as $CaCO_3$ and 10 to 16 mg/l as $CaCO_3$, respectively (Martin, 1994). Metal toxicity is mitigated by hardness and alkalinity. As alkalinity and hardness increase, the toxicity of a specific metal concentration decreases (Mount, 1966, Goettl and others, 1971, Howarth and Sprague, 1978). At a hardness of 10 mg/l $CaCO_3$, the acute Colorado copper standard assumed to be protective of sensitive aquatic species is 2.0 ug/l, whereas at a hardness of 100 mg/l $CaCO_3$ the copper standard is 17.7 ug/l (WQCC, 1993). Younger, recently hatched fish are more susceptible to metals than older fish (Goettl and others, 1971 and Chapman, 1978). The alkalinity and hardness of these waters may decrease during spring snowmelt while metal concentrations increase, a phenomenon common in most Colorado mountain streams. Seasonal increases in metals concentrations and decreases in hardness and alkalinity associated with snowmelt could possibly be fairly minor and still induce mortality to recently hatched cutthroat trout, a spring spawning species. Either a spring increase in metals associated with the onset of spring snowmelt an as yet undiscovered factor, such as an acid pulse which overwhelms the low alkalinities, may be the cause of this apparent reproductive failure.

Iron Creek enters the Alamosa River upstream of Alum Creek. Trout were not present in 1994 in the headwater area of Iron Creek upstream of Schinzel Flats due to gradient and lack of suitable habitat, not metal contamination (Martin 1994). Snake River cutthroat trout were found in Iron Creek in the Schinzel Flat area despite a substrate stained orange by precipitating metals, a dissolved copper concentration of 5.4 ug/l and alkalinity of 6 mg/l $CaCO_3$ (Martin, 1994). DOW toxicity studies determined that 5.3 ug/l dissolved copper induced a 74% mortality to rainbow trout in four days at an alkalinity of 10 mg/l $CaCO_3$ (Davies, oral commun., 1994). Although there are no written records, Iron Creek was stocked by the DOW once in 1980 (Alves, oral commun., 1994). There was no evidence of natural reproduction at this Iron Creek site as only two adult fish, six and nine inches in length, were collected in a 200-foot reach. The fish collected in 1994 were probably not 14 years old, but were the result of some natural reproduction in past years. Metal concentrations and alkalinity of Iron Creek in the Schinzel Flats stream reach were such that fingerlings stocked in 1980 survived and had at least limited natural reproduction, but a viable population has not persisted. Fishing pressure may also have contributed to the decline of this population. No fish were found at the mouth of Iron Creek. The acid level (pH 3.35) at the mouth of Iron Creek was acutely toxic to trout (DOW, unpub. data, 1993).

A naturally reproducing brook trout population has been documented in the Alamosa River stream segment that extends from some area downstream of Gold Creek to some area upstream of Alum Creek (Martin, 1994, Woodling, 1993). Angler reports for several years have also reported brook trout in Gold, Cascade and Asiatic Creeks, Alamosa River headwater tributaries in the same region. These fish may well be maintained by natural reproduction because the DOW has not stocked brook trout in these stream segments. This was the only naturally reproducing fish population found in the Alamosa River upstream of Wightman Fork.

Tributaries other than Wightman Fork introduce metals to the Alamosa River. Alum and Bitter Creeks, which are upstream of the Wightman Fork, drain portions of the same hydrothermal modification area that is drained by Wightman Fork. These tributaries introduce acutely toxic concentrations of cadmium, copper and zinc into the Alamosa River (Von Guerrard and others, this volume, Walton-Day, and others, this volume). Alum and Bitter Creeks were acidic to the point of acute toxicity to trout (Woodling, 1993). Fish were not in Alum or Bitter Creeks due to a combination of acidity, metals, steep gradient and lack of deep water areas for fish to overwinter. If acidity and metal levels decreased in Alum or Bitter Creeks, fish populations would still be precluded due to habitat

Table 3. Wightman Fork drainage fish sampling summary.

Station	Site	Year	Length feet	Width feet	Species	Number
Wightman Fork Upstream of South Fork	WF1	1993	125	3	Brook trout	52
Wightman Fork Above Summitville	WF2	1987	500	4.9	Brook trout	26
					Snake R. cutthroat	1
		1993	250	3	Brook trout	1
Pipeline Creek Above Summitville	PIC1	1993	380	3	Brook trout	68
Wightman Fork at Mouth	WF3	1993	125	3	—	0
Sawmill Creek	SC1	1994	92	2	—	0
	SC2	1993	137	2	—	0
Palmer Gulch	PG1	1994	200	2	—	0
	PG2	1993	75	2	—	0
Whitney Gulch	WG1	1993	100	2	—	0
Smallpox Gulch	SMG1	1993	100	2	—	0

limitations. Jasper Creek is located downstream of Wightman Fork. Metal concentrations flowing into the Alamosa River from the Jasper Creek Drainages introduced toxic levels of metals to the Alamosa River following a 1993 thunderstorm (Von Guerrard and others, this volume).

In 1993, fish were not in the mainstem Alamosa River from some point between Alum Creek and Wightman Fork downstream to a location below Terrace Reservoir (Woodling, 1993). Fish had disappeared from Terrace Reservoir and the Alamosa River upstream of Terrace Reservoir. Absence of fish was attributable to elevated metals, principally copper and acid levels. The physical habitat of the Alamosa River in this reach is typical of many Colorado trout streams and would support a fishery. If acid and metal levels were reduced a fishery could be developed. The extent of the fishery would depend on the degree of metal and acid reduction.

Qualitative sampling demonstrated that warmwater species, including fathead minnow and white sucker, were present in the Alamosa River where US Highway 285 crosses the river on the floor of the San Luis Valley in 1993 (Woodling 1993). Dilution and sedimentation have ameliorated the additional metal loading to a level that fish could survive. No data are available to indicate if there are any chronic affects such as reduced growth, fecundity or reproduction.

Rio Grande cutthroat in the Alamosa River

Sampling in headwater streams of the Alamosa River did not result in collection of any Rio Grande cutthroat upstream of the Wightman Fork (Martin 1994). Presence of Rio Grande cutthroat upstream of Wightman Fork, Alum, Bitter and Iron Creeks would demonstrate that fish had colonized the entire length of the Alamosa River prior to inception of intensive mining activities in the 1800s. The current absence of this sub-species does not mean the Rio Grande cutthroat did not inhabit the headwater areas at one time. Stocking of other salmonids, such as brook trout, may have resulted in the elimination of the Rio Grande cutthroat, as documented in other areas of Colorado. The only Rio Grande cutthroat in the Alamosa are in Rough Canyon Basin, a tributary entering the mainstem Alamosa just upstream of Terrace Reservoir. These fish, which maintain a naturally reproducing population, are the result of a DOW Rio Grande cutthroat restoration program.

La Jara Creek

The fish community of lower La Jara Creek is dependent on Alamosa River water quality. La Jara Creek is the Rio Grande tributary draining the area south of the Alamosa River basin (Pendelton and Posey, this volume). As the Alamosa River enters the Rio Grande Valley floor near Capulin, Colorado, water destined for irrigation use is diverted to mainstem La Jara Creek. If sufficient metal loadings were introduced to La Jara Creek, toxicity to fish could result.

Brown trout (Salmo trutta), white sucker, and two native species, the Rio Grande chub and longnose dace (Rhinicthyes cataractae), were collected at La Jara Creek sites upstream of where diverted Alamosa River water enters La Jara Creek (Woodling, 1993). No fish were collected downstream of where Alamosa River water enters La Jara Creek at a site near Capulin, Colorado. Further downstream where US Highway 285 crosses La Jara Creek, white sucker, fathead minnow and brook stickleback were collected. If metal loadings to La Jara Creek were returned to pre-Galactic levels, fish would recolonize the portion of the stream that was devoid of fish in 1993.

Park Creek

Park Creek arises in the drainage to the west of Wightman Fork and flows north to the Rio Grande near South Fork, Colorado. Although not tributary to the Alamosa River, there is a possibility that metals from the Galactic Summitville operation could reach Park Creek in groundwater. A naturally reproducing population of brook trout was documented in Park Creek headwater reaches in 1994 (Martin, 1994). This stream has not been stocked since 1980 (DOW, unpub data, 1980-1994). The stream substrate of Park Creek was stained orange by deposited metals at the sites where the brook trout were collected and water column metal levels were at, or near, detection limits. The source of the metals that stained the stream substrate could not be determined (Martin, 1994).

SUMMARY

As of 1889 the Alamosa River was a trout stream in the mountain portion of the drainage. In 1993 reproducing trout populations were found in only three regions within the basin. None of these three sites were in waters downstream of the Galactic Summitville operation discharges to Wightman Fork. Stocked Snake River cutthroat survived in some Alamosa River headwater locations but did not appear to reproduce successfully. The mainstem Alamosa River did not contain any fish from Alum Creek to a point some miles downstream of Terrace Reservoir. Downstream of Terrace Reservoir on the floor of the San Luis Valley, various warmwater species including minnows and suckers maintained reproducing populations. The existing fish community of the Alamosa River is severely degraded in comparison to most Colorado drainages where cutthroat and brook trout in high-mountain elevations would be replaced by brown and rainbow trout in the lower mountains and warmwater species on the plains of the San Luis Valley. Elevated metals and acid levels from various sources including Iron, Alum, Bitter and Jasper Creeks as well as the Wightman Fork preclude fish colonization in the mainstem Alamosa River from Alum Creek to the floor of the San Luis Valley, including Terrace Reservoir. Completely eliminating discharge of metals and acid from the Wightman Fork would not result in recolonization in all stream reaches currently devoid of fish. Without decreasing the metal and acid loading from Wightman Fork, fish will not be able to recolonize any of the stream reaches currently devoid of fish.

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PRELIMINARY INTERPRETATION OF SPATIAL AND TEMPORAL TRENDS IN THE CHEMISTRY OF TREE RINGS DOWNSTREAM FROM THE SUMMITVILLE MINE

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ABSTRACT

The element concentration levels in tree rings (dendrochemistry) of cottonwood and aspen, stream sediment, and surface water were examined at 10 sites along the Wightman Fork and Alamosa River in southern Colorado. Tree ring chemistry is used to chart potential spatial (down gradient) and temporal (over about 30 years) trace metal trends in drainage waters. Acid and metals in waters draining the basin are from both naturally altered geologic terrane (Alamosa River and its tributaries above Wightman Fork) and the mining and processing activities at the Summitville Mine (which drain into Wightman Fork). Analyses of tree rings in this study were obtained using laser-ablation ICP-mass spectrometry. Preliminary results for Ba, Br, Cd, Cu, Mo, Na, P, Pb, and Zn are presented. Spatial and temporal trends are noted; however, cause and effect relations are hard to establish with these data. Results for Cu and Zn do not show a clear association with mine drainage and trends for Mo and P are complicated by valley soil conditions and agricultural practices. Although the analytical method proved especially suited to this type of study, the limited number of analyses at this time preclude a detailed interpretation of the processes that may be affecting those results.

INTRODUCTION

The Summitville Mine, located near the old mining town of Summitville in Rio Grande County, Colorado, operated between July, 1986 and December, 1992 as a large-tonnage open-pit heap-leach gold mine. During its six years of existence the trace metal levels in drainage water from the mine site were elevated over historical (pre-1986) levels (Moran and Wentz, 1974) due to input from three sources--heap leach water, seeps that occur throughout the mine workings, and an increase in the metal load of water coming from the old Reynolds Adit. Mine-drainage waters flow into Wightman Fork, a small tributary of the Alamosa River, which in turn flows east into the San Luis Valley. The increase in the trace metal burden of the Alamosa River watershed is of concern to farmers, land owners, and Federal and State wildlife agencies.

PURPOSE AND OBJECTIVES

This study seeks to chart potential spatial and temporal trace metal trends in drainage water chemistry through the analysis of metal levels in individual tree rings from narrow-leaf cottonwood (*Populus angustifolia* James) and, to a lesser extent, quaking aspen (*Populus tremuloides* Michx.). Tree ring analysis was achieved using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Because of the experimental nature of the analytical method used here (this may be the first time this technique has been applied to tree ring studies) and due to the limited number of analyses performed, these data are considered preliminary. As stated below, the use of tree ring chemistry in the characterization of contaminated sites is a viable technique and its use in this regional study has promise.

DENDROCHEMISTRY

Dendrochemistry is the study of element concentrations within tree rings in relation to environmental conditions when the rings formed. Metals, absorbed through the roots and transported to the aerial portions of a tree (such as the cellulose tissue of which rings are composed), may reflect changes in the bioavailability and loading of metals being transported by both surface and ground water. Thus, element analysis of increment cores collected from the trunks of trees sometimes can be used to document the spatial extent and local onset of contamination. For example, rings from trees successively distant from a contaminated landfill in eastern Maryland contained concentrations of Fe, Ni, and Cl that permitted estimates of their respective transport velocities in ground water (Vroblesky and Yanosky, 1990; Yanosky and Vroblesky, 1992). Yanosky and Carmichael (1993) used ring-element concentrations near an abandoned wood-preserving facility to estimate the extent to which ground-water contaminants had reached down gradient parts of the aquifer. A positive relation was detected between trace-element concentrations in wetland trees and contaminated sediments in a southeastern river basin (Hupp and others, 1993), and concentrations of Cl, Na, and Br within baldcypress trees were used to estimate the onset of saltwater encroachment within a North Carolina estuary (Yanosky and others, 1995).

Many elements detected within tree rings are cations bound exchangeably to negatively charged conducting and strengthening cells (Momoshima and Bondietti, 1990). Additionally, elements are within a system of vascular rays running from the inside to the outside of the trunk, thus crossing many consecutive rings. Rays remain living within a zone of rings (sapwood) just inside the bark but are non living within rings to the inside of the sapwood (heartwood). During the conversion of sapwood into heartwood, some elements within rays may be translocated into sapwood rings farther from the heartwood/sapwood interface. The result is larger concentrations of the translocated element in sapwood than in heartwood rings, even though the availability and uptake of the element may have remained constant over time. Conversely, elements in rays sometimes are translocated permanently into rings converting from sapwood to heartwood, resulting in larger concentrations within heartwood than sapwood (Vroblesky and others, 1992; Yanosky and others, 1995). Nutrient cations and some anions seemingly are more likely translocated than are trace metals. Although element translocation from the inner to outer sapwood prevents inferences concerning the timing of environmental alteration, translocation into the innermost sapwood during the heartwood-forming process sometimes can be used for this purpose (Yanosky and others, 1995).

Other biological factors complicating the interpretation of dendrochemical data include poor understanding of the uptake, transport, and storage of elements in relation to tree species, age, size, and ring architecture (Yanosky and Vroblesky, 1992). Similarly, element concentrations within a ring vary along the ring circumference, although McClenahen and others (1989) determined that variability was greater among trees than among different radii from the same tree. A recent review by Cutter and Guyette (1993) summarizes additional factors affecting the choice of tree species for dendrochemical analysis.

METHODS

Field

The field studies were conducted between June 24-29, 1993. Samples of aspen were collected from riparian, mixed coniferous forest communities along the Wightman Fork and the Alamosa River from just above the confluence to just below (Sites B, C, and D, fig. 1). Samples of narrowleaf cottonwood were collected from the same communities along the Alamosa River at Sites E, F, G, H, I, J, and K. These sites were spaced about 3 miles apart from just below the confluence of the Alamosa River with the Wightman Fork to a point down river about 30 miles (fig. 1). Aspen was collected at Sites B-D because Site E was the elevational uppermost extent of cottonwood. The last four sites (H, I, J, and K) were located within the San Luis Valley.

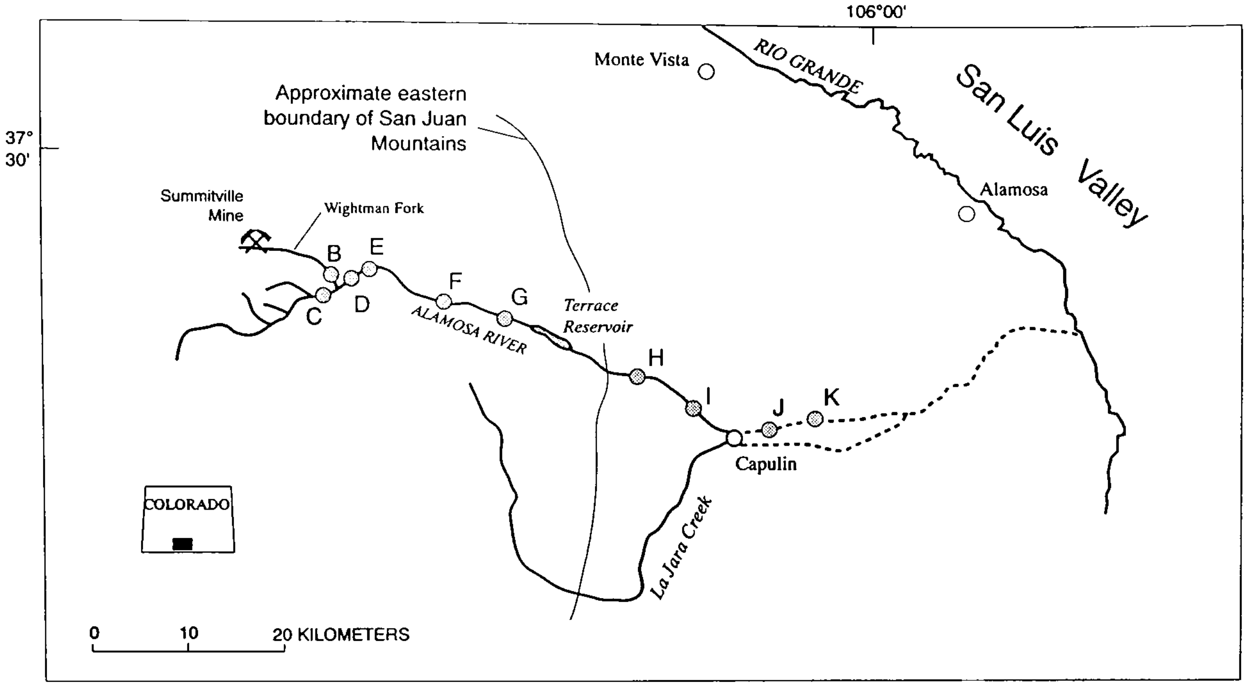

Figure 1. Map showing sampling sites for tree rings, sediments, and waters along the Alamosa River, southern Colorado. The dashed lines indicate that down stream of Capulin the Alamosa River and La Jara Creek are channelized but the subsurface hydrology of these streams is poorly understood.

Samples consisted of cores of xylem material collected at 1.5m above the ground. At each site cores were extracted from each of two adjacent mature trees. From one of the two trees a second core was extracted immediately parallel to the first one. Samples of river water and surface sediment were also collected at each of the sites using the methods outlined by Balistrieri, and others (this volume).

Laboratory

Tree rings were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The spectrometer was a VG Instruments PQII+ ICP MS equipped with a Spectron Laser Systems 500 mJ neodymium/yttrium-aluminum-garnet (Nd:YAG) laser operating at 1064 nm. The laser was operated in the free running mode, and produced holes in the tree cores approximately 300µm in diameter, that penetrated the entire core. Thus a constant volume of material was sampled from each site. This method has the capability of determining about 50 elements in plant material at the µg/g concentration level (Lichte, 1993; Lichte and others, 1994). Each annual ring was sampled in duplicate, and the results averaged. Most duplicate values were within 20%. However, small "cysts" within the tree material contain high amounts (>10x) of several metals especially Ca, Sr, Mg, and Ba. In those cases, the lower value was taken.

Table 1. Operating parameters for the ICP-MS instrument and associated laser conditions.

ICP	
Forward power	1250 watts
Gas flow rates	
Plasma	17 l/min.
Auxiliary	0.5 l/min.
Sample	
Argon	0.50 l/min.
Nitrogen	0.080 l/min.
Laser	
Flash voltage	1000 volts
Power	550 mJ
Mode of operation	free running
Repetition rate	7 - 20 Hz
Mass spectrometer	
Mass ranges	6-11, 13, 16-27, 29-38, 41-53, 55-210
Channels/amu	17
Dwell time/channel	40 µ sec.
Integration time	35 sec.

Experimental

Tree ring cores approximately 0.2 inches in diameter were examined under a microscope and annual rings were highlighted for easy identification during analysis. The core samples were then cut using a razor blade into 2.5- inch sections to fit into the laser sampling cell.

Laser energy was focused onto the in situ rings of interest using a high (15-20 Hz) laser repetition rate until charring began. The repetition rate was then lowered to 7 Hz for the remainder of the integration period. Standards and blanks were sampled at 7 Hz with a total of 140 laser shots.

Standardization was accomplished using a series of pressed pellets made of powdered cellulose which had been doped with solutions of the elements of interest. The calibration was verified for several elements by comparison to pellets made from NIST reference materials Apple Leaves, Pine needles, and Citrus Leaves. A high standard and blank were run with each tree core. All calculations were performed on a commercially available spreadsheet software. All integrated intensities were ratioed to carbon 13 in order to factor out the effect of variable tree-ring water content. Thus all values are reported on a 'dry weight basis'. It was assumed that all trees sampled in this study had a carbon concentration double that of the synthetic cellulose used for the calibration. This assumption was based on results from the NIST reference materials which more closely resembled tree material than the standard material.

The analysis of tree rings by LA-ICP-MS has several advantages over other analytical techniques applied to the element analysis of tree rings. Atomic emission spectrometry techniques (ICP and DCP) require extensive sample preparation and generally a large tissue mass which precludes the convenient analysis of individual rings. LA-ICP-MS permits the simultaneous analysis of up to 50 elements within individual rings or parts of rings, typically within 1-2 minutes/analysis with minimal prior sample preparation. Another method, proton-induced X-ray emission (PIXE), has the advantage of being essentially non-destructive and thus provides material for future analytical comparisons.

DISCUSSION

Dendrochemical Variability

Variability in the elemental concentrations of tree rings was partitioned among various sources including (1) analytical (see discussion under Experimental above), (2) between cores within a tree, (3) between trees at a site, and (4) among sites. Measurement of analytical and "natural" variability allows for the assessment of both temporal (among dated rings) and spatial (between sites across the watershed) element concentration trends.

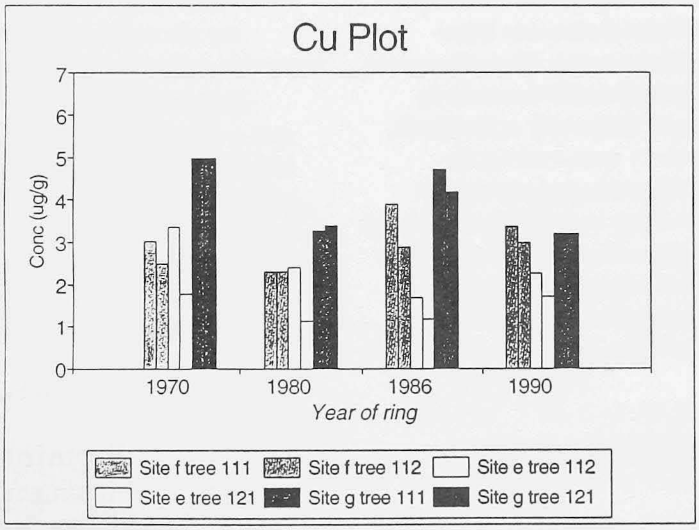

Figure 2. Variability of cottonwood tree-ring Cu analyses by LA-ICP-MS. The analyses for rings from Site F are for cores within a single tree (labeled samples 111 and 112) whereas those for Sites E (labeled 112 and 121) and G (labeled 111 and 121) are for rings from different trees.

Figure 2 shows comparisons in the concentration variability for Cu in tree-ring pairs. The plot gives analyses for rings from trees collected at three sites (Sites F, E, and G) and for four ages of rings (1970, 1980, 1986, and 1990).

Similar plots for Ba, Cd, Mg, and Zn were also examined and show similar trends, i.e., small variability between both separate cores from a single tree and for cores from separate trees. In general, for most elements, greater among-tree variability was observed for the older rings (1970 and 1980) rather than the more recent (younger) rings (1986 and 1990). The data for Zn indicate perhaps a somewhat greater among-tree variability.

In general, the data for these and other elements show that (a) element-concentration variability is small within cores collected from a tree (corresponds with the finding of McClenahen and others, 1989), (b) temporal and spatial trends for these and other elements should be interpretable, and (c) cottonwood may be a very good tree for use in dendrochemical studies.

Dendrochemical Trends

This report focuses on the results from the analysis of rings from four separate years and from six of the ten sites. These rings represent periods before modern mining began at Summitville (1970 and 1980), the year mining was initiated (1986), and the period during active mining (1990).

The translocation of elements between rings is a concern in the interpretation of dendrochemical trends (see discussion above). The small number of analyses per core in this study precludes definitive interpretation of element movement among rings; however, elements such as Br, Cl, Mg, Na, and P are mobile within the tree to some extent (Yanosky and others, 1995).

Balistrieri and others (this volume) detail the chemistry of sediment and water samples collected at the same time and at the same sites as the tree cores. Results of that study will not be repeated here; however, sediment and water chemistry trends downstream are used in the following interpretations.

COTTONWOOD TRENDS

Lead

Except for cottonwood rings collected at Site K (the site furthest from the mine) the uptake of Pb does not show either temporal or spatial trends (fig. 3). An order of magnitude increase is present at Site K over a thirty-year period. Several explanations are possible: either the amount of available Pb increased over time or the absolute amount of Pb did not change and the bioavailability of what was present did change. Baes and Ragsdale (1981) found that Pb was laterally mobile in selected southeastern hardwood tree species, i.e., Pb concentrations were greater in older than younger rings. The radial Pb concentration pattern that we observe (fig. 3) did not follow this pattern; however, our data covered only 30-40 years. The increase in Pb from older to younger rings remains unexplained.

Copper and Zinc

Copper and Zn are two of the major metals associated with area mineralization and are of great concern because of their toxicity to aquatic biota. High concentrations were found in the associated stream sediment and water samples (Balistrieri and others, this volume). Patterns in tree rings show that (a) they are most abundant in older tissue, (b) there are no obvious down-gradient trends, (c) there is a very high correlation between Cu and Zn in both their temporal and down gradient patterns, particularly within rings from the upper sites (E, F, and G; figs. 4 and 5). High concentrations of Cu in ground water are toxic to tree roots and uptake inhibition is a consideration.

Phosphorus

Both temporal and down-gradient trends are noted; P is translocated to younger tissue; P concentrations increase at sites I, J, and K (valley floor) and may be due to agricultural input or increases in its bioavailability (fig. 6).

Molybdenum

Molybdenum is associated with area mineralization and a down-gradient trend appears possible. The increased uptake of Mo at Site K is possibly due to oxic, saline soil conditions which are characteristic in large parts of the valley (fig. 7). The high values at Site E (near Wightman Fork) are unusual because this is an acidic environment (river water pH at this site was about 5.5) and the bioavailability of Mo at this site is not expected to be great. Except for Site E, there are no obvious temporal trends.

Bromine and Sodium

In this river basin environment, both are highly mobile. In addition, Br and Na appear to be laterally mobile within the trees (i.e., there is possibly some movement from younger to older rings). This mobility complicates down-gradient interpretations. The increased uptake of Br and Na at Site K is possibly due to oxic, saline soil conditions.

Cadmium

Although the precision of the analyses for Cd was good and variance between analyses and for cores at a site was small, the absolute amount of Cd measured in the rings was also small (<0.05 - 0.33 μg/g). Thus any patterns observed probably represent analytical "noise".

ASPEN TRENDS

The aspen and cottonwood data are not directly comparable because they are different species, may represent different ecological physiologies, and can occupy entirely different habitats. The aspen collected were from riparian communities, however, and occupied the same basic ecological niche as cottonwood. We note only general trends and do not compare absolute element concentrations.

Copper and Zinc

Cu and Zn are elements of environmental concern; no obvious impact from Wightman Fork because values above the confluence with the Alamosa River and in Wightman Fork were about the same; higher concentrations occur in older tissue.

Bromine

Both temporal and down-gradient trends are possible; impact from mine drainage may be observed; highly mobile element is associated with mineralization.

Barium

Both temporal and down-gradient trends are possible; impact from mine drainage may be observed.

ACKNOWLEDGMENTS

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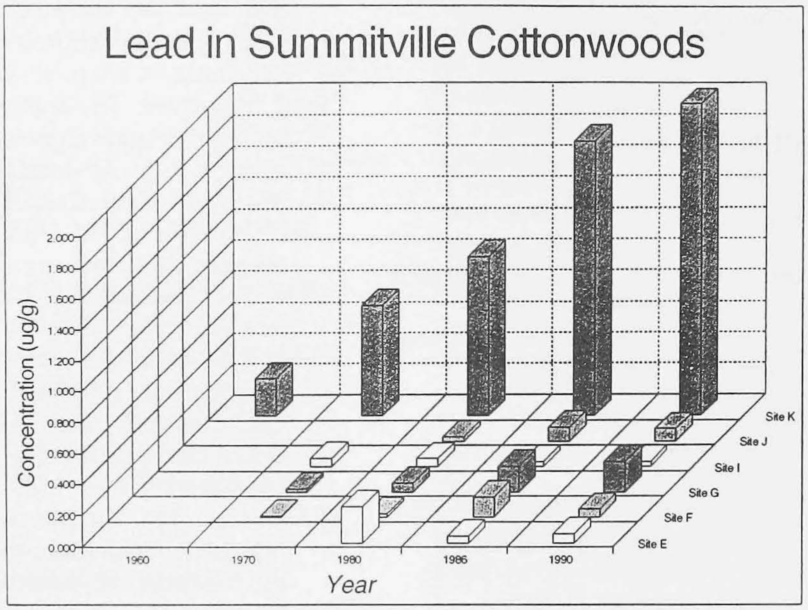

Figure 3. Lead in cottonwood tree rings (see fig. 1 for position of study sites).

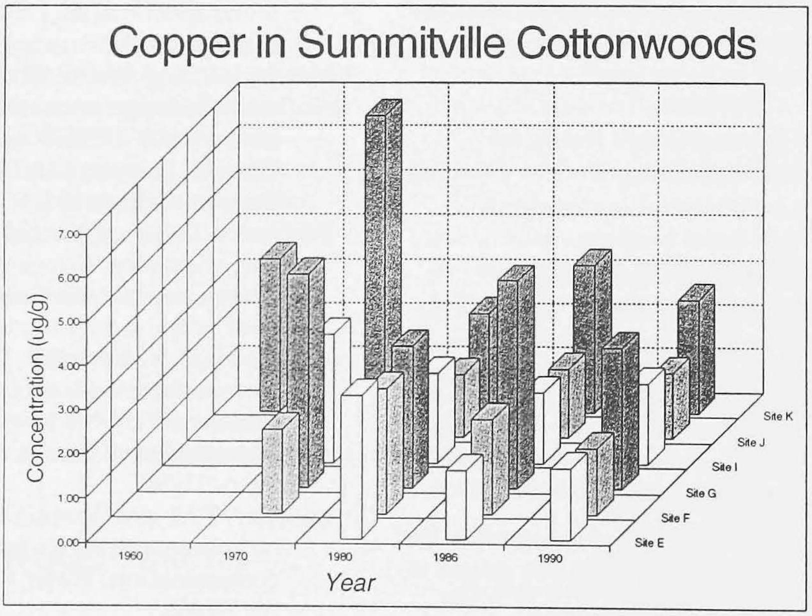

Figure 4. Copper in cottonwood tree rings (see fig. 1 for position of study sites).

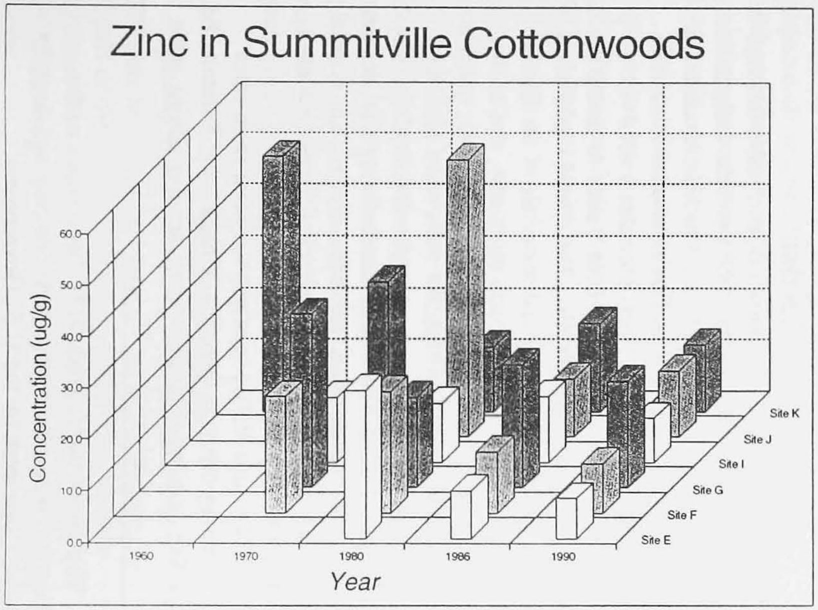

Figure 5. Zinc in cottonwood tree rings (see fig. 1 for position of study sites).

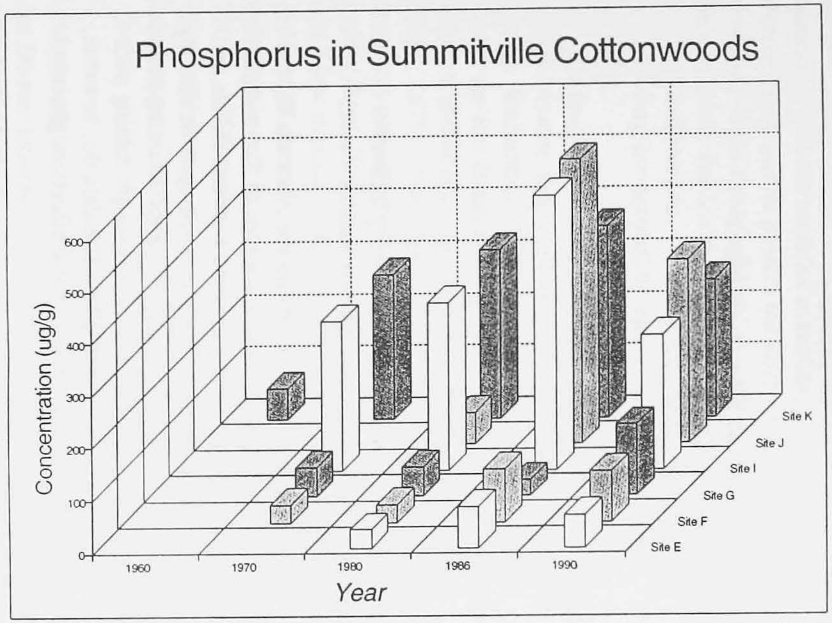

Figure 6. Phosphorus in cottonwood tree rings (see fig. 1 for position of study sites).

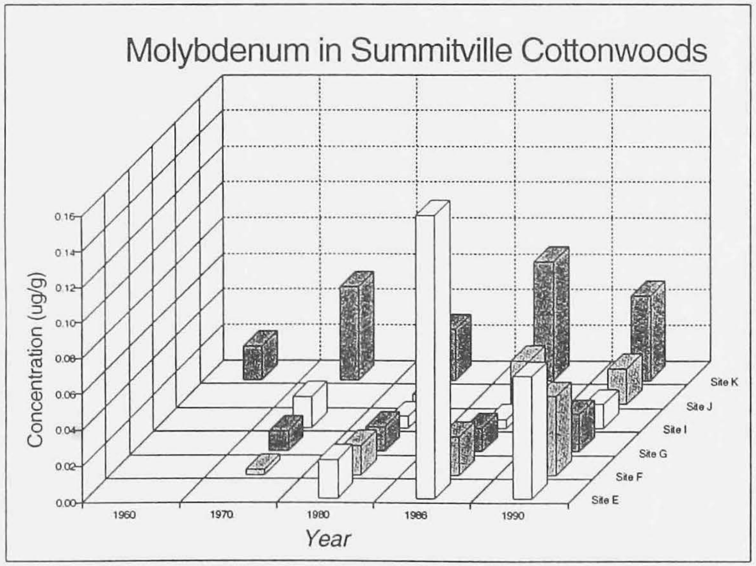

Figure 7. Molybdenum in cottonwood tree rings (see fig. 1 for position of study sites).

GEOCHEMICAL MAPPING OF SURFICIAL MATERIALS IN THE SAN LUIS VALLEY, COLORADO

by
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ABSTRACT

Samples of surficial materials, including soils, overbank sediments, and aeolian deposits were collected throughout the San Luis Valley in south-central Colorado to determine regional variations in chemical composition. Special emphasis was given to the alluvial fan of the Alamosa River in the southwest part of the valley because part of the watershed contains the Summitville mining district in the San Juan Mountains to the west. The samples were analyzed for total concentrations of 40 elements by inductively coupled plasma-atomic emission spectrometry (ICP). All samples were also analyzed for S and pH. Factor analysis, a multivariate statistical method, was used to aid in the interpretation of the analytical results based on 31 elements where data was complete. An optimum model of 7 factors describes 76 percent of the total variance in the data.

The element associations (compositions) that characterize each factor in descending order of element importance are as follows: Factor 1--Nd, Ce, La, Nb, Y, Th, and Yb; Factor 2--Fe, V, Ti, Co, Sc, and Ga; Factor 3--Mg, Ca, Sr, and S; Factor 4--Pb, and Zn; Factor 5--Cr, Ni, Co, and Sc; Factor 6--Na and K; Factor 7--As and Cu.

Maps of factor scores (a *score* is a multivariate statistical representation of each sample) show that the Alamosa River floodplain is characterized by both factors 4 and 7, factors indicative of material derived from weathering of sulfide mineralization. The probable sources for these sulfide assemblages on the Alamosa River floodplain are mineralized zones associated with the Summitville and/or Platoro calderas. In addition, other samples with probable mineralized origin were found on the Rio Grande floodplain (from the Creede area) and Kerber Creek (from the Bonanza caldera). Factor 3 characterizes evaporite deposits of alkaline-earth elements in the alkaline area of the north-central part of the valley. Factor 6 represents evaporites of Na and K, also located in the alkaline area and along the Rio Grande valley away from the river beyond the overbank sedimentation areas. Factors 2 and 5 are interpreted as being indicative of material derived from andesitic and basaltic rocks, respectively.

The presence of base metals on the Alamosa River fan results from several mineralized sources in the watershed. The present data do not differentiate between metals that might have been transported during prolonged weathering and erosional processes, during the historic mining period of the last 120 years, or during the open-pit mining period of the last decade at Summitville. The data do, however, indicate areas where studies of metal effects might best be directed.

Introduction[1]

Recent attention to the impact of acid-mine drainage in Colorado (Plumlee and others, 1993) and the designation of the Summitville mine site in the San Juan Mountains in southwest Colorado as a U.S. Environmental Protection Agency Superfund site in 1994, indicates a need for geochemical studies of the San Luis Valley to assess any potential impact on valley soils. The spatial distribution of elements in transported surficial materials of the San Luis Valley (including soils, overbank sediments, and aeolian deposits) reflects not only the composition of the materials but often their origin. In fact, the patterns of element dispersion on alluvial fans are a commonly used geochemical exploration tool to search for mineral deposits located within a watershed upstream. The extent of metal dispersion from known anthropogenic sources such as smelting or mining can also be determined.

The San Luis Valley receives sediment from three major mining districts, Bonanza, Creede, and Summitville, in the San Juan volcanic field, from smaller mining areas

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[1] The use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

in the Sangre de Cristo Mountains, and from unmined mineralized areas in the Alamosa River watershed. The purpose of this report is to define natural element associations in the surficial materials, to describe their distributions, and to predict the sources of elements where possible. Even though the valley extends into northern New Mexico, the study area consists only of the part that lies within Colorado. The San Luis Hills are excluded because they are uplifted blocks (horst) rather than alluvium.

The San Luis Valley has long been a locus of geologic studies because it is a component of the Rio Grande rift system (Siebenthal, 1910; Tweto, 1979). Studies have shown the Rio Grande rift zone to be one of high heat flow which is essential for geothermal resources (Reiter and others, 1975). Burroughs (1981) shows that a zone of high heat flow extends from central New Mexico into the San Luis Valley. The presence of several geothermal springs and a few thermal wells supports continuing interest in geothermal resource development in the valley. Investigations of groundwater resources (Siebenthal, 1910; Powell, 1958; Emery and others, 1971) and groundwater quality (Edelmann and Buckles, 1984) were inspired by the dependence of agriculture on groundwater.

Acknowledgments

We wish to thank U.S. Geological Survey chemists in the Denver laboratories for contributions that make this report possible. Christine McDougal directed sample flow through the analytical laboratories and Pete Theodarkos prepared all samples. Paul Briggs and David Fey performed analyses by inductively coupled plasma-atomic emission spectrometry (ICP). Clara Papp and Joe Curry analyzed S, and James Crock measured soil pH.

We also thank the many land owners who graciously permitted access to their land. The cooperation of the administration of the Alamosa and Monte Vista Wildlife Refuges helped to fill in significant areas.

STUDY AREA

The San Luis Valley is located in south-central Colorado between the Sangre de Cristo Mountians on the east and the San Juan Mountains on the west. The character and configuration of the valley are the product of regional structure, extensive nearby volcanism, and prolonged erosion and valley fill.

Geologic setting

The San Luis Valley is the northern extension of the San Luis basin, an intermontane structural depression that is part of the Rio Grande rift system, which extends from El Paso, Texas, to north of Leadville, Colorado (Tweto, 1979; Burroughs, 1981). The valley is bounded on the east by a steep fault scarp along the front of the Sangre de Cristo Mountains that represents about 7 km of structural relief (Davis and Keller, 1978) and on the west by the San Juan volcanic field, otherwise known as the San Juan Mountains.

The following description is summarized from Burroughs (1981). Structurally, the basin is a complex hinged graben tilting to the east. The southern part of the valley is interrupted by the San Luis Hills, a series of upthrown blocks (horst) that are both a physiographic barrier and a structural divide between the Alamosa Basin to the north and the Taos Plateau to the south (Thompson and Machette, 1989). The Alamosa Basin is underlain about mid valley by a north-trending fault block, the Alamosa horst. The Baca graben lies to the east between the horst and the Sangre de Cristo Mountains. The Monte Vista graben lies to the west between the horst and the San Juan Mountains. About 10,000 feet of valley fill covers the Monte Vista graben and tapers to zero depth toward the west; about 5400 feet of fill covers the Alamosa horst, and about 19,000 feet of fill covers the Baca graben.

The San Juan volcanic field borders the entire western side of the valley and covers about 25,000 km^2. The evolution of the field was described by Lipman and others, (1970). Steven and Lipman (1976) identified 15 calderas and postulated 3 more based on the complex stratigraphy of 18 major ash-flow sheets (Steven and others, 1974).

The Summitville and Platoro calderas in the southeastern part of the field contribute sediments to the San Luis Valley through the Alamosa and Conejos Rivers. Sediment from a proposed caldera (Karig, 1965) in the vicinity of the old mining camp of Bonanza enters the north end of the valley, primarily by way of Kerber Creek. Sediment from calderas of the central San Juan volcanic field--Bachelor, Creede, La Garita, and Mount Hope--is carried to the valley by the Rio Grande.

Other sources of volcanic sediment include the Los Mogotes shield volcano (Lipman, 1975), which borders the southwest side of the valley between La Jara Creek and the Conejos River. The Cat Creek stock, which stands at the head of Cat Creek, was interpreted by Lipman (1975) to be the center of a former large (25 km basal diameter) stratovolcano, the erosional remnants of which make up the mixture of lava flows and breccias on Green Ridge near Rock Creek. The Summer Coon volcano described by Lipman (1968, 1976), Zielinski and Lipman (1976), and Noblett and Loeffler (1987) lies just north of Del Norte. Summer Coon is an Oligocene stratovolcano eroded down to its base. Sediment from this volcano is carrried to the valley by both the Rio Grande and La Garita Creek.

Physiographic setting

The valley is an arid basin about 150 miles (240 km) long with a maximum width of 50 miles (80 km) and an average elevation of about 7700 feet (2350 m). The principal drainage is the Rio Grande, which enters the valley from the west and departs at the south end. Streams from the west side drain large watersheds and are long with broad, gently sloping alluvial fans. Streams from the east side of the valley emerge from short, steep canyons of the Sangre de Cristo Mountains and tend to have short alluvial fans. The northern end of the valley is defined by the convergence of the Sangre de Cristo Mountains and the Sawatch Range. The southern end is rather diffuse and was arbitrarily placed about 15 miles south of the New Mexico border by Siebenthal (1910) and about 60 miles south by Upson (1939). Upson divided the valley into 5 physiographic subdivisions, each with distinctive geologic and topographic characteristics: these included the Alamosa Basin, the Costilla Plains, the Culebra Reentrant, the San Luis Hills, and the Taos Plateau. Only the first two are included in the study area (see Figure 1).

The *Alamosa Basin* constitutes the major part of the study area. It is the flat, nearly featureless central part of the valley extending from Antonito in the southwest to the northern end of the valley. It is underlain by alluvium of coalescing fans that constitute the upper part of the Alamosa Formation (upper Pliocene and Pleistocene). The central part is a broad fan of the Rio Grande and is the source material for the Great Sand Dunes northeast of Alamosa (Johnson, 1967). An east-west hydrologic divide that lies just north of the Rio Grande directs drainage to the south into the Rio Grande. Drainage to the north of this divide is internal into the *Alkaline Area*, so named because the waters and soils are alkaline.

The *Costilla Plains* are located along the southeast side of the valley and extend from Sierra Blanca Peak southward into New Mexico. The area is composed of westward sloping alluvial fans that originate near the edge of the Culebra Range. The alluvium consists of fine, sandy, unconsolidated deposits that clearly reflect the Precambrian rocks of the Culebra Range. Topographically, the Costilla Plains are similar to the Alamosa Basin, but the former are erosional and the latter is depositional.

METHODS

Field

Soil samples were collected from a depth of 0-12 inches (0-30 cm) whereever the soil was atleast that deep using a stainless-steel auger. Dry samples were sieved through a 2 mm, stainless-steel sieve[2] in the field if dry; wet samples were sieved in the laboratory after air drying. Material passed through the sieve was retained for analysis and coarser material was discarded. Many of the sampling areas were in cultivated fields or pastures. In some cases, especially in the lowlands near the lower end of the Alamosa River and La Jara Creek, native hay fields were sampled even though seasonally covered with water.

Sample sites south and west of the Rio Grande were located at approximately one-mile intervals near the section corners. Each site was located at least 200 feet away from roads or farm buildings to minimize the possibility of contamination. Sites elsewhere in the valley were located at approximately 5-km intervals. Some areas could not be sampled because of inaccessibility.

Laboratory methods

All samples were air dried either in the field or the laboratory with ambient temperature. Samples that were not sieved in the field were disaggregated with a mechanical, ceramic mortar and pestal sufficient and sieved through a 2 mm, stainless-steel sieve. A 4 oz. subsample was ground between ceramic plates to -100 mesh (Peacock, 1990).

A 100-mg portion of each sample was decomposed with multiacids--HNO_3, $HClO_4$, and HF--and analyzed for 40 elements by ICP (Lichte, Golightly, and Lamothe, 1987). Soil pH was determined by specific-ion electrode in a 10-gm sample of the -100 mesh material in a 1:2 soil-water suspension. The suspension was equilibrated overnight and stirred immediately before measurement. The pH electrode came to equilibrium within about 1 minute (J.G. Crock, oral communication). Soil pH is typically determined on -10 mesh material, but the -100 mesh material comes to a stable equilibrium much more rapidly. The lower limits of determination for the methods are shown in Table 1.

Statistics

The analytical data were interpreted with the aid of factor analysis, a multivariate procedure based on correlations among the elements (Jöreskog and others, 1976). An oblique model with the factor axes adjusted to extreme elements was used. In a natural geochemical system, certain chemical elements tend to be associated in one of several groups because each group is controlled by a unique process. Such associations are more easily recognized with a multivariate technique that allows all of the elements to be viewed simultaneously rather than interpret individual elements. Each sample is described in terms of a factor score (a multivariate statistical representation) which can be plotted on a map to show the geographic components contained in the data. Scores are dimensionless numbers with a mean of zero and a standard deviation of one that express the relative similarity of the composition of a given sample with the composition of a theoretical end-member (factor). A large positive score fo a sample indicates that the composition of that sample is closely similar to the end-member composition.

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[2] The 2-mm sieve constitutes a standard definition of soil material.

Table 1. Lower limits of determination for analytical methods used in this study.

Element	Lower limit of determination	Element	Lower limit of determination
Al, percent	0.005	Ga, ppm	4
Ca, percent	.005	La, ppm	2
Fe, percent	.02	Li, ppm	2
K, percent	.01	Mo, ppm	2
Mg, percent	.005	Nb, ppm	4
Na, percent	.006	Nd, ppm	4
P, percent	.005	Ni, ppm	3
Ti, percent	.005	Pb, ppm	4
Mn, ppm	4	Sc, ppm	2
Ag, ppm	4	Sn, ppm	5
As, ppm	10	Sr, ppm	2
Au, ppm	8	Ta, ppm	40
Ba, ppm	1	Th, ppm	6
Be, ppm	1	U, ppm	100
Bi, ppm	10	V, ppm	2
Cd, ppm	2	Y, ppm	2
Ce, ppm	5	Yb, ppm	1
Co, ppm	2	Zn, ppm	2
Cr, ppm	2	S, percent	.05
Cu, ppm	2	pH	--
Eu, ppm	2		

The technique requires that the data set for all elements must be complete (not censored), that is, without indeterminate values[3]. For several elements that were no more than 20 percent censored, indeterminate values were replaced with an arbitrarily small value equal to 0.7 times the lower limit. Such replacements are justified providing that final interpretations are not appreciably altered. Replacements were made for S because of the importance of the element even though it was about 50 percent censored.

Color-filled contour maps were made to display factor scores because of their utility to summarize and smooth scattered data observations. Contoured surfaces were estimated using the computer software, Earthvision©, by Dynamic Graphics. The gridding algorithm is a minimum tension procedure. Because factor scores are dimensionless values that have meaning only in a comparative context, the frequency distribution of each score data set was divided according to percentiles. Our primary interest is in the large positive scores because they indicate samples that have compositions most nearly like the end-member factor compositions. Thus only the 50th, 80th, 90th, 95th, and 99th percentiles are contoured. The entire range of pH data is plotted. A moderate smoothing

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[3] Indeterminate values are those reported as below or above the limit of determination by the method used. For example, with a lower detection limit of 5 ppm, an indeterminate value would be reported as <5 or 5L.

factor of 0.5 (from a possible range 0-10) was applied to eliminate minor noise in the estimated surface. Sample sites are shown on the contour maps as black dots. The validity of the estimated surface is of course dependent on the density of sample locations, which is much greater in the southwestern part of the valley. The Great Sand Dunes and vicinity have little or no supporting data at all. In some cases single, isolated, anomalous samples without neighboring support cause a spurious "bullseye" which should be viewed with caution.

Estimates of means and deviations are based on the entire sample set. Analytical data for some elements were transformed to logarithms if their frequency distributions were rendered more nearly normal on a logarithmic scale. The means and deviations of log-transformed data are expressed as geometric means and geometric deviations (antilog of the arithmetic mean and standard deviation of log values). Otherwise, the arithmetic mean and standard deviation are used as the best measures of central tendency for nontransformed elements. The means and deviations of censored elements were estimated by the method of Cohen (1959). Estimates for some elements, notably Cd, Eu, and Sn, are based on extremely small numbers of samples and should be viewed with caution.

RESULTS

The minimum, maximum, mean, deviation and number of indeterminate values for all elements are shown in Table 2. Average values for soils of the western U.S. are included for comparison. Those 31 elements included in the factor analysis are indicated with an asterisk.

In an optimum model, we attempt to define a minimum number of factors that best describe the variance in the data; here that number is 7. The determination is based on several considerations, (1) number of eigenvectors with a value greater than one, (2) the magnitude of the communalities (amount of variance of each element explained by the model), (3) stability of the factor compositions as the number of factors is increased, (4) do the residuals (unexplained variance) have any geographic components or are they randomly distributed,and (5) do the factor compositions make geologic sense. Finally the factor scores are computed for each sample and plotted on maps as shown in Figures 1 to 7. Factor compositions are expressed in terms of correlations between the factor scores and the element values; thus a sample with a high score and a high concentration of, say Fe, will have a high correlation and a dominant role in the composition as in factor 2. The factor compositions are shown in Table 3.

Factor description

Factor 1--the composition of this factor consists of lithophile elements (Nd, Ce, La, Nb, Y, Th, and Yb) which suggests evolved silicic rocks (rocks enriched in silica such as granites and their volcanic equivalent, rhyolites). The plot of factor scores shown in figure 1 shows a dominant cluster of samples at the north end of the valley that probably reflects inputs from rhyolites in the Bonanza district. Sediments of similar composition just north of the Rio Grande are derived from volcanic terrain to the west. Another small area near the southeastern corner of the valley probably reflects a granitic source in the Culebra Range.

Factor 2--this factor, which contains Fe, V, Ti, Co, Sc, and Ga, is suggestive of a rock of intermediate composition rock such as andesite, which is common in the San Juan Mountains. The distribution of factor scores shown in figure 2 indicates that samples of this type occur on the floodplain of the Rio San Antonio. The Summer Coon volcano is also a possible source area.

Factor 3--alkaline-earth evaporites comprised of Mg, Ca, Sr, and S have accumulated in the alkaline area of the valley shown in figure 3. Internal drainage, a high water table, and evapotranspiration contribute to the accumulation of these elements probably as soluble sulfates and carbonates. The lava field of the Los Mogotes volcano between La Jara Creek and Conejos River is also a source of Ca and Mg though these elements do not likely occur as evaporites. A separate plot of S (not shown) indicated that S has also accumulated in the central basin area along the Alamosa River and La Jara Creek where the water table is shallow.

Factor 4--sulfide mineralization is reflected by base metals, Pb and Zn. Three source areas are indicated by the distribution of factor scores in figure 4. First, evidence of mineralization from the Bonanza area is well represented. Second, metal-enriched sediments from the upper Rio Grande, probably from the Creede mining district, and possibly from Summer Coon volcano highlight the Rio Grande floodplain. A well defined dispersion pattern also appears on the Alamosa River floodplain. The source of these metals could be any of several mineralized zones associated with the Summitville and Platoro calderas. These mineralized areas are not primarily Pb-Zn deposits and the association of metals is weaker along the Alamosa River compared to the other two areas. Sulfur has accumulated on the lower reaches of the Alamosa River floodplain; therefore the absence of S in the factor composition suggests that base-metal sulfides have been oxidized and the S was transported downstream from the metals in the sulfate form.

Factor 5--the association of Cr, Ni, Co, and Sc is suggestive of sediments derived from basalt, a more mafic volcanic rock than represented by factor 2. Several areas are indicated on the distribution map in figure 5. The lava flow from the Los Mogotes volcano is the principal source for this type. The Pliocene Servilleta Formation (Thompson and Machette, 1989) at the south edge of the valley and the Summer Coon volcano and adjacent areas to

Table 2. Number of uncensored (valid) values, number of indeterminate values, ranges, means, and deviations for soils of the San Luis Valley, and means for western U.S. soils[1]
[ppm, parts per million. --, not determined. <, less than value shown. *, Element included in factor analysis. Means and deviations are geometric except as noted.]

Element	Number of valid values	Number of (L) indeterm.	Range	Mean	Deviation	Mean, western soils
Al, percent*[2]	986	5	1.5-8.9	7.29	0.67	7.4
Ca, percent*	986	0	.2-20	2.52	1.64	1.8
Fe, percent*[2]	986	0	.6-7.3	3.99	1.06	2.6
K, percent*[2]	986	0	.88-3.7	2.52	0.40	1.8
Mg, percent*	986	0	.27-5	0.85	1.41	.74
Na, percent*[2]	986	0	.64-5.3	1.95	0.45	1.2
P, percent*	986	0	.04-.62	0.11	1.34	.032
S, percent*	441	545	.05-9.4	0.15	3.0	.13
Ti, percent*[2]	986	0	.07-.9	0.44	0.11	.26
Mn, ppm*	986	0	210-3000	783	1.33	380
Ag, ppm	0	986	<2	--	--	--
As, ppm*[3]	85	901	<10-26	12	1.25	5.5
Au, ppm	0	986	<8	--	--	--
Ba, ppm*[2]	986	0	23-1500	826	168	670
Be, ppm*[3]	980	6	<1-4	1.7	1.36	.68
Bi, ppm	0	986	<10	--	--	--
Cd, ppm[3]	4	982	<2-3	2.5	1.26	--
Ce, ppm*	986	0	17-280	72	1.2	65
Co, ppm*[2]	986	0	3-28	14	4.1	9.0
Cr, ppm*	986	0	6-110	24	1.6	41
Cu, ppm*	986	0	5-140	22	1.5	21
Eu, ppm[3]	3	983	<2-4	.07	3.36	--
Ga, ppm*[2]	986	0	4-22	17	1.9	19

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[1] Shacklette and Boerngen (1984)

[2] Arithmetic mean and standard deviation

[3] Mean and deviation of censored distribution estimated by method of Cohen (1959).

Element	Number of valid values	Number of (L) indeterm.	Range	Mean	Deviation	Mean, western soils
La, ppm*	986	0	10-130	40	1.2	30
Li, ppm*	986	0	7-86	18	1.3	22
Mo, ppm[3]	14	972	<2-4	2.8	1.38	.85
Nb, ppm*	986	0	2.8-42	14	1.2	8.7
Nd, ppm*	986	0	6-140	33	1.2	36
Ni, ppm*	986	0	2-54	11	1.6	15
Pb,_ppm*	986	0	2.8-380	19	1.5	17
Sc, ppm*	985	1	3-15	9	1.2	8.2
Sn, ppm[3]	4	982	<5-14	7.4	1.57	.9
Sr, ppm*	986	0	88-2900	477	1.3	200
Ta, ppm	0	986	<40	--	--	--
Th, ppm*	986	0	2.8-19	9.1	1.3	9.1
U, ppm	0	986	<100	--	--	2.5
V, ppm*[2]	986	0	18-220	104	33.0	70
Y, ppm*	986	0	3-80	20	1.2	22
Yb, ppm*	986	0	.7-7	2	1.3	2.6
Zn, ppm*	986	0	27-660	86	1.4	55
pH[2]	986	0	5.5-10.6	8.4	0.8	--

the north are also source areas. A source in the Sangre de Cristo Mountains near the northeast side of the valley may consist of rocks that are Early Proterozoic gneiss (Johnson and others, 1984a).

Factor 6--the association of Na and K characterizes a saline-evaporite-type deposit. The source of these elements is most likely shallow groundwater. The distribution shown in figure 6 coincides with areas where the water table of the unconfined aquifer is within 6-12 feet (2-4 m) of the surface (Edelmann and Buckles, 1984). The distribution also overlaps areas with medium to very high Na hazard in shallow groundwater and areas with alkali-affected soils. Edelmann and Buckles (1984) report that high amounts of dissolved solids result from both natural (leaching of soil and minerals, ion exchange, and evapotranspiration) and manmade causes (irrigation water, fertilizers, and waterlogging of soils).

Factor 7--factor analysis partitioned out a second mineralization association comprised of As and Cu (see figure 7). Samples with high scores occur on the Alamosa River floodplain suggesting that the association could derive from the mineral, enargite (Cu_3AsS_4), which is a common ore mineral at the Summitville mine (Steven and Ratté, 1960). In the northwest part of the valley, metal-enriched sediment originates from diverse volcanic terrain which could include the La Garita caldera near the headwaters of Saguache Creek and a source on the eastern flank of Bonanza caldera. Scattered geochemical anomalies are found along the western flank of the Sangre de Cristo Mountains mostly as Au- and Ag-bearing veins (Johnson and others, 1984b; Zimbelman, 1989). One or more of these may be the source of the As-Cu association shown at the northern end of the Sangre de Cristo Mountains.

Table 3. Factor compositions arranged in descending order of element dominance according to correlations between factor scores and concentrations of elements.

Correlation coefficients						
Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Nd, 0.953	Fe, 0.965	Mg, 0.917	Pb, 0.922	Cr, 0.895	Na, 0.882	As, 0.705
Ce, .942	V, .922	Ca, .849	Zn, .858	Ni, .882	K, .651	Cu, .616
La, .934	Ti, .892	Sr, .662		Co, .635		
Nb, .827	Co, .870	S, .456		Sc, .632		
Y, .822	Sc, .809					
Th, .683	Ga, .631					
Yb, .647						

Soil pH

The distribution of soil pH values is shown in figure 8. Most valley soils are alkaline, some with values as high as 10.6. Soils with pH above 10 occur in the alkaline area of the north-central part of the valley and the area between Rock Creek and the Rio Grande. If pH had been included in the factor analysis, it would have associated with factor 6, Na-K. Acid surface waters appear to have some impact on the reservoir of alkalinity in the soils around the edges of the valley but relatively little in the interior of the valley. The only exception of note is the upper part of the Alamosa River floodplain where numerous values less than 7.5 and a few values less than 6.6 are found. The lowest value measured, 5.5, was found on the Alamosa River floodplain very near the mountain front. The equilibration between acid waters (river and irrigation) and alkaline soils tends to progress toward the valley center. From an agricultural point of view, the rare acid or neutral soils would be a welcome abatement to the harsh and difficult alkaline conditions. From the standpoint of base-metal solubility, metals should be more readily available in acid soils.

DISCUSSION

In terms of overall averages, the soils of the San Luis Valley differ little in composition, with a few minor exceptions, from the averages of most elements in soils reported for the western United States (Shacklette and Boerngen, 1984). Valley soils tend have elevated amounts of mafic elements, Co, Fe, Mn, and V, probably because of the high proportion of volcanic rocks in the surrounding mountains. The soils are more enriched in the alkalies, Na and K, and the alkaline-earths, Ca, Mg, and Sr, because of the unique groundwater system in the valley. In spite of the presence of mineralized source rocks, only As and Zn exhibit elevated means. Although Mo and Sn appear to be enriched, the numbers of samples measured above the limits of detection are too small to make reliable interpretations. Our estimated mean for Cd, which is based on only 4 samples above a limit of determination of 2 ppm, is 2.5 ppm. This compares with data reported by Holmgren and others (1993) for samples from the San Luis Valley that are in the range of 0.16-.32 ppm.

The factor analysis model helped to categorize the valley soils in terms of 7 fundamental element associations. Each association is believed to represent a common source and a common process of transport and weathering. While valley soils may not seem particularly unusual in terms of average composition, there are important local geochemical anomalies that have been identified. The accumulation of alkalies and alkaline-earth elements in the north-central part of the Alamosa Basin reaffirms knowledge acquired by farmers and researchers long ago. These particular associations are consistent with the pattern of groundwater movement as reported by Emery and others (1971) which shows water migrating toward the alkaline area and San Luis Lake.

Two major volcanic rock types have been described in the San Juan volcanic field (Steven and Lipman, 1976). The earliest eruptions in the San Juan volcanic field about 35 to 30 m.y. ago were largely of intermediate-composition rocks, such as andesite, rhyodacite, and mafic quartz latite. The period from about 28 to 26.5 m.y. was characterized by large-volume ash flows of rhyodacite, latite, and rhyolite. The character of erupted rocks changed in early Miocene time (about 25 m.y. ago) from andesitic type rocks to bimodal rocks consisting of basalts with some associated high-silica alkali-rich rhyolites. This change to bimodal coincided with basin-and-range-faulting in the San Luis Valley segment of the Rio Grande trough (Lipman and Mehnert, 1975) and may also reflect a rise in the batholith that is believed to underlie most of the calderas of the area (Plouff and Pakiser, 1972). We believe that factors 2 and 5 reflect the compositions of sediments derived from andesites and basalts, respectively.

It is noteworthy that even though the dispersion of several base metals from known mineralization sources had been suggested previously from very limited NURE[4] sample coverage in the valley (Broxton and others, 1979; Shannon, 1978; Shannon and others, 1980a,b; Tidball and others, 1994), factor analysis partitioned such metals into two associations, Pb-Zn and As-Cu. Each association has some unique occurrences, but they both occur on the Alamosa River floodplain and are partially overlapping in distribution.

An important question is whether the recent mining at Summitville has caused any impact on valley soils? The whole area south from Summitville and across the Alamosa River and east to Jasper is a zone of scattered hydrothermal alteration and mineralization associated with the intersections of intrusive and extrusive centers and the marginal ring fracture structures formed during subsidence of the Platoro caldera complex (Lipman, 1975). Lipman defined a probable late collapse of the northwest part of the Platoro caldera as the Summitville caldera. Minerals associated with the Summitville ore deposits include pyrite, enargite, native S, barite, galena, and sphalerite (Steven and Ratté, 1960; Plumlee and others, this volume). Thus we must interpret that the Alamosa River floodplain contains a composite of sediment from these various sources, and unless minerals or element suites from various local alteration zones could be uniquely fingerprinted, it would be impossible on the basis of the present data to specify the actual source of any part of the sediment.

Parts of the Alamosa River floodplain are enriched in As, Cu, Mn, Mo, Pb, and Zn. Levels of enrichment for these elements compared to background levels (in parentheses) taken from averages of western U.S. soils (Shacklette and Boerngen, 1984) are as follows: As, 11-26 ppm, (5.5); Cu, 35-140 ppm, (21); Mn, 900-1400 ppm, (380); Mo, 3-4 ppm, (0.8); Pb, 25-74 ppm, (17); and Zn, 120-140 ppm, (55). The higher concentrations, especially for less mobile elements, tend to occur closer to the mountain front. Whether these enhanced concentrations are of importance to agriculture is beyond the scope of this study, but other studies in this same volume address effects on agriculture.

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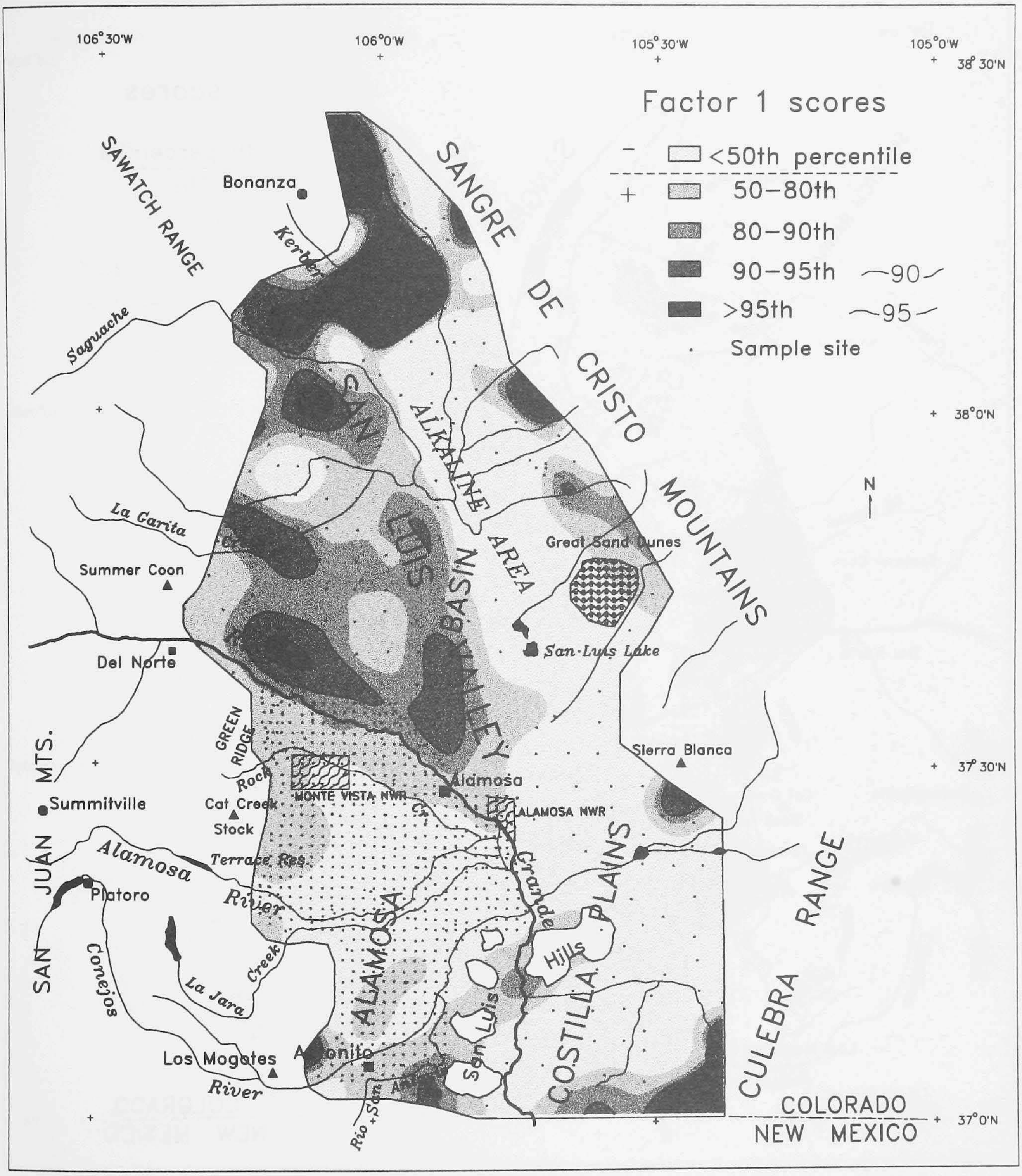

Figure 1. Factor 1 scores showing the distribution of multielement composition for valley soils. The composition consists of lithophile elements, Nd, Ce, La, Nb, Y, Th, and Yb.

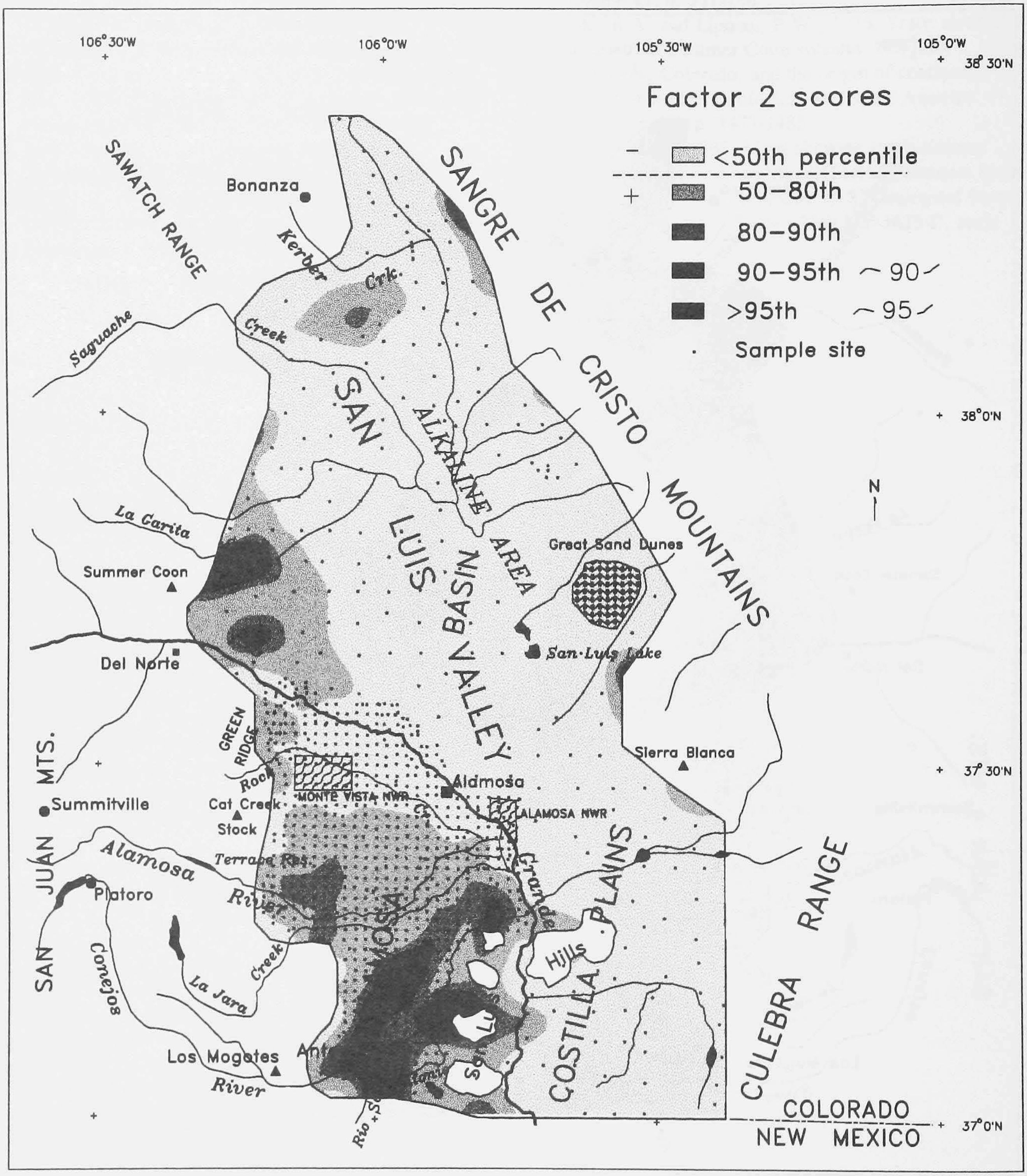

Figure 2. Factor 2 scores showing the distribution of multielement composition in valley soils. This andesitic composition consists of Fe, V, Ti, Co, Sc, and Ga.

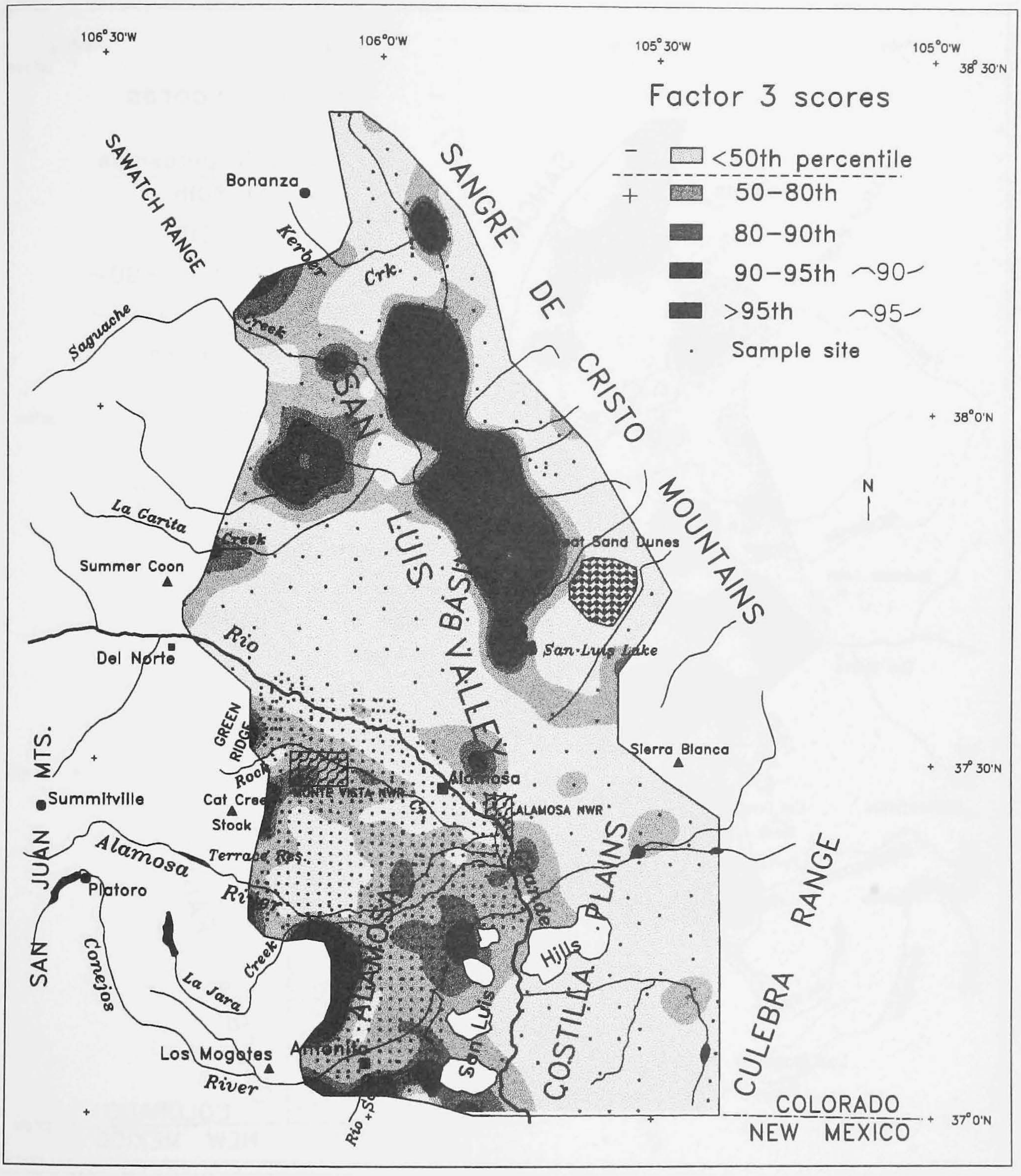

Figure 3. Factor 3 scores showing the distribution of multielement composition in valley soils. This alkaline-earth evaporite composition consists of Mg, Ca, Sr, and S.

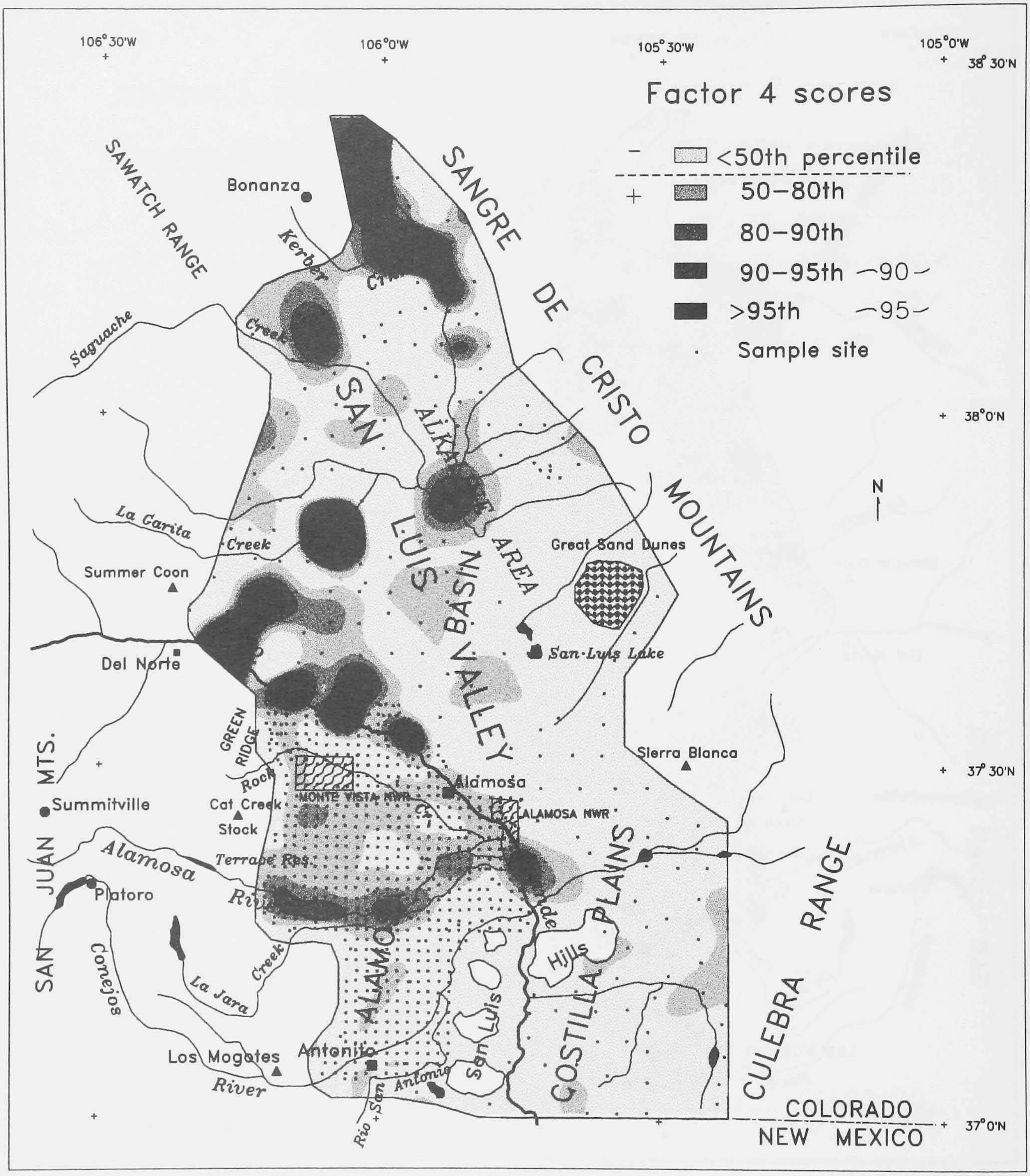

Figure 4. Factor 4 scores showing the distribution of multielement composition in valley soils. This sulfide mineralization composition consists of Pb and Zn.

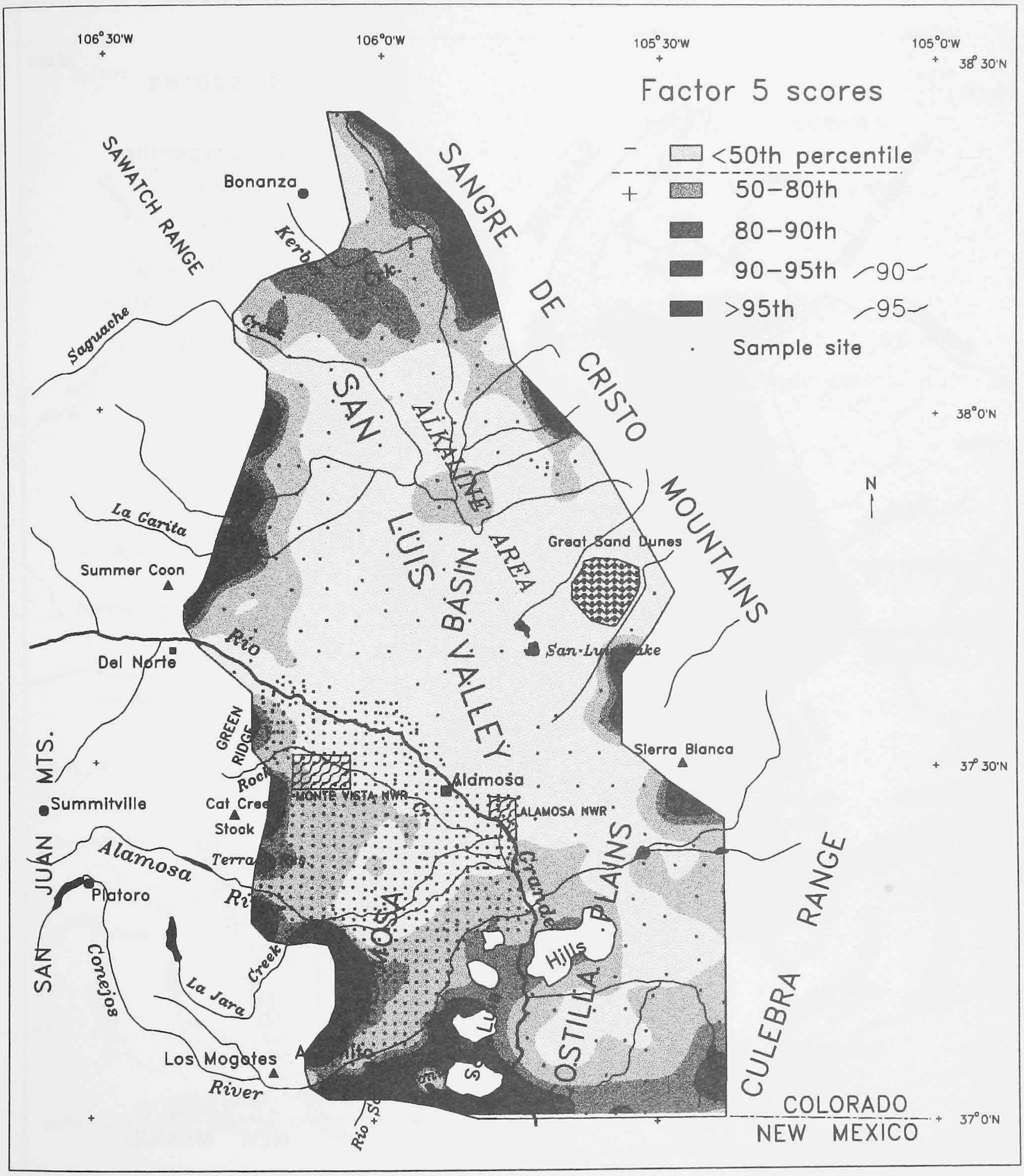

Figure 5. Factor 5 scores showing the distribution of multielement composition in valley soils. This basaltic composition consists of Cr, Ni, Co, and Sc.

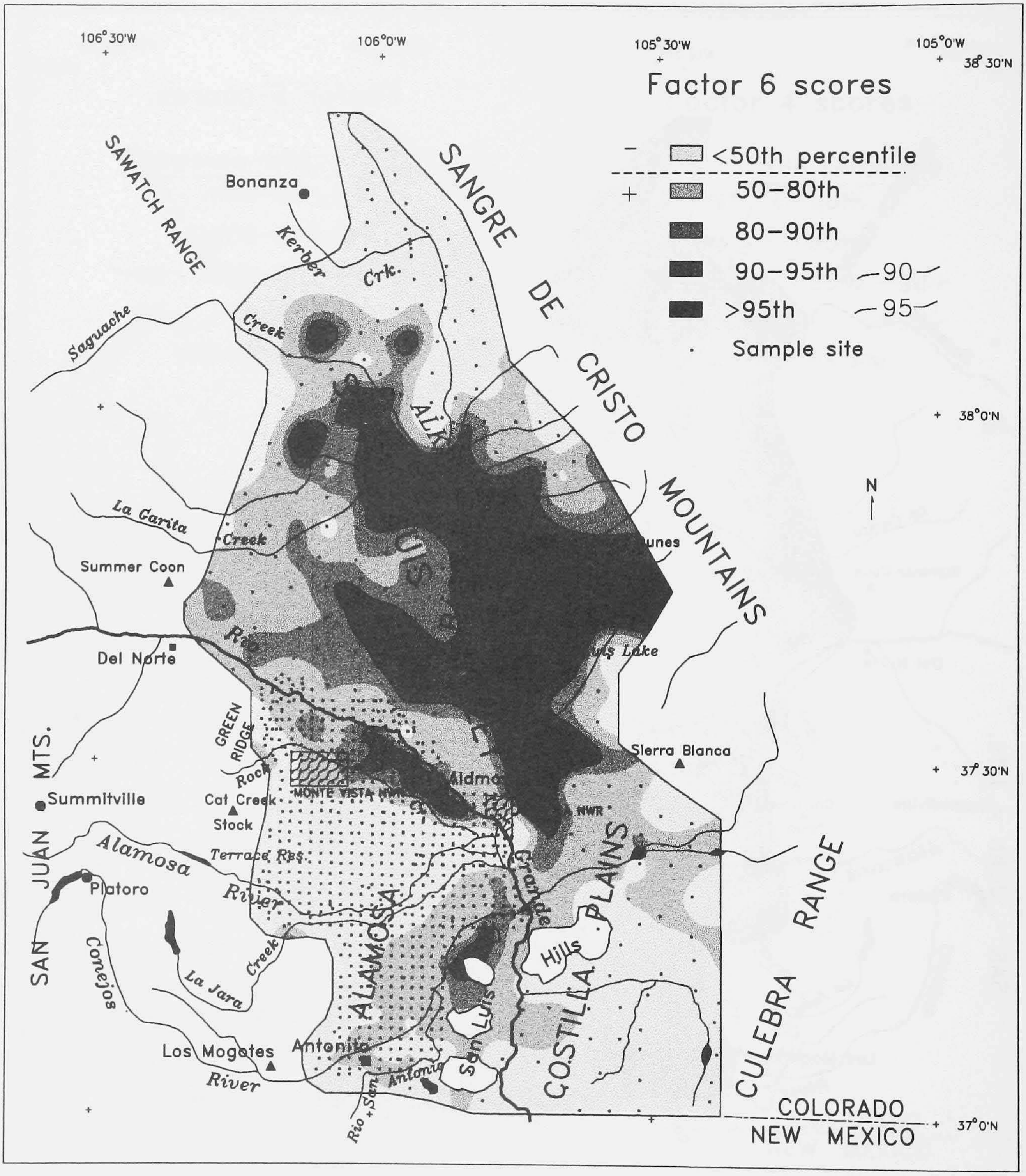

Figure 6. Factor 6 scores showing the distribution of multielement composition in valley soils. This saline-evaporite composition consists of Na and K.

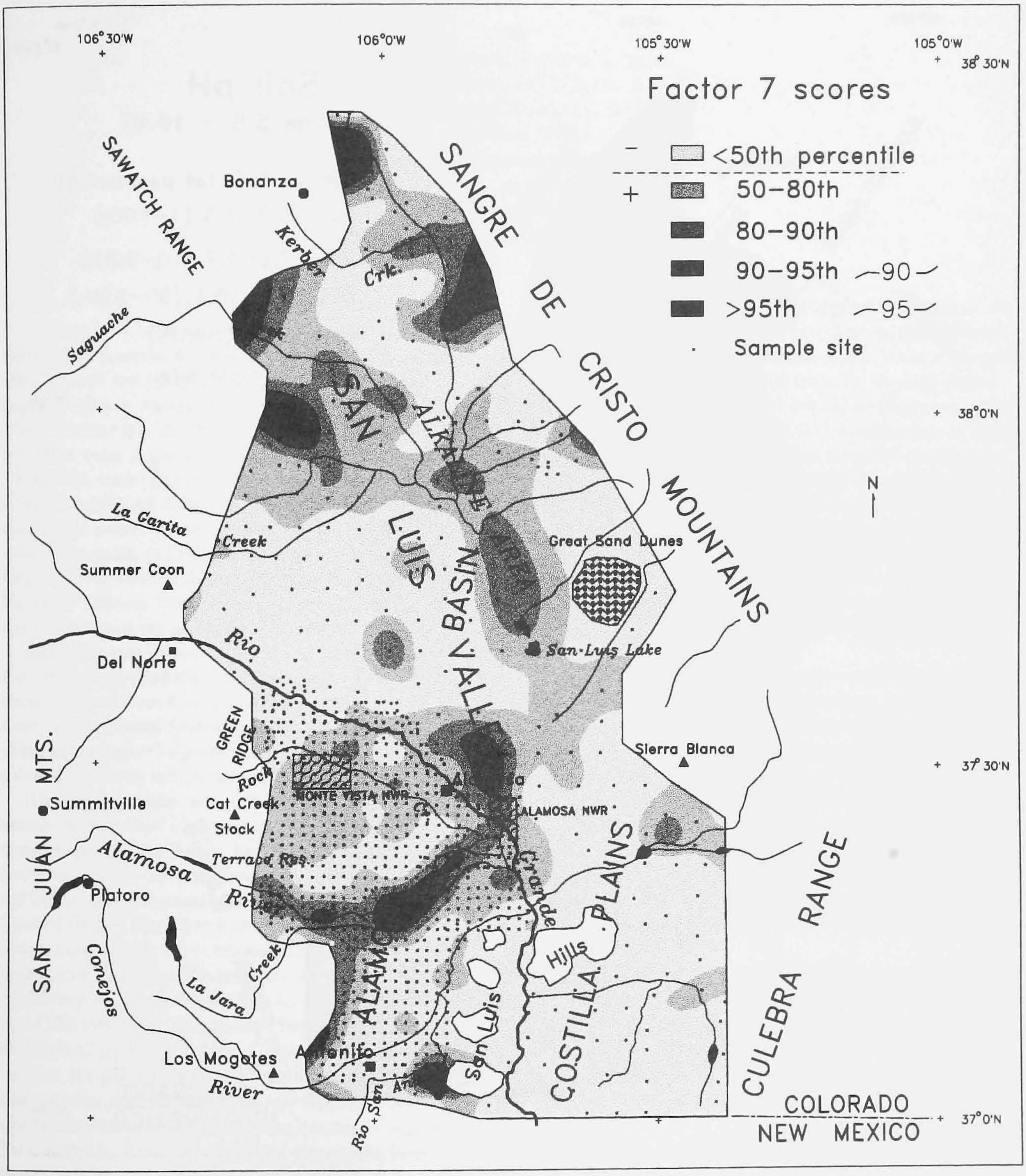

Figure 7. Factor 7 scores showing the distribution of multielement composition in valley soils. The As-Cu composition suggests enargite, a commonly occurring ore mineral at Summitville mine.

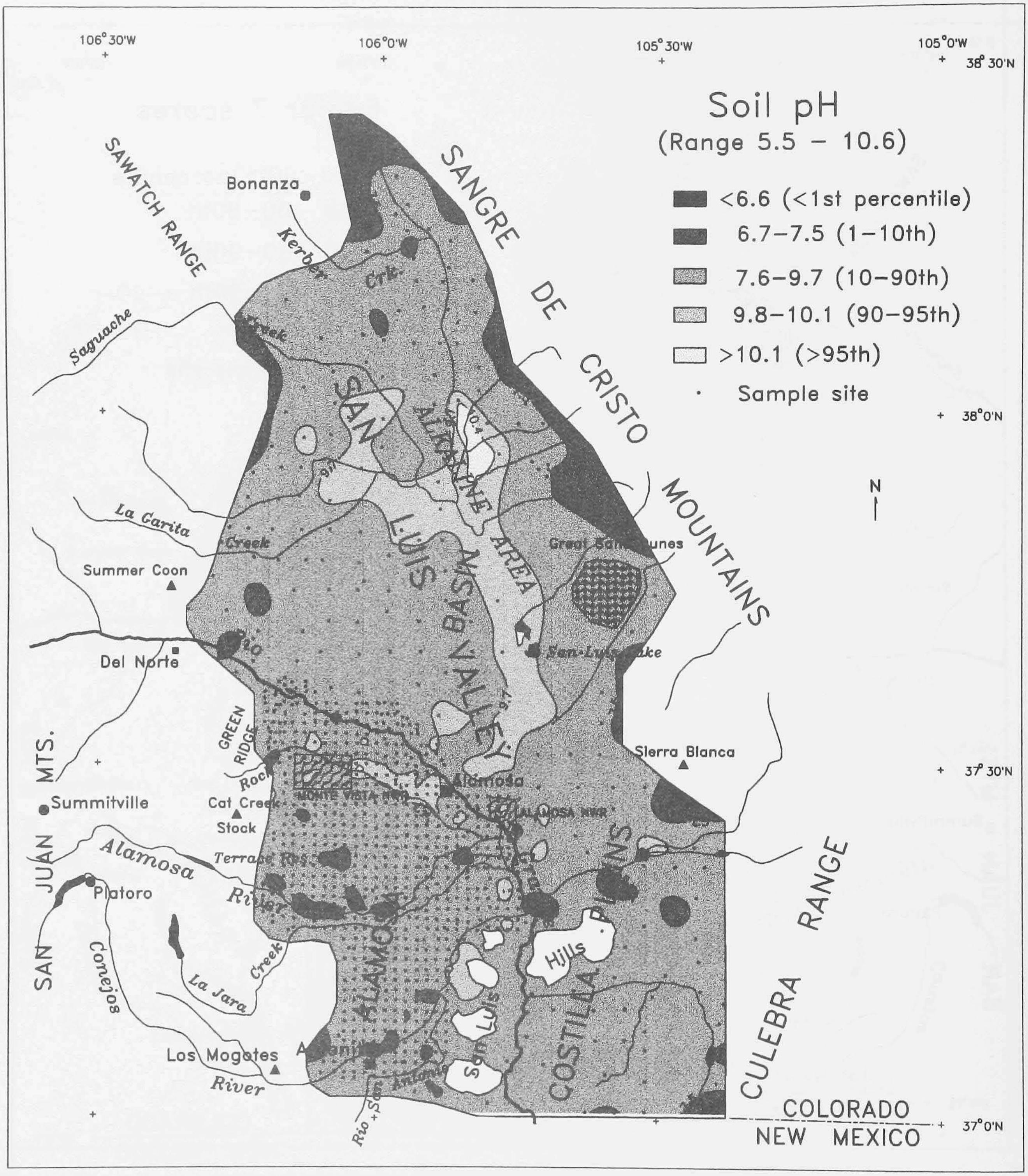

Figure 8. Distribution of pH in valley soils.

IMPACT OF ALAMOSA RIVER WATER ON ALFALFA, SOUTHWESTERN SAN LUIS VALLEY, COLORADO

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ABSTRACT

Contamination from the Summitville gold mine in the San Juan Mountains, Colorado, has raised concerns over the effects of low pH and metal-laden—particularly copper—surface waters carried down the Alamosa River. These waters enter the Terrace Reservoir, which provides irrigation water to the southwestern part of the San Luis Valley. The main purpose of this study was to assess whether significant differences exist between the effects of two source waters on the composition of alfalfa. The two source waters are (1) Terrace Reservoir water and (2) Rio Grande River water and (or) confined ground water ("control" waters). We also assessed the effects of these source waters on the associated agricultural soils.

Sampling was conducted June 3-6, 1993, just prior to the first cutting of alfalfa. Irrigation water, soils, and alfalfa were collected from four sprinkler-irrigated Terrace Reservoir fields and from similarly irrigated control fields using an analysis-of-variance design. Four sites were selected randomly within each of the eight fields.

The water samples were taken from the irrigation system of each field. Fields irrigated with waters originating from the Terrace Reservoir received more acidic water and higher concentrations of dissolved metals than did fields using irrigation waters from another source (control fields). The pH values of the Terrace Reservoir waters ranged from 5.6 to 6.8 and the samples contained no measurable alkalinity. These waters also contained high concentrations of cobalt (6-13 μg/L), copper (60-350 μg/L), zinc (150-190 μg/L), manganese (360-520 μg/L), and nickel (8-12 μg/L), in unfiltered, acidified samples. In contrast, the pH of irrigation waters originating from sources other than Terrace Reservoir ranged from 7.6 to 9.2, and the concentration of metals was less than 1 μg cobalt/L, 3 μg copper/L, 22 μg zinc/L, 40 μg manganese/L, and 1 μg nickel/L.

Except for copper, results of total concentrations of elements in soils from sites irrigated with Terrace Reservoir water are similar to those of the soils irrigated with other sources of water. Differences in copper concentrations were statistically significant at the 95-percent confidence level—higher in soils irrigated by Terrace water. When compared with geometric means for soils from the Western United States, the soils we collected from the southwestern part of the San Luis Valley contain higher concentrations of many elements, including cobalt, copper, zinc, and manganese. These higher concentrations probably reflect, at least in part, the composition of the alluvial-fan parent material from which the soils were derived. This material is detritus shed from weathering of volcanic rocks and mineralized areas in the Alamosa River drainage basin. All of our soil data from the southwestern part of the San Luis Valley are within geochemical baselines for soils from the Western United States.

Stem-and-leaf samples of alfalfa were collected from 10 points within a 1-m radius of each soil pit. An analysis-of-variance of 15 elements showed that concentrations of copper, manganese, and nickel were significantly higher at the 95-percent confidence level in alfalfa from the Terrace fields than in alfalfa from the control fields. More importantly, concentrations of these metals in alfalfa affected by both water sources (1) meet published nutritive requirements for cattle, (2) are far below maximum tolerable levels reported for cattle, and (3) are comparable to concentrations in alfalfa found in other parts of the country.

In conclusion, our results indicate that the metal concentrations of the irrigation water from Terrace Reservoir are anomalous. Yet these waters have had only a minor effect on the total soil chemistry and seem to have enhanced the bioavailability of copper and manganese to optimum levels for alfalfa growth.

INTRODUCTION

Recent open-pit mining and the abandonment of the Summitville gold mine in the San Juan Mountains late 1992 have led to serious problems with acid-mine drainage (Environmental Protection Agency, 1993). Other sources of acid-mine drainage and natural acid-rock drainage, however, also occur in the Alamosa River watershed (Miller and McHugh, 1994), but the main source of high levels of dissolved copper (Cu), zinc (Zn), and to a lesser extent manganese (Mn) in the Alamosa River stems from Wightman Fork below the Summitville mine site (Kirkham and others, this volume).

Downstream concerns focused, in part, on the impact this contamination might have on the nutritional quality of the crops grown in the San Luis Valley where alfalfa is a major crop. According to the Environmental Protection Agency (1993), water from Terrace Reservoir (fig. 1) irrigates approximately 45,000 acres of farmland in Alamosa, Conejos, and Rio Grande counties in south-central Colorado.

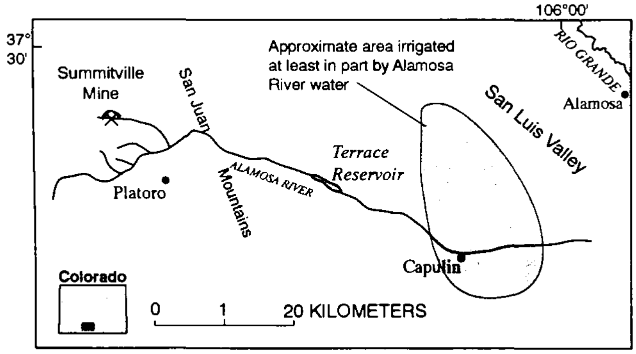

Figure 1. Index map showing location of Summitville mine and Terrace Reservoir with respect to farmlands irrigated with Alamosa River water.

This study, funded by the U.S. Geological Survey, was designed to assess whether alfalfa from fields irrigated by the two water sources differs significantly in element content. Whether or not significant differences do occur, the more important concern is this: Given that significant differences are found, are they nutritionally meaningful?

METHODS

Sample Collection

Sampling was conducted June 3-6, 1993, just before the first cutting of alfalfa. Flushing of metal-laden salts from soils commonly occurs before and during the early part of the irrigation season (Naftz and others, 1993, p. 124). In our study area the first flush occurred after spring melt-off about April 1 and peak flow was measured June 2 (Douglas Cain, Water Resources Division/USGS, oral commun., November 1993). According to Royce Reinhardt, one of the cooperating irrigators (oral commun., November 1993), a third of the season's water is applied by the first cutting.

Irrigation water, soils, and alfalfa were collected from eight center-pivot, sprinkler-irrigated fields. Four of these fields were irrigated by water from Terrace Reservoir and four "control" fields were irrigated by water from other sources that included River Grande River water and ground water. Eight fields with similar soil types were selected, using the soil survey maps available for Alamosa, Conejos, and Rio Grande counties (Pannell and others, 1973; Yenter and others, 1980; and Pannell and others, 1980). Sampling was conducted according to a balanced, four-level nested analysis-of-variance design (fig. 2). The term analysis-of-variance refers to a statistical technique "whereby the total variation is being analyzed or divided into meaningful components" (Walpole and Myers, 1978).

Four sites were randomly selected from each field and marked with a survey flag. A large handful of tillers (stems) of alfalfa in the vegetative (prebud) growth stage was then collected from approximately ten points within a 1-m radius of the flag. Finally, a channel sample of plow-zone soil (0-30 cm depth) was dug and composited with a tiling spade at each site.

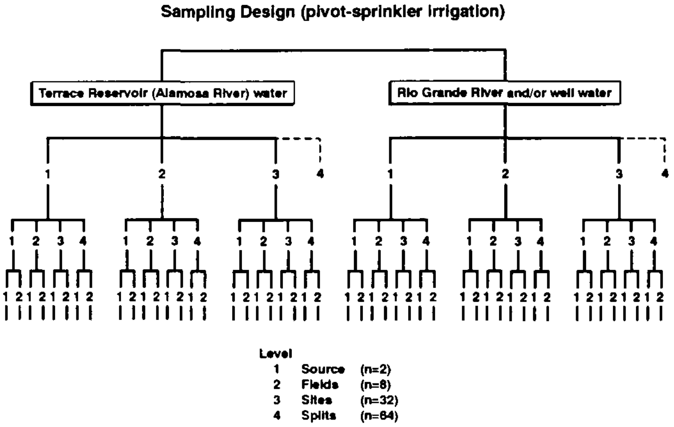

Figure 2. Schematic of the four-level analysis-of- variance sampling design.

Water pH and specific conductance were measured on site in both filtered and unfiltered samples from the irrigation system of each field (fig. 3). However, only the results for the unfiltered samples were used in this report because the agricultural-use standards for Colorado are based on total rather than dissolved constituents. Our unfiltered data are more comparable with those standards than are our filtered data. After examination of the irrigation-water data we decided to eliminate two fields in our data analysis that did not fit our population definitions. One of the control fields (Control Field #3, Appendix Table 2) was not included because drain water was used for irrigation; the drain water contained much higher concentrations of total dissolved solids than water from the other fields. One of the Terrace-irrigated fields (Terrace Field #4, Appendix Table 1) was likewise excluded because Terrace and well water were mixed for irrigation. This mixture yielded a water decidedly lower in metal concentrations compared to those found in water from the other Terrace fields.

Figure 3. The alfalfa field shown here is one of eight that were studied to determine the impact of the Summitville mine on alfalfa, including the irrigation water and associated soils. This field is irrigated by water from the Terrace Reservoir, which is supplied by the Alamosa River.

Laboratory and Analytical Procedures

Samples were handled according to prescribed quality assurance/quality control (Arbogast, 1990) and chain-of-custody protocol.

Unfiltered water samples were acidified with concentrated nitric acid to dissolve acid-soluble particulates. Major elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Trace elements were determined by atomic absorption spectrophotometry in the analytical laboratories of the U.S. Geological Survey (USGS), Denver. USGS water standards, samples, and duplicates were submitted in a randomized sequence for analysis.

The soil samples were air-dried, disaggregated, and sieved to minus 2 mm (10 mesh). A portion was ground to minus-100 mesh and digested for total analysis by ICP-AES in the analytical laboratories of the U.S. Geological Survey, Denver (Peacock, 1990; Briggs, 1990).

Alfalfa samples were air-dried and ground in a Wiley mill to pass a 1.3-mm sieve. They were not washed, since they were meant to represent hay as fed to cattle. A portion of each sample was ashed at ~500°C in a muffle furnace, digested in a mixed-acid solution, and analyzed by ICP-AES. Ash yield was calculated to allow conversion to the dry-weight basis used in nutritional studies (Peacock, 1992).

Duplicates of all soil and alfalfa samples were prepared with a Jones splitter; these splits were used to estimate procedural, often referred to as analytical, error. Two samples of the Standard Reference Material 1547, Peach Leaves (National Institute of Standards and Technology) were included in each job of 40 samples for both soils and alfalfa. All samples—including duplicates and NIST standards—were submitted in a randomized sequence to convert any systematic error that might occur in either sampling or analysis into random error.

Statistical Methods

The limited number of water samples precluded a statistical analysis of the water data. Moreover, the strong differences in the character of water from the two source areas are so clear that such a test is unnecessary.

The soil data were first converted to a logarithmic basis because geochemical data are generally logarithmically distributed. However, the alfalfa results were not based on such a transform because the results of the analysis-of-variance (Grundy and Miesch, 1988) on both the raw data and the transformed data were similar. Where concentrations for a few samples were reported to be below the lower limits of determination, such as for the metal nickel (Ni) in alfalfa (Appendix Table 2), the qualified value "<" was replaced with a concentration seven-tenths the lower limit. No statistical test was run for lithium and molybdenum in alfalfa because of extensive censoring of the data; that is, an excessive number of samples with concentrations below the lower limit of detection.

RESULTS

Water

The concentrations of Cu, Zn, and Mn were considerably higher in water samples from the fields irrigated by Terrace Reservoir water than those from fields irrigated by other source waters (fig. 4). The Cu levels in many samples of water from the Terrace fields exceeded Colorado's agricultural-use standard (200 μg/L) for stock watering and or irrigation (Colorado Department of Health, 1994). All water samples from the Terrace fields contained Mn that exceeded the 200 μg/L use standard. None of the water samples from the two source waters exceeded State agricultural-use standards of 200 and 2,000 μg/L for Ni and Zn, respectively. Standards for cobalt have not been established.

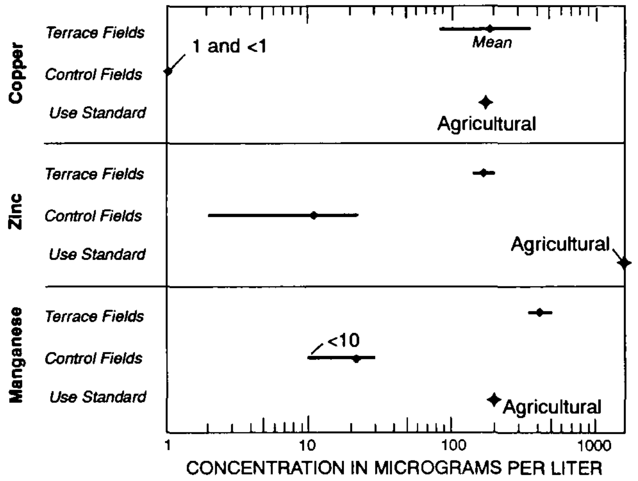

Figure 4. Comparison of levels of Cu, Zn, and Mn in water samples collected from fields irrigated by Terrace Reservoir and other sources.

Soils

In contrast to the water results, total analyses of the bulk soil samples revealed only minor differences in the concentrations of Cu, Zn, and Mn between fields irrigated by the two source waters. Only the Cu concentrations were significantly higher in soils from the Terrace fields (fig. 5). The means for this metal, however, fall well within the baseline for Cu in soils from the Western United States (Shacklette and Boerngen, 1984).

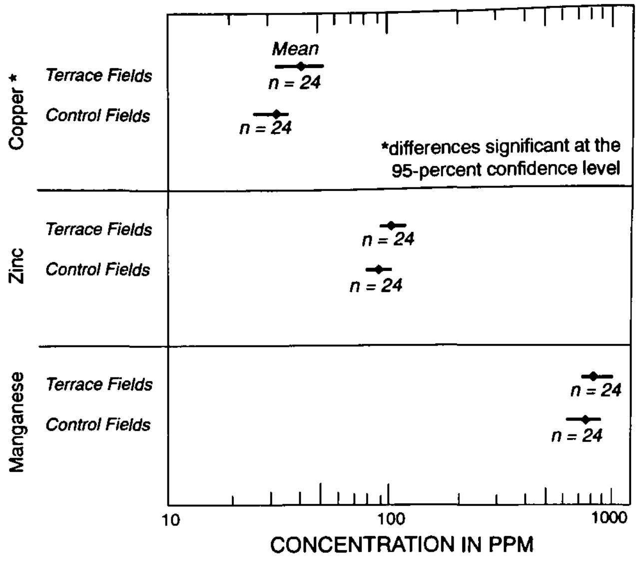

Figure 5. Comparison of levels of Cu, Zn, and Mn in soil samples collected from fields irrigated by Terrace Reservoir and other sources.

Alfalfa

We have chosen to interpret the alfalfa results in three ways, where data permit. We compare the ranges and means for the alfalfa samples collected from fields irrigated by the two source waters with the following:
(1) ranges and means in alfalfa from several other studies in western United States; (2) nutrient requirements of beef cattle (National Research Council, Subcommittee on Beef Cattle Nutrition, 1984, table 4)—requirement ranges and maximum tolerable levels; and (3) nutrient-status requirements of alfalfa (Jones and others, 1991).

The importance of (1) lies not only in the recency of the other studies, but in the fact that they were also conducted by the U.S. Geological Survey. More importantly, the samples were analyzed by the same methods in its laboratories. The use of requirement range rather than a requirement value recognizes that requirements for most minerals are affected by a variety of dietary and animal factors, such as body weight, sex, and rate of gain (see Brown, this volume).

Of 15 elements that were compared in the alfalfa from fields irrigated by both water sources, only the concentrations of three—Cu, Mn, and Ni—were significantly different, higher by about 50 percent in samples from the Terrace fields.

Copper is not easily translocated from the roots to shoots, even where excess Cu has been observed in soils (Kabata-Pendias and Pendias, 1984). The significant differences observed, therefore, are notable. On the other hand, Mn is taken up and translocated rapidly within plants.

According to Kabata-Pendias and Pendias (1984), the most readily available Mn occurs in acid soil. These same authors report that the availability of Ni, too, is most pronounced in acid soils.

As shown in figure 6, the Cu concentrations in alfalfa from the Terrace fields lie within the ranges in alfalfa reported in studies from California, Wyoming, and western Colorado. The range of concentrations for Cu in all the alfalfa that we sampled was comparable to the ranges found in the Wyoming and Colorado studies; it was small compared with the range found in the California study. The Cu levels in alfalfa from both the Terrace and control fields meet the dietary-requirement range and are well below the maximum tolerable level for cattle (fig. 7). However, a comparison with the nutrient-status requirement of alfalfa, as reported by Jones and others (1991), suggests that some of the samples from the control fields are in the low range. In this respect, the Cu-laden irrigation water from Terrace Reservoir may be slightly beneficial.

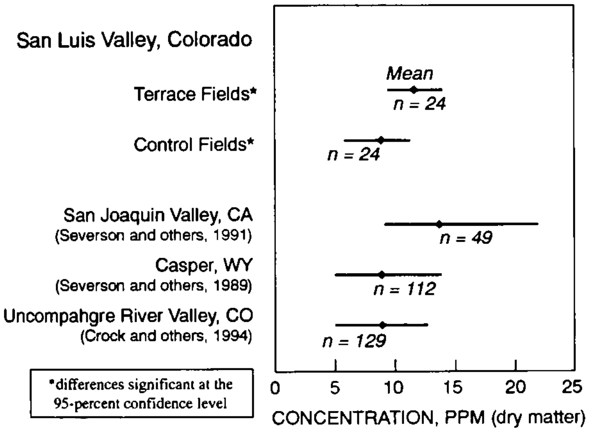

Figure 6. Levels of Cu in alfalfa samples collected from fields irrigated by Terrace Reservoir and other sources compared with Cu levels in alfalfa from three other regions in Western United States.

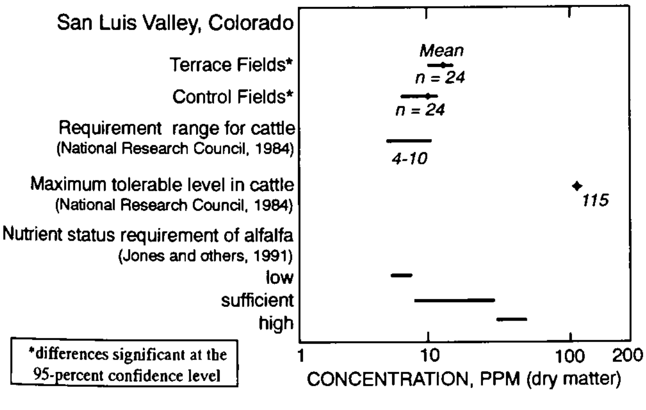

Figure 7. Levels of Cu in alfalfa samples collected from fields irrigated by Terrace Reservoir and other sources compared with nutrient requirements for Cu in cattle and in alfalfa.

Results for Mn are quite similar to those of Cu, although the ranges of values do not overlap as they do with Cu (fig. 8). As with Cu, the concentrations of Mn in alfalfa from this study meet the requirements for cattle and clearly do not approach a toxic level of 1,000 ppm (fig. 9). Based on growth requirements for alfalfa, some samples of alfalfa taken from the alfalfa taken from the control fields appear to be low in this essential element.

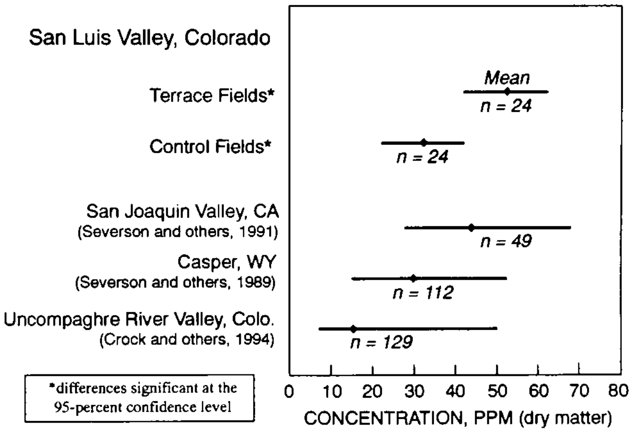

Figure 8. Levels of Mn in alfalfa samples collected from fields irrigated by Terrace Reservoir and other sources compared with Mn levels in alfalfa from three other regions in Western United States.

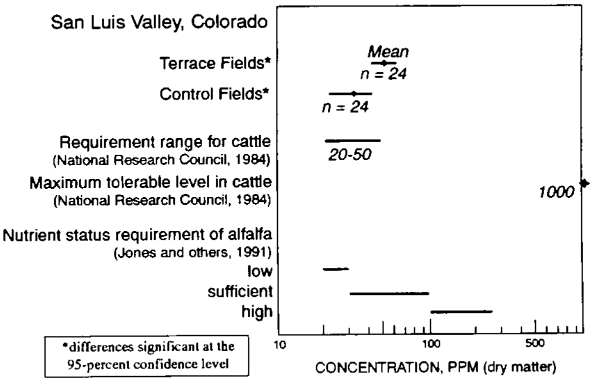

Figure 9. Levels of Mn in alfalfa samples collected from fields irrigated by Terrace Reservoir and other sources compared with nutrient requirements for Mn in cattle and in alfalfa.

Our interpretation for Ni—the final element of concern—focuses only on a comparison with the three other alfalfa studies (fig. 10) because nutrient requirements for cattle and alfalfa were not found. Nickel levels in the alfalfa from Terrace fields also differ significantly from alfalfa in the control fields. The ranges found in all alfalfa sampled in this study, regardless of the source waters, are at the low end of ranges given for alfalfa from the three other regions. This observation suggests that if Ni constitutes part of the contamination suite of metals in the Alamosa River the impact has little importance on the nutritional quality of alfalfa.

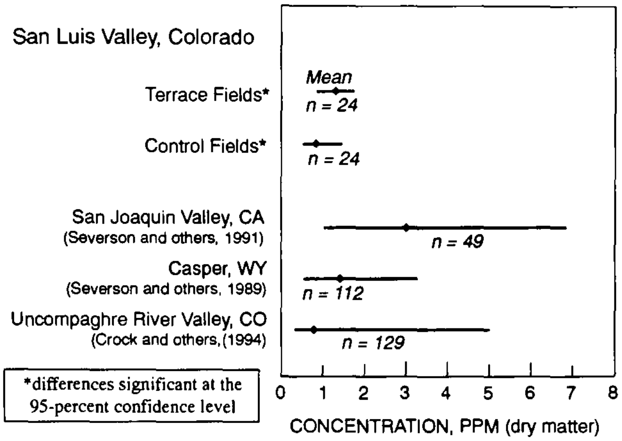

Figure 10. Levels of Ni in alfalfa samples collected from fields irrigated by Terrace Reservoir and other sources compared with Ni levels in alfalfa from three other regions in Western United States.

CONCLUSIONS

- Irrigation water from Terrace Reservoir is clearly more acid (pH 5.6-6.8) and higher in some metals than water from other sources (pH 7.6-9.2).
- Water samples taken from Terrace-Reservoir irrigated fields contained Cu and Mn levels that exceed the Colorado Surface-Water Standards for Agricultural Use.
- Although all soil data from the study area are within the geochemical baselines for soils from the Western United States, Cu concentrations were significantly higher in soil samples from fields irrigated by Terrace-Reservoir water.
- Small but significant differences were seen in the concentrations of Cu, Mn, and Ni in alfalfa irrigated by the two water sources. *Yet the levels for Cu and Mn are well below published maximum tolerable levels and meet nutritive requirements for cattle.* Similar criteria for Ni are unknown.
- The nutrient status requirement for Cu and Mn in alfalfa sampled in June 1993 may have been slightly enhanced by irrigation water from the Terrace Reservoir.

ACKNOWLEDGEMENTS

We thank the cooperating farmers for their approval to sample their fields. James Crock, Paul Briggs, John McHugh, David Fey, and Peter Theodorakos, with the Analytical Chemistry Services Group (USGS), provided the sample preparation and analyses under difficult chain-of-custody protocol. Graphics were prepared by Dick Walker, also with the USGS.

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Appendix Table 1. Analytical results for alfalfa collected from fields irrigated with Terrace Reservoir water, southwestern San Luis Valley, Colorado, June 3-6, 1993.

[Concentrations expressed on a dry-weight basis; paired samples are analytical duplicates; shaded columns indicate significant differences were found between source waters.]

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Li ppm	Mn ppm	Mo ppm	Na ppm	Ni ppm	Sr ppm	Zn ppm
Terrace Field #1																	
T11A	2.1	3.4	0.27	0.52	37	27	0.62	0.25	11	98	<.49	63	0.49	530	1.2	120	27
T11R	2.1	3.5	0.29	0.55	39	27	0.52	0.26	11	100	<.52	60	0.65	520	1.3	120	30
T12A	2.0	3.9	0.25	0.51	53	27	0.53	<.27	11	93	<.53	61	<.53	210	1.5	110	32
T12R	1.9	4.0	0.25	0.52	53	27	0.67	0.40	11	110	<.53	60	<.53	210	1.3	110	33
T13A	1.9	4.1	0.27	0.49	53	23	0.67	0.40	13	120	<.53	57	<.53	210	1.2	98	28
T13R	1.6	4.3	0.25	0.45	50	23	0.50	0.38	12	110	<.5	46	0.5	200	1.0	94	26
T14A	1.8	3.6	0.27	0.48	110	27	0.49	0.37	12	150	<.49	52	<.49	140	1.1	100	28
T14R	1.8	3.8	0.28	0.49	180	28	0.50	0.38	13	180	<.5	49	<.5	110	1.1	98	30
Terrace Field #2																	
T21A	2.2	3.1	0.30	0.43	130	32	0.48	0.36	13	160	<.48	54	<.48	230	1.7	160	34
T21R	2.0	3.2	0.31	0.42	120	34	0.59	0.35	13	180	<.47	52	<.47	220	1.2	150	33
T22A	2.1	3.1	0.31	0.44	120	33	0.59	0.35	14	170	<.47	58	<.47	240	1.4	150	34
T22R	2.0	3.1	0.30	0.44	120	32	0.23	<.23	14	160	<.46	52	<.46	230	1.5	150	35
T23A	1.9	3.5	0.29	0.47	36	24	0.48	0.24	13	96	<.48	48	<.48	160	1.4	120	36
T23R	1.7	3.5	0.27	0.44	34	24	0.45	0.23	12	90	<.45	42	<.45	150	1.4	110	34
T24A	2.1	2.8	0.29	0.43	88	30	0.55	0.22	14	140	<.44	51	<.44	180	1.2	130	31
T24R	1.9	3.0	0.29	0.42	77	31	0.55	<.22	14	130	<.44	47	<.44	180	1.2	130	31
Terrace Field #3																	
T31A	1.9	4.0	0.28	0.48	40	20	0.40	0.27	11	80	<.53	48	0.53	200	0.93	100	19
T31R	1.9	4.0	0.29	0.49	29	20	0.57	0.29	11	86	<.57	47	<.57	200	1.1	100	19
T32A	2.0	3.7	0.27	0.55	40	25	0.53	0.40	13	110	<.53	53	<.53	210	1.3	110	28
T32R	1.9	3.9	0.25	0.53	40	27	0.40	0.40	12	93	<.53	51	<.53	200	1.1	110	28
T33A	2.0	3.9	0.27	0.53	42	36	0.56	0.42	11	98	<.56	50	<.56	180	1.7	120	25
T33R	1.8	3.9	0.26	0.50	27	35	0.54	0.27	11	81	<.54	45	<.54	180	1.4	120	23
T34A	1.7	3.9	0.27	0.48	65	29	0.39	0.39	10	100	<.52	55	<.52	220	0.91	110	23
T34R	1.7	4.1	0.28	0.48	28	29	0.41	0.41	9.3	97	<.55	50	<.55	210	0.80	120	23
Terrace Field #4																	
T41A	2.4	3.4	0.36	0.49	27	30	0.54	0.27	10	95	<.54	47	<.54	430	1.1	150	34
T41R	2.3	3.3	0.35	0.49	26	29	0.39	0.39	10	91	<.52	44	<.52	400	0.90	140	34
T42A	2.2	3.6	0.33	0.52	26	29	0.51	0.38	9.2	90	<.51	47	<.51	600	1.0	140	27
T42R	2.2	3.3	0.33	0.53	26	29	0.39	0.26	9.0	100	<.52	48	<.52	570	1.0	130	27
T43A	2.1	3.1	0.34	0.48	24	27	0.47	0.35	10	83	<.47	44	<.47	600	1.2	140	30
T43R	2.1	3.2	0.34	0.49	25	27	0.37	0.25	10	86	<.49	44	<.49	600	1.2	150	31
T44A	2.3	3.5	0.35	0.52	27	31	0.53	0.40	11	80	<.53	47	<.53	510	1.1	160	28
T44R	2.2	3.4	0.34	0.52	26	29	0.39	0.26	10	91	<.52	43	<.52	480	1.3	140	29

Appendix Table 2. Analytical results for alfalfa collected from fields irrigated with non-Terrace Reservoir water, southwestern San Luis Valley, Colorado, June 3-6, 1993.

[Concentrations expressed on a dry-weight basis; paired samples are analytical duplicates; shaded columns indicate significant differences were found between source waters.]

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Li ppm	Mn ppm	Mo ppm	Na ppm	Ni ppm	Sr ppm	Zn ppm
Control Field #1																	
C11A	1.8	3.3	0.26	0.47	65	18	0.52	0.52	6.8	120	<.52	31	2.5	460	1.6	110	25
C11R	1.6	3.4	0.24	0.41	63	18	0.25	<.25	5.9	100	<.5	26	1.9	430	1.0	110	23
C12A	2.3	3.2	0.27	0.47	93	23	0.40	0.40	7.6	120	<.53	37	2.3	310	1.1	130	20
C12R	2.3	3.2	0.27	0.49	95	24	0.41	0.27	7.8	120	<.54	39	2.4	310	1.1	140	20
C13A	2.1	3.2	0.24	0.45	170	18	0.42	0.42	8.5	180	<.56	34	2.8	530	1.1	130	22
C13R	2.2	3.5	0.25	0.46	160	19	0.58	0.44	9.1	170	<.58	35	2.6	550	1.0	130	22
C14A	2.0	3.8	0.25	0.49	130	25	0.44	0.29	8.3	160	<.58	42	3.2	170	0.87	130	22
C14R	2.0	3.6	0.24	0.48	130	22	0.56	0.28	8.1	150	<.56	39	3.1	170	0.84	120	21
Control Field #2																	
C21A	2.1	3.9	0.24	0.34	82	15	0.49	<.33	7.2	110	<.65	36	1.0	110	0.81	110	13
C21R	2.0	3.8	0.24	0.35	92	15	0.46	0.31	7.8	140	<.61	37	1.1	120	0.77	110	13
C22A	2.0	3.8	0.26	0.38	27	15	0.41	<.27	7.6	95	<.54	43	1.2	110	0.67	120	13
C22R	2.0	4.1	0.25	0.39	28	14	0.56	0.28	7.6	98	<.56	41	1.1	110	0.70	120	13
C23A	2.1	4.1	0.27	0.36	30	10	0.44	<.3	8.4	74	<.59	36	2.4	190	0.59	140	14
C23R	2.2	4.0	0.29	0.34	31	10	0.31	<.31	8.1	93	<.62	37	2.5	190	<.62	140	13
C24A	2.6	4.5	0.42	0.59	52	15	0.52	<.35	11	120	<.69	38	1.9	970	0.86	190	29
C24R	2.0	4.1	0.33	0.45	50	14	0.50	0.33	6.6	83	<.66	38	2.0	230	0.66	140	16
Control Field #3																	
C31A	1.8	3.4	0.28	0.34	36	9.2	0.48	0.24	8.2	84	<.48	26	2.6	800	0.48	160	19
C31R	1.7	3.3	0.28	0.34	37	9.2	0.49	<.25	8.4	74	<.49	27	2.7	800	0.62	160	20
C32A	1.9	3.1	0.26	0.43	38	9.8	0.50	<.25	8.6	100	<.5	29	1.3	700	0.50	140	20
C32R	1.4	3.1	0.22	0.32	26	9.2	0.38	0.26	4.2	64	<.51	26	1.3	170	<.51	100	11
C33A	1.9	3.6	0.29	0.44	100	10	0.29	<.29	8.8	130	<.58	32	2.9	1000	<.58	140	20
C33R	1.9	3.6	0.30	0.42	87	11	0.58	0.44	8.7	120	<.58	30	2.8	1000	<.58	140	20
C34A	2.0	3.4	0.30	0.41	68	14	0.27	0.27	8.9	95	<.54	32	1.6	700	<.54	150	20
C34R	2.0	3.4	0.30	0.41	68	14	0.41	<.27	8.6	110	<.54	31	1.6	700	<.54	150	20
Control Field #4																	
C41A	1.8	3.3	0.25	0.37	130	30	0.46	<.23	9.0	130	<.46	23	1.5	200	0.80	130	25
C41R	1.8	3.4	0.25	0.41	140	30	0.49	0.25	10	140	<.49	25	1.6	210	0.86	140	27
C42A	1.8	3.8	0.27	0.42	70	29	0.28	0.28	9.0	84	<.56	27	1.8	240	0.56	170	18
C42R	1.9	3.7	0.30	0.43	83	32	0.28	0.28	8.6	97	<.55	28	1.7	250	0.69	170	18
C43A	1.8	3.8	0.26	0.41	90	26	0.26	0.38	10	100	0.64	24	1.5	670	0.90	140	24
C43R	1.7	3.7	0.28	0.41	67	27	0.53	0.27	10	110	0.67	24	1.5	650	0.93	130	25
C44A	1.6	3.5	0.25	0.36	92	24	0.35	0.35	11	140	0.46	22	1.6	290	0.80	130	25
C44R	1.6	3.6	0.27	0.38	98	25	0.49	0.25	11	110	0.49	22	1.7	280	0.86	140	27

METAL UPTAKE BY MORAVIAN III BARLEY IRRIGATED WITH WATER AFFECTED BY ACID MINE DISCHARGE IN SAN LUIS VALLEY, COLORADO.

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ABSTRACT

The objectives of this study were to examine whether the use of water from the Terrace Reservoir on the Alamosa River significantly increased metal uptake in malt barley (*Hordeum vulgare* cv. Moravian III) and to determine relationships between soil chemistry and plant-metal concentrations.

The pH of water samples collected from the Terrace-irrigated fields averaged 6.0 and ranged from 5.3 to 6.7. The pH for control-field water was significantly higher and averaged 8.2 with a range of 7.3–9.2. Fields irrigated with water from the Terrace Reservoir clearly receive more acidic water than do fields irrigated with water from other sources. As with the pH of the irrigation waters, the soil pH of the Terrace fields was significantly lower than that of the control fields.

Results of total analyses of soils show some differences between fields irrigated with Terrace Reservoir water and control fields. Concentrations of Co, Cu, Fe, Mn, Pb, V, and Zn were significantly higher in soils from the Terrace-irrigated fields than in soils from the control fields. On the other hand, concentrations of Ca, Li, Mg, Na, and Sr were significantly higher in the soils from the control fields than in those from the Terrace-irrigated fields. Equally important, metal concentrations in all the soils sampled were within ranges for Western U.S. soils given by Shacklette and Boerngen (1984).

Results of the barley analyses showed that Ba, Cu, K Ni, and Zn were present in significantly greater concentrations in the barley grain of the fields irrigated with Terrace Reservoir water than in the barley grain of the control fields. Grain concentrations of Cu and Ni also were strongly, negatively correlated to soil pH and strongly, positively correlated with DTPA- extractable Cu and Ni in the soils. Strontium concentrations were significantly greater in the grain of the control fields. Greater loading rates of Cu, Ni and Zn were evident. Lower soil and water pH, appears to be making some metals, particularly Ba, more available to barley. Although the differences in barley and soil metal concentrations of the two water treatments were statistically significant, they were not large and all concentrations were well within the reported ranges for barley grain grown in other regions of the U.S.

INTRODUCTION

Mining activities in Colorado, both current and historic, have affected Colorado's water resources for many years. Acidic discharges from mining activity can alter the pH of natural waters and dissolve many metals that would otherwise be sequestered in unavailable forms. This can harm aquatic life and reduce the quality of the affected water for agricultural use.

The San Luis valley of south-central Colorado has approximately 45,000 acres of farm land in Alamosa and Conejos Counties irrigated with water from Terrace Reservoir (EPA, 1993). Terrace Reservoir is fed by the Alamosa River and this water is in turn distributed to the valley through a series of canals. As a result of mining activities at Summitville and other sites in the upper reaches of the Alamosa's watershed, the reservoir has been affected by imported metals and increased acidity (EPA, 1993).

The purpose of this study was to examine the effects of irrigation with water from the Terrace Reservoir on barley and the associated soils in the San Luis valley. Primarily, this study was designed to determine if significant differences in metal concentrations in soils and barley (*Hordeum vulgare* cv. Moravian III) were observable between fields irrigated with Terrace Reservoir water and fields irrigated from other water sources and if these concentrations were higher than ranges reported in the literature. Also, this study sought to determine if any temporal changes were observable in the soil chemistry within the season sampled.

Several soil extractions and data analyses were utilized to help elucidate the effects of the irrigation water. 1) analysis of variance (ANOVA) was utilized to examine differences in water, soil and barley metal concentrations between water sources; 2) results of this study were compared to values found in the literature; 3) correlations between soil pH, estimated bioavailable metals (using diethylene triamine pentaacetic acid, DTPA, extractions) and metal concentrations in plants were examined.

MATERIALS AND METHODS

Soil Sampling Design

Soil samples were taken over the course of the summer of 1993 to estimate the metal concentration in the soil and observe if the concentrations were changing over the course of the season sampled. Soils were sampled at three intervals: June 8-10; July 17-20 and August 10-13. Six fields were selected in the Capulin area using the soil survey maps available for Conejos and Alamosa counties (Soil Conservation Service, 1973; 1980). Fields with similar physical soil types were selected.

Of the fields chosen, three were irrigated with water from Terrace reservoir (hereafter referred to as Terrace fields) and three were irrigated with either water from the Rio Grande River brought by the Monte Vista canal or deep well water derived from the lower confined aquifer (hereafter referred to as control fields). All the fields were irrigated by center-pivot irrigation systems except for one Terrace field that was flood irrigated.

All the fields were planted in Moravian III malting barley, though two Terrace fields were under-planted with alfalfa (for next year's crop). The fields were not ideally similar due to difficulty in finding fields that met all the physical parameters and to which the land owner would permit access.

Each of the six fields was divided into quarters and three quarters were randomly selected for sampling. Within each quarter, a depth-composited sample of the top 20 cm was collected and the location of the soil pit recorded. Care was taken so that the shovel contacted only one side of the hole. A channel sample was then removed from the opposite side of the hole and set on the ground while still on the shovel ensuring the sample never contacted the ground. The sample was squared so that equal volumes of the 20 cm depth could be taken. This was placed in a plastic dish pan and any plant material or large rocks were removed. A sub-sample of this composite was then placed in a paper soil-sample envelope. Thus, three composited soil samples per field were collected at each of the sampling periods. Compositing was used to obtain three representative samples from each field.

Soil samples were prepared in a manner consistent with the standard USGS soil preparation protocol (Peacock, 1990) prior to extractions.

A modified version of a procedure outlined by Crock and Severson (1980) was used to determine soil pH using a 5:1 ratio of water to soil instead of a 1:1 ratio.

The DTPA extraction for bioavailable metals procedure used was outlined in Crock and Severson (1980). A solution of 0.005 M DTPA, 0.01 M calcium chloride, and 0.1 M triethanolamine adjusted to pH 7.3 was freshly prepared and used in this study.

To determine bulk soil metals a mixed acid digestion procedure outlined in Crock and others (1983) and Briggs (1990) was used. All extraction analyses were done using inductively coupled plasma atomic emission spectroscopy (ICP-AES) performed by the USGS analytical laboratories at the Federal Center Denver, Colorado.

Plant Sampling Design

The plant sampling design was identical to that used for soil sampling. Plant samples consisted of equal volumes of ripe barley heads hand harvested within 2 m of each soil pit. The sampled grain from each of the three sites was placed in a clean cloth bag. Thus, three composited grain samples were collected per field, including one field duplicate, for a total of 19 samples.

Five of the fields were sampled from August 10 to 13, 1993 within a week of being harvested. The sixth field was planted later than the other fields and was sampled at a separate, later time so that it would be of equivalent ripeness to the other fields.

The plant samples were returned to Denver and prepared in a manner consistent with the procedure outlined by Peacock (1992). Samples were first threshed and cleaned. Afterwards, the grain was washed with deionized water to remove surface contaminants.

The samples were then dried in a locked drying oven at 40°C for 48 hours. Samples were removed from the oven and ground to a powder using a Wiley mill and a coffee grinder. These were then dry ashed in muffle furnaces that ramped up to approximately 500°C at 100°C per hour for 8 hours. The ashed samples were then digested by the same multi-acid digestion procedure as the total soil metal extraction (Crock and others 1983; Briggs 1990). The extractant was then analyzed using ICP-AES in the same manner as the soil samples.

Water Sampling Design

One water sample was taken from the sprinkler system of each field. The sample was collected at either a spigot on the sprinkler or a sprinkler head. If no water was flowing through the sprinkler, a sample was taken from the reservoir that fed the sprinkler; this was avoided when possible for sample consistency.

Samples were filtered through a 0.45μm disposable filter pod attached to a plastic syringe and acidified in the field with metal free nitric acid. Analysis of the water samples was done by ICP-AES (Crock and others, 1983) performed by the USGS analytical laboratories.

Quality Control And Assurance

Samples were collected with utensils that had been decontaminated before use. For soil sampling, spades, dishpans and any other tool directly contacting the samples were cleaned before each use. This involved scrubbing the utensils with a wet plastic bristle brush, rinsing the utensil with clean, deionized water and drying the utensil with a paper towel. Also, soil samples were only touched with clean utensils or a gloved hand (a new latex glove was used on each composite sample). For plant sampling, a plastic dish pan was rinsed between samples and dried with a paper towel. For water sampling, new disposable syringes, filter pods and sample bottles were used for each sample and were pre-rinsed with sample water. Sample bottles for cation analyses also were acid washed with 10% HCl. Any instrument that was reused was thoroughly rinsed with deionized water.

Numerous standards, duplicate, replicates and blanks were inserted into all sample sets to assure both accuracy and precision of the results. Samples were submitted to the USGS labs in random order and chain-of-custody forms were kept for all samples.

Statistical Analysis

Descriptive statistics were calculated for each data set. Each sample population was tested using a Kolmogorov-Smirnov (Montgomery, 1991) test to determine distribution. Log-normal populations were log transformed before any statistical tests were run using the data.

Differences between means were tested using Statgraphics 6.0 using a 3-level, balanced, nested analysis of variance (ANOVA) with all fixed effects. Means also were examined with respect to time using an ANOVA (for soil data sets, which were collected at different times over the season). For all statistical tests, significance was assigned at the 0.01 probability level. Correlations between barley concentrations of each metal and each soil fraction as well as soil pH were calculated. Thus, correlations between barley metals and soil bulk chemistry, DTPA extractable metals in the soil and soil pH were found. Means and ranges for each water source are given.

RESULTS

Water Results

The pH values for the Terrace water source were significantly lower than the control sources (Table 1) and many of the metal concentrations were higher in the Terrace water source than in the control sources (Table 2). No ANOVA's were run on the metal concentrations in the irrigation water because many results for the control field water sources were below detection limits for many of the.

From the water analysis (Table 2) it was obvious that the Terrace water source was chemically different from the control sources.

Soil Results

The Terrace-irrigated fields had significantly lower soil pH values than did the control fields (Table 1).

Terrace-irrigated fields had statistically higher bulk soil chemistry concentrations of Co, Cu, Fe, Pb, Mn, V and Zn (Table 3). The control fields had higher soil concentrations of Ca, Li, Mg, Na and Sr. These differences, though statistically significant, were small and all the results were well within the ranges for soils of the Western U.S. reported by Shacklette and Boerngen (1984).

Soils from the Terrace irrigated fields had significantly higher extractable concentrations of Ce, Cu, Mn, Ni, and Zn, whereas the control-field soils had significantly higher extractable concentrations of Ca (Table 4).

Table 1. Water and soil pH values
for terrace and control fields

Water pH	**Mean**	**Range**
Terrace	6.0	5.3-6.7
control	8.2	7.3-9.2
Soil pH		
Terrace	7.2	5.4-7.9
control	8.2	7.6-8.5

No significant temporal changes were observed for any soil metal concentration over the course of the season sampled.

Plant Results

Grain from the Terrace-irrigated fields had higher concentrations of Ba, Cu, K, Ni and Zn (Table 5). The grain from the control fields had higher concentrations of Sr. Though these differences were statistically significant, they were small and all results were well within reported ranges for metals in barley.

Several significant correlations also were evident in the data collected. Plant Cu concentrations were negatively correlated with soil pH (correlation coefficient = -0.81). A positive correlation between plant Cu concentrations and DTPA extractable Cu also was observed (correlation coefficient = 0.70).

Ni also was correlated negatively with soil pH (correlation coefficient = -0.74) and a positive correlation between plant Ni concentrations and DTPA extractable Ni

Table 2. Results of water analysis for unfiltered samples (n=3). All results reported in ppb. Below detection limits are reported as <Detection limit. Populations assumed normal.

	Values for Terrace fields		Values for control fields	
Metal	Mean	Range	Mean	Range
Al	500	500-500	<10	NA
Ba	29	24-33	24	19-28
Ca	1700	1700-1700	1500	1200-3300
Cd	2	2-2	<2	NA
Co	13	11-14	<5	NA
Cu	700	460-920	<10	NA
Fe	2000	600-3000	<50	NA
K	900	900-900	2000	1000-3000
Mg	1500	1000-3000	1400	2000-3000
Mn	600	530-620	20	8-27
Na	4000	3000-5000	5000	3000-6000
Ni	14	13-15	<5	NA
Si	8000	4000-9000	11000	2000-20000
Sr	130	120-140	100	72-230
Zn	200	90-260	<10	NA

was observed (correlation coefficient = 0.71). Plant Zn concentrations were negatively correlated with soil pH (correlation coefficient = -0.51) and positively correlated with DTPA extractable Zn (correlation coefficient = 0.77). Plant Ba concentrations also were negatively correlated with soil pH (correlation coefficient = -0.33).

No relationships between bulk soil chemistry and plant metal concentrations were observed.

DISCUSSION

Copper

Copper is a vital component in a wide variety of biochemical processes in plants. Copper is associated with numerous enzymes that regulate various reduction/ oxidation reactions (Gupta, 1979). Photosynthesis, respiration, carbohydrate distribution, nitrogen reduction/oxidation and protein metabolism are all reactions regulated by copper containing compounds (Kabata-Pendias and Pendias, 1984). Copper also acts as a prosthetic group and activator. Proper nutritive concentrations of Cu improve the utilization of NH_4^+ as a nitrogen source (Gupta, 1979).

The concentration of Cu in the barley grain was strongly related to the soil pH. This is consistent with Gupta (1979), Thornton (1979), Kabata-Pedias and Pendias (1984) who concluded that Cu is primarily available in its ionic form, which would be strongly affected by the soil pH (Pickering, 1979). Xian (1989) found that in cabbage plants, the plant concentration of Cu was strongly related to the exchangeable and carbonate fractions that again are strongly affected by pH. In ryegrass and wheat, soil pH also was shown to be the overriding factor in plant Cu concentration (Sauerbeck, 1991). As seen in the Terrace fields, higher plant concentrations of Cu are associated with the lower soil pH. It is reasonable to conclude that not only is the pool of Cu being increased by the addition of Cu in the irrigation water, but this Cu is more available to the plants due to the decreased soil pH.

The negative relationship between grain-Cu concentrations and soil pH indicates that the uptake and translocation mechanisms are dependent on ionic Cu. Laurie and others, (1991) discuss that the chelating agent has an impact upon the amount of Cu extracted by the plant and that at a lower pH more Cu may be chelated. This is consistent with the positive relationship found between DTPA extractable Cu in the soil and plant-Cu concentrations.

Although statistically significant differences were established between the water sources, the higher Cu concentrations in Terrace-irrigated barley do not exceed normal reported ranges for Cu in barley (Table 5).

Nickel

There is no evidence of a physiological requirement of Ni for plant metabolism or function, but nickel appears to be mobile in plants and may accumulate in leaves or seeds

Table 3. Bulk soil chemistry results (n=32). All populations were log-normal distributions. Table compares Terrace fields and control fields to literature values.

	Values for Terrace fields			Values for control fields			Literature values for Western U.S. soils*	
Metal	GM‡	Range	GD	GM	Range	GD	GM	Range
Al (%)	7.4	7.1-7.7	1.7	7.3	6.6-7.7	1.6	5.8	0.5->10
Ca(%) †	1.1	1-1.3	2.4	2.3	1.4-4.2	0	1.8	0.06-32
Fe (%) †	5.3	4.7-5.8	1.27	4.7	4.1-5	1.4	2.1	0.1->10
Mg (%) †	0.7	0.63-0.83	2.8	0.87	0.75-1.1	2.2	0.74	0.03->10
P (%)	0.12	0.1-0.16	3.9	0.14	0.12-0.15	6.9	320	40-4,500
K (%)	2.3	2-2.6	1.8	2.3	2.2-2.5	2.6	1.8	0.19-6.3
Na (%) †	1.5	1.2-1.8	1.6	1.7	1.6-1.9	2.7	0.97	0.05-10
Ti (%)	0.52	0.42-0.64	4.6	0.51	0.44-0.55	1.6	0.22	0.05-2.0
Ba (ppm)	790	680-870	4.2	800	740-850	3	580	70-5000
Be (ppm)	1.6	1-2	1	1.4	1-2	1	0.68	<1-15
Ce (ppm)	63	60-69	1.1	64	60-69	1	65	<150-300
Cr (ppm)	26	16-36	1.7	27	19-33	1.2	41	3-2,000
Co (ppm) †	18	15-23	1	15	14-17	1.9	7.1	<3-50
Cu (ppm) †	43	33-60	2.1	31	28-35	1	21	2-300
Ga (ppm)	16	15-18	0	16	14-18	1	16	<5-70
La (ppm)	33	31-37	0	34	31-37	1.1	130	30-200
Pb (ppm) †	25	19-35	1.6	21	17-24	1.1	17	<10-700
Li (ppm) †	14	12-17	1	16	14-18	1.1	22	5-130
Mn (ppm) †	870	740-980	4.3	800	740-890	3.7	380	30-5,000
Nd (ppm)	28	25-31	1	28	25-32	1	36	<70-300
Ni (ppm)	13	10-16	1	13	10-15	1	15	<5-700
Nb (ppm)	13	10-15	0	14	12-15	1	8.7	<10-100
Sc (ppm)	10	9-11	1	10	9-11	1	8.2	<5-50
Sr (ppm) †	420	400-450	2.4	480	430-570	3.5	200	10-3,000
Th (ppm)	8.7	6-11	0	8.3	7-11	1.2	9.1	2.4-31
V (ppm) †	140	120-170	2.8	130	110-150	9.3	70	7-500
Yb (ppm)	1.4	1-2	0.67	1.9	1-2	0	2.6	<1-20
Y (ppm)	15	12-18	0.58	18	17-19	1.1	22	<10-150
Zn (ppm) †	110	91-130	2.4	94	81-100	5	55	10-2,100

* Shacklette, H. T., J. G. Boerngen (1984).

† Indicates that the Terrace and control populations were significantly different at the 0.01 probability level

‡GM denotes geometric mean, GD denotes geometric deviation

(Welch and Cary, 1975). This mobility may account for the relative toxicity of Ni. Typical toxic symptoms are predominantly chlorosis and restricted plant growth (Kabata-Pendias and Pendias, 1984). One suggested mechanism of toxicity is Ni interactions with Fe thus resulting in Fe deficiencies in plants (Wallace et al., 1977).

The Ni results are consistent with other studies in which strong negative relationships were found between soil pH and plant Ni concentrations (Bates and others, 1980; Kabata-Pendias and Pendias, 1984; Saurbeck, 1991). Garrels and Christ (1965) described Ni solubility in soil solution increasing with decreasing soil pH. The negative relationship between plant-Ni concentrations and soil pH may be a result of more inorganic species becoming available to chelates. Similar to Cu, Ni^{2+} is readily chelated (Kabata-Pendias and Pendias, 1984) and with decreasing pH, more Ni may be in the Ni^{2+} form. Cataldo and others, (1978) found that in soybean plants Ni uptake was positively correlated with soluble Ni concentrations in the soil solution.

The relationship between DTPA-extractable Ni and plant concentrations also is consistent with Keeney and

Table 4. DTPA extractable soil metal results (n=27). Values are reported in ppm.
All populations were log-normal distributions. Values are reported for metals above detection limits.

	Values for Terrace fields			Values for control fields		
Metal	GM	Range	GD	GM	Range	GD
Ba	1.8	1-4	1.1	0.87	0.12-4	1
Ca †	300	200-780	4	1,400	800-2,100	6
Ce †	2.7	1.6-4	1	0.84	0.6-1.6	2
Cu †	4.6	2-12	1	1.6	0.8-2	1.9
Pb	0.2	0.11-.4	4.9	0.42	0.16-0.8	3.9
Mg	160	130-190	2.3	180	62-580	4.1
Mn †	33	22-54	2.6	13	8-30	1.8
Ni †	0.73	0.4-1.0	2.4	0.21	0.14-0.4	3.5
Sr	12	6-10	1	14	10-24	0.74
Zn †	1.4	0.14-4	1	0.29	0.056-1.6	1.4

† indicates differences significant at the 0.01 probability level

Walsh (1980) who found a strong positive relationship between DTPA-extractable Ni and plant-Ni concentrations in sludge-amended soils. Garrels and Christ (1965) comment that organic chelated forms of Ni are the most available to plants, which may account for the high bioavailable Ni concentrations in sludge amended soils.

As with Cu, Ni is present in significantly greater concentrations in the soils and grains of the Terrace-irrigated fields. Nickel also is significantly more concentrated in the Terrace-irrigation water. These results would indicate that irrigating with Terrace Reservoir water is altering the Ni concentrations both in the soil and in the barley. Though these differences are significant , the concentrations of Ni in the soil and plants are well within normal ranges reported in the literature (Tables 3 and 5).

Zinc

Within a plant, Zn has numerous physiologic functions, typically being associated with enzymes such as dehydrogenases and protenases. Zinc also affects the permeability of membranes. Tinker (1981) reported Zn being generally bound to low molecular weight, soluble proteins. Zinc also is reported to have varying mobility within the plant depending upon species and period in growth cycle (Kabata-Pendias and Pendias, 1984). Zinc uptake seems primarily metabolically mediated (Kabata-Pendias and Pendias, 1984).

The results of this study were consistent with Xian (1989) who reported a strong negative relationship between soil pH and plant-Zn concentrations in cabbage plants. Bates and others (1980), Saurbeck (1991), Levy and others (1992), and Chlopecka (1993) reported that plant-Zn concentrations increased with increased application rates of both ionic Zn and sewage sludge amendments. Lindsay and Norvell (1978) and Keeney and Walsh (1980) reported plant-Zn concentrations increasing with increasing DTPA extractable Zn concentrations.

The mobility and bioavailability of Zn has been reported as dependent on the concentration of Zn^{2+} (Kabata-Pendias and Pendias, 1984). This would make pH among the most important factors affecting Zn availability and mobility. Norrish (1975) reported that Zn is typically associated with the Fe-and Mn-oxide soil fractions and that this is the most bioavailable pool of Zn. Levy and others, (1992) also found Zn mostly associated with Fe and Mn oxides in contaminated soils near Leadville, Colorado and indicated that soluble forms of Zn were most available to plants. Wallace (1989) reported that Zn uptake in grasses and other monocots was increased by the availability of NH_4^+. Lindsay (1972) proposed different mechanisms for Zn adsorption for acid soils and basic soils. In acid soils, Zn adsorption is related to cation exchange sites and in alkaline soils adsorption is influenced more by the ability of organic ligands to bind Zn.

Results indicated that the Terrace-irrigated fields had higher Zn concentrations in the bulk soil, DTPA soil extractions and in the barley grain. This indicates that Zn may have become more available in the Terrace irrigated fields due to the increased concentration of Zn in the irrigation water and the lower soil pH values. Though Terrace-irrigated barley had statistically higher zinc

Table 5. Metal concentrations in San Luis Valley barley grain (n=19). All values are by dry weight in ppm. Table includes all metals above detection limits. All populations are normal distributions.

	Values for Terrace fields			Values for control fields			Literature values for barley grain		
Metal	Mean	Range	SD•	Mean	Range	SD	Mean	Range	Source
Al	6	2-30	2	3	2-7	0.6	-	-	-
Ca	550	500-600	10	550	500-600	10	900	300-1500	7
Fe	40	30-50	3	40	30-100	5	70	40-220	7
Mg	1330	1200-1400	20	1300	1200-1400	10	1600	1200-7800	5,7
P	4400	4000-6500	50	4200	3800-4900	90	3500	2400-4400	7
K †	5200	4400-6500	200	4300	4000-5000	70	5600	3400-9200	4,7
Ba †	4.6	3.4-7.3	0.025	2.7	0.3-4.7	0.43	2.3	<1.5-3.4	4
Cr	0.4	0.23-0.51	0.02	0.41	0.23-0.50	0.02	-	-	-
Cu †	6.5	4.9-7.3	0.14	4.4	3.5-5.7	0.19	5.5	1-15	1,2,3,4,5,6,8
Mn	17	13-30	1.6	14	13-16	0.27	15	9-23	3,9
Ni †	0.15	0.07-0.22	0.01	0.09	0.02-0.15	0.001	0.35	0.16-0.67	1,4,5
Sr †	4.5	3.8-5.5	0.16	5.4	4.8-7.1	0.19	0.98	0.42-2.8	4
Zn †	30	18-44	2.6	21	14-34	1.7	28	12-48	1,2,3,5

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1. Bansal (1991).
2. Chlopecka (1993).
3. Dudas and Pawluk (1977).
4. Ebens and Shacklette (1982)
5. Erdman and Moul (1982).
6. Greaves and Andersen (1936).
7. Greaves and Hirst (1929).
8. Liu, Pomeranz and Robbins (1974).
9. Underwood, Robinson and Curnow (1947).

† Indicates that the Terrace and control populations were significantly different at the 0.01 probability level.

• SD indicates standard deviation

concentrations, these concentrations were well within reported ranges for zinc in barley (Table 5).

Barium

Barium readily precipitates as sulfates and carbonates and is strongly adsorbed by clays (Birkeland, 1984). Thus, Ba in soils is predominantly in forms unavailable to plants. Weinberg (1977) indicates that plants may be able to easily extract Ba from acid soils. This may explain the higher Ba concentrations in the Terrace irrigated barley grain. The slightly more acidic soils of the Terrace fields may be allowing the barley to extract Ba^{2+}.

The relationship between soil pH and plant-Ba concentrations may explain why the Terrace grain had higher concentrations of Ba. Thus the effect of irrigation with Terrace water would appear to be related to its effect on the soil pH rather than by its Ba load, since no significant differences in Ba concentrations were found between water sources.

CONCLUSION

Significantly higher barley grain concentrations of Ba, Cu, Ni, and Zn were evident in the Terrace-irrigated barley. Soil pH appeared to be the major soil chemistry factor affecting plant-metal concentrations. Because other factors were controlled as much as was possible in the field study, the higher concentrations of metals in the Terrace irrigated fields most likely were due to irrigation with water from Terrace Reservoir. Also, it appears that changes in Cu, Mn and Zn can be traced to increased concentrations in the irrigation water from the Alamosa River. Barium may be more available to plants due to decreases in soil pH which is a result of irrigating with Terrace Reservoir water. Thus, irrigation with Terrace Reservoir water has significantly altered the plant-metal concentrations of Ba, Cu and Zn by increased loads in the irrigation water as well as by lower pH.

Although significant differences were observed between the Terrace and control fields, most of the metal concentrations were within values reported for barley grown in other areas of the U.S. The exception, Sr, was present in higher concentrations in the grain of the control fields than reported values, possibly due to high naturally occurring Sr in the soils. These results indicated that irrigation with water affected by acid-mine discharge did not adversely affect the barley crops. It also was evident from the results that any changes in soil chemistry likely are occurring at a relatively slow pace, since no temporal changes in soil chemistry were observed over the season sampled.

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METAL CONTENT OF WHEAT AND POTATO TISSUE AND ASSOCIATED SOILS IRRIGATED WITH ALAMOSA RIVER WATER

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INTRODUCTION

Acidic, natural and mine-drainage waters carrying high levels of dissolved metals, have been documented entering streams and irrigation waterways along the Alamosa River in the San Luis Valley of Colorado (Sullivan, 1993). This water conceivably presents a considerable source of metal contamination to the crops and soils irrigated with it. This study was conducted to determine whether irrigation with Alamosa River water results in higher metal content of wheat and potato tissue and associated soils when compared to commercial agricultural materials irrigated with other water sources in the valley and from different locations across the nation.

METHODS

Cooperator Selection

Wheat and potato growers were contacted throughout the Alamosa River basin and invited to cooperate in this study. Growers were selected from among those utilizing 100% Alamosa River water and 100% Rio Grande River water (supplied by the Monte Vista and Empire canals). Fields that received a mixture of river water and groundwater were not selected due to the lack of control on the origin of the groundwater. The crop and soil samples from the Rio Grande-irrigated fields were used as uncontaminated controls for comparison. Data for wheat, potato, and agricultural soil metal content was obtained from the literature to determine if unexpectedly high metal contents resulted from irrigation with Alamosa River water.

Wheat sampling and preparation

Eight wheat fields were selected for sampling. Four each were irrigated with the two irrigation water sources. All fields were irrigated by center-pivot sprinkler. To obtain representative samples under pivot irrigation, normal random sampling can not be done. Irrigation uniformity varies along the pivot line resulting in variations in water application amounts radially out from the center of the circle. To account for the variability this may impose, the sampling scheme illustrated in Figure 1 was employed. Sixteen random locations about the pivot point were selected and samples were taken at three equidistant points along the radius originating at each point. Samples were taken at 25%, 50% and 75% of the length of the radius measured from the pivot point. The samples from the above three points from a single radius were composited to represent the whole radius. Sixteen composite samples resulted. Each sample was threshed and cleaned and the straw and grain portions saved for analysis. After threshing, all samples were dried and ground. In all grinding operations (including those for potato and soil), the equipment was cleaned between samples to minimize cross contamination.

Potato sampling and preparation

Three potato fields irrigated with 100% Rio Grande

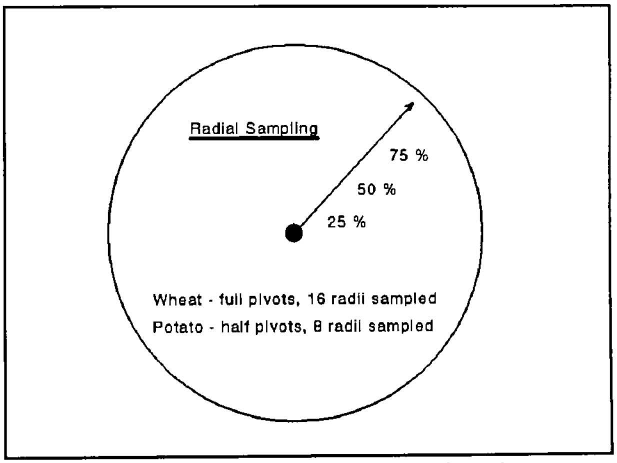

Figure 1. Radial sampling design used for wheat, potato, and soil.

River water were selected for sampling. Only one field of commercial fresh market potatoes irrigated with 100% Alamosa RIver water was available for sampling. The potato fields were also irrigated by center-pivot sprinkler and in each case only half of the pivot-covered area was planted to potatoes. To account for possible irrigation nonuniformity, the radial sampling scheme discussed above was used. To ensure that the sampling density was the same for potato as for wheat, only eight random radii were selected for sampling on the potato fields. Three to four tubers were taken at each of the three locations along each radius and composited. Eight composite samples resulted.

The potatoes were washed and scrubbed and then peeled to minimize contamination of the potato samples from soil adhering to the tuber. After the potatoes were peeled, they were diced and then dried in an oven at 60o C until the sample weight stabilized (3-4 days). After drying, the samples were ground.

Soil Sampling and preparation

Soil sampling was performed using the same radial design outlined above for wheat and potatoes. Samples were taken along the radii at the locations from which the plant samples were obtained. Samples were taken from each foot increment of depth down to 2 feet or any impeding gravel layer, whichever was shallower. Samples for each depth increment from the three points along each radius were composited as described for the plant samples. The samples were then dried and ground.

Chemical Analysis

The wheat and potato samples were wet-acid digested and the solutions analyzed for metal content using ICP-ES at Colorado State University's Soil, Water, and Plant Analysis lab. A full metal analysis was done, but only values for Copper, Cadmium, Lead, Manganese, Nickel and Zinc will be presented. These metals are those for which national comparison data could be obtained (Wolnik et al., 1983a,b)

Soil samples were acid-extracted for total metal analysis and DTPA-extracted for bioavailable metals determination. Metal content of the extracts was accomplished using ICP-ES with the exceptions of Arsenic and Selenium which were analyzed by Atomic Adsorption with hydride generation. National comparison data for soils was more readily available (Shacklette and Boerngen, 1984) in the literature and, therefore, results for more elements will be presented.

RESULTS AND DISCUSSION

Wheat

The results of the metal analysis on wheat grain samples is given in Table 1. The fields numbered 1-4 are those that were irrigated with 100% Alamosa River water. The others were irrigated with 100% Rio Grande River water. Statistically, the data shows quite a bit of scatter. However, there is no consistent difference in metal contents measured for the two water sources.

In these samples, a general elevation in the mean metal contents, compared to national baseline samples, was observed. However, the means are all within the baseline ranges established in the literature as normal for wheat across the nation. The only exceptions are the mean Manganese contents from fields 3 and 8 (one from each water source) which are above the normal baseline range. The values, however, are close to the baseline maximum and do not pose any health risk. The fact that the two means are from two different water sources implies that the elevations are due to high native content of Manganese in the soils of this area rather than in the water sources. The same explanation is likely for the generally higher mean metal contents overall, compared to wheat across the nation.

Potato

The potato tissue analysis results are given in Table 2. Fields 1-3 are those that were irrigated with Rio Grande River water. Field 4 is the Alamosa River water-irrigated field. In all cases for potato, there are no consistent differences in metal content between the two water sources. Unlike wheat, the data is much more homogeneous. All the means are near or below the national comparison data except for Lead. Lead has a higher mean on all 4 fields, suggesting an influence of the parent soils of the area rather than water source. In all cases the metal contents are within the baseline ranges for national comparison samples.

Soils

The total soil metal analysis results are given in Table 3. Statistical comparison between soils irrigated by different water sources revealed no significant difference at the 90% confidence limit. The data in Table 3, therefore, is the aggregate data for all soils under wheat and potato for both sources of water. Elevations in the measured mean metal content compared to the baseline data were found for Copper, Iron, Lead, Manganese, Phosphorus, Vanadium, and Zinc. The measured means however, fall well within the baseline ranges, and are, therefore, not abnormally high.

Table 1. Metal content (mg/kg) of wheat grain raised with Alamosa River water (fields 1-4) and Rio Grande River water (fields 5-8).

Field	Cd	Cu	Fe	Mn	Zn	Pb
1	0.12bc	6.84a	44.43b	62.04bc	45.03a	0.21ab
2	0.09c	5.22c	58.66a	47.17de	37.73b	0.21ab
3	0.18a	4.06d	37.46bc	80.98a	28.13cd	0.30a
4	0.06d	4.80cd	29.37c	38.62e	23.19e	0.007b
5	0.13b	4.19d	44.49b	58.34cd	23.21e	0.13ab
6	0.09c	5.58bc	42.02b	59.62c	25.29de	0.16ab
7	0.10c	5.35c	43.99b	55.76cd	23.94e	0.16ab
8	0.14b	6.25ab	48.43b	71.23ab	29.66c	0.36a

For comparison, the following means and ranges have been found for the above elements in wheat from around the U.S.:

Element	Mean	Range
Cadmium(Cd):	0.049	<0.002-0.210
Copper(Cu):	5.0	3.0-61
Iron(Fe):	36.9	24-68
Manganese(Mn):	43	18-68
Zinc(Zn):	31	12.9-68
Lead(Pb):	0.042	<0.0011-0.725

Note: Means followed by the same letter are not different from others in the same column at the 95% confidence limit.

Table 2. Metal content (mg/kg) of potatoes raised with Alamosa River water (field 4) and Rio Grande River water (fields 1-3).

Field	Cd	Cu	Fe	Mn	Zn	Pb
1	0.21a	2.01a	19.58a	6.90a	7.77a	0.89a
2	0.11b	4.46b	13.90a	4.01a	7.72a	1.04a
3	0.18a	2.77a	17.05a	7.56a	7.61a	0.98a
4	0.20a	2.61a	20.45a	7.69a	7.38a	1.04a

For reference, the following means and ranges have been found for the above elements in potatoes from around the U.S.:

Element	Mean	Range
Cadmium(Cd):	0.161	0.016 - 0.703
Copper(Cu):	4.970	1.110 - 10.400
Iron(Fe):	19.950	10.300 - 25.500
Manganese(Mn):	7.300	5.710 - 14.300
Zinc(Zn):	16.100	8.730 - 27.000
Lead(Pb)	0.047	0.0016-1.429

Note: Means followed by the same letter are not different from others in the same column at the 95% confidence limit.

Table 3. Total metal analysis (units noted in table) measured on agricultural soils in the Alamosa River basin and compared with baseline data from around the U.S.

Element	Baseline Range	Baseline Geometric Mean	Measured Range	Measured Geometric Mean
Aluminum (%)	1.5 - 23	5.8	1.7 - 5.1	2.8
Barium (ppm)	200 - 1700	580	48.3 - 444.5	231.4
Calcium (%)	0.19 - 17	1.8	0.4 - 4.7	0.9
Chromium (ppm)	8.5 - 200	41	2.9 - 17.4	10.2
Copper (ppm)	4.9 - 90	21	19.1 - 54.0	28.6
Iron (%)	0.55 - 8.0	2.1	2.0 - 6.1	4.1
Lead (ppm)	5.2 - 55	17	2.0 - 25.5	11.6
Magnesium (%)	0.15 - 3.6	0.74	0.5 - 0.9	0.7
Manganese (ppm)	97 - 1500	380	432 - 872	706.4
Nickel (ppm)	3.4 - 66	15	7.6 - 16.6	11.9
Phosphorus (%)	0.006 - 0.17	0.032	0.06 - 0.14	0.11
Potassium (%)	0.38 - 3.2	1.8	0.4 - 1.5	0.7
Sodium (%)	0.26 - 3.7	0.97	0.03 - 0.1	0.6
Strontium (ppm)	43 - 930	200	75.9 - 241.5	105.7
Titanium (ppm)	0.069 - 0.7	0.22	0.06 - 0.3	0.19
Vanadium (ppm)	18 - 270	70	58.2 - 150.1	103.5
Zinc (ppm)	17 - 180	55	46.7 - 107.5	85.1

The elevation in metal content is consistent with the hypothesis that these soils are naturally high in metal elements due to their parent materials from which they are derived rather than from metals applied by irrigation. The soils of this area are derivied from alluvial materials washed from the San Juan Mountains, a range renown for its rich mineral content.

CONCLUSION

The data presented in this paper clearly shows that in general, crops and soils in the Alamosa River basin have slightly higher metal content on average when compared to baseline data from around the U.S., but that the elevations are within the expected, normal range for these materials. The lack of significant differences in metal content for the crops and soils between the two irrigation water sources suggests that the elevated mean metal contents are most likely due to the native soil mineral composition and not from application of water high in these elements. Other studies show that the Alamosa

River, in fact, has higher concentrations of acid and metals than other water sources in the area (Erdman and Smith, 1993). However, the soil metal chemistry is such that these additions make little difference to the overall composition of the soils or bioavailability of the metals.

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SURVEY OF IRRIGATION STRUCTURE CONDITION IN THE ALAMOSA RIVER BASIN

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INTRODUCTION

Acidic waters from natural seeps and from mine tailings and drains flow into the Alamosa River (Sullivan, 1993). This water flows to the Terrace reservoir where it is stored for the irrigation of approximately 45,000 acres in the southwestern San Luis Valley of Colorado. Erdman and Smith (1993) found that the pH of water in Terrace reservoir ranged from 5.6 to 6.8 and contained no measurable alkalinity. Other water sources in the San Luis Valley have pH levels ranging from 7.6 to 9.2. There has been much anecdotal evidence of increased wear of irrigation equipment and structures in the areas utilizing Alamosa River water (Maya ter Kuile, personal communication). This study was conducted to inventory and survey the irrigation structures in the Alamosa River basin to determine if increased wear or deterioration results from exposure to these acidic irrigation waters.

The structures were classified to be in good, fair, or poor condition based on the following criteria:

Good --	Very little rust or deterioration. Generally, some water staining or surficial rust occurring where water contacts the structure.
Fair --	Rusting (not staining) or deterioration apparent where water is in contact with the structure. No rotting or metal flaking occurring.
Poor --	Rusting or deterioration not necessarily confined to water contact areas. Flaking of rusted metal, rotting, or holes developing in places, especially where water contacts the structure.

METHODS

In consultation with Joe McCann, the deputy water commissioner for the Alamosa River at the time of this study, a survey was devised to determine the following information on all irrigation structures in the basin: location (for mapping purposes), material (wood, plastic, steel, etc.), age of the structure (since manufacture), date of installation, the ditch from which water flows through the structure, the relative amounts of water from the various possible sources flowing through the structure (Alamosa River, La Jara Creek, Rio Grande River, groundwater, tailwater), the grower's personal opinion of the structure's condition, and an independent assessment of the structure's condition (by Joe McCann using a set of criteria). The survey was well received by almost all growers with two or three exceptions. Because of this cooperation, over 900 structures on over 50 farms were inventoried and evaluated.

Numeric values of 1, 2, and 3 were assigned to the good, fair, and poor classifications, respectively. This allowed us to calculate a mean condition for common groups of structures.

To quantify the amount of exposure to Alamosa River water on a given structure, an appropriate index was developed. The Exposure Index was calculated by multiplying the 10-year average flow (in cfs) through the ditch feeding the structure by the proportion of Alamosa River water carried by that ditch and ranged from a low of 0.91 to a high of 34.11. The Exposure Index and age of each structure were then tested for correlation to structure condition. These correlation tests were done for material groupings of structures (plastic, steel, etc.). Because the values for condition are not measured quantities, chi-square tests of independence were conducted. A confidence level of 95% was used in all statistical comparisons.

RESULTS AND DISCUSSION

The grower and independent assessments of structure condition were highly linearly correlated. A regression analysis between the data resulted in an intercept close to zero (0.04) a slope close to 1 (0.93) and a correlation coefficient of 0.93. These results indicate that the two estimates were nearly equivalent. Because the independent assessment was used as the abscissa variable, the regression results also indicate that this estimate was slightly shifted toward the "poor" end of the condition scale.

For all material groups other than steel, the only factor that correlated with the condition of the structure was age. The poorest conditions were observed on the oldest structures. Structures were considered steel structures if any steel (including coated steel) component was in contact with water. Some steel structures were combinations of steel and wood, plastic, or other material.

Histograms showing the comparison of the distribution of conditions for various combinations of Exposure Index and age are given as Figures 1-5. For convenience, three Exposure Index groupings (Index≤10, 10<Index≤20, Index>20) and two age groupings (age<15 years, age>15 years) were evaluated. The chi-square results are noted in each figure. For any comparison, a chi-square result greater than 5.99 indicates a significant relationship between condition of the structure and the combination of age and Exposure Index. Because no true "control" structures were included in the sample, the group combining the lowest exposure classification (Exposure Index≤10) with the youngest age classification (age<15 years) was compared to the other groups.

The two chi-square results greater than 5.99 show that a significant shift in condition (when compared to the young/low exposure group) has occurred within the young/high exposure group and the old/low exposure group. In both cases, it is interesting to note that the shift is toward better condition (shift towards numeric values of 1 or good). In no case does a significant decrease in structure condition occur for any of the comparisons.

To more clearly determine the factor (age or Exposure Index) that affects condition the most, observations were summed over each age within each Exposure Index group and over each Exposure Index group within each age (Figures 6-8). Surprisingly, no significant relationship was detected between age and condition. The only significant shift in condition was between the lowest and highest Exposure Index groups. Again, the shift, though small, is toward better condition in the high exposure group and is consistent with the comparisons in Figures 1-5.

From the comparisons in Figures 6-8, Exposure Index is clearly related to structure condition. The results, however, of improved condition with higher exposure to Alamosa River water, and no relationship of age to condition, are seemingly inconsistent with intuition. In the survey there are several examples of young structures classified as poor in condition. These cases, however, can be expected as normal, in that a certain number of material failures will occur naturally. Statistically, these cases do not appear to establish any significant trend of rapid structure deterioration with exposure to Alamosa River water. However, there are several considerations that must be examined in more detail before definitive conclusions about the effects of Alamosa River water on irrigation structures can be made.

The first consideration is that there are many fewer samples at the high Exposure Index values compared to the other two categories. The sample size, therefore, may be influencing the results. Further tests may be possible to see if the distribution of classes is too discrete (i.e. too few classes). It may be possible to develop intermediate classes that would result in a distribution of observations that better account for the shifts in condition.

Secondly, as yet, detailed multiple-overlay maps of structure location, Exposure Index, age, and condition have not been made. All the data for such maps has been collected and will be used in future projects. The geographical data should be one of the most instructive indicators of the effects of Alamosa River water on irrigation structures. Some of the ditches with the highest flows and, hence, a high Exposure Index value, are some of those farthest downstream on the Alamosa River. At these locations downstream, the water in the river has picked up sufficient alkalinity to be neutral or slightly alkaline in pH. Detailed multiple-overlay maps developed with Geographic Information System (GIS) software will show if significant spatial distributions of condition exist, for example, if areas of poor condition upstream and closer to Terrace reservoir exist, regardless of age or Exposure Index level. Geographic analysis may also aid in determining the cause for the lack of a significant relationship between age and condition as found in this study. If a spatial relationship exists, it would likely span all age classes. This may have influenced the result found in the analysis presented above.

CONCLUSIONS

For irrigation structures not having steel components in contact with water, the only factor that correlated with the condition of the structures was age. The poorest conditions were observed on the oldest structures. For steel irrigation structures (those having steel components in contact with water) a statistically significant relationship between the condition of the structures and exposure to Alamosa River water was found. The shift in condition was small and tended to be toward better condition. In

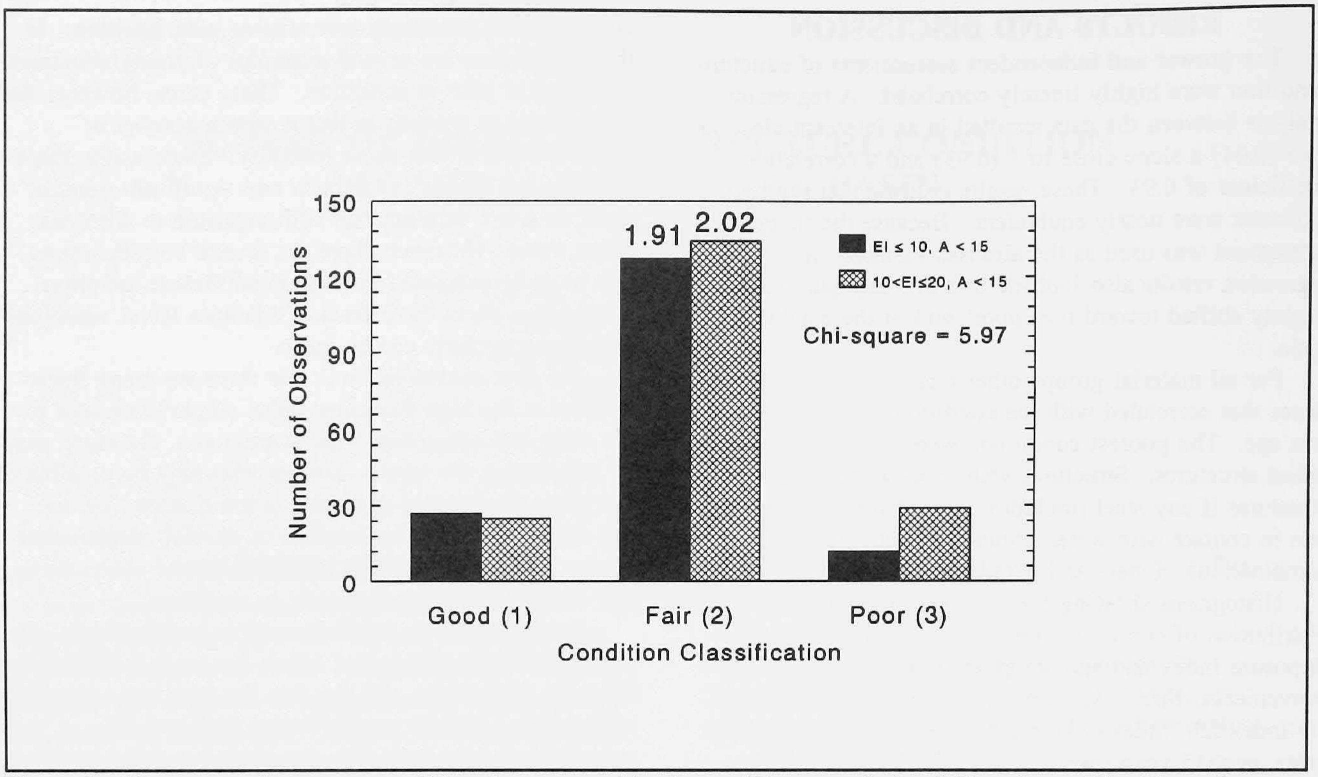

Figure 1. Histogram of structure condition for two combinations of Exposure Index (EI) and age (A). The values over the "fair" bars are the means for the group over which they are placed.

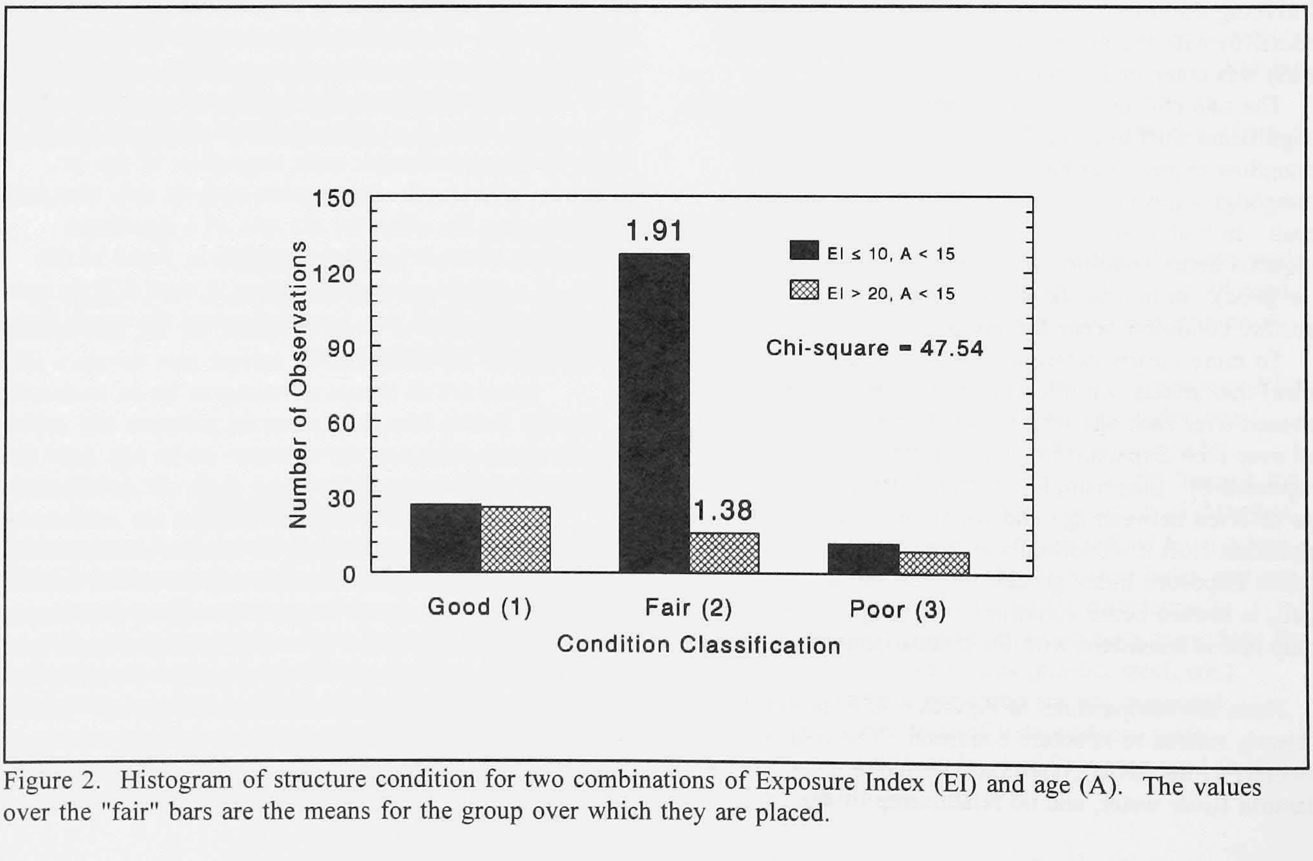

Figure 2. Histogram of structure condition for two combinations of Exposure Index (EI) and age (A). The values over the "fair" bars are the means for the group over which they are placed.

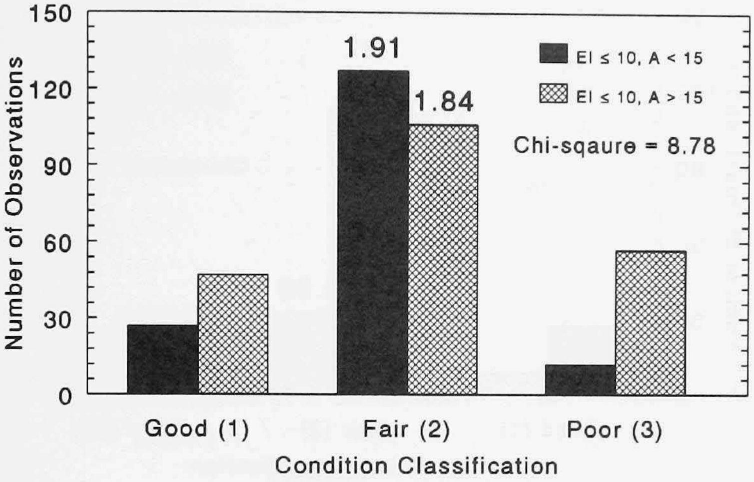

Figure 3. Histogram of structure condition for two combinations of Exposure Index (EI) and age (A). The values over the "fair" bars are the means for the group over which they are placed.

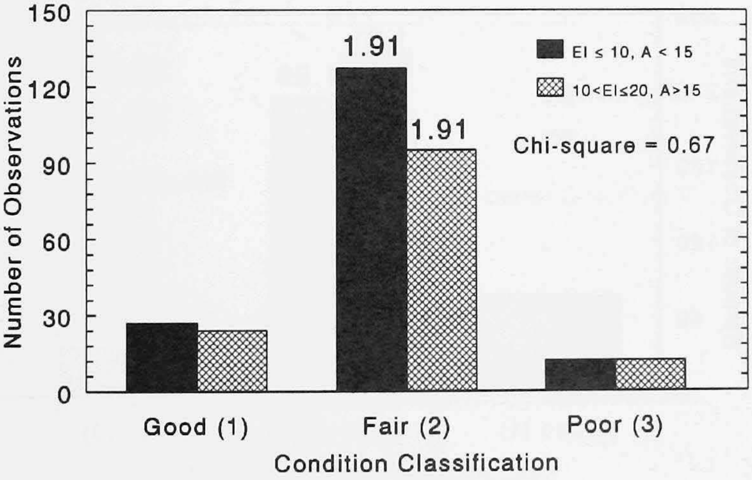

Figure 4. Histogram of structure condition for two combinations of Exposure Index (EI) and age (A). The values over the "fair" bars are the means for the group over which they are placed.

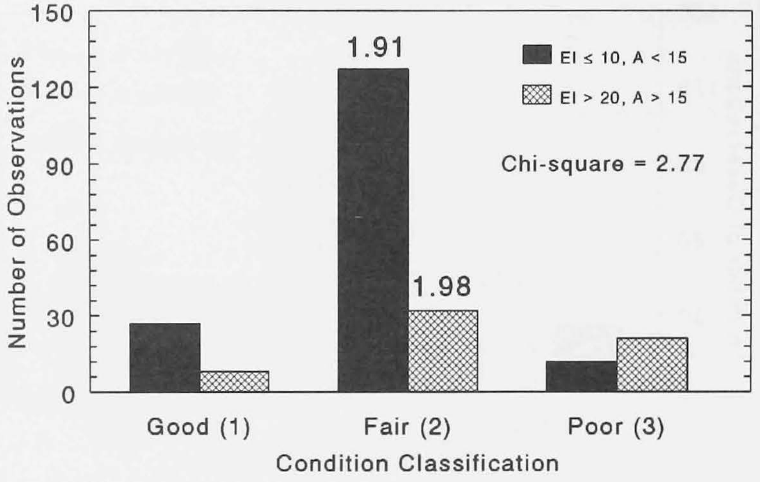

Figure 5. Histogram of structure condition for two combinations of Exposure Index (EI) and age (A). The values over the "fair" bars are the means for the group over which they are placed.

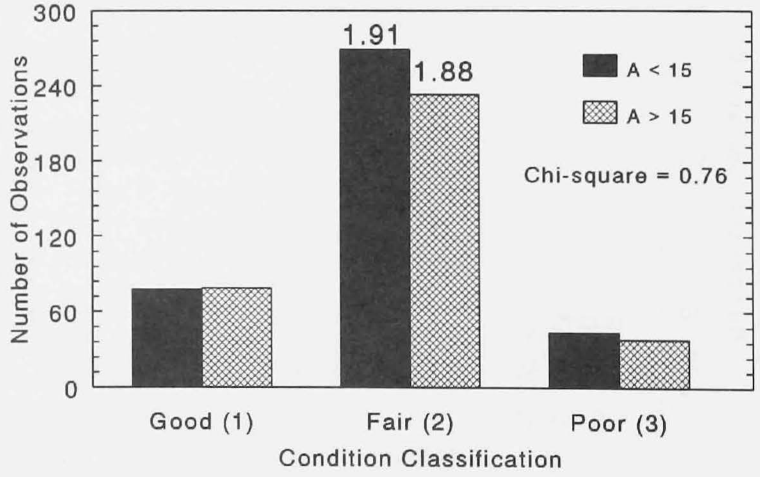

Figure 6. Histogram of structure condition for the two age (A) groups (over all Exposure Index groups). The values over the "fair" bars are the means for the group over which they are placed.

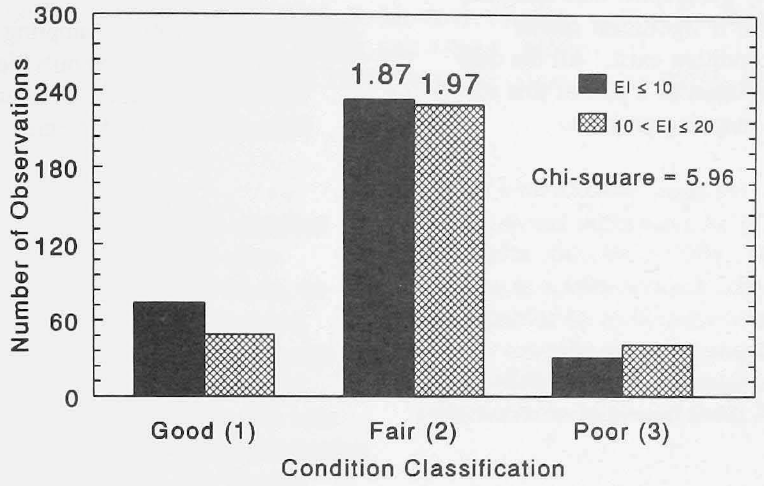

Figure 7. Histogram of structure condition for two Exposure Index (EI) groups (over all age groups). The values over the "fair" bars are the means for the group over which they are placed.

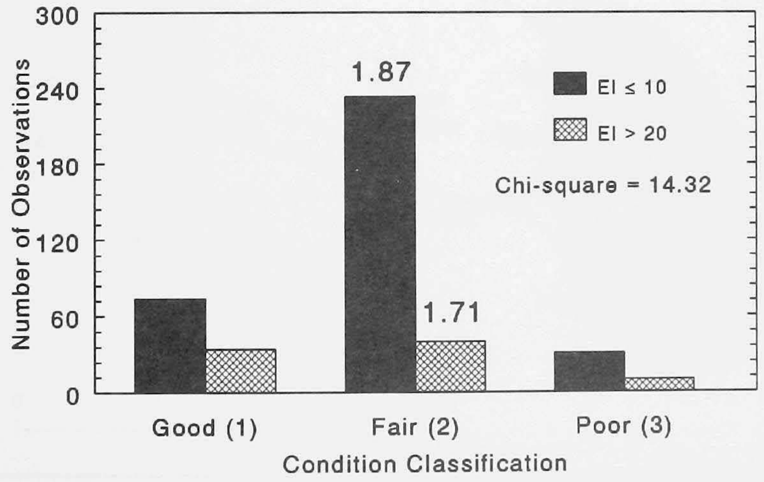

Figure 8. Histogram of structure condition for two Exposure Index (EI) groups (over all age groups). The values over the "fair" bars are the means for the group over which they are placed.

other words, steel structures exposed to the greatest amounts of Alamosa River water are in slightly better condition, on a basin-wide basis, than those exposed to the least amount of Alamosa River water. No relationship was found between age and the condition of steel structures. The two latter results suggest a need for further analysis, particularly geographic data analysis, which would help determine if significant spatial distributions of structure condition exist. All the data necessary for mapping was taken as a part of this survey and will be used in future mapping projects.

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YEARLY AND SEASONAL VARIATIONS IN ACIDITY AND METAL CONTENT OF IRRIGATION WATERS FROM THE ALAMOSA RIVER, COLORADO

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ABSTRACT

Concern about the impact of acidic, metal-enriched drainage from the Summitville mine site, and other mineralized areas in the upper Alamosa River basin, on irrigation waters in the San Luis Valley, south-central Colorado led us to study two irrigation canals during the spring and summer of 1993 and 1994. Farmers in the northern part of the southwestern portion of the San Luis Valley use water from the Alamosa River for crop irrigation through a network of canals and ditches. The Terrace Main Canal is a concrete-lined canal that extends about 15 km north of the Alamosa River. The El Viejo Ditch is a smaller canal that extends about 7 km northeast of the Alamosa River. This ditch was unlined until late summer, 1994. Data from a synoptic study performed in June, 1993 show little pH variation between the lined and unlined canals; however, there does appear to be some loss of copper with distance along the unlined ditch. We noted large seasonal differences for pH and metal concentrations in samples collected in 1994. There was a 100-fold increase in acidity between early June and late July, 1994, accompanied by an increase in metal concentrations. Copper concentrations increased about 7-fold, manganese concentrations increased about 1.5-fold, and zinc concentrations increased about 2-fold.

INTRODUCTION

The southwestern portion of the San Luis Valley, Colorado, contains approximately 45,000 acres of farm land irrigated with water from the Alamosa River that is stored in Terrace Reservoir (EPA, 1993) (see Figure 1). This water is distributed from the Alamosa River to farm lands through a network of canals and ditches. There is

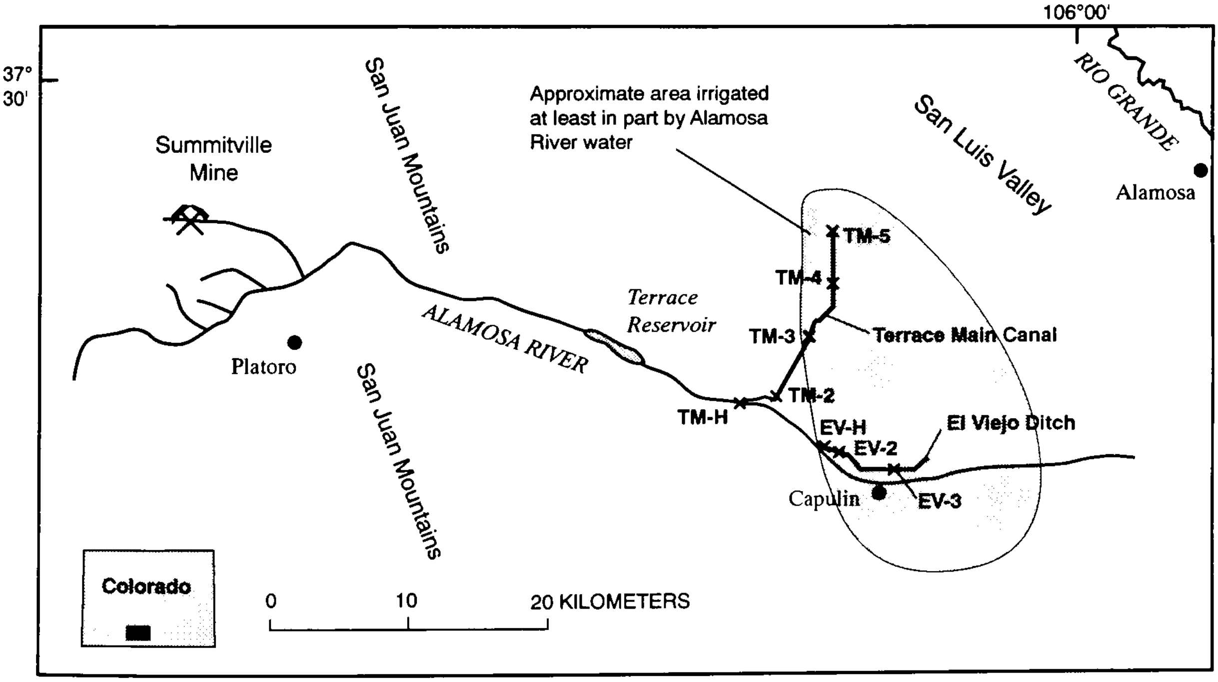

Figure 1. Map showing location of Summitville mine site, Alamosa River, Terrace Reservoir, Terrace Main Canal, El Viejo Ditch, sampling sites, and farmlands irrigated with Alamosa River water (modified from Colorado Dept. of Natural Resources, Division of Water Resources, and U.S. Dept. of Agriculture, Soil Conservation Service, 1994, unpub. map).

concern that historic and recent mining activities at the Summitville mine site (see Figure 1), as well as drainage from other mineralized areas, have been deleterious to the irrigation water quality in the Alamosa River and Terrace Reservoir. Copper (Cu), manganese (Mn), zinc (Zn), cadmium (Cd), iron (Fe), and nickel (Ni) concentrations and acidity in the Alamosa River downstream of Terrace Reservoir have increased since 1986 (Agro Engineering, 1992).

In late June, 1993, we undertook a study of two irrigation canals and associated storage ponds in the southwestern San Luis Valley that receive water from the Alamosa River downstream of Terrace Reservoir. The Terrace Main Canal (Figure 1) extends about 15 km north of the Alamosa River and was rebuilt and lined with concrete during late 1992. The El Viejo Ditch (Figure 1) is a smaller canal that extends about 7 km northeast of the Alamosa River. This ditch was unlined until late summer, 1994. The 1993 study focused on both a survey of water quality in these canals and storage ponds, and compared water quality between canals and between sampling sites (Figure 1) to determine if the concrete lining had an effect on metal concentrations or pH.

A follow-up study of water quality was conducted from early June through late September, 1994, on Terrace Main Canal, El Viejo Ditch, and a storage pond. This study was designed to assess seasonal changes in the irrigation water quality. Many of the water quality data in this report are still preliminary, however, overall trends in the data are evident from the illustrations.

METHODS

Sample Collection and Field Methods

On June 24, 1993 a synoptic sampling along Terrace Main Canal and El Viejo Ditch was conducted. A synoptic sampling refers to a simultaneous sampling method. Several persons were stationed along each canal and at three storage ponds to collect samples at the same time. In this way, we were able to produce a "snapshot" of the water quality at a specific time. Each person simultaneously collected a bottle of untreated water and measured the temperature at each sampling site. The sample bottles were kept cool and transported to a common location for pH and specific conductivity measurements. Subsamples were then prepared for major- and minor-element analysis. Both filtered (F, 0.45 µm) and unfiltered (U) samples were prepared for each site.

On June 7, July 27, and September 12, 1994, water quality samples were collected at the headgates of Terrace Main Canal and El Viejo Ditch, at a site along Terrace Main Canal approximately 15 km north of the headgate, and at a storage pond along the El Viejo Ditch approximately 7 km northeast of the headgate. Specific conductivity, pH, and temperature were measured at the site. Both filtered (F, 0.2 µm) and unfiltered (U) samples were collected at each site.

Chain-of-custody protocol was followed for sample collection, transport, storage, and analysis.

Sample Preparation and Storage

Some filtered and unfiltered water samples were acidified (A) with concentrated nitric acid (to $pH < 2$) for subsequent metal analysis. Portions of the filtered (unacidified) water were saved for anion and alkalinity determinations. Samples for anion and alkalinity determinations were refrigerated prior to analysis.

Analytical Methods

Samples were arranged in random sequence for analysis to reduce the effect of any systematic errors. For graphical purposes throughout this report, when elements were below the determination limit of the analytical method, those values were replaced by a value equal to 70% of the determination limit (Miesch, 1976). This procedure allows us to illustrate samples having low concentrations and does not alter data interpretation.

Twenty-eight major and minor element concentrations were simultaneously determined for filtered acidified (FA) and unfiltered acidified (UA) water samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in the laboratories of the U.S. Geological Survey, Branch of Geochemistry (Lichte and others, 1987; Briggs, 1990). Several elements in the water samples that were near or below the determination limit of ICP-AES were also determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Alkalinity was determined for filtered unacidified samples collected in 1994. A Gran's plot potentiometric titration method was used for these determinations (Stumm and Morgan, 1981).

RESULTS AND DISCUSSION

June 24, 1993 Synoptic Study

The synoptic study conducted along Terrace Main Canal and El Viejo Ditch on June 24, 1993 showed little variation in pH (Figure 2) or specific conductivity. Differences in Cu concentrations, shown in Figure 3, are for unfiltered acidified (UA) water samples; there was little concentration difference between the unfiltered and filtered samples. No measurable Cu attenuation took place along the concrete-lined Terrace Main Canal, but some Cu loss did take place along the unlined El Viejo Ditch (Figure 3). This slight attenuation along the El Viejo Ditch and in the storage ponds likely was due to Cu interactions with minerals along the ditch or in the ponds. This is also a

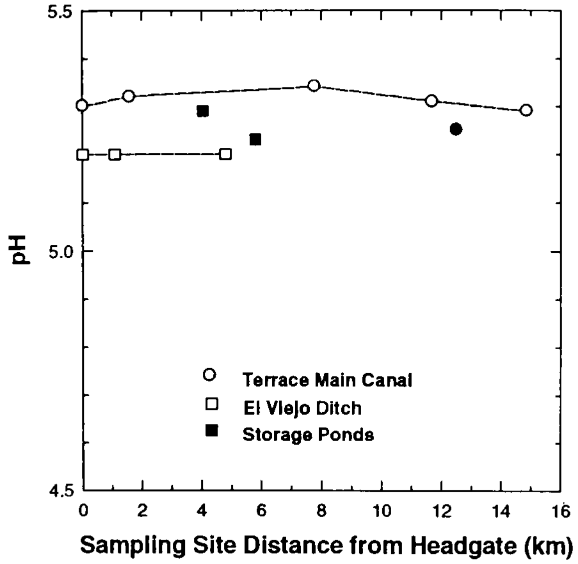

Figure 2. Plot of irrigation water pH data from the June 24, 1993 synoptic sampling along Terrace Main Canal (concrete-lined) and El Viejo Ditch (unlined) as a function of distance from the headgate on the Alamosa River.

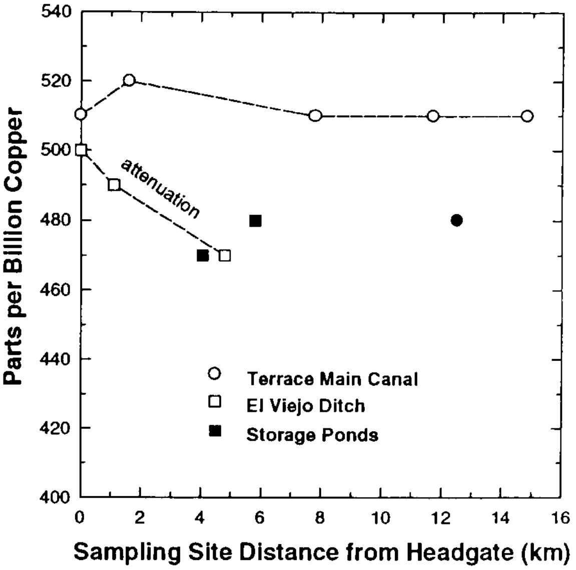

Figure 3. Plot of irrigation water copper concentration for the June 24, 1993 synoptic sampling along Terrace Main Canal (concrete-lined) and El Viejo Ditch (unlined) as a function of distance from the headgate on the Alamosa River. Copper concentrations shown are from unfiltered acidified (UA) water samples.

Table 1. Alkalinity determinations and field pH measurements for irrigation water from Terrace Main Canal and El Viejo Ditch, San Luis Valley, Colorado. Site TM-5 is approximately 15 km north of the Terrace Main Canal headgate, and site EV-P is a storage pond approximately 7 km northeast of the El Viejo Ditch headgate.

Sampling Site	Sampling Date	Field pH	Alkalinity (mg $CaCO_3$/L)
TM-H (Terrace Main headgate)	June 7, 1994	6.4	0
TM-5 (Terrace Main - 15 km dist.)	June 7, 1994	7.0	3.9
EV-H (El Viejo headgate)	June 7, 1994	6.5	1.7
EV-P (El Viejo pond - 7 km dist.)	June 7, 1994	6.6	2.3
TM-H (Terrace Main headgate)	July 27, 1994	4.3	0.51
TM-5 (Terrace Main - 15 km dist.)	July 27, 1994	4.6	1.1
EV-H (El Viejo headgate)	July 27, 1994	4.6	0.30
EV-P (El Viejo pond - 7 km dist.)	July 27, 1994	4.7	0.26
TM-H (Terrace Main headgate)	Sept. 12, 1994	4.4	0
TM-5 (Terrace Main - 15 km dist.)	Sept. 12, 1994	5.0	2.4
EV-H (El Viejo headgate)	Sept. 12, 1994	4.1	0
EV-P (El Viejo pond - 7 km dist.)	Sept. 12, 1994	4.2	0

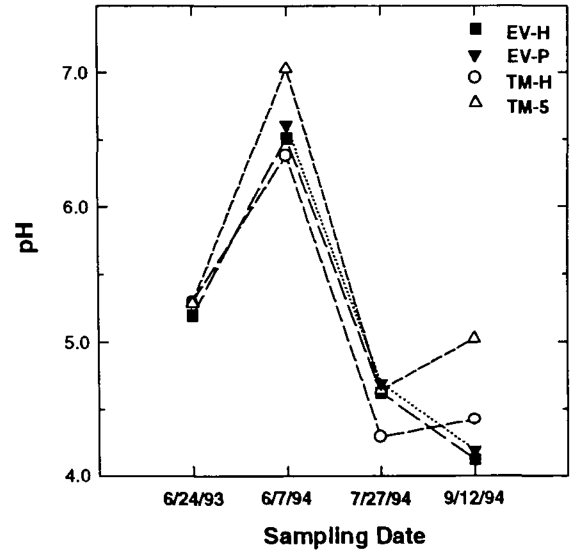

Figure 4. Plot of irrigation water pH data for the seasonal study from June, 1993 to September, 1994. TM-H is the Terrace Main Canal headgate on the Alamosa River, TM-5 is a site along the Terrace Main Canal approximately 15 km from the headgate, EV-H is the El Viejo Ditch headgate on the Alamosa River, and EV-P is a storage pond along the El Viejo Ditch approximately 7 km from the headgate.

likely explanation for the decrease in Cu concentration in the Terrace Main storage pond. No attenuation was observed for Mn or Zn along either canal.

Comparison of Yearly and Seasonal Trends in pH

There were large differences in the pH of the irrigation waters between June, 1993, and June, 1994, as well as seasonal variations during 1994 (Figure 4). The acidity of the irrigation waters decreased by 10-fold or more between June, 1993 and June, 1994 as illustrated by the increase in pH over that time (from a median value of pH 5.3 to pH 6.5). In contrast, between June, 1994 and July, 1994 a 100-fold increase in acidity was measured, as illustrated by the steep drop in pH (from a median value of pH 6.5 to pH 4.5). The pH remained low through September, 1994.

Data from a study conducted during 1993 (Stout, 1994) indicate that a similar degree of acidification of irrigation waters during the summer months, as noted in 1994, did not occur during 1993. Also, in 1993, the lowest pH measured at the Terrace Reservoir outflow during sampling between April and September was 5.5 (K. Walton-Day, U.S. Geological Survey, oral commun., 1994). Differences in acidification of irrigation waters between 1993 and 1994 may be partly due to differences in the amount of

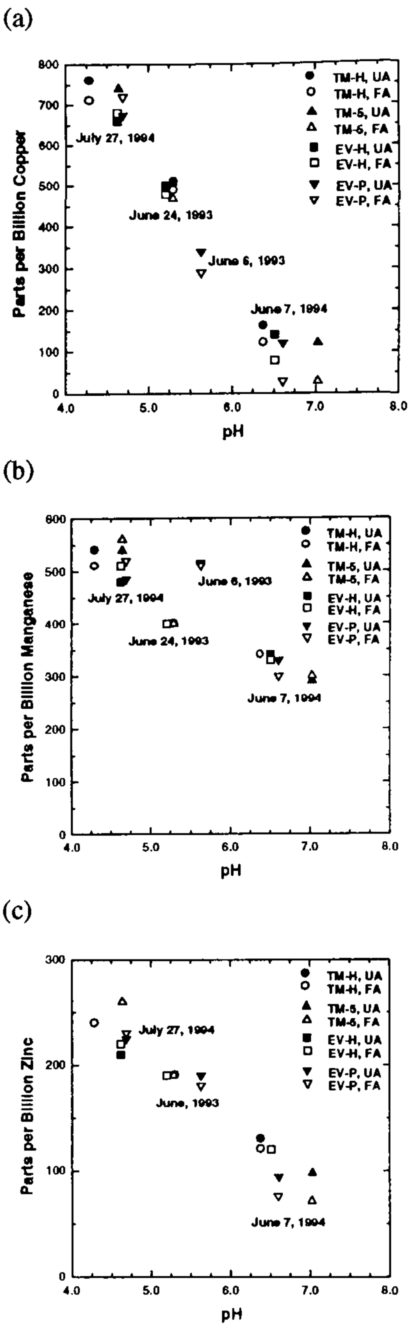

Figure 5. Plot of irrigation water metal concentration as a function of pH for (a) copper, (b) manganese, and (c) zinc from June, 1993 to July, 1994. TM-H is the Terrace Main Canal headgate on the Alamosa River, TM-5 is a site along the Terrace Main Canal approximately 15 km from the headgate, EV-H is the El Viejo Ditch headgate on the Alamosa River, and EV-P is a storage pond along the El Viejo Ditch approximately 7 km from the headgate. UA refers to unfiltered acidified water samples and FA refers to filtered (0.45 μm in 1993 and 0.2 μm in 1994) acidified water samples.

precipitation during the year. The percent of average snowpack in the Alamosa River Basin reported for May 1, 1993 was 150% (SCS, 1993) and for May 1, 1994 was 91% (SCS, 1994). Monthly storage in Terrace Reservoir was 8,200 acre-feet in May, 1993 and 11,700 acre-feet in May, 1994 (Colorado Dept.of Natural Resources, Division of Water Resources, unpub. data).

Alkalinity is a measure of the capacity of a water to buffer acid. This property is determined by titration with a strong acid. In most natural waters, alkalinity is due to the presence of dissolved bicarbonate and carbonate, and is often reported in terms of amount of calcium carbonate ($CaCO_3$). Bicarbonate and carbonate concentrations in natural water are generally controlled by carbonate equilibria. The bicarbonate concentration of rainwater is commonly below 10 mg/L, and most surface waters contain less than 200 mg/L (Hem, 1989).

Alkalinity data for the irrigation waters we studied are listed in Table 1. These data show that the irrigation waters have little to no alkalinity and thus have very little capacity to resist acidification. Differences in pH and alkalinity between the Terrace Main Canal headgate and the site about 15 km north may indicate that the concrete liner in the canal is reacting with the irrigation waters, thus increasing pH and alkalinity.

Comparison of Yearly and Seasonal Trends for Cu, Mn, and Zn

Preliminary water-quality trends in metal concentrations appear to relate strongly to the pH of the irrigation waters (Figure 5). Copper, Mn, and Zn all show higher concentrations in the more acidic (lower pH values) waters. Also, most of these metals are dissolved as shown by the similarity between the unfiltered acidified (UA) and filtered acidified (FA) samples. Between June and July, 1994, Cu concentrations increased by about 7 fold (from about 100 ppb to about 700 ppb), Mn concentrations increased by about 1.5 fold (from about 350 ppb to about 500 ppb), and Zn concentrations doubled (from about 100 ppb to greater than 200 ppb). Both Cu and Mn exceeded the Colorado Surface-Water Standards (CDH, 1993) for Agricultural Use of 200 µg/L (roughly equal to 200 ppb) during July, 1994, and Mn also exceeded the standard during June, 1994. No water-quality analyses are available as yet for September, 1994.

Miller and McHugh studied natural acid drainage in the upper Alamosa River Basin and report that a significant amount of acidity, Mn, and Zn may originate from natural sources in the basin (Miller and McHugh, 1994). However, little Cu has been detected in these natural sources. A study of mine-related drainage from the Summitville mine site shows very acidic waters (pH 2.2 - 3) with large concentrations of Cu (as high as 500,000 ppb), Mn (as high as 360,000 ppb), and Zn (as high as 400,000 ppb) produced on-site (Plumlee and others, 1995, this volume). It appears that much of the Cu in the irrigation waters originates from the Summitville mine site, but the high acidity and elevated Mn and Zn concentrations may be of mixed origin.

SUMMARY

We conducted a two-year study of irrigation waters in the southwestern San Luis Valley that originate from the Alamosa River and are stored in the Terrace Reservoir. In June, 1993, we compared water quality along a concrete-lined canal and an unlined ditch and observed some Cu attenuation along the unlined ditch. Our 1994 seasonal data document large increases in acidity and metal content of these waters during the spring and summer. Although some of our water-quality data are still preliminary, they clearly show that Cu, Mn, and Zn concentrations have increased about 7-, 1.5-, and 2-fold, respectively, between early June and late July, 1994. These increases in metal concentrations were accompanied by a 100-fold increase in acidity of these irrigation waters; the pH dropped from near-neutral in early June to about 4.5 in late July, 1994.

ACKNOWLEDGMENTS

We thank the Terrace Irrigation Company and owners of the El Viejo Ditch and the storage ponds for allowing us sampling access. We also thank Joe McCann for showing us around and helping us choose sampling locations. We would like to acknowledge the assistance of Laurie Balistrieri, Larry Gough, Phil Hageman, Harry Posey, Charlie Severson, Kathleen Stewart, and Ron Tidball during the June, 1993 synoptic sampling. Mollie Malcolm and David Fey provided analytical assistance, and Chris Murphy and Pete Theodorakos provided chain-of-custody assistance for sample storage and management. Reviews by Stan Church, Ian Ridley, and Harry Posey helped the quality of this report.

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CONCENTRATIONS OF KEY DIETARY ELEMENTS IN HAY RAISED WITH ALAMOSA RIVER WATER IRRIGATION

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SUMMARY

Seventeen hay samples raised with Alamosa River irrigation water were analyzed to determine whether key element concentrations were within dietary guidelines for beef cattle and sheep. Concentrations of copper, manganese, zinc and molybdenum, elements that are important micro-minerals in livestock diets, were within dietary recommendations. The Cu:Mo ratio, which is important in assessing the potential for a Mo induced-secondary Cu deficiency, was above the minimum recommended in 12 samples and below the minimum recommended in 5 samples. Concentrations of aluminum, arsenic, cadmium and lead, elements that may be toxic above certain levels, were found to be lower than the maximum tolerable levels in all samples.

INTRODUCTION

Heavy metal loading in the Alamosa River increased between 1986 and 1991 (Agro-Engineering, 1992). This situation came into public awareness in the spring of 1993, creating concern about possible effects on the environment, animals, and people of the Alamosa River watershed.

The elements included in an EPA list of "pollutants of concern" for the Alamosa River include Al, Cd, Cu, Fe, Pb, Mn, Hg, Ag, and Zn (Dana Allen, written commun, 1993). Elements such as Cu, Mn, and Zn are important dietary micro-minerals in livestock nutrition. Copper is of primary concern in livestock nutrition as either toxicities or deficiencies can result in poor animal health (NAS), and Cu levels in the Alamosa River have been measured in excess of agricultural use standards (Agro Engineering, 1992). Deficiencies of Mn and Zn result in poor animal health also, and while elevated levels rarely cause toxicity problems, they can interfere with absorption or metabolism of other elements, thus causing secondary deficiencies. Aluminum, As, Cd, and Pb are less important in nutritional management of livestock, but they are important because they are considered potentially toxic to livestock.

Virtually all livestock raised in the Alamosa River watershed rely solely on a diet of conserved hay from January until May each year, hay that is raised with irrigation water from the Alamosa River. If heavy metal loading in forage plants is occurring, it could result in livestock eating a diet with high concentrations of elements for an extended time and increase the risk of dietary toxicities. The objective of this study was to sample a variety of hay types raised with Alamosa River water and determine whether they contain element concentrations which might be harmful to livestock.

METHODS

In February 1994, samples were collected from seventeen hay lots. Each lot was identified by the farm and field from which it was harvested, the year in which it was harvested, the year in which it was grown, the type of forage and whether it was the first or second cutting (Table 1). Using a hay core sampler, a minimum of 15 sub-sample cores were collected randomly from each lot and combined into a composite lot sample.

Samples were submitted to the United States Geological Survey (USGS) for analysis. The samples were placed in a locked drying oven at 40 C for 48 hours to dry completely. Samples were removed from the oven and ground to a powder using a willow mill and coffee grinder. This was then dry ashed in muffle furnaces that ramped up to approximately 500 C at 100 C per hour. A mixed acid extraction as outlined by Briggs (1990) was used on the ashed samples. The extraction analysis was done using inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) performed by the USGS analytical laboratories at the Federal Center Denver, Colorado. Three blind-split samples were used to monitor analytical precision.

Of the forty elements screened, Cu, Mn, Zn, Mo, Al, As, Cd, and Pb have been chosen for

Table 1. Identification and characterization of hay samples collected February 8, 1994

SAMPLE NUMBER	FARM	FIELD	CUT	YEAR	TYPE
01	01	01	1st	1993	Alfalfa Hay
02	01	02	1st	1993	Grass Hay
03	01	03	1st	1993	Alfalfa Hay
04	02	01	2nd	1993	Alfalfa Hay
05	02	02	1st	1993	Grass Hay
06	02	03	1st	1993	Grass Hay
07	02	04	2nd	1993	Alfalfa-Grass Mix
08	02	01	1st	1993	Alfalfa Hay
09	03	01	1st	1993	Alfalfa Hay
10	03	01	2nd	1993	Alfalfa Hay
11	04	01	2nd	1993	Alfalfa-Grass Mix
12	04	01	1st	1993	Alfalfa-Grass Mix
13	04	01	2nd	1992	Alfalfa-Grass Mix
14	04	02	1st	1993	Oat Hay
15	04	01	1st	1993	Alfalfa Hay
16	05	02	1st	1993	Alfalfa Hay
17	05	03	1st	1993	Grass Hay

Table 2. Element concentrations in blind split samples[a]

Sample Number	Sample (ppm)			
	Mn	Cu	Mo	Zn
9	19	8.9	1.2	21
9	22	9.3	1.2	21
12	47	12.7	<0.4	21
12	49	12.7	<0.4	22
15	20	7.9	1.6	18
15	21	7.9	1.7	17

[a] This high level of repeatability within blind split samples indicates excellent laboratory technique precision

interpretation and reporting. These eight elements are all important in livestock nutrition and, with the exception of Mo, are considered elements of concern in the on-going monitoring of Alamosa River water quality. Data interpretation is by comparing the concentrations found in each forage sample to the suggested range that would meet dietary requirements of cattle and sheep, and to the suggested maximum tolerable levels (National Research Council 1984, 1985). Molybdenum was chosen for reporting because it interferes with Cu metabolism. The ratio of Cu:Mo is therefore calculated and compared to the minimum ratio of 4:1 suggested by Hamar (personal communication, 1994).

RESULTS

Results of the blind split sampling are shown in Table 2 and indicate excellent analytical precision. The observed ranges of element concentrations along with the suggested ranges and maximum tolerable levels (MTL) for cattle and sheep are listed in Table 3. The distribution of the seventeen Cu concentrations is shown graphically in Figure 1. Animals consuming hay from lots 6, 10, 11, and 15, which are all above the suggested range, would likely consume more than their minimum daily Cu requirement and this might result in higher-than-normal biological concentrations in the animal. Whether higher-than-normal biological concentrations would actually occur in the animal depends upon the interrelationship of Cu with other dietary elements present. More important in the scope of this study, however, is that all samples are below the MTL for sheep (25 ppm) and cattle (115 ppm). Because the concentration of sample 15 (17.9 ppm) is approaching the MTL for sheep, a producer would be wise to limit this hay to a portion of the diet, rather than feeding it as the sole diet for sheep.

Manganese distributions are shown in Figure 2. There are two samples above the suggested range for cattle and two additional samples above for sheep. Far more important, all samples are well below the MTL (1000 ppm). Animals consuming these forages

Table 3. Observed ranges, suggested ranges and maximum tolerable levels of Cu, Mn, Zn, Mo, Al, As, Cd, and Pb (ppm)

Element	Observed Range	Cattle[a]		Sheep[b]	
		Suggested Range[c]	MTL	Suggested Range[c]	MTL
Cu	3.6-17.9	4-10	115	7-11	25
Mn	13-58	20-50	1000	20-40	1000
Zn	14-28	20-40	500	20-33	750
Mo	<0.4-3.6	---	6	0.5	10
Al	.01-.07%		0.1%		0.1%
As	<2.5[d]		50		50
Cd	<0.48[d]		0.5		0.5
Pb	<0.95[d]		30		30
Cu:Mo	2.4-38	>4:1[e]			

[a] NRC, 1984

[b] NRC, 1985

[c] The listing of a dietary concentration range in which animal requirements are likely to be met

[d] The ICP-AES analysis did not detect any As, Cd, or Pb. The concentrations listed represent the maximum possible concentration for these forage samples at the minimum detection limit.

[e] Hamar, personal communication, 1994

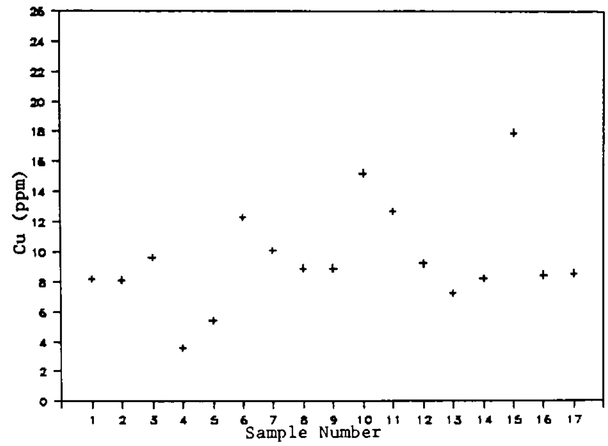

Figure 1. Copper concentration distributions.

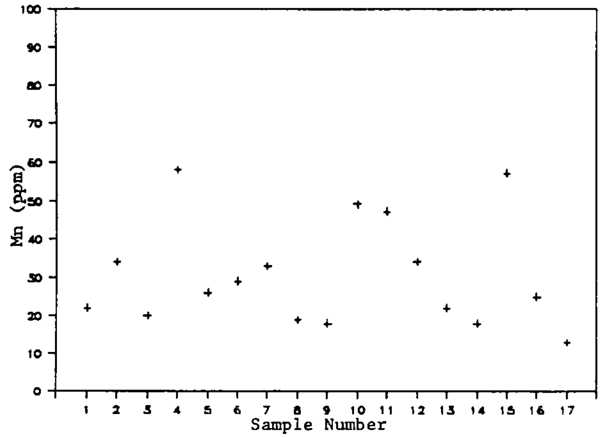

Figure 2. Manganese concentration distributions.

are not likely to experience toxicities or imbalances of Mn. The Zn distributions shown in Figure 3 also indicate that animals consuming these forages would be in no danger of Zn excesses.

Eleven of the samples contain Mo concentrations above the suggested level for sheep (.5 ppm), but all are well below the MTL for sheep (10 ppm) and cattle (6ppm)(Figure 4). The most important problem with high Mo concentrations is its inference with Cu metabolism. Thus, high Mo concentrations can result in a secondary Cu deficiency (NRC, 1984). Baldwin and Hamar (1981) suggest a Cu:Mo ratio of 6:1 to 10:1 is considered optimum for growth and reproduction in cattle and sheep. Hamar (personal communciation, 1994) reports clinical symptoms of secondary Cu deficiency occuring at ratios of 4:1 and lower. Samples 1, 3, 4, 16 and 17 have Cu:Mo below 4:1. In some cases this is due to relatively low Cu concentrations, in other cases to relatively high Mo.

Animals consuming these forages would be at risk of developing a secondary Cu deficiency. A producer would be wise to feed these forages as only a portion of the diet, or to provide a mineral supplement with appropriate levels of supplemental Cu.

At the ICP-AES minimum detection limit for As, Cd, and Pb, samples would have 2.5 ppm, 4.8 ppm and .95 ppm, respectively. Since the analysis did not detect any As, Cd, or Pb, the actual levels are less than these values (Table 3). Therefore, As, Cd, and Pb concentrations are below MTL indicating that animals would not experience toxicities of these three elements from consuming these forages. Likewise, Al concentrations are below MTL, indicating animals would not develop Al toxicity from consuming these forages.

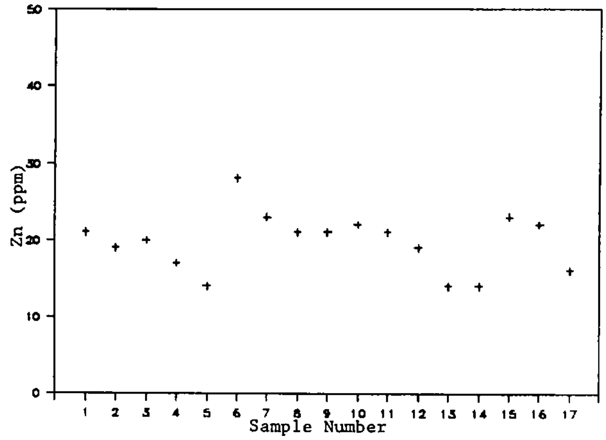

Figure 3. Zinc concentration distributions.

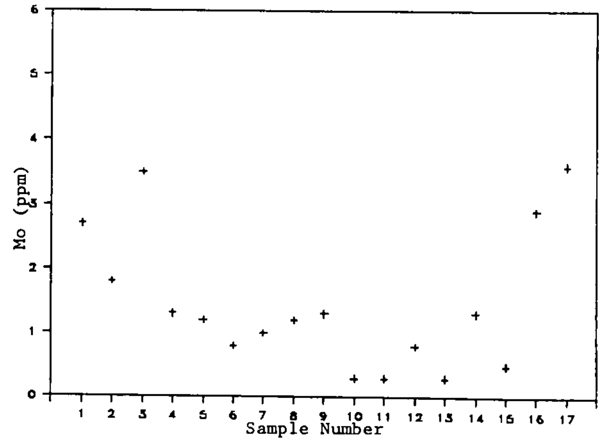

Figure 4. Molybdenum concentration distributions.

CONCLUSION

All seventeen hay lots sampled, which were irrigated with Alamosa River water, are within dietary recommendations for Cu, Mn, Zn, Mo, Al, As, Cd, and Pb. Twelve meet the dietary requirement for Cu:Mo ratio. These results indicate that animals consuming these forages would not experience toxicities due to element concentrations in the forage. Moreover, these forages generally meet the dietary requirements of beef cattle and sheep, although several might require appropriate mineral supplementation.

This study was designed as a point-in-time sampling and does not address possible accumulation over time. Neither was this study designed to compare Alamosa River irrigated forage to forage irrigated by other water sources, or to correlate concentration differences between hay samples to field location, irrigation method or soil fertility management.

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BIOLOGICAL CONCENTRATIONS OF KEY ELEMENTS IN BLOOD, HAIR AND WOOL OF LIVESTOCK RAISED IN THE ALAMOSA RIVER WATERSHED
PART 1: VETERINARY DIAGNOSTIC ANALYSIS

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SUMMARY

Sixty beef cows and forty sheep from four ranches were used to evaluate mineral levels in the blood, hair and wool of livestock raised in the Alamosa River watershed. Interpretation of the data using veterinary diagnostic standards reveals no copper, selenium, zinc, lead, cadmium, or arsenic toxicities in these four herds in 1993. Body condition score (BCS) distributions on the cattle and sheep were consistent with distributions expected in healthy, well managed herds. One decreasing BCS trend was apparent in the sheep on Ranch C, but this study can not determine the cause.

Despite elevated Cu concentrations in Alamosa River water, blood Cu levels in exposed livestock tended to be below normal or deficient, a common condition of livestock raised in southern Colorado. The levels of Se, Cu, and Cd tended to increase from the first sampling time to the second time. Statistical analysis of these data are reported in Part 2, a separate paper. It would be prudent to enact a yearly monitoring program to assess long term trends, until water quality in the Alamosa River returns to 1986 levels.

INTRODUCTION

Heavy metal loading in the Alamosa River increased between 1986 and 1991 (Agro-Engineering, 1992). This situation came into public awareness in the spring of 1993, creating concern about possible effects on the environment, animals, and people of the Alamosa River watershed.

Health of livestock raised in the watershed was one concern. This study was conducted as a rapid, reconnaissance action to assess the biological mineral status of exposed livestock. Our objective was to measure the levels of key dietary minerals and toxic elements in the blood stream and hair of exposed animals, and to use veterinary diagnostic standards to assess mineral deficiencies, toxicities and imbalances.

METHODS

Livestock species exposed to Alamosa River water include cattle, sheep, horses, goats, and swine. Cattle and sheep are the most numerous and also represent the major economic concern. Therefore, cattle and sheep were chosen for this study.

The Conejos County Agricultural Stabilization and Conservation Service office has approximately one hundred livestock operations on record in the Alamosa River watershed. Time and funding constraints at the outset of the study did not allow a sample size large enough to adequately represent either the exposed livestock population or the exposed number of operations. The study design team thus chose a rationale of screening two cattle and two sheep herds at various locations along the watershed, and to include adequate numbers within each herd to be representative of that sub-population. The information gleaned would thus provide an indication of the mineral status of cattle and sheep in the Alamosa River watershed.

The constraints at the outset also influenced the biological tests used and the elements chosen for analysis. Copper was chosen as a primary element of concern as Cu levels in the Alamosa River had been measured in excess of NAS livestock standards (Agro-Engineering, 1992). Although the design team recognizes liver biopsy and tissue analysis as the diagnostic method of choice for Cu, this method was not possible because of time and personnel constraints. Instead, blood serum analysis was used to indicate element intake and metabolism in the seven to ten days immediately prior to sampling, combined with hair or wool analysis which indicates element intake and metabolism during the forty-five to sixty day period prior to sampling. Selenium and Zn were chosen for analysis because they play on important role in Cu metabolism. Glutathione peroxidase, a red blood cell, Se containing enzyme, was used as an indicator of Se in the blood. Arsenic, Cd, and Pb were also chosen for study because they are potentially toxic to livestock and because they were listed as elements of concern in the Alamosa River.

Cattle

Forty beef cows from cooperating Ranch A and twenty beef cows from cooperating Ranch B were individually identified using plastic and metal ear tags, in May 1993. Cattle at each ranch were divided into two study groups. The first group had been drinking Alamosa River water for six weeks prior to the first sampling. The second group had been drinking water pumped from wells. All cattle were consuming forage produced in the Alamosa River watershed. Cattle on each ranch were receiving a mineral supplement. The supplements used were different on each ranch.

The entire cow herd was removed from each ranch in late June and moved to various locations for summer and fall grazing. All summer grazing locations were outside the Alamosa River watershed. Within ten days of returning to the home ranch, a second set of blood and hair samples were collected. Body condition was assessed on all cattle (Richards, et al., 1986) at both sampling times. The number of observations for ranch, study group and sampling time are listed in Table 1a.

At each sampling time, two blood samples were collected from each animal by jugular vena-puncture. One sample was collected in a heparinized tube for whole blood analysis and was refrigerated until analysis. The second sample was collected in a sterile serum tube, held at room temperature and centrifuged within 8 hours of collection. The serum was then separated and refrigerated until laboratory analysis.

Hair samples were collected from each animal by clipping closely against the skin immediately behind the shoulder. Clipped hair was stored in whirl-pack bags until laboratory analysis.

Sheep

Twenty ewes from cooperating Ranch C and twenty ewes from cooperating Ranch D were individually identified for the study using plastic and metal ear tags, in June 1993. Sample collection and handling methods were identical to the methods described for cattle. Unlike the cattle, all sheep remained in the Alamosa River watershed throughout the year. None of the sheep were receiving mineral supplementation. A second set of samples was collected in the fall of 1993. Body condition was assessed on all sheep (American Sheep Producers Council, 1988) at both sampling times. The number of observations for ranch and sampling time are listed in Table 1b.

Table 1a. Number of cattle observations at each ranch, study group and sampling time

Ranch	Study Group[a]	Number of Observations		
		May 12, 1993	October 12, 1993	February 14, 1994
A	1	20		16
	2	20		18
B	1	10	10	
	2	10	10	

[a] 1=River Water; 2=Well Water

Table 1b. Number of sheep observations at each ranch and sampling time

Ranch	Number of Observations	
	June 8, 1993	November 2, 1993
C	20	18
D	20	18

Lab Technique

All laboratory analyses were conducted by the Colorado State University Veterinary Diagnostic Laboratory, Fort Collins, Colorado. Glutathione peroxidase (GP) was measured in whole blood according to procedures outlined by Ageraard and Jensen (1982).

All other elements were measured using various methods of atomic absorption spectrophotometry. Hair and wool samples were thoroughly cleaned and wet ashed (EPA, 1992) in preparation for analysis. Arsenic and Se were measured using vapor generation as described by Brodie, et al. (1983) and Siemar (1975). Copper and Zn in both serum and wet ash samples, as well as Pb, and Cd in wet ash samples were measured using standard flame atomic absorption photometric techniques (Varian Techtrom, 1972).

Veterinary Diagnostic Analysis

The elements screened in this study were chosen either because they were listed as elements of concern in the Alamosa River and are potentially toxic to livestock, or because they have significant dietary interaction with the elements of concern.

Levels of all elements were measured in parts per million by the diagnostic laboratory, and then categorically classified as toxic, above normal, normal, below normal or deficient. Ranges for each of these categories were suggested by the CSU Veterinary Diagnostic Laboratory and are listed in Table 2 (Puls, 1988). The number and proportion of animals in each diagnostic category were used to diagnose whether or not herd level toxicities or imbalances existed.

Table 2. Standards used to rank each sample into diagnostic categories (ppm)

---CATTLE--- Diagnostic Category	Blood			Hair					
	GP[a]	Cu	Zn	As	Cd	Cu	Pb	Se	Zn
Toxic		>2.5	>3.0	>3.4	>40		>10.0	>5.0	
Above Normal	>1000	1.2-2.5	1.4-3.0	3.0-3.4	0.6-16	>32	5-10		>150
Normal	250-1000	0.8-1.2	0.7-1.4	<3.0	<.6	6.7-32	<5.0	≤.50	100
Below Normal		0.6-0.8	0.4-0.7						
Deficient	<250	<0.6	<0.4			<6.7			<100

[a] GP unit of measure is mmole/l/sec, all other units are ppm

---SHEEP--- Diagnostic Category	Blood			Wool					
	GP[a]	Cu	Zn	As[b]	Cd	Cu	Pb	Se	Zn
Toxic		>2.5	>30.0		>20		>25		>145
Above Normal	>1000	1.2-2.5	1.4-30.0		1.2-2.0	>10	7-25	>4.0	130-145
Normal	250-1000	0.8-1.2	0.7-1.4		0.55-1.2	3.0-10.0	4.0-7.0	0.80-4.0	70-130
Below Normal		0.6-0.8	0.4-0.7		<0.55	2-3	<4	0.03-0.08	
Deficient	<250	<0.6	<0.4			<2.0		<0.03	<70

[a] GP units of measure is mmole/l/sec, all other units are ppm
[b] no reference found for wool As standards

RESULTS

The following results are reported separately by species and by blood, hair or wool, and body condition. These results (Part 1) are reported strictly from a veterinary diagnostic approach and not from statistical analysis. A statistical analysis of these data are reported in a separate paper (Part 2).

Cattle

Blood

The ranges of GP, Cu and Zn measured in individual cattle within each study group are listed in Table 3. Each individual animal was then categorized into a veterinary diagnostic category for each blood element screened. The corresponding diagnostic distributions for each group are shown in Table 4.

The diagnostic distributions for blood GP, Cu and Zn follow a very similar pattern on each ranch, with most of the animals being in the normal range for GP and Zn. There are no animals diagnosed in the toxic category for any of the three elements. There is a tendency for Zn levels to be above the normal range on some animals. There is a definite pattern of below normal and deficient blood levels of Cu. Copper is of great concern because substantial increases have been measured in the Alamosa River with levels recorded above NAS livestock use standards (Agro-Engineering, 1992). At the same time, much of the western United States, including southern Colorado, is known to have relatively low soil Cu concentrations, resulting in forage with low Cu and frequent symptoms of Cu deficiency in livestock (Baldwin et al., 1981, Tanner et al., 1988). It is noteworthy in this study that cattle blood Cu levels remained in below normal and deficient ranges, even though they were exposed to water with high Cu concentrations.

Table 3. Range of blood GP, Cu, and Zn measured in cattle

Element	Study Group[a]	Time	Ranch A	Ranch B
			Range	Range
GP[b]	1	1	301-551	532-875
		2	298-768	457-961
	2	1	394-897	639-1004
		2	318-717	567-817
Cu	1	1	0.50-0.89	0.60-0.79
		2	0.39-0.68	0.50-1.00
	2	1	0.46-0.75	0.53-0.75
		2	0.39-0.83	0.45-0.80
Zn	1	1	0.83-1.41	0.90-1.29
		2	1.03-1.80	0.75-1.94
	2	1	0.87-1.45	1.02-1.48
		2	1.11-1.80	0.83-1.31

[a] 1= River Water, 2=Well Water

[b] GP unit of measure is mmole/l/sec, all other units are ppm

Table 4. Diagnostic category distribution for blood GP, Cu, and Zn for cattle

Element	Study Group[a]	Time	Ranch A					Ranch B				
			Diagnostic Category[b]					Diagnostic Category				
			T	AN	N	BN	D	T	AN	N	BN	D
GP	1	1			20					10		
		2			16					10		
	2	1			20				1	9		
		2			18					10		
Cu	1	1			2	12	6				10	
		2				8	8			3	4	3
	2	1				13	6				8	2
		2			1	11	6			2	5	3
Zn	1	1		1	19					10		
		2		4	12				1	9		
	2	1		1	18				2	8		
		2		7	11					10		

[a] 1=River Water, 2=Well Water

[b] T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

Hair

The ranges of As, Cd, Cu, Pb, Se and Zn measured in individual cattle within each study group are listed in Table 5. The corresponding diagnostic distributions are shown in Table 6.

The diagnostic distributions for hair follow similar patterns on each ranch, with the exception of Pb. Seven cows on Ranch A had Pb levels above normal and one in the toxic category at sampling time 1. These cows were all in the river water group, and furthermore, all had returned to the normal category after spending the summer away from the Alamosa River watershed. Because all river-water cows on Ranch B were in the normal range for Pb at sampling time 1, it is not clear if the high Pb levels in Ranch A cows was a result of drinking river water or if there was a different source of lead unique to Ranch A. There were no other cows with toxic ranking for any other elements.

There was a definite trend of above normal Cd levels in cows on both ranches, and this was more pronounced in the cattle drinking river water than in those drinking well water. Animals on each ranch had deficient hair Cu levels, which is consistent with the results of blood Cu.

There were 14 river-water cows from Ranch A and 4 river-water cows from Ranch B that were deficient in hair Zn. This is in direct conflict with the blood Zn results, which showed a small number of cows with above normal Zn. This would indicate higher dietary intake of Zn close to the first sampling date, or perhaps a shift in the balance of minerals, allowing better use of the available Zn.

All cows were in the normal category for hair As and Se, and the cows on Ranch B were all in the normal category for Pb.

Table 5. Range of hair As, Cd, Cu, Pb, Se, and Zn found in cattle (ppm)

Element	Study Group[a]	Time	Ranch A Range	Ranch B Range
As	1	1	0.03-2.7	0.03-1.70
		2	0.03-1.3	<0.01-0.14
	2	1	<0.01-0.35	<0.01-0.06
		2	0.03-0.20	<0.01-0.08
Cd	1	1	0.5-11.7	<0.5-1.3
		2	<0.5-0.6	<0.5
	2	1	0.5-1.4	<0.5-1.4
		2	<0.5-1.5	<0.5
Cu	1	1	4.3-11.4	5.7-10.4
		2	3.5-8.5	6.28-9.73
	2	1	4.6-7.9	5.4-7.6
		2	3.6-8.9	6.19-8.55
Pb	1	1	<2-10.5	<2
		2	<2	<2
	2	1	<2-2.8	<2-2.8
		2	<2	<2
Se	1	1	0.46-1.03	0.49-1.31
		2	0.60-1.19	0.15-0.77
	2	1	0.36-1.17	0.71-1.18
		2	0.53-1.33	0.18-0.83
Zn	1	1	79.5-124	94.6-145
		2	105-129	110-129
	2	1	97.1-124	109-149
		2	106-137	114-185

[a] 1=River Water, 2=Well Water

Table 6. Diagnostic category distribution for hair As, Cd, Cu, Pb, Se, and Zn for cattle

Element	Study Group[a]	Time	Ranch A					Ranch B				
			Diagnostic Category[b]					Diagnostic Category				
			T	A N	N	B N	D	T	A N	N	B N	D
As	1	1			20					10		
		2			16					10		
	2	1			20					10		
		2			18					10		
Cd	1	1		13	7				7	3		
		2		1	15					10		
	2	1		19	1				8	2		
		2		2	16					10		
Cu	1	1			10		10			6		4
		2			6		10			8		2
	2	1			4		16			6		4
		2			6		12			9		1
Pb	1	1	1	7	12					10		
		2			16					10		
	2	1			20					10		
		2			18					10		
Se	1	1			20					10		
		2			16					10		
	2	1			20					10		
		2			18					10		
Zn	1	1			6		14			6		4
		2			16					10		
	2	1			19		1			10		
		2			18				1	9		

a 1=River Water, 2=Well Water
b T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

Body Condition

The body condition scoring (BCS) system is used as an indication of nutritional adequacy and general health of the animal. A cow's body condition will naturally fluctuate within the range of 4 to 7, depending on weather conditions, nutrition, and the cow's stage of production. BCS distributions are shown in Table 7.

These BCS distributions are all within normally expected ranges for healthy, productive cows. They do not suggest that a serious nutritional imbalance exists on either ranch or in either study group.

Sheep

Blood

The ranges of GP, Cu, and Zn measured in individual sheep are listed in Table 8. The corresponding diagnostic distributions are listed in Table 9.

There were no sheep diagnosed in the toxic category for blood GP, Cu, or Zn. There is a definite pattern of animals shifting from normal GP levels at sampling time 1 to above normal levels at sampling 2 on each ranch. The two sheep on Ranch C and one on Ranch D which were deficient at sampling 1 also shifted to a higher category. This would indicate an increase in dietary intake of Se prior to sampling 2. Sheep on both ranches are mostly in the normal and below normal categories for blood Cu, although there is more variability on Ranch C both within and between sampling time. Blood Zn appears to be normal in sheep on both ranches.

Table 7. BCS distributions for cows

Sample Time[a]	Study Group[b]	Ranch A				Ranch B			
		BCS				BCS			
		4	5	6	7	4	5	6	7
1	1	3	7	8	2		3	7	
	2	2	8	7	3			9	1
2	1	5	3	6	2		3	6	1
	2	1	12	3	2			8	2

[a] Sampling time 1=May 1993; Sampling time 2=February 1994 for Ranch A; Sampling time 2=October 1993 for Ranch B

[b] 1=River Water; 2=Well Water

[c] Cattle BCS system ranges from 1 = emaciated, 5 = average, 9 = obese

Table 8. Range of blood GP, Cu, and Zn measured in sheep (ppm)

Element	Time	Ranch C	Ranch D
		Range	Range
GP[a]	1	180-1339	288-743
	2	475-1508	729-1274
Cu	1	0.55-1.21	0.63-1.10
	2	0.62-1.74	0.65-1.00
Zn	1	0.87-1.92	0.72-1.30
	2	0.61-1.21	1.01-1.40

[a] GP unit of measure is mmole/l/sec, all other units are ppm

Table 9. Diagnostic category distributions for blood GP, Cu, and Zn for sheep

Element	Time	Ranch C					Ranch D				
		Diagnostic Category[a]					Diagnostic Category				
		T	AN	N	BN	D	T	AN	N	BN	D
GP	1		1	17		2			19		1
	2		13	5				11	7		
Cu	1		1	13	5	1			12	8	
	2		4	8	6				11	7	
Zn	1		1	19					20		
	2			17	1				18		

[a] T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

Wool

The sheep on Ranch D had been shorn one week prior to the June 8 sampling. Therefore, we did not have wool element levels for sampling 1 on Ranch D. The ranges of wool As, Cd, Cu, Pb, Se, and Zn found in individual sheep are listed in Table 10. The corresponding diagnostic distributions are shown in Table 11.

There is more variability between ranches in the wool diagnostic distributions than in any of the distributions previously compared. Although we found no reference of diagnostic levels of wool As, the highest level tested of 0.4 ppm is well below the As level referenced as toxic (>3.4 ppm) in cattle hair.

Sheep on Ranch C show a definite increase in wool Cd from sampling time 1 to sampling 2, which indicates higher dietary Cd through the summer period than in the spring. Wool Cu levels of sheep on Ranch D are normal and below normal, consistent with both the cattle distributions and the sheep blood distributions. However, sheep on Ranch C are in the normal and above normal categories, inconsistent with all other distributions. The reason for this is not known. The possible reasons include higher water Cu concentrations at that location on the Alamosa River, dietary and management differences, or this may be due to chance alone. The importance of this observation can not be determined in a single year study.

While sheep on Ranch C are normal for wool Pb, sheep on Ranch D are all below normal at sampling time 2. Because high Pb is a potential health concern but low Pb is not, this is not considered important. Wool Se is consistently normal at sampling 2 on each ranch, and there is a definite trend of wool Se increasing from sampling time 1 to sampling 2 on Ranch C. This is consistent with the trend noted in blood GP for sheep, and is an indication of increased Se intake through the summer. One sheep on Ranch C is in the toxic category for Zn at sampling time 2. All other sheep on both ranches are in the normal category at sampling time 2 which is consistant with blood Zn results. Moreover, seventeen sheep from Ranch C are in the normal category with three in the deficient category at sampling time 1. Therfore, this does not indicate a toxicity problem in either herd in 1993. There are no other sheep with toxic levels of any other element screened.

Body Condition

The body condition scoring system for sheep is numerically different than the cattle system, but it is used in the same manner as an indicator of animal health and nutritional state. A sheep's body condition will naturally fluctuate within the range of 2 to 4, depending on weather conditions, nutrition and stage of production. The BCS distributions are listed in Table 12.

The BCS distribution was excellent in June for both ranches, and the sheep on Ranch D increased in body condition at sampling 2, indicating good health and nutrition. On Ranch C, the individual sheep that dropped in condition from 2 to 1 was one of the oldest ewes in the study, which was likely a major factor in the decline. There is a notable trend of declining condition scores between June and November on Ranch C. However, sixteen of the eighteen sheep scored on Ranch C in November have a BCS of either 3 or 4, which is within the appropriate range.

Table 10. Range of wool As, Cd, Cu, Pb, Se, and Zn measured in sheep (ppm)

Element	Time	Ranch C Range	Ranch D[a] Range
As	1	<0.01-0.08	
	2	0.03-0.4	<0.01-0.20
Cd	1	<0.5	
	2	<0.5-1.7	<0.5-1.8
Cu	1	6.8-14.0	
	2	2.07-4.95	2.02-8.92
Pb	1	<2-3.1	
	2	<2	<2
Se	1	<0.01-0.09	
	2	0.09-0.51	0.09-2.13
Zn	1	65.8-105.0	
	2	87.1-164.0	94.5-118.0

[a] Wool samples were not analyzed at sampling time 1 for Ranch D

Table 11. Diagnostic category distribution of wool As, Cd, Cu, Pb, Se, and Zn for sheep

Element	Time	Ranch C Diagnostic Category[a]					Ranch D[c] Diagnostic Category				
		T	A N	N	B N	D	T	A N	N	B N	D
As[b]	1										
	2										
Cd	1				20						
	2		12	2	4			5	3	10	
Cu	1		9	11							
	2		3	15					12	6	
Pb	1			20							
	2			18						18	
Se	1			2	13	5					
	2			18					18		
Zn	1			17		3					
	2	1		17					18		

[a] T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

[b] No reference found for diagnostic levels of wool As

[c] Wool samples were not analyzed at sampling time 1 for Ranch D

Table 12. BCS distributions for sheep

Sampling Time[a]	Ranch C					Ranch D				
	BCS[b]					BCS[b]				
	1	2	3	4	5	1	2	3	4	5
1		1	1	18				1	19	
2	1	1	5	11				2	4	11

[a] 1=June 1993; 2=November 1993

[b] Sheep BCS system ranges from 1=emaciated, 3=average, 5=obese

Conclusion

Veterinary diagnostic techniques were used to assess the mineral status and health of two beef cattle and two sheep herds. There are no indications of mineral toxicities in either cattle herd, whether drinking river water or well water. In spite of increasing Cu concentrations in the Alamosa River, these data show tendencies for cattle to have below normal and deficient Cu levels in blood and hair. Above normal Cd levels appear to be specific to cattle drinking river water and should be monitored.

There are no indications of mineral toxicities in either sheep herd. The increase in both Se and Cd between sampling time 1 and 2 in sheep warrants future monitoring. Sheep on Ranch D were in excellent body condition, and while the majority of sheep on Ranch C were in adequate condition, the trend of declining BCS raises concern. While several management factors, such as grazing fall forage low in dietary protein, or late weaning of the lambs could be responsible for this trend, a subclinical imbalance of dietary minerals is also within the realm of possibility.

APPLICATION AND IMPLICATIONS

The results of this reconnaissance study suggest that two cattle herds and two sheep flocks in the Alamosa River watershed were in a normal mineral status in 1993. A statistical analysis performed to assess the cause and significance of trends noted herein is reported in a separate paper.

While this study assessed short term trends in levels of key elements in the blood, hair, and wool, it does not provide adequate information to assess long-term trends. Therefore, if heavy metal loading in the Alamosa River should decrease to 1986 levels, there would be little concern for potential toxicities to livestock. If, however, concentrations of heavy metals in the Alamosa River continue to increase, or even if they stabilize at the current elevated levels, then the possibility of animals loading elements and experiencing mineral toxicities or imbalances still exists. Therefore, it would be prudent to enact a yearly monitoring of these animals until water quality returns to 1986 levels.

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BIOLOGICAL CONCENTRATIONS OF KEY ELEMENTS IN BLOOD, HAIR AND WOOL OF LIVESTOCK RAISED IN THE ALAMOSA RIVER WATER SHED
PART 2: STATISTICAL ANALYSIS

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SUMMARY

Biological data from sixty beef cattle and forty sheep were statistically analyzed to determine whether drinking Alamosa River water (treatment 1) versus drinking well water (treatment 2) had a significant effect on element concentrations in blood or hair, and on classification into diagnostic categories of toxic, above normal, normal, below normal or deficient. Treatment had a significant effect on glutathione peroxidase (GP) and Zn concentrations in cattle blood, and on As, Cd, Pb and Se concentrations in cattle hair. Cattle drinking river water had higher concentrations of As, Cd, and Pb, and lower concentrations of GP, Se and Zn than cattle drinking well water. Treatment was a significant source of variation in ranking hair Zn into diagnostic categories with more cattle drinking river water ranked deficient. Treatment did not have a significant effect in categorizing any of the other elements for cattle. There were no treatment subgroups for sheep, thus only geographic location and management effects were tested. Both location and management had significant influence on element concentration in sheep blood. Sheep on Ranch C, further upstream, had lower GP and higher Cu concentrations than sheep on Ranch D. The magnitude of changes likely due to diet or water quality varied for the different ranches. Sampling time had a significant influence on ranking sheep GP into diagnostic categories, with an obvious shift from normal to above normal categorization from sampling time 1 to time 2.

INTRODUCTION

Heavy metal loading in the Alamosa River increased between 1986 and 1991 (Agro-Engineering, 1992). This situation came into public awareness in the spring of 1993, creating concern about possible effects on the environment, animals, and people of the Alamosa River watershed.

Health of livestock was one such concern. Several of the elements included on a US-EPA list of "pollutants of concern" for the Alamosa River are either key dietary micro-minerals in livestock nutrition or are considered potentially toxic elements for livestock. A rapid reconnaissance action was taken to assess the biological mineral status of exposed livestock by measuring levels of key elements in the blood, hair and wool, and comparing these levels to veterinary diagnostic standards. While the results of the diagnostic evaluation revealed animals in a normal mineral status, or in the case of Cu, in a low to deficient status which is consistent with historical findings in Cu status (Baldwin), there were notable differences in element levels among ranches, study groups and sampling times. The objective of part 2 of this study was to determine which of these differences were significant and due to Alamosa River water exposure.

METHODS

Livestock species exposed to Alamosa River water include cattle, sheep, horses, goats, and swine. Cattle and sheep are the most numerous and also represent the major economic concern. Therefore, cattle and sheep were chosen for this study.

The Conejos County Agricultural Stabilization and Conservation Service office has approximately one hundred livestock operations on record in the Alamosa River watershed. Time and funding constraints at the outset of the study did not allow a sample size large enough to adequately represent either the exposed livestock population or the exposed number of operations. The study design team thus chose a rationale of screening two cattle and two sheep herds at various locations along the watershed, and to include adequate numbers within each herd to be representative of that sub-population. The information gleaned would thus provide an indication of the mineral status of cattle and sheep in the Alamosa River watershed.

The constraints at the outset also influenced the biological tests used and the elements chosen for analysis. Copper was chosen as a primary element of concern as Cu levels in the Alamosa River had been measured in excess of NAS livestock standards (Agro-Engineering, 1992). Although the design team recognizes liver biopsy and tissue analysis as the diagnostic method of choice for Cu, this method was not possible because of time and personnel constraints. Instead, blood serum analysis was used to indicate element intake and metabolism in the seven to ten days immediately prior to sampling, combined with hair or wool analysis which indicates element intake and metabolism during the forty-five to sixty day period prior to sampling. Selenium and Zn were chosen for analysis because they play an important role in Cu metabolism. Glutathione peroxidase, a red blood cell, Se containing enzyme, was used as an indicator of Se in the blood. Arsenic, Cd, and Pb were also chosen for study because they are potentially toxic to livestock and because they were listed as elements of concern in the Alamosa River. In this paper, Cu, Zn, Cu-h and Zn-h stand for blood cooper, blood zinc, hair copper, and hair zinc, respectively.

Cattle

Forty beef cows from cooperating Ranch A and twenty beef cows from cooperating Ranch B were individually identified using plastic and metal ear tags, in May 1993. Cattle at each ranch were divided into two study groups. The first group had been drinking Alamosa River water for six weeks prior to the first sampling. The second group had been drinking water pumped from wells. All cattle were consuming forage produced in the Alamosa River watershed. Cattle on each ranch were receiving a mineral supplement. The supplements used were different on each ranch.

The entire cow herd was removed from each ranch in late June and moved to various locations for summer and fall grazing. All summer grazing locations were outside the Alamosa River watershed. Within ten days of returning to the home ranch, a second set of blood and hair samples were collected. Body condition was assessed on all cattle (Richards, et al., 1986) at both sampling times. The number of observations for ranch, study group and sampling time are listed in Table 1a.

At each sampling time, two blood samples were collected from each animal by jugular vena-puncture. One sample was collected in a heparinized tube for whole blood analysis and was refrigerated until analysis. The second sample was collected in a sterile serum tube, held at room temperature and centrifuged within 8 hours of collection. The serum was then separated and refrigerated until laboratory analysis.

Hair samples were collected from each animal by clipping closely against the skin immediately behind the shoulder. Clipped hair was stored in whirl-pack bags until laboratory analysis.

Table 1a. Number of cattle observations at each ranch, study group and sampling time[a]

Ranch	Study Group[b]	Number of Observations		
		May 12, 1993	October 12, 1993	February 14, 1994
A	1	20		16
	2	20		18
B	1	10	10	
	2	10	10	

[a] Total number of observations = 114

[b] 1=River Water; 2=Well Water

Sheep

Twenty ewes from cooperating Ranch C and twenty ewes from cooperating Ranch D were individually identified for the study using plastic and metal ear tags, in June 1993. Sample collection and handling methods were identical to the methods described for cattle. Unlike the cattle, all sheep remained in the Alamosa River watershed throughout the year. None of the sheep were receiving mineral supplementation. A second set of samples was collected in the fall of 1993. Body condition was assessed on all sheep (American Sheep Producers Council, 1988) at both sampling times. The number of observations for ranch and sampling time are listed in Table 1b. Wool data is incomplete because sheep on Ranch D were shorn immediately prior to sampling time 1 and are therefore not presented.

Lab Technique

All laboratory analyses were conducted by the Colorado State University Veterinary Diagnostic Laboratory. Glutathione peroxidase (GP) was measured in whole blood according to procedures outlined by Ageraard and Jensen (1982).

All other elements were measured using various methods of atomic absorption spectrophotometry. Hair and wool samples were thoroughly cleaned and wet ashed (EPA, 1992) in preparation for analysis. Arsenic and Se were measured using vapor generation as described by Brodie, et al. (1983) and Siemar (1975). Copper and Zn in both serum and wet ash samples, as well as Pb, and Cd in wet ash samples were measured using standard flame atomic absorption photometric techniques (Varian Techtrom, 1972).

Categorical Classification

The elements screened in this study were chosen either because they were listed as elements of concern in the Alamosa River and are potentially toxic to livestock, or because they have significant dietary interaction with the elements of concern. Concentrations of all elements were measured in parts per million by the diagnostic laboratory, and then categorically classified as toxic, above normal, normal, below normal or deficient. Ranges for each of these categories were suggested by the CSU Veterinary Diagnostic Laboratory and are listed in Table 2 (Puls, 1988).

Statistical Analysis

Two types of analysis were performed: 1) analysis of variance for the continuously distributed absolute element concentration data; 2) categorical, logistic analysis of the categorically classified data.

Table 1b. Number of sheep observations at each ranch and sampling time[a]

Ranch	Number of Observations	
	June 8, 1993	November 2, 1993
C	20	18
D	20	18

[a] Total number of observations = 76

Analysis of Variance

The significance and magnitude of factors potentially influencing element contents in ppm (continuous response variable) were analyzed with least squares analysis of variance (Steele and Torrie, 1960) using the general linear models procedure in SAS (SAS, 1988).

Preliminary analyses were preformed to determine if treatment differences existed in element concentration content at the first measurement time. These analyses included the fixed, main effects of treatment and ranch and the two-way interaction. When differences were detected a repeat measures model was employed to analyze data from both measuring times. Independent variables tested included the following fixed, main effects: treatment, ranch, time and all two-way and three-way interactions, as well as the fixed main effect of subject.

Categorical Analysis

Element concentrations were also analyzed as categorical response variables. In this analysis element concentration classified as toxic, above normal, normal, below normal and deficient, were analyzed with a linear, logistic procedure using the catmod procedure in SAS (1988).

Preliminary analyses were preformed to determine whether differences existed in the categorical, ranking at the first measurement time. When differences were detected a repeat measures model was employed to analyze data from both measuring times. The same independent variables were used in the preliminary and final categorical analyses as in the least squares analyses.

Body condition score analyses were preformed using both analysis of variance and categorical, logistic analysis. The assumptions of the categorical analysis were more consistent with the BCS data (SAS, 1988) and were therefore considered more reliable.

Table 2. Standards used to rank each sample into diagnostic categories (ppm)

---CATTLE--- Diagnostic Category	Blood			Hair					
	GP[a]	Cu	Zn	As	Cd	Cu	Pb	Se	Zn
Toxic		>2.5	>3.0	>3.4	>40		>10.0	>5.0	
Above Normal	>1000	1.2-2.5	1.4-3.0	3.0-3.4	0.6-16	>32	5-10		>150
Normal	250-1000	0.8-1.2	0.7-1.4	<3.0	<.6	6.7-32	<5.0	≤.50	100
Below Normal		0.6-0.8	0.4-0.7						
Deficient	<250	<0.6	<0.4			<6.7			<100

[a] GP unit of measure is mmole/l/sec, all other units are ppm

---SHEEP--- Diagnostic Category	Blood			Wool					
	GP[a]	Cu	Zn	As[b]	Cd	Cu	Pb	Se	Zn
Toxic		>2.5	>30.0		>20		>25		>145
Above Normal	>1000	1.2-2.5	1.4-30.0		1.2-2.0	>10	7-25	>4.0	130-145
Normal	250-1000	0.8-1.2	0.7-1.4		0.55-1.2	3.0-10.0	4.0-7.0	0.80-4.0	70-130
Below Normal		0.6-0.8	0.4-0.7		<0.55	2-3	<4	0.03-0.08	
Deficient	<250	<0.6	<0.4			<2.0		<0.03	<70

[a] GP units of measure is mmole/l/sec, all other units are ppm

[b] no reference found for wool As standards

RESULTS

Cattle

Biological Concentrations

Preliminary analysis of element concentration at the first measurement time suggested that treatment differences existed. Therefore, all data from both measurement times were pooled and analyzed. The significance of factors potentially influencing element concentration measured in ppm from both measurement times are listed in Table 3.

R-square values for GP, Cu, Zn, As, Cd, Cu-h, Pb, Se and Zn-h were .859, .761, .642, .594, .931, .741, .779, .879 and 8.30, respectively. Hence, the effects listed in Table 3 accounted for most of the differences in element concentration.

Because animals in both treatment groups were subjected to similar conditions between measurement times, overall treatment differences could be masked by the similar conditions between groups at the second sampling. Therefore, the effect most useful to detect true treatment differences is the treatment*time interaction.

While copper was of primary concern, the treatment*time interaction was not significant for either Cu or Cu-h. The treatment*time interaction was significant for GP, As, Cd, and Pb. This suggested that treatment differences existed, but those differences depended on the time of measurement. As expected, linear contrasts showed that the significance of the treatment*time interaction was due to differences between treatment groups at the first measurement, and therefore a result of whether the cows were drinking river water or well water. Treatment groups were not different at the second measurement. Least square means for treatments at the first measurement are listed in Table 4.

Treatment one (river water) had higher levels of Cu, Cu-h, As, Cd, and Pb; whereas, treatment two (well water) had higher levels of GP, Se, Zn, and Zn-h.

In some instances a significant 3-way interaction could also suggest treatment effects were important. However, this interaction must be carefully inspected to be properly interpreted. One scenario that can result in a significant 3-way interaction is the differences in the rate of change between treatment groups over time was not the same for the two ranches. In other words, the magnitude and significance of the treatment*time interaction was not the same on the two ranches.

The treatment*time interaction was not significant, but the 3-way was significant for Zn and Se. Appropriate linear contrasts for both elements suggested the magnitude and sometimes direction of change from sampling time 1 to sampling time 2 were different for both treatment groups at both ranches (compare reference numbers 1 vs. 3 and 2 vs. 4, Table 5). For testing the two-way interaction the differences in Table 5 were in effect pooled across ranches (add references numbers 1 + 3 and 2 + 4). The differences between magnitude and sign of the within-ranch two-way interaction tended to cancel or dilute each other, resulting in a nonsignificant, overall treatment*time interaction.

Table 3. Probability values for significance of factors potentially influencing heavy metal content in parts per million.

Element	P Values for						
	Subject	Ranch	Treatment	Time	Treatment*Time	Treatment*Ranch	3-Way[a]
GP	.020	.001	.001	.561	.004	.337	.008
Cu	.001	.001	.143	.510	.233	.291	.406
Zn	.709	.008	.021	.034	.804	.340	.001
As	.504	.611	.009	.129	.033	.171	.006
Cd	.001	.001	.021	.001	.019	.004	.570
Cu-h	.009	.001	.032	.370	.241	.520	.063
Pb	.494	.002	.003	.001	.002	.001	.001
Se	.001	.001	.045	.001	.901	.072	.001
Zn-h	.001	.001	.001	.001	.097	.212	.056

[a] This is the 3-way, treatment*time*ranch interaction

Table 4. Least square means for treatment*time interaction subclasses at the first measurement in cattle[a]

Element	Treatment 1[b]		Treatment 2	
GP	572.6[c]	(18.1)	706.1	(18.4)
Cu	0.659	(.013)	0.620	(.014)
Zn	1.077	(.038)	1.182	(.039)
As	0.187	(.030)	0.034	(.031)
Cd	1.245	(.087)	1.016	(.089)
Cu-h	6.907	(.199)	6.224	(.203)
Pb	3.320	(.188)	2.117	(.191)
Se	0.704	(.024)	0.756	(0.024)
Zn-h	101.322	(1.79)	116.418	(1.81)

[a] Cell values are least square means in parts per million, standard errors in parenthesis

[b] Treatment 1= River Water; Treatment 2= Well Water

[c] Cell values for GP are Least Square Means in mmole/l/sec

Table 5. Differences between element concentration at measurement times one and two for treatment*ranch subclasses

Reference Number	Ranch	Treatment[a]	Change (Round 1 - Round 2)	
			Se	Zn
1	A	1	.110	.173
2	A	2	.253	.277
3	B	1	-.306	.019
4	B	2	-.447	-.124

[a] Treatment 1= River Water; Treatement 2= Well Water

In short, treatment had a significant effect on both ranches for GP, As, Cd, and Pb. Treatment was also significant for Se but had the opposite effect on each ranch. Treatment was significant for Zn, but only on ranch 1. Treatment did not have a significant effect on Cu, Cu-h or Zn-h.

Diagnostic Category

Although statistical differences in element concentration were suggested by the analyses in parts per million, those analyses did not clarify if those differences were biologically important. The categorical analyses were better suited to answer this question.

The significance of factors potentially influencing element concentration, at the first measurement time, expressed categorically are listed in Table 6.

Treatment was only a significant source of variation for Zn-h and differences approached significance for Cd. The number of observations in each category are listed in Table 7. As the P values in Table 6 indicate, the small numeric differences seen in Table 7, for all variables except Zn-h, were likely due to chance alone. For Zn-h, the relatively small numeric difference in ppm caused a significantly greater percentage of animals in treatment 1 to be deficient because the mean Zn-h content was close to the cut off between normal and deficient.

Table 6. Probability values for significance of factors potentially influencing element concentration for cattle expressed in categories

Element	P Values For		
	Treatment	Ranch	Treatment*Ranch
GP	.695	.005	.695
Cu	.619	.388	.514
Zn	.404	.015	.483
As	*	*	*
Cd	.132	.065	.448
Cu-h	.241	.036	.248
Pb	.324	.356	.324
Se	*	*	*
Zn-h	.002	.752	.272

* Indicates all responses were in one category. With no differences in responses, significance tests for differences are meaningless.

Table 7. Number of observations in heavy metal content categories for cattle

Element	Treatment[a]	Category[b]				
		T	AN	N	BN	D
GP	1			30		
	2		1	29		
Cu	1			2	22	6
	2				21	8
Zn	1		1	29		
	2		3	26		
As	1			30		
	2			30		
Cd	1		20	10		
	2		27	3		
Cu-h	1			16		14
	2			10		20
Pb	1	1	7	22		
	2			30		
Se	1			30		
	2			30		
Zn-h	1			12		18
	2			29		1

[a] 1= River Water; 2= Well Water
[b] T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

Body Condition Score

Categorical analysis of BCS indicated that treatment was not a significant source of variation at the first measurement time.

For analysis of variance of BCS as a continuous variable, the treatment*time interaction was again the appropriate term for assessing if treatment had a significant influence on body condition score. The treatment*time interaction was significant. However, as can be seen in the least square means in Table 8, mean BCS were almost identical at the first measurement time. The differences were significant only due to changes in BCS that occurred after the animals left the Alamosa watershed - and therefore are not due to treatment differences.

Furthermore, element concentration was not a significant source of variation when included as a covariate in analysis of variance of BCS.

Sheep

Biological Concentrations

The meaningful comparisons that can be made from these sheep data are differences due to geographical location along the river and management differences between the two ranches. Probability values for significance of factors potentially influencing element concentration and BCS are listed in Table 9, and least square means for these variables are listed in Table 10. Model R-square values were .796, .788, .794, and 829 for GP, Cu, Zn, and BCS, respectivley.

Ranch, time and the time*ranch interaction were significant sources of variation for most variables. Apparently, geographic and managerial differences between the ranches had an influence on element concentration and BCS. Time was likely a significant source of variation due to changes in diet as a result of changes in forage and location. However, as the time*ranch interaction indicated, the magnitude of changes likely due to diet or water quality were different for the different ranches.

Diagnostic Categories and Body Condition

Differences in categorization of element concentration between ranches, times and ranch*time subclasses, listed in Table 11a, were small and as the P values in Table 12 indicate, likely due to chance alone. The one exception was that time was significant for GP, and the differences in the numbers per category were large.

Differences in BCS categorization, listed in Table 11b, were markedly greater than the differences in element concentration categorization; and, as the P values in Table 12 indicate, not likely due to chance alone.

Table 8. Least square means for treatment*time interaction subclasses of BCS in cattle

Time	Treatment[a]	LSMeans	
		BCS	Standard Error
1	1	5.42	(.096)
	2	5.44	(.104)
2	1	5.75	(.098)
	2	6.15	(.100)

[a]Treatment 1= River Water; Treatment 2= Well Water

Table 9. Probability values for significance of factors potentially influencing element concentration in parts per million and body condition score of sheep

Element	P Values for			
	Subject	Ranch	Time	Time*Ranch
GP	.842	.039	.001	.934
Cu	.001	.001	.435	.036
Zn	.040	.808	.001	.001
BCS	.002	.001	.504	.001

Table 10. Least square means for ranch*time interaction subclasses in sheep[a]

Ranch	Time	LSMeans			
		Variable			
		GP	Cu	Zn	BCS
C	1	620.8 (46.1)	.866 (.038)	1.08 (.039)	3.85 (.135)
	2	500.6 (48.6)	.947 (.040)	1.04 (.041)	3.46 (.147)
D	1	1138.5 (46.1)	.848 (.038)	.90 (0.39)	3.95 (.035)
	2	1026.6 (48.6)	.808 (.040)	1.25 (.041)	4.47 (.147)

[a] Cell values are least square means in parts per million, standard errors in parenthesis

[b] Cell values for GP are least square means in mmole/l/sec

Table 11a. Number of observations in element concentration categories for sheep

Element	Ranch	Category[a]				
		T	AN	N	BN	D
GP	C		14	22		2
	D		11	26		1
Cu	C		5	21	11	1
	D			23	15	
Zn	C		1	36	1	
	D			38		
	Time					
GP	C		1	36		3
	D		24	12		
Cu	C		1	25	13	1
	D		4	19	13	
Zn	C		1	39		
	C			25	1	

[a] T=Toxic; AN=Above Normal; N=Normal; BN=Below Normal; D=Deficient

Table 11b. Number of observations in body condition score categories for sheep

Ranch	Category				
	1	2	3	4	5
C	1	2	6	29	
D		3	23	11	
Time					
1		1	2	37	
2	1	1	7	15	11

Table 12. Probability values for significance of factors potentially influencing element concentration of sheep expressed in categories

Element	P Values For		
	Ranch	Time	Ranch*Time
GP	.369	.001	.788
Cu	.461	.511	.628
Zn	.889	.781	.963
BCS	.001	.001	.001

CONCLUSION

Statistically significant differences in element concentrations existed between cattle who drank river water versus those who drank well water. Thus, element concentrations in river water did influence biological concentrations in the animals. However, the concentration differences resulted in significant differences in the numbers of animals in toxic, deficient, normal, above normal, or below normal categories only for Zn-h. Whether this river water vs well water effect would result in significant changes in diagnostic category ranking with longer exposure can not be answered in this single year study.

Ranch, time and ranch*time interaction were all significant sources of variation for element concentrations and BCS in sheep, but did not influence diagnostic categorization.

Source of water did not have any effect on the BCS in cattle. This study did not assess if water source had any effect on the productivity of the livestock.

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A CASE - CONTROL STUDY OF BEEF HERDS AND SHEEP FLOCKS THAT WERE OR WERE NOT EXPOSED TO WATER AND FORAGE IN THE ALAMOSA RIVER WATERSHED

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SUMMARY

Cattle and sheep producers, whose livestock were either exposed or not exposed to water and forage in the Alamosa River watershed, were surveyed to determine the effects of exposure to heavy metal loading in the river on livestock morbidity, mortality, and productivity. In general, exposure to the water and forage had no effect on morbidity rates, mortality rates, or animal performance. However, the exposed population had a higher median calf morality between 24 hours and three weeks of age in 1991 and 1993 (3.7% vs. 0.6%, P=.03; 5.8% vs. 1.0%, P=.003, respectively). The exposed population had lower median lamb birthing rate in 1992 (94.2% vs. 98.8%, P=.05) and higher median total lamb mortality in 1992 (12.2% vs. 3.4%, P=.03). These may be true exposure effects, however the probability is high that climate and management factors contributed to these differences. There were no differences in total morbidity rates for adult cattle, calves, adult sheep, or lambs between exposed and non-exposed populations for any year surveyed. There were no differences in median total mortality rates for adult cattle, calves, or adult sheep between populations in any year surveyed. Total lamb mortality was not different between treatment groups in 1991 or 1993. There were no differences in cattle birthing rates or weaning weights between the populations in any year surveyed. There were not differences in lamb birthing rates in 1991 or in lamb weaning weight in either year.

Four veterinarians who serve clients with both exposed and non-exposed livestock reported no difference in number or type of calls for the two groups.

Components of the data set indicate possible exposure effects, but the overall data set does not. Conclusions should be drawn cautiously from this survey because the majority of data is based on livestock producers' memory rather than written record.

INTRODUCTION

Heavy metal loading in the Alamosa River increased between 1986 and 1991 (Agro-Engineering, 1992). This situation came into public awareness in the spring of 1993, creating concern about possible effects on the environment, animals, and people of the Alamosa River watershed.

One concern was for the health of livestock raised in the watershed. This study was conducted as a rapid, reconnaissance action to assess the morbidity, mortality and productivity rates of beef cattle and sheep in the affected area. Our objective was to assess whether an epidemic caused by mineral toxicities and imbalances existed in exposed livestock, and locate the ranches affected if there was an epidemic.

METHODS

This study was conducted consistent with epidemiological survey techniques and statistical analyses, as designed by the Department of Environmental Health at Colorado State University. Twenty-seven beef cattle producers and thirteen sheep producers were interviewed.

Survey

Sample Selection

The exposed population was defined as animals from the ranches located in the Alamosa River watershed. Some of these animals remained in the Alamosa watershed year-round, while others were only in the watershed for a portion of the year. The non-exposed population was defined as the animals from ranches located outside the Alamosa River watershed. Participants were selected according to the following protocol. First, a list of livestock producers was obtained from the Conejos County Agricultural Stabilization and Conservation Service and was considered the most accurate compilation of the total study population. Next, the list was stratified by whether the ranch was or was not located in the Alamosa River watershed, (exposed vs non-exposed), whether the producer raised cattle or sheep, and by the size of operation (Table 1).

The proportion of each size category relative to the total population was determined: 40%, 20%, and 40% for small, medium, and large operations, respectively. The total Alamosa watershed population was approximately 100 livestock operations, of which 20 were interviewed to obtain a minimum sampling of 20 percent of the population. Attempting to achieve proportional numbers while maintaining randomness, eight producers each were selected randomly from within the small and large categories, and four were selected randomly from within the medium category. Several producers declined interviews and were replaced by the same selection process. The non-exposed sampling population was chosen in the same manner.

Instrument

The survey instrument employed was adapted from the USDA-National Animal Health Monitoring System (NAHMS, King, 1985) for beef cattle and sheep. NAHMS survey forms were modified to collect yearly data for the three year period 1991 through 1993. Six specific interview forms were used (Table 2).

Statistical Analysis

The parameters of interest were the same for beef cattle and sheep. Production parameters include birth rate, the number of breeding females that gave birth divided by the number of females exposed to breeding, and weaning weight of the offspring adjusted to a common weaning age.

Morbidity parameters were analyzed for both adult animals and for the offspring born each year. Disease classes analyzed for adult animals include respiratory, diarrhea, foot rot, mastitis, retained placenta or uterine infection, abortion, skeletal-muscular problems, birth defects, and total morbidity. Diseases classes for the offspring include diarrhea, respiratory, foot rot, skeletal-

Table 1. Number of Animals used to categorize operation size

Species	Category		
	Small	Medium	Large
Cattle	≤ 75	75-200	>200
Sheep	< 75	75-400	>400

Table 2. Summary of information requested by survey form

Form	Information
Cover Form	General ranch and operator information
Beef Health	Morbidity, mortality, and productivity of beef herds
Beef Management	Management factors that may affect morbidity, mortality and productivity
Sheep Health	Morbidity, mortality, and productivity of sheep flocks
Sheep Management	Management factors that may affect morbidity, mortality and productivity
Veterinarian Form	Actual veterinary response to health problems

muscular problems and total morbidity. Morbidity rates were calculated for each disease class for every herd during each year

Mortality rates were also analyzed for both adult animals and offspring. Adult mortality was simply analyzed as a yearly total. Mortality in the young animals was analyzed by age at death, including stillbirth, birth to 24 hours, 24 hours to three weeks, three weeks to weaning, and the yearly total.

Preliminary analyses indicated that the values of these parameters were not normally distributed, with the exception of weaning weights. Therefore, the weaning weight means were compared using the Students t test, and the medians were compared for all other parameters using the Mann-Whitney U test (Snedecor, 1967). All comparisons were made between the exposed population and the non-exposed population within each year. These analyses provide an indication of whether there was a significant difference for each parameter between the exposed and non-exposed populations. However, any differences between the two groups could have also been caused by other factors such as climate or management.

RESULTS AND DISCUSSION

The management survey included a question to determine whether the responses to production, morbidity and mortality questions were taken from written records or from producer memory. It is important to note that the vast majority of responses were from memory only. Therefore, it would be prudent to be cautious when drawing conclusions based on these data, especially when differences are small or subtle.

Cattle

The number of beef cattle herds in the exposed and non-exposed groups, along with the number of breeding females and beginning date of the birthing season for each year are reported in Table 3. The differences in median herd size and beginning calving date were not significant during any study year.

Table 3. General description of the beef cattle herds that were or were not exposed to water and forage in the Alamosa River watershed

VARIABLE	N	1991	N	1992	N	1993
Number of Females Calving						
Median: Exposed	13	75.0	13	80.0	14	107.5
Non-Exposed	12	205.5	12	245.0	13	241.0
		(P=.35)[a]		(P=.43)		(P=.50)
Range: Exposed	13	17-360	13	17-350	14	14-400
Non-Exposed	12	10-800	12	13-800	13	6-800
Beginning Date of the Calving Season						
Median: Exposed	13	Feb. 4	13	Feb. 10	14	Feb. 9
Non-Exposed	12	Feb. 1	12	Feb. 1	13	Feb. 1
		(P=.45)		(P=.13)		(P=.82)
Range: Exposed	13	Jan. 1 - Feb. 15	13	Jan. 7 - Mar. 1	14	Jan. 7 - Feb. 25
Non-Exposed	12	Jan. 1 - Mar. 15	12	Jan. 1 - Mar. 15	13	Jan. 10 - Mar. 17

[a] P values for differences between medians

Production Parameters

Birthing rates and adjusted weaning weights for the two populations are reported in Table 4. At the time this survey was conducted in 1993, calves were still being born at some ranches and none of the calves had been weaned. Thus, only 1991 and 1992 data are reported. There was no significant difference in median birthing rate for the two groups. Adjusted weaning weight means were normally distributed and are therefore used to compare the exposed and non-exposed populations. There were no significant differences in adjusted weaning weights between exposed and non-exposed herd in either year.

Morbidity Parameters

Total morbidity rates for calves and adult cows are reported in Table 5. There were no significant differences in total morbidity between exposed and non-exposed herds for either adult cattle or calves in any year. There were no significant differences between median morbidity rates for any disease class in any year, except for pink-eye in adult cattle in 1992. During that year, the exposed population had a median incidence of pink eye of 0.0% compared to 2.0% in the non-exposed population. Although significant (P=.04), this difference is small and is not considered biologically important, because morbidity rates were similar for all other disease classes in the exposed and non-exposed herds, these data are reported in the appendix only.

Table 4. Birthing rates of females and adjusted weaning weights of calves in beef herds that were or were not exposed to water and forage from the Alamosa River watershed

VARIABLE	N	1991	N	1992
Calving Rate[a]				
Median: Exposed	13	97.1	14	94.9
Non-Exposed	12	94.3	13	94.9
		(P=.83)[c]		(P=.35)
Range: Exposed	13	48.5-100.0	14	53.2-100.0
Non-Exposed	12	88.7-100.0	13	88.9-100.0
Adjusted Weaning Weight[b]				
Mean: Exposed	13	499.5	13	523.8
Non-Exposed	11	493.9	11	494.9
		(P=..84)		(P=.62)
Range: Exposed	13	400.0-608.8	13	400.0-725.8
Non-Exposed	11	410.0-605.0	11	399.0-585.9

[a] A calving rate was determined for each herd during each year by dividing the number of females that calved by the number of females exposed to breeding and multiplying by 100.

[b] An adjusted weaning weight for calves was calculted for each herd during each year by using the following formula: ((actual weaning weight - 80)/age at weaning * 250) + 80.

[c] P values for differences between medians

Table 5. Morbidity rates of calves and adult cows that were or were not exposed to water and forage in the Alamosa River watershed

		N	1991	N	1992	N	1993
Total Morbidity of Calves[a]							
Median:	Exposed	11	11.0	12	13.0	13	13.0
	Non-Exposed	11	7.0	11	8.0	12	7.0
			(P=.92)[c]		(P=.44)		(P=.48)
Range:	Exposed	11	0.0-28.0	12	0.0-39.0	13	0.0-28.0
	Non-Exposed	11	0.0-109.0	11	0.0-54.0	12	0.0-27.0
Total Morbidity of Adult Cows[b]							
Median:	Exposed	13	6.0	13	6.0	14	6.0
	Non-Exposed	11	5.0	11	10.0	12	5.5
			(P=.58)		(P=.58)		(P=.72)
Range:	Exposed	13	0.0-20.0	13	0.0-21.0	14	0.0-20.0
	Non-Exposed	11	0.0-56.0	11	0.0-55.0	12	0.0-20.0

[a] A morbidity rate was calculated for each disease class for every herd during each year by dividing the number of cases of disease by the total number of calves born minus the number of calves that were born dead and multiplying by 100

[b] A morbidity rate was calculated for each disease class for every herd during each year by dividing the number of cases of disease by the number of adult cows calving and multiplying by 100.

[c] P values for differences between medians

Mortality Parameters

There were no significant differences between populations in calf stillbirths or death from birth to 24 hours in any year (Table 6). The median mortality rate for calves between 24 hours and three weeks of age was higher for the exposed population (3.7% vs 0.6%, P=.03) in 1991 and in 1993 (5.8% vs 1.0%, P=.003). From three weeks of age to weaning, there were no significant differences in calf mortality. Total calf mortality tended to be higher in 1992 and 1993 (P=.09 and P=.06, respectively) in the exposed herds compared with that in the non-exposed herds. These are important differences to note in the scope of this study. Factors potentially contributing to these differences include climate, and management factors such as nutritional management and herd health management. While the mortality differences may be a true exposure effect, they are more likely due to cumulative effects of the other contributing factors. Climate especially in 1991 and 1992, could have been a major contributing factor to calf mortality as both years were abnormally cold during the winter and spring.

Mortality rates of the adult females are reported in Table 7. There were no significant differences between populations in any year surveyed.

Sheep

The number of sheep flocks in each population, along with the number of breeding females and beginning date of the birthing season for each year are reported in Table 8. The differences in medium flock size and beginning lambing date were not significant between groups for any of the three years surveyed.

Table 6. Mortality rates[a] of calves in beef herds that were or were not exposed to water and forage in the Alamosa River watershed

Age at Death		N	1991	N	1992	N	1993
Stillbirth							
Median:	Exposed	13	0.0	13	0.4	14	0.3
	Non-Exposed	11	0.7	11	0.0	12	0.0
			(P=.90)[b]		(P=.48)		(P=.37)
Range:	Exposed	13	0.0-5.9	13	0.0-5.9	14	0.0-7.1
	Non-Exposed	11	0.0-4.0	11	0.0-3.5	12	0.0-2.6
Birth to 24 hours							
Median:	Exposed	13	0.0	13	1.9	14	0.4
	Non-Exposed	11	0.8	11	0.4	12	0.8
			(P=.31)		(P=.76)		(P=.68)
Range:	Exposed	13	0.0-23.3	13	0.0-12.0	14	0.0-2.9
	Non-Exposed	11	0.0-10.0	11	0.0-4.3	12	0.0-33.3
24 hours to 3 weeks							
Median:	Exposed	13	3.7	13	2.6	14	5.8
	Non-Exposed	11	0.6	11	1.7	12	1.0
			(P=.03)		(P=.18)		(P=.003)
Range:	Exposed	13	0.0-12.1	13	0.0-12.5	14	0.0-23.4
	Non-Exposed	11	0.0-6.5	11	0.0-6.5	12	0.0-6.4
3 weeks to weaning							
Median:	Exposed	13	0.0	13	1.0	14	0.0
	Non-Exposed	11	1.0	11	1.0	12	0.7
			(P=.11)		(P=.86)		(P=.96)
Range:	Exposed	13	0.0-3.9	13	0.0-6.8	14	0.0-14.6
	Non-Exposed	11	0.0-3.0	11	0.0-3.0	12	0.0-1.9
Total Mortality							
Median:	Exposed	13	6.3	13	8.6	14	9.3
	Non-Exposed	11	3.8	11	3.3	12	3.3
			(P=.30)		(P=.09)		(P=.06)
Range:	Exposed	13	0.0-32.6	13	2.5-16.7	14	2.5-35.7
	Non-Exposed	11	0.0-13.3	11	0.0-13.3	12	0.0-33.3

[a] A mortality rate was calculated for each age at death class for every herd during each year by dividing the number of calf deaths during that period by the number of calves that were still alive at the beginning of the period and multiplying by 100.

[b] P values for differences between medians

Table 7. Mortality rates of adult cows in beef herds that were or were not exposed to water and forage in the Alamosa River watershed

Mortality Rate[a]		N	1991	N	1992	N	1993
Median:	Exposed	13	1.1	13	1.1	14	1.1
	Non-Exposed	11	0.4	11	0.4	12	0.2
			(P=.54)[b]		(P=.27)		(P=.16)
Range:	Exposed	13	0.0-9.3	13	0.0-11.8	14	0.0-5.6
	Non-Exposed	11	0.0-5.3	11	0.0-5.3	12	0.0-33.3

[a] A mortality rate was calculated for each herd during each year by dividing the number of females that died by the number of females calving

[b] P values for differences between medians

Table 8. General description of the sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

VARIABLE		N	1991	N	1992	N	1993
Number of ewes lambing							
Median:	Exposed	10	425.0	10	425.0	9	380.0
	Non-Exposed	3	300.0	3	235.0	3	300.0
			(P=.86)[a]		(P=.86)		(P=.52)
Range:	Exposed	10	30-1025	10	30-1025	9	30-1025
	Non-Exposed	3	40-1500	3	40-1600	3	38-450
Beginning date of the lambing season							
Median:	Exposed	10	Mar. 13	10	Mar. 13	9	Mar. 26
	Non-Exposed	3	Mar. 16	3	Mar. 16	3	Apr. 1
			(P=.86)		(P=.86)		(P=.35)
Range:	Exposed	10	Jan. 16 - Apr. 5	10	Feb. 5 - Apr. 5	9	Feb. 5 Apr. 1
	Non-Exposed	3	Mar. 15 - Mar. 20	3	Mar. 15 - Mar. 20	3	Mar. 15 - May 12

[a] P values for differences between medians

One must be cautious when interpreting these data because the data are primarily based on producer memory rather than production records, and because the sample size in the non-exposed population is small.

Production Parameters

Birthing rates and weaning weights for the exposed and non-exposed flocks are reported in Table 9. Data for 1991 and 1992 only are reported as the 1993 lamb crop was not yet weaned at the time of the survey. Median lambing rate was higher in the non-exposed population than in the exposed population in 1992 (98.8% vs 94.2%, P=.05). This difference is not large but it may be important. It may be a true effect of exposure to drinking water and forage in the Alamosa River watershed, or it may be a result of differences in nutritional management and breeding management. There were no significant differences in mean weaning weight between the two populations in either year.

Morbidity Parameters

Total morbidity rates for lambs and adult ewes are reported in Table 10. There were no differences in median total morbidity rates for either age group in any of the three years. Neither were there any differences in median morbidity rates for any specific disease class for lambs or adult ewes in any year. The disease class data are reported in the appendix.

Table 9. Birthing rates of ewes and adjusted weaning weights of lambs in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

VARIABLE		N	1991	N	1992
Lambing rate[a]					
Median:	Exposed	10	95.0	10	94.2
	Non-Exposed	2	97.4	2	98.8
			(P=.09)[c]		(P=.05)
Range:	Exposed	10	90.0-97.7	10	89.4-97.7
	Non-Exposed	2	97.4-97.5	2	97.6-100.0
Adjusted weaning weight[b]					
Mean:	Exposed	9	93.6	10	98.9
	Non-Exposed	3	90.6	3	92.5
			(P=.78)		(P=.60)
Range:	Exposed	9	69.1-122.2	10	69.1-138.8
	Non-Exposed	3	80.3-102.0	3	85.9-102.0

[a] A lambing rate was determined for each flock during each year by dividing the number of ewes that lambed by the number of ewes exposed to breeding and multiplying by 100.

[b] An adjusted weaning weight for lambs was calculated for each flock during each year by using the following formula: ((actual weaning weight)/age at weaning * 170).

[c] P values for differences between medians

Table 10. Morbidity rates of lambs and adult ewes in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

DISEASE CLASS		N	1991	N	1992	N	1993
Total morbidity of lambs[a]							
Median:	Exposed	9	5.0	9	7.0	8	3.0
	Non-Exposed	3	4.0	3	4.0	3	4.0
			(P=.45)[c]		(P=.23)		(P=.76)
Range:	Exposed	9	0.0-44.0	9	0.0-43.0	8	0.0-20.0
	Non-Exposed	3	0.0-5.0	3	0.0-5.0	3	0.0-5.0
Total morbidity of adult ewes[b]							
Median:	Exposed	9	9.0	10	8.5	9	8.0
	Non-Exposed	3	29.0	3	29.0	3	13.0
			(P=.31)		(P=.45)		(P=.31)
Range:	Exposed	9	1.0-22.0	10	1.0-70.0	9	0.0-23.0
	Non-Exposed	3	2.0-53.0	3	4.0-53.0	3	4.0-29.0

[a] A morbidity rate was calculated for each disease class for every flock during each year by dividing the number of cases of disease by the total number of lambs born minus the number of lambs that were born dead and multiplying by 100.

[b] A morbidity rate was calculated for each disease class for every flock during each year by dividing the number of cases of disease by the number of ewes lambing and multiplying by 100.

[c] P values for differences between medians

Mortality Parameters

Lamb mortality rates are reported in Table 11. There were no significant differences between the two populations in any year for the median rate of lamb deaths at birth, from birth to 24 hours, from 24 hours to three weeks, or from three weeks to weaning. However, total lamb mortality was higher in the exposed population than in the non-exposed population in 1992 (12.2% vs 3.4%, P=.03). As with the calf mortality from 24 hours to three weeks of age, the difference in lamb mortality is more likely a cumulative result of climate and management effects rather than a pure exposure effect.

Mortality rates for the adult ewes are reported in Table 12. There were no significant differences in median mortality rates of ewes between populations for any year surveyed.

Veterinarian Survey

The veterinary survey collected only qualitative data and responses were made from veterinarian memory. The four veterinarians surveyed reported no increased response to animal health cases for exposed herds compared to that of non-exposed herds. There were no reports of cases they would consider unusual in the exposed group.

Table 11. Mortality rates[a] of lambs in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

AGE AT DEATH	N	1991	N	1992	N	1993
Stillbirth						
Median: Exposed	10	1.6	10	1.6	9	1.3
Non-Exposed	3	1.0	3	1.3	3	1.3
		(P=.87)[b]		(P=.35)		(P=.78)
Range: Exposed	10	0.0-10.0	10	0.4-12.0	9	0.0-4.4
Non-Exposed	3	0.6-3.4	3	0.4-1.7	3	1.0-3.7
Birth to 24 hours						
Median: Exposed	10	1.6	10	1.6	9	1.0
Non-Exposed	3	0.6	3	0.4	3	1.3
		(P=.20)		(P=.15)		(P=.93)
Range: Exposed	10	0.0-12.2	10	0.0-13.6	9	0.0-6.3
Non-Exposed	3	0.0-1.0	3	0.0-1.3	3	1.0-1.9
24 hours to 3 weeks						
Median: Exposed	9	1.5	9	2.7	8	1.8
Non-Exposed	3	1.8	3	0.6	3	2.0
		(P=.78)		(P=.40)		(P=.84)
Range: Exposed	9	0.0-5.4	9	0.0-17.7	8	0.0-6.8
Non-Exposed	3	0.9-3.5	3	0.0-4.3	3	1.0-3.9
3 weeks to weaning						
Median: Exposed	9	1.5	9	1.8	8	1.7
Non-Exposed	3	1.0	3	0.6	3	5.1
		(P=.93)		(P=.12)		(P=.61)
Range: Exposed	9	0.0-20.0	9	0.0-12.6	8	0.0-14.6
Non-Exposed	3	0.0-7.2	3	0.4-1.8	3	0.0-7.2
Total mortality						
Median: Exposed	9	8.3	9	12.2	8	6.8
Non-Exposed	3	5.1	3	3.4	3	10.0
		(P=.40)		(P=.03)		(P=.31)
Range: Exposed	9	3.6-33.3	9	3.6-28.0	8	3.2-22.2
Non-Exposed	3	3.1-12.2	3	2.1-7.1	3	7.4-11.1

[a] A mortality rate was calculated for each age at death class for every flock during each year by dividing the number of lamb deaths during that period by the number of lambs that were still alive at the beginning of the period and multiplying by 100.

[b] P values for differences between medians

Table 12. Mortality rates[a] of adult ewes in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

MORTALITY RATE[a]		N	1991	N	1992	N	1993
Median:	Exposed	10	7.0	10	7.8	9	3.7
	Non-Exposed	3	1.7	3	1.6	3	3.3
			(P=.13)[b]		(P=.15)		(P=.71)
Range:	Exposed	10	0.0-29.3	10	0.0-32.0	9	0.0-14.3
	Non-Exposed	3	0.7-2.6	3	0.9-2.5	3	0.7-5.1

[a] A mortality rate was calculated for each flock during each year by dividing the number of ewes that died by the number of ewes lambing.

[b] P values for differences between medians

CONCLUSION

In general, our study does not indicate that exposure to the water and forage in the Alamosa River watershed increased morbidity or mortality rates, or reduced animal performance in beef herds and sheep flocks. However, certain components within the data indicate a possibility of exposure effects. To more accurately document effects of exposure, management and climate, further study based on written production records rather than memory would be required. If current Alamosa River water quality is improved compared to 1991 data, the risk of exposure effects is low and the need for further study is minimal. Conversely, if Alamosa River water quality is the same as in 1991, or if quality has declined, then there is a moderate risk of exposure effects and further animal health monitoring should be enacted.

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Appendix Table 1. Morbidity rates[a] of calves in beef herds that were or were not exposed to water and forage in the Alamosa River watershed

Year	N	Diarrhea	N	Respiratory	N	Pink eye	N	Foot rot	N	Skeletal-muscular problems
1991										
Median: Exposed	11	3.0	11	1.0	13	0.0	13	1.0	13	0.0
Non-Exposed	11	3.0	11	1.0	11	1.0	11	1.0	11	0.0
		(P=.97)[b]		(P=.86)		(P=.38)		(P=.79)		(P=.12)
Range: Exposed	11	0.0-28.0	11	0.0-5.0	13	0.0-10.0	13	0.0-5.0	13	0.0-0.0
Non-Exposed	11	0.0-92.0	11	0.0-5.0	11	0.0-6.0	11	0.0-10.0	11	0.0-1.0
1992										
Median: Exposed	12	6.5	12	1.0	13	0.0	13	1.0	13	0.0
Non-Exposed	11	4.0	11	1.0	11	1.0	11	1.0	11	0.0
		(P=.58)		(P=.90)		(P=.25)		(P=.86)		(P=.86)
Range: Exposed	12	0.0-27.0	12	0.0-6.0	13	0.0-10.0	13	0.0-3.0	13	0.0-1.0
Non-Exposed	11	0.0-25.0	11	0.0-13.0	11	0.0-5.0	11	0.0-10.0	11	0.0-1.0
1993										
Median: Exposed	14	6.0	13	0.0	14	0.0	14	1.0	14	0.0
Non-Exposed	12	2.5	12	1.0	12	0.5	12	0.5	12	0.0
		(P=.31)		(P=.69)		(P=.30)		(P=.33)		(P=1.0)
Range: Exposed	14	0.0-45.0	13	0.0-5.0	14	0.0-10.0	14	0.0-6.0	14	0.0-4.0
Non-Exposed	12	0.0-18.0	12	0.0-15.0	12	0.0-5.0	12	0.0-10.0	12	0.0-1.0

[a] A morbidity rate was calculated for each disease class for every herd during each year by dividing the number of cases of disease by the total number of calves born minus the number of calves that were born dead and multiplying by 100.

[b] P values for differences between medians

Appendix Table 2. Morbidity rates[a] of adult cows in beef herds that were or were not exposed to water and forage in the Alamosa River watershed

Year	N	Respiratory	Diarrhea	Pink eye	Foot rot	Cancer eye	Mastitis	Retained Placenta/ Uterine Infection	Abortion	Skeletal-muscular problems	Birth Defects
1991											
Median:Exposed	13	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
Non-Exposed	11	1.0	0.0	2.0	1.0	0.0	0.0	1.0	0.0	0.0	0.0
		(P=.14)[b]	(P=.28)	(P=.04)	(P=.34)	(P=.77)	(P=.10)	(P=.98)	(P=.68)	(P=.76)	(P=1.0)
Range: Exposed	13	0.0-4.0	0.0-0.0	0.0-8.0	0.0-8.0	0.0-3.0	0.0-2.0	0.0-6.0	0.0-2.0	0.0-1.0	0.0-0.0
Non-Exposed	11	0.0-50.0	0.0-1.0	0.0-5.0	0.0-5.0	0.0-2.0	0.0-4.0	0.0-5.0	0.0-2.0	0.0-2.0	0.0-0.0
1992											
Median:Exposed	13	0.0	0.0	0.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0
Non-Exposed	11	1.0	0.0	1.0	1.0	0.0	0.0	1.0	1.0	0.0	0.0
		P=.13)	(P=.28)	(P=.12)	(P=.91)	(P=.33)	(P=.23)	(P=.78)	(P=.06)	(P=.84)	(P=1.0)
Range: Exposed	13	0.0-4.0	0.0-0.0	0.0-8.0	0.0-8.0	0.0-8.0	0.0-2.0	0.0-6.0	0.0-1.0	0.0-3.0	0.0-0.0
Non-Exposed	11	0.0-50.0	0.0-1.0	0.0-3.0	0.0-6.0	0.0-2.0	0.0-4.0	0.0-7.0	0.0-2.0	0.0-5.0	0.0-0.0
1993											
Median:Exposed	14	0.0	0.0	0.0	2.5	0.5	0.0	0.5	0.0	0.0	0.0
Non-Exposed	12	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
		(P=.66)	(P=.28)	(P=.43)	(P=.15)	(P=.28)	(P=.57)	(P=.76)	(P=.76)	(P=1.0)	(P=1.0)
Range: Exposed	14	0.0-6.0	0.0-0.0	0.0-8.0	0.0-8.0	0.0-7.0	0.0-2.0	0.0-6.0	0.0-1.0	0.0-0.0	0.0-0.0
Non-Exposed	12	0.0-20.0	0.0-1.0	0.0-3.0	0.0-4.0	0.0-2.0	0.0-5.0	0.0-5.0	0.0-2.0	0.0-0.0	0.0-0.0

[a] A morbidity rate was calculated for each disease class for every herd during each year by dividing the number of cases of disease by the total number of adult cows calving and multiplying 100.

[b] P values for differences between medians

Appendix Table 3. Morbidity rates[a] of lambs in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

Year	N	Diarrhea		Respiratory		Foot rot		Skeletal-muscular problems
1991								
Median: Exposed	10	1.0	10	0.0	10	0.0	9	1.0
Non-Exposed	3	0.0	3	0.0	3	2.0	3	2.0
		(P=.06)[b]		(P=.70)		(P=.63)		(P=.50)
Range: Exposed	10	0.0-33.0	10	0.0-8.0	10	0.0-15.0	9	0.0-3.0
Non-Exposed	3	0.0-0.0	3	0.0-1.0	3	0.0-2.0	3	0.0-2.0
1992								
Median: Exposed	10	1.0	10	0.0	10	0.0	9	1.0
Non-Exposed	3	0.0	3	0.0	3	2.0	3	2.0
		(P=.10)		(P=.70)		(P=.71)		(P=.50)
Range: Exposed	10	0.0-33.0	10	0.0-8.0	10	0.0-40.0	9	0.0-3.0
Non-Exposed	3	0.0-0.0	3	0.0-1.0	3	0.0-2.0	3	0.0-2.0
1993								
Median: Exposed	9	0.0	9	0.0	9	1.0	8	1.0
Non-Exposed	3	0.0	3	0.0	3	2.0	3	2.0
		(P=.19)		(P=.60)		(P=.77)		(P=.59)
Range: Exposed	9	0.0-10.0	9	0.0-8.0	9	0.0-4.0	8	0.0-3.0
Non-Exposed	3	0.0-0.0	3	0.0-1.0	3	0.0-2.0	3	0.0-2.0

[a] A morbidity rate was calculated for each disease class for every flock during each year by dividing the number of cases of disease by the total number of lambs born minus the number of lambs that were born dead and multiplying by 100.

[b] P values for differences for medians

Appendix Table 4. Morbidity rates[a] of adult ewes in sheep flocks that were or were not exposed to water and forage in the Alamosa River watershed

Year	N	Respiratory	Diarrhea	Foot rot	Mastitis	Retained Placenta/ Uterine Infection	Abortion	Skeletal-muscular problems	Birth Defects
1991									
Median: Exposed	10	0.0	0.0	0.0	2.0	0.0	1.0 (N=9)	0.0	0.0
Non-Exposed	3	1.0	0.0	25.0	1.0	0.0	1.0	0.0	0.0
		(P=.36)[b]	(P=.58)	(P=.14)	(P=.44)	(P=.77)	(P=.85)	(P=.42)	(P=1.0)
Range: Exposed	10	0.0-3.0	0.0-10.0	0.0-15.0	0.0-8.0	0.0-3.0	0.0-10.0	0.0-3.0	0.0-0.0
Non-Exposed	3	0.0-2.0	0.0-0.0	0.0-50.0	0.0-2.0	0.0-1.0	0.0-1.0	0.0-0.0	0.0-0.0
1992									
Median: Exposed	10	0.0	0.0	1.0	1.5	0.0	1.5	0.0	0.0
Non-Exposed	3	1.0	0.0	25.0	1.0	0.0	1.0	0.0	0.0
		(P=.36)	(P=.58)	(P=.49)	(P=.55)	(P=.77)	(P=.80)	(P=.30)	(P=1.0)
Range: Exposed	10	0.0-3.0	0.0-10.0	0.0-67.0	0.0-8.0	0.0-3.0	0.0-4.0	0.0-3.0	0.0-0.0
Non-Exposed	3	0.0-2.0	0.0-0.0	0.0-50.0	0.0-2.0	0.0-1.0	1.0-2.0	0.0-0.0	0.0-0.0
1993									
Median: Exposed	9	0.0	0.0	1.0	2.0	0.0	1.0	0.0	0.0
Non-Exposed	3	0.0	0.0	10.0	1.0	0.0	1.0	0.0	0.0
		(P=.76)	(P=.56)	(P=.40)	(P=.51)	(P=1.0)	(P=.39)	(P=.72)	(P=1.0)
Range: Exposed	9	0.0-3.0	0.0-10.0	0.0-12.0	0.0-8.0	0.0-1.0	0.0-3.0	0.0-3.0	0.0-0.0
Non-Exposed	3	0.0-1.0	0.0-0.0	0.0-25.0	0.0-2.0	0.0-1.0	1.0-2.0	0.0-2.0	0.0-0.0

[a] A morbidity rate was calculated for each disease class for every flock during each year by dividing the number of cases of disease by the number of ewes lambing and multiplying by 100.

[b] P values for differences between medians.

THE PROCESS AT SUMMITVILLE - IS CERCLA WORKING?

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ABSTRACT

The Comprehensive Environmental Response, Compensation and Liability Act, (CERCLA or Superfund), was originally crafted to deal with industrial dump sites, things such as Love Canal or Valley of the Drums in Kentucky. Such sites are typically addressed through comprehensive studies which lead to the selection of a series of fairly typical treatment and cleanup techniques. These techniques are selected because they will achieve a reduction in contaminant levels consistent with existing environmental standards.

Summitville is not such a site. First, the magnitude of the problems is much greater than the typical dump site. Second, use of emergency response actions has avoided the bulk of the studies that normally would have been completed prior to implementation of cleanup options. Third, cleanup activities such as waste rock movement and adit plugging, have been implemented without adequate consideration of results and objectives.

CERCLA

The scheme under CERCLA is designed around a fairly well defined process of study, evaluation, selection of remedial options and execution of these options. This process is outlined in a body of regulations adopted by the U.S. Environmental Protection Agency (EPA) known as the National Contingency Plan (NCP). This process is designed to first fully understand the nature of the problems at a site. Once these problems are known and, especially, once the mechanisms by which these problems might harm human health or the environment are known, the NCP process is designed to select appropriate remedies.

Under CERCLA a remedy involving no action must be considered. The point of considering no action is simply to make certain that remedies are rational. CERCLA contains the concept that remedies selected under CERCLA must be economically reasonable. In other words, not only must the remedy be designed to achieve environmental standards - a process discussed later - but the remedy must also be economically reasonable in light of other available remedies.

Liability for the costs associated with the process is placed with the owner of the site, the operator of the site and those that arranged for hazardous substances to be placed at the site. Allocation of responsibility among these parties is not a process defined by CERCLA. Instead, liability is typically strict, joint and several. Simply put, any person having any liability is potentially liable for the entire cost without regard of fault or other factors typically considered in allocating responsibility.

This liability concept obviously creates the potential for fundamental unfairness. It runs contrary to our general system of liability based upon some concept of fault or responsibility. Should the party that sent one drum to a dump site be responsible for the entire cleanup? Should the owner of the property be held liable for the actions of a tenant operator? Should one operator have liability for the actions of a prior or successor operator?

Under CERCLA such parties most certainly can be held responsible for the entire cleanup. The only defenses available are arguments that the contamination occurred because 1) it resulted from an act of God, 2) it resulted from acts of a third person to whom you have no relationship, or 3) it resulted from an act of war.

On first blush these defenses seem to present the potential for an argument that the problems at the site where caused by someone else. Unfortunately, CERCLA does not work in this fashion. All the government need prove is that the defendant was the owner, operator, or arranged for the placement of hazardous substances at the site. (Hazardous substances include anything having the potential for harming human health or the environment.) Once this proof is made, liability is established. The only remaining question is how much money will be paid.

The liability scheme under CERCLA obviously creates tremendous leverage for the government. Not surprisingly defendants are frequently put in the situation of accepting unfair settlement because there is no reasonable way to defend against liability.

At mining sites, there are CERCLA issues that complicate the process. Obviously, there has typically been a succession of owners and operators. Many of these entities may not be viable. Given the succession of mining activities, it is typically unclear what sort of work occurred at different times.

One of the more confusing issues is the question of whether mining waste rock is a hazardous substance. Some courts have decided that the waste rock is not a hazardous substance, but that acid mine drainage that may come from tailings or other depositories of waste rock, is a hazardous substance. This puts agencies and responsible parties in the position of trying to evaluate environmental damage in a fashion that considers management of acid mine drainage but not overtly considering the management of waste rock.

SUMMITVILLE

Summitville has been a mining district since the 1870s. Extensive underground workings were established by a variety of entities. Substantial ore was removed and tailings were produced. Adits were driven in remove ore and to drain the mountain, which has resulted in highly acidic drainage.

There is no evidence that the area streams have ever supported fish. Undisturbed drainages nearby have very low pHs and are known to be impacted by mineral seeps and exposed sulfur bearing rocks.

Even though it is likely that mining activities have had an impact by increasing the discharge of acidic materials, the magnitude of this impact is unknown and may not be very significant in comparison to native conditions.

In this century, several mining companies operated on the site. Some held leases to evaluate and expand the existing underground workings. Others contemplated more extensive operations.

Ultimately, Galactic resources obtained the assignment of a lease for the property. They bought designs for a heap leach operation from a prior operator and set about to obtain the necessary permits and approvals for operations.

The process of obtaining these permits and the technical quality of these permits is discussed in a paper entitled *The Summitville Mine: What Went Wrong* written as an official document by a member of the Mined Land Reclamation Board at the time of the permitting. It is not my purpose to re-discuss this report, other than to note that there were many reasons the operator went bankrupt. Among these reasons was the inability of the operator to obtain permits necessary for continued operation.

At the time of the bankruptcy, the agencies believed that imminent hazards existed at the site. They believed that water treatment systems would fail causing acidic waters to be discharged at increasing rates. They also believed that water would overflow the heap leach retention dam causing a catastrophic failure and the discharge of cyanide and tailings materials into the local drainage.

EPA came onto the site to run an emergency response action under CERCLA. The identified emergencies included not only conditions caused by Galactic but also discharges from the adits and certain tailings piles that had been present for decades.

Both EPA and the State of Colorado were aware of conditions at Summitville well in advance of the bankruptcy. At least one year prior to the bankruptcy, both the State and EPA were on-site conducting studies.

In fact, EPA had spent a substantial amount of money in evaluating the area for listing as a National Priorities List site under CERCLA. The site was "scored" to determine whether it presented levels of potential environmental risk high enough for listing as early as May 1993. The site "scored" well in excess of the necessary levels.

EMERGENCY RESPONSE

Emergency response actions do not follow the typical CERCLA process. Instead, the agency decides what it wants to do and does it. There is no public oversight. There is no opportunity for public comment. There is no potential for the review of their activities until the much later point where they attempt to collect the costs from the responsible parties.

EPA simply sweeps onto the site and excludes past operators and the owner. It does what it feels is necessary, without consideration of the impacts of these actions save that they address the emergency conditions.

In the typical case, emergency response deals with train wrecks, abandoned drums and other situations in which there is an immediate risk to human life. Other emergency response actions in Colorado have both been limited in time and scope to the bare minimum necessary to eliminate the risk. Emergency response is not intended to complete or even dictate the ultimate solution for a site. In fact, in most cases the location of an emergency response does not end up being listed as a NPL site.

In the case of Summitville, EPA has issued an access order against the land owners that denies them access to their property absent prior permission. The land owners may not sell this property absent prior notice to EPA and then only with conditions that would require the new owner to accept EPA.

EPA is treating water from the adits and from the heap leach. They are recovering gold and other metals from the waste water treatment sludges without even an accounting to the property owners. They are moving large quantities of waste rock back into the mining pit and plan on re-filling the mining pits. They are plugging adits. Ultimately they plan on either moving the entire heap leach or hydrologically isolating it from the surrounding area.

None of these remedies has been subjected to a public analysis. It is not at all clear that all these steps are truly necessary to address emergencies at the site. The ultimately environmental goal of these actions have not been determined. Instead, these activities have been selected because the seem to be the correct actions given the EPA's view of proper efforts.

As of October 1994, EPA has finally proposed certain remedial actions for public comment. Typically these actions are justified on the basis that they are continuations of the prior emergency response actions. These remedies are also justified of the basis of restoring in-stream water quality to a level not historically or biologically justified.

The tax payers are currently paying for these efforts. As of October 1994 some $50 million has been spent. Completion of the remedies proposed is estimated to reach over $90 million.

Given the nature of an emergency response action and its high cost, one would hope that EPA's efforts were the bare minimum necessary to stabilize the site. Instead the EPA seems focused on completing a cleanup of this site within their view of appropriate ultimate solutions. These solutions are not consistent with additional mining of the site, but instead seem designed to achieve EPA's views on the future use of this property. CERCLA does not give EPA the right to decide future land use. In the case of Summitville, EPA is acting as though it is a land use regulatory agency. Rather than anticipate that future mining might be reasonable, EPA is acting to foreclose such a use.

The CERCLA process in routine situations is designed to consider future use of the property and these other factors. Not only would EPA normally consider these factors, but they would do so with an opportunity for fully public comment and review.

CONCLUSION

CERCLA was never designed for mining sites. Much less, the emergency response process was intended for quick operations designed to achieve an immediate reduction in risk from leaking drums or other uncontrolled conditions. At Summitville, the emergency response process is being used to accomplish cleanup of a site for reasons and to standards that may make no sense in the context of this site. The emergency response process is being subverted at Summitville to avoid public comment and input on the appropriate remedies and goals.

THE SUMMITVILLE LEGACY: WHERE DO WE GO FROM HERE?

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INTRODUCTION

In just eight years, the Summitville mine progressed from initial permitting to the U.S. Environmental Protection Agency's (EPA) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)[1] national priorities list.

Since the former site operator, the now-bankrupt Summitville Consolidated Mining Company, Inc. (SCMCI), and its parent corporation, the Canadian-based Galactic Resources, Ltd., abandoned operations in December 1992, there has been enormous national and international interest in ongoing developments at the mine. The magnitude of the cost and extent of environmental damage have spurred a state investigation,[2] and the Federal Bureau of Investigation and U.S. Department of Justice have launched a criminal investigation.[3] The events at Summitville have been portrayed repeatedly in the national and world media, with varying degrees of accuracy. They have played a major role in debate over the future of the 1872 General Mining Law.

Summitville suggests that environmental damage from mining is not a relic of the distant past, as some in the mining industry have suggested, but a very modern concern. If a mine can become a Superfund site in less than 10 years, environmental regulation of domestic mining remains a significant problem.

Summitville provides evidence that involvement of reputable technical firms does not alone guarantee success. Engineers, scientists, and other technical professionals need to ask themselves some challenging questions based on the Summitville example. The technical professional must be sensitive to the possibility that his or her well-earned reputation for competence and integrity may be presented to regulators as a basis for allowing a permit to issue or construction to begin. There is no guarantee, of course, that once the credibility of the technical professional has been used as assurance of a rigorous approach to technical issues to obtain regulatory approval, that the company will continue to follow the engineering recommendations. Summitville is a reminder that permit conditions cannot be relaxed, or important technical questions allowed to go unanswered. Personnel can be changed, and permits can be transferred. Although the regulation of mine operations has been strengthened, there is still no rule or policy requiring or encouraging third parties, such as technical engineers, to inform the regulatory body if new information comes to light or the third party becomes aware that the operator is not adhering to the assumptions underlying technical judgment of the permit requirements or such assumptions turn out to be invalid.

BACKGROUND

The Site

The Summitville site covers 1,400 acres on the northeast flank of South Mountain in the San Juan range,

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42 U.S.C. §§9601-9675, ELR Stat. CERCLA §§101-405. For a discussion of CERCLA liability for abandoned mines, see Jan G. Laitos, *Federal CERCLA Liability for Abandoned Mines*, 23 Colo. Law 371 (1994). *See also* National Priorities List for Uncontrolled Hazardous Waste Sites, Proposed Rule No. 14, 58 Fed. Reg. 27507 (May 10, 1993) (proposal to list the Summitville site on the CERCLA national priorities list).

[2] Katie Kerwin, *Romer Orders Inquiry Into Mining Company*, Rocky Mtn. News, Apr. 7, 1993, at 3A.

[3] Mark Obmascik, *Summitville Mess Probed*, Denver Post, Jan. 25, 1994, at 1A.

within two miles of the Continental Divide. Twenty-one acres of the site was public land administered by the U.S. Forest Service, available for mining under the General Mining Law of 1872.[4] The remainder was private land, leased from private individuals. Mine site altitude varies from 11,400 to 12,500 feet, with long winters and short, cool summers. Winter snowfall is heavy.

Summitville, like many other mining districts, has experienced a boom-bust cycle. Following lode discoveries from 1872-73, Summitville saw significant activity from 1875 to 1887.[5] At that time, the amount of high-grade ore declined. It had become less profitable to mine the remaining low-grade sulfide ores. The district became relatively idle by 1890; Mining resumed in 1926 when lessees discovered the "Pickens Cut," a lode yielding $500,000 in gold.[6]

The 1930's saw the formation of Consolidated Mining Companies.[7] Several companies acquired groups of claims and mined them in larger units with more capital. The years 1940 to 1950 saw declining activity at Summitville. In 1950, the district experienced several exploration programs and some rehabilitation, and in 1962, some copper, gold and silver were produced from the Reynolds Tunnel. For the most part, activity was limited to exploration and improvement work until Galactic Resources began the Summitville project in 1984.[8]

Historic Water Degradation

The Summitville region is highly mineralized. Studies indicate considerable heavy metal loading and high acidity, even in small tributary streams where no mining has occurred.[9] Naturally occurring exposed reactive geologic formations have contributed to water degradation in the Alamosa River,[10] and several tributaries have been contaminated by historic mining activity. The Wightman Fork, a tributary that flows by the Summitville site and ultimately joins the Alamosa River, was contaminated prior to Galactic's Summitville project by acid drainage from historic tunnels such as the Reynolds Adit. A recent report cites studies that identified water degradation in the Alamosa River and several of its tributaries as far back as the early 1900s.[11]

Table I below shows the extent to which naturally exposed geologic formations have caused high metal concentrations in some area streams. Two of the streams--Alum Creek and Bitter Creek--have little known history of mining activity.[12]

Table 1. Metal loads from discharging adits and streams draining altered mineralized areas in the Alamosa River Basin during September 1986.[13]

LOAD IN POUNDS PER DAY

Streams	Al	Fe	Mn	Cu	Zn	Ni	Mo	Cd	Cr	Pb
Iron*	179.	285.	14.85	1.02	1.54	0.51	<0.51	<0.51	<0.51	<2.56
Alum	1154.	3686.	93.1	11.25	17.85	2.91	1.36	0.58	0.58	4.08
Bitter	159.	331.	26.4	0.81	2.43	0.27	0.27	<0.27	0.27	0.27
Wightman Fork*	77.6	52.1	32.8	33.0	15.36	0.65	<0.16	0.16	0.16	<0.81

*Includes some mine drainage

It is impossible now to obtain detailed information on water quality prior to the commencement of mining in the 1800s, or even on the water quality prior to the opening of the Summitville mine in 1984. Regulators, SCMCI, and various companies that may be designated as potentially responsible parties (PRPs)[14] are engaged in a running debate on this subject, which may be fairly abstract, given the lack of substantive scientific data on baseline water quality in the Alamosa and its tributaries.

Despite evidence of natural stream acidity and heavy-metal content, it is indisputable that recent operations at Summitville have contributed directly and substantially to water quality problems downstream from the mine. Drainage from waste piles, repeated unpermitted discharges of contaminated water from the land application system, and increased contaminated loading from the Reynolds Adit and other mine-related sources have resulted in a measurable increase in metal concentrations and a decrease in pH in Wightman Fork and possibly in the Alamosa River.[15] There have been allegations that these discharges led to fish kills in the

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[4] 30 U.S.C. §§22-54 (1988).

[5] Knight Piesold & Co., Chronological Site History, Summitville Mine 16 (May 25, 1993).

[6] *Id.* at 17.

[7] *Id.*

[8] Knight Piesold & Co., *supra* note 9, at 21.

[9] J. David Holm & Robert M. Kirkham, *Environmental Problems and Reclamation Activities At Inactive Metal Mine and Milling Sites in San Luis Valley*, Water in the Valley (Colorado Groundwater Ass'n ed. 1989).

[10] *Id.* at 1.

[11] Knight Piesold & Co., *supra* note 9, at 43.

[12] The very fact that local creeks bear names such as Iron Creek, Bitter Creek, and Alum Creek is some indication of the natural level of mineralization. Almost two tons of iron per day flows down Alum Creek alone. Holm & Kirkham, *supra* note 14.

[13] Holm & Kirkham, *supra* note 14. September is a relatively low flow month and it would not be surprising if spring and summer loading was a good deal higher.

[14] 42 U.S.C. §9607, ELR Stat. CERCLA §107.

[15] Knight Piesold & Co., *supra* note 9, at 43-51.

Alamosa.[16] Limited baseline data on fish populations exist to substantiate or refute these reports. Certainly, at this point, there are few, if any, fish to be found below Iron Creek through the Terrace Reservoir. The exposed acid generating surface area in the waste piles, the open pit, and the leach pad will continue to react chemically and produce pollution for hundreds or thousands of years if not remediated.

Government agencies are now spending a great deal of money in an attempt to determine, post facto, the extent of Galactic's responsibility and the extent of the responsibility attributable to prior operations or natural conditions. Not only has the lack of definitive baseline data heightened an already futile debate, but as will be seen below, it has contributed directly to on-site problems and hurt the position of the company and others who will become PRPs now that Summitville has become a Superfund site.

THE COLORADO PERMITTING PROCESS AS IT RELATED TO SUMMITVILLE

The Colorado Mined Land Reclamation Act in 1984[17]

Most regulatory responsibility for environmental aspects of mining operations, other than coal mines, falls on the states. In Colorado, mining operations are regulated under the Colorado Mined Land Reclamation Act of 1976,[18] which is administered through the Colorado Division of Minerals and Geology (DMG)[19] of the Colorado Department of Natural Resources. The Colorado Mined Land Reclamation Board (MLRB) oversees the DMG's activities. The MLRB is a seven-member citizen board appointed by the governor and confirmed by the Colorado Senate.[20] It has the authority to grant permits and hear allegations of violations.[21]

The Act makes it unlawful to mine without a permit,[22] and requires that all land disturbed after 1976, the effective date of the Act, be reclaimed to a beneficial use.[23] Permit applicants must submit a mining plan[24] and a reclamation plan[25] and post a bond adequate to fulfill the reclamation plan should the operator default or the permit be revoked.[26]

Operators must provide public notice of their intention to mine a site. They must notify the commissioners of the county in which the project is located,[27] publish a legal notice in a local newspaper,[28] and notify by mail any owners of property within 200 feet of the land affected by the mining operation.[29]

The standards for denying a Regular permit are strict.[30] In addition, DMG must inspect the site and render a decision within 120 days after receiving a complete application, or the permit issues automatically.[31] The MLRB or DMG bears the burden of demonstrating the noncompliance required to deny the permit.[32]

The Summitville Permit: Contents of Application

In 1984, SCMCI began a series of pilot-scale heap leach tests at the Summitville site to determine the viability of a large-scale, open-pit cyanide heap leach.

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[16] Kit Miniclier, *Mine's Toxic Leaks Render River Lifeless*, Denv. Post, Nov. 11, 1991, at 1A; *see also* Memorandum from Donald P. Holmer, Professional Engineer, Colorado Water Quality Control Division, to J. David Holm, Director of Water Quality Control, Colorado Water Quality Control Division (Aug. 2, 1990) (on file with the Colorado Division of Minerals and Geology); Memorandum from J. David Holm, Director of Water Quality Control, Colorado Water Quality Control Division, to Pat Nelson and Robert Shukle, Professional Engineers, Colorado Water Quality Control Division (Aug. 2, 1990) (on file with the Colorado Division of Minerals and Geology).

[17] In this section, references to the Colorado Mined Land Reclamation Act are to the Act as it existed in 1984 unless otherwise noted. While the Act, partly as a result of the events at Summitville, has been substanitally amended, this basic framework has continued.

[18] Colo. Rev. Stat. §§34-32-101 to -127 (1991). An excellent analysis of the Act is contained in a study by the Environmental Law Institute. *See* Envtl. Law Inst., *Regulation of Mining Waste in Colorado, in* State Regulation of Mining Waste: Current State of the Art (1992).

[19] At the time of the permit issuance, the DMG was known as the Mined Land Reclamation Division.

[20] Colo. Rev. Stat. §34-32-105 (1991). The seven members are appointed to represent various constituencies. *Id.* §34-32-105(2). One of the authors is a member of the MLRB, appointed to represent the conservation community.

[21] *Id.* §34-32-107; *see also id.* §34-32-105.

[22] *Id.* §34-32-109(1).

[23] *Id.* §34-32-102(3)(b).

[24] *Id.* §34-32-112(2).

[25] *Id.* §34-32-112(1).

[26] *Id.* §34-32-117.

[27] 2 Colo. Code Regs. §407-1 (Rule 2.2.1(1)) (1988).

[28] *Id.*

[29] *Id.*

[30] Colo. Rev. Stat. §34-32-115(3) (1991); *see also* Envtl. Law Inst., *supra* note 22, at 8.

[31] Colo. Rev. Stat. §34-32-115(1) (1991).

[32] *Id.* §34-32-115(4).

The company planned to mine the same ore zone that had previously been mined by underground methods through surface methods, using a cyanide leaching process to extract the gold from the ore.

Initially, the company sought a permit under §110 of the Act, which applies to mines affecting less than two acres and extracting less than 70,000 tons per year of mineral or overburden.[33] The company designed the pilot-scale heap leaching to test the feasibility of a larger mine. As the §110 pilot operation proceeded, the company applied for a §112 permit for a full-scale mine operation on August 31, 1984.[34]

A review of Summitville's §112 permit application and of subsequent developments at the mine reveals the inadequacy of the statutes governing permitting,[35] the failure of the DMG and MLRB to consider fully all aspects of the application before approval, and the failure of the company to comply with the mining and reclamation plan set forth in the permit application. In retrospect, while it can be argued that Summitville's permit application, at least in most respects, complied with the minimal requirements of the Act, the documents and information submitted by the company were, as allowed by existing rules and practice,[36] scant relative to the proposed size of operations. One of the most noticeable features of the application was the paucity of baseline data.

Other regulations left the submission of any substantive baseline data to the discretion of the operator, and required little more than general descriptions of existing environmental conditions.[37] Baseline data on water quality for tributaries below the mine site, consisted mainly of studies done by a previous company.[38] The climatological data, essential to determining the water balance in the heap leach pad, were drawn from precipitation and evaporation rates at other locations, and were not site specific.[39]

The absence of any comprehensive baseline data requirement and the confusion that later arose from this absence, demonstrate the inadequacy of the regulations which were in effect at that time. Although SCMCI's §112 permit application may appear incomplete or hastily assembled, it nevertheless complied in most respects with 1984 baseline data requirements, which required only general descriptions of water, wildlife, soil, vegetation and climatology.[40] This led to several problems during the mine's operations. A faulty water balance calculation, based on non-site-specific climatological data, led to significant problems with the water balance in the heap leach pad. A lack of water quality baseline data led to last-minute, time-consuming negotiations with the Water Quality Control Division. The lack of data led to delay at other critical points, as experts argued over the reasons for the occurence on the site. The lack of baseline data ultimately caused disputes over allocating liability for the site's various environmental problems. Had the Act or rules and regulations contained more stringent requirements for baseline data these problems could have been prevented.[41]

The relative leniency of the original Act and the MLRB's permit requirements reveal the extent to which legislators had originally conceived the Act as a post-mining reclamation statute. This emphasis is evident from the terms of the Act itself.[42] Regulations under the Act required the applicant to submit both a mining plan[43] and a reclamation plan; however, the reclamation plan[44] requirements were far more specific than those for the

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[33] *Id.* §34-32-110(1)(a).

[34] Galactic Resources, Inc. Regular (112) Permit Application M-84-157 (Aug. 31, 1984) [hereinafter August 1984 Permit Application] (on file with the DMG); *see also* Danielson & McNamara, The Summitville Report: What Went Wrong 6 (Mar. 25, 1993) (on file with Colo. Dep.t of Natural Resources).

[35] For a discussion of these inadequacies, see Envtl. Law Inst., *supra* note 22, at 53-55.

[36] Colo. Rev. Stat. §34-32-202-127 (1991); 2 Colo. Code Regs. §407-1 (Rules 1-8) (1988).

[37] 2 Colo. Code Regs. §407-1 (Rule 2.1.2(8)-(12)) (1988).

[38] While SCMCI did supply some baseline data, most of this was based on studies done by consultants to prior operations, and was inadequate for determining average flow and loading rates. When SCMCI ultimately was forced to apply for a discharge permit, the Colorado Water Quality Control Division officials found the data inadequate. *See* Danielson & McNamara, *supra* note 40, at 34.

[39] Knight Piesold & Co., *supra* note 9, at 34-35.

[40] 2 Colo. Code Regs. §407-1 (Rule 2.1.2(8)-(11), (K)) (1988) ("(K)," which appears in the *Code of Colorado Regulations*, should probably read "(12)").

[41] The Colorado Revised Statutes, as amended by Act of June 3, 1993, require an "environmental protection plan" for all operations classified as "designated mining operations." Colo. Rev. Stat. §34-32-116-5 (1993) (Colorado Revised Statutes §34-32-103(3.5) defines "designated mining operations"). Proposed amendments to the Mineral Rules and Regulations of the MLRB require extensive baseline for designated mining operations as a provision of the environmental protection plan. Proposed Amendment to the Mineral Rules and Regulations of the Colorado Mined Land Reclamation Board, Rule 6.4.20 (to be codified at 2 Colo. Code Regs. §407-1). Under the amended statute, Summitville would have been classified as a "designated mining operation." Colo. Rev. Stat. §34-32-112.5 (1993).

[42] For a comprehensive analysis of the regulation of Colorado's mining waste, see Envtl. Law Inst., *supra* note 22.

[43] 2 Colo. Code Regs. §407-1 (Rule 2.1.2(4), (5)) (1988).

[44] Colo. Rev. Stat. §34-32-116 (1991).

mine plan. Regulations effective at the time of permitting required that the mine plan only identify affected land,[45] give a general timetable for operations,[46] and describe the ore body to be mined and adjacent land.[47] The reclamation plan included more specific description for water, wildlife, soil, and vegetation. The 1984 regulations required this information solely for reclaiming the mined land at the end of the mining operation.[48]

Experience has taught that reclamation is not solely a "post-mining" activity and that concerns for environmental protection and successful reclamation must be integrated into mining operations throughout the life of the mine. These concepts were not widely recognized when Summitville was permitted, as reflected in the limited material required, submitted, and approved for the mine plan.

The mine operator was also clearly to blame. SCMCI often changed, omitted, or completely altered key design features outlined in its permit application without consulting the DMG or the MLRB. Key features, such as the winter geomembrane cover over the heap, were just simply omitted. This clearly violated the Act, which requires a formal amendment process.[49] Many of these changes occurred early in the construction phase, but were not reported by the company or discovered by the DMG until after completion.

Agency Review of Permit Application

The regulatory agency's review of SCMCI's permit application was inadequate. It took place in an atmosphere of political boosterism. County officials, legislators, and others communicated repeatedly to the Board both the need for haste in approving the permit and their boundless faith in the project. Perhaps it might have been wise to ask what the Town of Del Norte, which asserted tht al environmental concerns had been satisfied, actually knew about the technical issues it was so sure had been fully dealt with, or why a soundly conceived project could not go through the permit process without shortcuts. These questions were not asked. SCMCI submitted its permit application on August 31, 1984, and the MLRB approved it on October 25, 1984. MLRB approval was conditional on the company's promptly reporting any cyanide spills, submitting construction reports or as-built modifications of the leach pad, and submitting a detoxification leachate model study.[50]

This conditional approach was a critical mistake. The company provided documents piecemeal, repeatedly changed consultants and contractors, and altered key design features of the mine plan without informing the DMG. Certainly, the documents on file when the permit was approved did not describe or contemplate the operation's actual physical structure.[51]

In addition, the MLRB approved the permit before the public comment period had expired.[52] The Mined Land Reclamation Act requires that, after publication of the last legal notice, the public be given 20 days to comment on the proposal and the opportunity to appear at a hearing to contest the application.[53] Although the MLRB made early permit approval conditional on not receiving opposing comments within the statutory time, early approval may be an indication of both unseemly haste and the low importance that the MLRB placed on public participation. Also, the MLRB was no doubt responding to substantial pressure from local and county officials, local organizations, and businesses to process the permit quickly. Furthermore, no one expressed any objection, before or after the approval.[54]

Citizen environmental organizations could have played a key role in preventing the MLRB's premature decision. However, no one objected to the result. While it may be easier to rally supporters in the wake of an environmental disaster than to participate in the tedious process of preventing one, the rules and regulations allow for public comment because this activity is critical to the mine permitting process functioning effectively.

In this respect, however, things may not have changed in the 10 years since Summitville was approved. In September 1993, after Summitville's problems were clearly known, the MLRB was again asked to approve a permit for a high-altitude cyanide heap leach. The Agency anticipated hard questioning and much public comment. But there was very little.[55] The Cresson Project,

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[45] *Id.* §34-32-103(1.5); 2 Colo. Code Regs. §407-1 (Rule 2.1.3(4)(d)) (1988)

[46] 2 Colo. Code Regs. §407-1 (Rule 2.1.2(5)(e)) (1988).

[47] *Id.* §407-1 (Rule 2.1.2(5)(f)).

[48] *Id.* §407-1 (Rule 2.1.2(8)-(11)) (1988).

[49] Colo. Rev. Stat. §34-32-112(8) (1991); *see also* Envtl. Law Inst., *supra* note 22, at 8.

[50] Galactic Resources Inc. Mining and Reclamation 112 Permit No. M84-157 (Oct. 25, 1984) (on file with the DMG).

[51] August 1984 Permit Application, *supra* note 40.

[52] Colorado Mined Land Reclamation Division, Minutes, Oct. 14, 1984; *see also* Danielson & McNamara, *supra* note 40, at 9.

[53] Colo. Rev. Stat. §34-32-114 (1993).

[54] Danielson & McNamara, *supra* note 40, at 8.

[55] It should be noted that the mine did attract some initial opposition, prompting the formation of a group, Citizens for Victor! (Victor is a small Colorado town located approximately one mile east of the Cresson Project.) However, the group's concerns were negotiated with the company before the permit came to the attention of the MLRB. Citizens for Victor! agreed to withdraw formal

approximately five times the size of Summitville, was approved without comment from any of the state's environmental organizations. At the same time, over 1500 individuals and groups, including many of those same environmental organizations, sought formal party status in a single suburban gravel pit quarry application.[56]

MINE OPERATION AND AGENCY ENFORCEMENT

Construction Phase

Summitville began construction of the heap leach pad and liner in the fall of 1985 and continued construction throughout the winter of 1985-86. Many of the problems that would later plague the mine during its operating life may have resulted directly from the company's decision to complete construction of the liner during the winter.

Critical to the success of a heap leaching operation is an impermeable liner under the crushed ore material. This liner has two functions. First, it collects the "pregnant" cyanide solution that has percolated through the heap in order to convey it to the processing plant where the gold is ultimately removed from the solution. Second, it prevents the solution from entering the environment.

While liners do exist which will bond at low temperatures in laboratory conditions, this fails to account for fatigue of workers spending hours in near-zero conditions, or the fact that there have to be very clear understandings of the conditions of moisture, wind, and weather which will lead to shutdown of installation, how installed materials will be protected during shutdown, and what inspection procedures will be used. An independent QA/QC organization, operating under clear guidelines, is also very important in any liner installation.

Despite the importance of the liner for environmental control, the permit did not restrict winter installation,[57] nor did it adequately address conditions of installation or other QA/AC issues. Liner construction occurred through the depth of the 1985 winter.

This ill-advised winter construction, compounded by frequent snowslides, led to liner rips and tears and inadequately sealed seams that probably culminated in cyanide leaks soon after the company began initial operations in June 1986.[58] A Canadian Broadcasting Corporation report described the severe problems experienced during winter construction:

"The pad was built under nightmarish conditions--subzero temperatures, 35 feet of snow, and avalanches that crashed into the construction site. In the words of one report, the pad liner froze, buckled, cracked and eventually leaked."[59]

In proceeding with winter construction of the liner, the company acted contrary to common sense and its own consultant's advice. It was later alleged that the company was under pressure to meet gold production deadlines to fulfill the terms of a bank loan commitment.[60] Such haste during the critical phase of construction led to friction between the company and its consultants and contractors. On December 17, 1985, SCMCI fired the initial liner construction company, which then sued SCMCI.[61] Ultimately, the company became involved in litigation with the successor installation contractor, as well.[62]

The company and the consultants blamed each other with zeal, something which continues. It is unfortunate that the company and its consultants could not have directed some of this zeal toward dealing with the growing environmental problems on site.

This haste also led to significant design changes that were neither submitted to the state regulators for approval as permit amendments nor thoroughly thought out.[63] Safeguards built into the process by one set of designers failed to be implemented by the next set of engineers as the project saw a veritable revolving door of consultants.

For example, the mining plan proposed in the

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opposition to the mine after the company agreed to keep all mine facilities out of the Wilson Creek drainage. Telephone Interview with Roger Flynn, Director, Western Mining Action Project, and Attorney for Citizens for Victor! (Feb. 16, 1994).

[56] Bradley Family Partnership, South Table Mountain Quarry, Permit M-92-112 (on file with the DMG).

[57] However, a consultant's report submitted as part of the permit application does include general provisions for liner construction during dry conditions. *See* Klohn Leonoff, Hydrological and Geotechnical Engineering, Summitville Heap Leach Facility, vol. 1, at v-9, 14, 26 (Aug. 29, 1984) (on file with the DMG).

[58] Anne Baldridge et al., Inspection Report of Summitville Project (June 18, 1986) (on file with the DMG).

[59] *The Fifth Estate* (Canadian Broadcasting Corporation television broadcast, Sept. 21, 1993).

[60] Summitville Consol. Mining Co. v. Klohn Leonoff Ltd., No. C880756, slip op. at 16-17 (Sup. Ct. Brit. Colum. July 19, 1989); *see also* Danielson & McNamara, *supra* note 40, at 18-19.

[61] Gundle Lining Sys., Inc. v. Summitville Consol. Mining Co., No. 86-M-15 (D. Colo. Jan. 6, 1986).

[62] *Klohn Leonoff Ltd.*, slip op. at 16-17.

[63] Company management implemented as many as six sets of design changes during construction without a formal application for permit amendment. Paul Jones, former Chairman of the Board, Colorado Mining Association, and current Chairman of the Summitville Mine Task Force, Colorado Mining Association, Statement at the Earth Resources Consortium, Denver, Colorado (Oct. 7, 1993).

application suggested that the operation would contain three relatively small separate heap leaches.[64] In fact, the company, without amending its permit, designed and built one large heap leach.[65] Once the rizing heap leach fluid level diluted the processing solution, making it impossible to recover the gold, the company placed an intermediate liner on the heap and piled more ore on top of that. The leached ore in the heap is now 127 feet high, with a number of intermediate liners. These intermediate liners complicated detoxification of the heap material. This system was not approved when the permit was granted.[66] Nor was it approved before it was built.

Similarly, because of concern that precipitation would cause moisture to rise in the heap, potentially causing overflow of toxic material, the initial application provided that each November, prior to the snow season, a 20-mil polyvinyl chloride cover would be installed on top of the heap to prevent infiltration from snow melt.[67] In addition, the ore heaps would be graded to provide better drainage. These features were never implemented, which contributed to later problems.

The company also changed the location of the waste rock pile. The South Cropsy waste pile was constructed in 1986, at a location not specified in the company's permit. The company did not submit any design or permitting documents to the DMG. Only in 1987, after Summitville was in operation, did SCMCI finally submit an application for an amendment to conform its permit to the mine it had already built and started to operate.[68]

This clearly violated the terms of the Mined Land Reclamation Act as it existed in 1984.[69] The Act required a permittee seeking to increase affected acreage or otherwise revise its reclamation plan to obtain approval for a permit amendment.[70] In this respect, the statute and regulations were adequate; but neither the regulators nor the company had a systematic approach to monitoring construction at the site. Monitoring and managing an enormous and complex construction process under tight time limits is a very difficult task. In this case, the project got out of control of both the company and regulators.

More stringent regulations governing construction inspection and reporting requirements could have prevented some of the problems surrounding construction of the heap leach pad. Existing regulations contained no requirement for a quality assurance or quality control program, no requirement that the consultants report noncomplying installation to the DMG, and no clear guidance to the DMG or its inspectors on how to treat noncomplying site conditions. The 1984 statutes and regulations provided almost no specific construction requirements for mining operations.

The only reporting requirement in the statute in 1984 was the requirement of an annual report.[71] The statute did not even require the company to report emergencies to the DMG.[72] It did not require the DMG to make critical point inspections to ensure integrity of the liner or require the company to certify compliance with design conditions or to stop construction if major problems arose.[73] In short, the essential QA/QC elements were not present.

The Act provided very limited authority to the DMG's inspectors to issue cease and desist orders in the field.[74] Under most circumstances, only the MLRB could issue cease and desist orders,[75] and the grounds for issuing such orders were very limited.[76]

DMG files reveal that while staff performed several inspections of the site during the winter and spring of 1986, heavy snow prevented inspectors from making any comprehensive inspections of the entire heap leach pad area. It was not until a May 29, 1986 inspection that DMG inspector Anne Baldridge identified serious damage to the integrity of the heap leach liner. Records at the DMG show that staff inspectors continued to inspect the mine throughout that spring and made a total of three inspections during June 1986.[77] Clearly, DMG was inspecting the site, and the frequency of inspections may indicate serious concern. Despite the growing seriousness of the problems detailed in inspection reports, DMG management apparently favored a "wait and see" policy rather than issuing citations. The basic problems with the heap leach liner were in fact promptly identified by the inspectors,[78] but responsible officials made no record of

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[64] August 1984 Permit Application, *supra* note 40, at D24.

[65] Knight Piesold & Co., *supra* note 9, at 27.

[66] August 1984 Permit Application, *supra* note 40, at D25-D34.

[67] Klohn Leonoff, *supra* note 64, at 15.

[68] Knight Piesold & Co., *supra* note 9, at 32.

[69] Colo Rev. Stat. §34-32-109(7) (1984).

[70] *Id.* §34-32-112(8).

[71] *Id.* §34-32-116(3).

[72] *Id.* §34-32-101 to -127.

[73] *Id.*

[74] *Id.* §34-32-123, -124.

[75] *Id.* §34-32-124(2).

[76] *Id.* §34-32-124.

[77] Anne Baldridge et al., Inspection Report of Summitville Project (June 18, 1986) (on file with the DMG); Anne Baldridge, Inspection Report of Summitville Project (June 23, 1986) (on file with the DMG); Anne Baldridge, Inspection Report of Summitville Project (June 27, 1986) (on file with the DMG).

[78] *See supra* note 84.

their thoughts, if any, regarding the situation.[79]

Operation and Enforcement

On June 5, 1986, Summitville began leaching operations. The lower compacted clay liner was completed, but only part of the upper geomembrane liner was done. Leaching began where both liners were finished, while construction continued on the remainder of the upper liner. On June 11, the company reported to the DMG that cyanide had begun to appear in the leak detection system between the upper and lower liners. The company reported cyanide solution entering the system at just under one-half gallon per minute (gpm).[80]

When state regulators began questioning the source of this contamination, SCMCI, through its consultants, responded with a barrage of technical arguments and explanations. The company argued forcefully that while the cause could be a leak in the upper liner, it was probably due to "overspray," where cyanide sprayed over the edge of the completed portion of the upper liner infiltrated back under that liner through the leak detection system.[81] The company asserted that more careful measures to prevent overspray and completion of the upper liner would solve the problem.

Under the Mined Land Reclamation Act, a violation of a permit condition or term authorizes the MLRB to issue a cease and desist order, suspend or revoke the permit,[82] or impose civil penalties.[83] Yet during this period the MLRB failed to exercise any of these options. The DMG never recommended that they be exercised. The MLRB easily could have found that the cyanide leaks constituted a violation of permit conditions or the statutory requirement that off-site areas be protected from damage.[84] Instead, while the project continued to operate, the DMG attempted to address the applicant's technical arguments. At this critical point, the agency failed to take any enforcement actions against the company for its failure to contain cyanide solutions.[85]

Despite its apparent reluctance to take vigorous enforcement actions against the company for failure to contain cyanide solutions, the DMG did not waste time in noting other unrelated violations soon after the company began operations. In July 1986, following a DMG inspection report that noted possible violations, the MLRB issued its first notice of violation (NOV) and assessed a $3,600 civil penalty against the company.[86]

In June 1986, after the heap was loaded and the mine was in full operation, it became obvious to inspectors[87] that the cyanide solution improperly existing under the upper liner was not primarily the result of "overspray," but the result of leaks in the liner itself.[88] By June 18, it became clear that the lower clay liner was also leaking.[89]

This led to an immediate problem: by the time it became clear that the lower liner was also leaking and that heavy metal bearing cyanide solution was entering the French drain under the liner system, the heap was loaded with a substantial amount of ore.[90] The company asserted that it would be uneconomical to remove this material from the leach pad in order to repair the liner. Further, the heap already contained a large volume of cyanide solution, which would require storage during the attempted repair, and there was no place to put it.

In September 1986, SCMCI submitted a technical revision to the MLRB and DMG requesting permission to install a permanent sump and pump back system.[91] This would enable the company to pump the contaminated liquids from under the heap leach pad and prevent groundwater contamination. However, the only place to put this liquid was back into the heap. Every time the liquid cycled, more groundwater was brought into the

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[79] While there may have been some communication between DMG inspectors and management, no record of any such communication exists in the DMG's Summitville files. Research of DMG files (Feb. & Mar. 1993, Oct. & Nov. 1993).

[80] Letter from Roger Leonard, General Manager, SCMCI, to Anne Baldridge, Reclamation Specialist, DMG (June 11, 1986) (on file with the DMG).

[81] Memorandum from Anne Baldridge, Reclamation Specialist, DMG, to file (July 15, 1986) (on file with the DMG); *see also* Danielson & McNamara, *supra* note 40, at 25-27.

[82] Colo. Rev. Stat. §34-32-124(6) (1991).

[83] *Id.* §34-32-124(7).

[84] *Id.* §34-32-124.

[85] Danielson & McNamara, *supra* note 40, at 46.

[86] The MLRB issued the NOV and assessed the civil penalty for failure to comply with the mine plan, failure to salvage topsoil completely, and sediment control problems. *See* Letter from Anne Baldridge, Reclamation Specialist, DMG, to Roger Leonard, General Manager, SCMCI (July 29, 1986) (on file with the DMG).

[87] *See supra* note 84.

[88] Knight Piesold & Co., *supra* note 9, at 28-29.

[89] Anne Baldridge, Inspection Report of Summitville Project (June 18, 1986) (on file with the DMG).

[90] A report claims that by June 18, 1986, the heap leach pad had already been loaded with approximately 209,000 tons of ore, placed across an area spanning roughly 1.5 acres. The highest ore placement was approximately 40 feet thick. *See* Summitville Consolidated Mining Company, Inc., Heap Leach System Report, vol. 1, at 17 (Apr. 1, 1992) (on file with the DMG).

[91] Letter from Roger Leonard, General Manager, SCMCI, to Anne Baldridge, Reclamation Specialist, DMG (Sept. 29, 1986) (on file with the DMG).

system and more liquid would go into the heap.

The feasibility of putting this liquid back into the heap depended critically on the water balance calculation: did natural evaporation of the site exceed precipitation (negative water balance) or fall short of precipitation (positive water balance)? In short, left to its own devices, would the heap tend to dry out over time or to accumulate water? The DMG believed, based on the company's baseline data, that evaporation exceeded precipitation, making it safe to add more liquid to the heap. The baseline data were wrong,[92] and, therefore, the conclusion also proved wrong.

In October, the DMG and MLRB approved the revision[93] and a permanent sump--known as the French drain sump--was constructed downstream from the mine to intercept the contaminated liquid, which was pumped back into the heap leach pad. Continuous circulation of the contaminated water required that the circulation pumps operate constantly, effectively requiring continued operation of the leaching system.

The implementation of the pump back system appeared to be a feasible temporary solution to the problem. However, by June 1987, the system began to experience repeated failures. This resulted in nine cyanide spills over the course of the summer, with the system releasing a cumulative total in excess of 85,000 gallons of contaminated fluids into Cropsy Creek.

Up to this point, the Colorado Water Quality Control Division (WQCD) had not been involved with the Summitville project. However, in December 1989, following the cyanide spills, the WQCD issued a NOV and assessed a $27,000 penalty. A month earlier, the MLRB had also issued an NOV, but refrained from assessing a fine because the WQCD was also taking action.[94]

Water Quality Control Division Enforcement Actions and Permitting

By 1988, it had become obvious to the company that new means were needed to deal with the cyanide solution escaping the heap leach pad.[95] Since the contaminated groundwater had been pumped back into the heap, the accumulation rate in the heap had doubled. Increased liquid depth in turn increased the hydrostatic head on the liner and the rate of leakage from the heap.[96]

Unanticipated water balance problems in the heap exacerbated the problem. Natural precipitation exceeded evaporation, gradually increasing the water level in the heap. The problem was also furthered by the failure to install a winter cover over the heap to prevent snow melt infiltration, a design feature recommended by Summitville's own consultants, but never implemented by the company.[97]

Prior to this point, the company was unable to consider discharging the fluids from the heap because Summitville had not acquired a Colorado Pollutant Discharge System (CPDS) permit: the company had represented that the project would be a "zero discharge facility," and thus avoided any CWA permitting. Faced with the prospect of rising heap leach pad fluids, however, the company entered into negotiations with the WQCD to obtain a CPDS permit.[98]

Summitville faced many hurdles in obtaining this permit. Because there were no good baseline data available, water quality regulators were extremely hesitant to accept the company's view of the extent of prior contamination in local streams. Water quality regulators, therefore, required the company, if it was to discharge the fluids, to demonstrate compliance with the stringent water quality standards applicable to pristine waters. In its application, Summitville was forced to comply with best available technology (BAT) standards, which the company was ultimately unable to meet.[99]

In May 1989, the WQCD approved Summitville's discharge permit. A month earlier, the company had obtained the DMG's and MLRB's approval of a process solution water treatment plant, which the company would use to treat water before discharging it into the Wightman Fork. Treating the water and discharging it was seen as a solution to the continued ominous rise of the liquid level in the heap. By June 1989, it became apparent that the

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[92] It has been reported that the company based its precipitation levels on records from Wolf Creek pass. It was later discovered that Summitville receives 35 feet more snowfall than the Wolf Creek site. This led to a severe miscalculation in Summitville's water balance, which would eventually contribute to the threat of overflow at the heap spillway. *See* Mark Obmascik, *Mine Becomes Bottomless Money Pit*, Denv. Post, Feb. 21, 1993,at 14A. It also appears that the company, not wanting to take the time to gather evaporation data from its own site, submitted evaporation data gathered at a mine site several miles away, which turned out to show a higher evaporation rate than existed at Summitville.

[93] Letter from Anne Baldridge, Reclamation Specialist, DMG, to Roger Leonard, General Manager, SCMCI (Oct. 27, 1986) (on file with the DMG).

[94] Chronological Summary of Events, SCMCI Permit M-84-157 (on file with the DMG).

[95] A report commissioned by SCMCI in 1988 predicted that at normal winter precipitation, the heap would overflow a spillway heap pad elevation of 11,552 feet by December 1989. At maximum precipitation, the heap would overflow by June 1989. *See* Golder Associates, Heap Leach Pad Water Balance Estimate (Apr. 1988) (on file with the DMG).

[96] Knight Piesold & Co., *supra* note 9, at 29.

[97] Klohn Leonoff, *supra* note 64, at 53.

[98] Knight Piesold & Co., *supra* note 9, at 38.

[99] Danielson & McNamara, *supra* note 40, at 33-34.

water treatment plant was incapable of treating water to the extent required by water quality regulators.[100] Further, the stringent water quality standards imposed on the company lowered the output rate of the treatment plant. Meeting the silver standard was a particular problem. This limited the ability of the water treatment plant to lower the water level in the heap. The water treatment plant could slow but not prevent the inexorable rise of fluid.

By this point, SCMCI may well have been regretting the absence of WQCD involvement in the initial permitting of the mine and the lack of any water quality baseline data. Had such baseline data been provided, more realistic effluent levels would have been established. This would have given the company a better chance of complying with effluent limits.

The Federal Water Pollution Control Act,[101] commonly known as the Clean Water Act (CWA), seeks to restore and maintain the chemical, physical, and biological integrity of the nation's waters.[102] It reasonably could be expected that mining operations, which commonly use or affect water sources, would be regulated under the CWA. Historically, however, the CWA has only regulated "point source discharges," as defined by the CWA[103] and the Colorado Water Quality Act (CWQA).[104]

Despite the conservation objectives of the CWA and the CWQA, the regulatory control of the CWA over many mining operations is hindered by the mining operation's assertion that they will function as nondischarge facilities. Amendments to the CWA have sought to broaden environmental protection by expanding federal and state authority. These requirements might have played a critical role in Summitville's mining operation if they had existed at the time the permit was granted. The stormwater regulations prescribed by CWA §1342(p)[105] and embodied in EPA's rules at 40 C.F.R. §122.26(b)(14)[106] provide for the state to require a permit for certain discharges composed entirely of stormwater. In addition, Congress has authorized a "nonpoint source program" under the CWA for more generalized runoff.[107] This program, however, only became effective in Colorado in 1989, when the federal government provided funding for a nonpoint source program. The program was not an effective regulatory tool at the time of the Summitville permitting.

The Colorado legislature has now adopted enabling legislation for the stormwater program, which became effective September 30, 1993.[108] The WQCD then began the process of subjecting sites such as Summitville to the stormwater program. The WQCD, through its Industrial Permits and Enforcement Unit, is also developing a formal Division policy that will require permits for certain "zero discharge" facilities. Cyanide heap leach mines, like Summitville, are one type of facility that will be required to obtain a water quality permit even at the zero discharge level. The existence of these requirements during Summitville's initial permitting process would have involved water quality regulators earlier in the project and could have reduced the environmental damage the mining operation caused.

Land Application

On realizing that its water treatment plant would never meet the BAT effluent standards prescribed by the WQCD, SCMCI was forced to consider other options for eliminating accumulating heap liquids. The company submitted yet another technical revision to the DMG, this time for a land application system. The company was to spray contaminated liquid as a fine mist over a relatively flat piece of land, where the liquid would evaporate and percolate at a controlled rate into the ground. The lack of substantive groundwater regulations allowed the MLRB to approve this type of land application system.[109]

Unfortunately, regulators failed to require, and the company failed to complete, an adequate analysis of the subsurface conditions for the land application system. While the company did submit information on subsurface conditions, this information contained nothing to indicate that a clay layer existed a short distance below the surface, preventing water from percolating to the extent expected. Further, the company did not own all of the land on which the land application was to occur. SCMCI was unable to obtain permission from one private landowner to use a portion of his land that was proposed and approved for the land application system. As a result, the amount of liquid initially proposed to be sprayed over roughly 17 acres of land was sprayed over five to six acres. This change was not promptly called to the attention of the DMG. Nor was it the subject of a

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[100] Knight Piesold & Co., *supra* note 9, at 38.

[101] 33 U.S.C. §§1251-1387, ELR Stat. FWPCA §§101-607.

[102] *Id.* §1251(a), ELR Stat. FWPCA §101(a).

[103] *Id.* §1362, ELR Stat. FWPCA §502. Point source discharges as defined by CWA §502 excluded agricultural storm water discharges and return flows from irrigated agriculture. *Id.*

[104] Colo. Rev. Stat. §25-8-103(14) (1990).

[105] 33 U.S.C. §1342(p), ELR Stat. FWPCA §402(p).

[106] Mining is specifically addressed at 40 C.F.R. §122.26(b)(14)(iii) (1992).

[107] 33 U.S.C. §1329, ELR Stat. FWPCA §319.

[108] 2 Colo. Code Regs. §407-1 (Rule 6.4.2) (1988).

[109] *See* Envtl. Law Inst., *supra* note 22, at 17-18.

permit amendment. All of these factors contributed to overland runoff of solution into the Wightman Fork.[110]

In a July 1990 inspection of the site, WQCD inspectors discovered that the land application system was resulting in overland flow of contaminated fluids into the Wightman Fork. The Agency did not act until February 4, 1991, when it issued a NOV for discharging without a permit.[111]

Settlement Agreement

By this time the signs of accumulating environmental problems had become easy to read. The land application system was discharging large amounts of contaminated liquid into the Wightman Fork. Water quality in the Wightman Fork showed a decrease in pH from 1989 to 1990, and an increase in metals and cyanide. In addition, drainage from the improperly located Cropsy waste pile was resulting in toxic seepage, probably the biggest long-term water quality problem at the site. This was discharging to the Cropsy Creek from the "550 Diversion." Breakdowns of the pump back system were also contributing to unpermitted discharges, which continued throughout 1991.[112] In February 1991, SCMCI received NOVs from both the WQCD and the MLRB due to these problems.[113]

On July 1, 1991, SCMCI, the MLRB, and the WQCD signed a settlement agreement addressing SCMCI's accumulating violations.[114] The two agencies and the company drafted the agreement in response to the problems that prompted the February 1991 NOVs. The settlement agreement, while not addressing every shortcoming of the Summitville operation, succeeded in achieving some very significant on-site environmental improvements and resolving some of the legal and permitting problems.[115] The company and the agencies signed a later amendment to the agreement on July 20, 1992.[116] In addition to addressing stormwater requirements, the amendment raised the company's bond by $5 million.[117]

The stipulations of the 1991 agreement are indicative of the rigorous analysis and straightforward enforcement that should have been exercised from the beginning of the mine's operation. It is true that because SCMCI had applied as a nondischarge facility, it avoided dealing with the more detailed discharge permit requirements. However, had the DMG and MLRB exercised the same attention to detail in their review of the permit application in 1984, many of these problems might never have occurred.

The regulators' guarded optimism that the company had committed itself to a program that would remedy some of the site's worst problems was dashed in December 1992, when the company declared bankruptcy without warning, terminating its commitment to pay for continuing operation of the water treatment plant and the complex system of pumps and pipes that was keeping massive active discharges of contaminants from overflowing the heap. The company's withdrawal from its agreements with 11 days' notice was a supreme act of corporate irresponsibility. The bankrupt mining operation left both state and federal regulators, without any advance warning, heirs to an abandoned mine at the beginning of one of the most severe winters in recent history.[118] The timing of the bankruptcy was extremely unfortunate and has been the subject of much deserved criticism.[119]

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[110] Telephone interview with Harry Posey, Geologist, DMG (Oct. 8, 1993).

[111] Knight Piesold & Co., *supra* note 9, at 38-39.

[112] Knight Piesold & Co., *supra* note 9, at 30.

[113] Knight Piesold & Co., *supra* note 9, at 39.

[114] 1991 Settlement Agreement (July 1, 1991) (on file with the DMG).

[115] In this agreement, the MLRB and WQCD assessed fines of $57,000 and $43,000, respectively. In addition, the agreement required that SCMCI submit a Surface Water Management Plan and Best Management Practices Plan. The settlement agreement's compliance plan called for significant on-site improvements. The compliance plan required treatment of water from the Cropsy Waste Pile 550 Diversion, the submittal of an application for a CPDS permit for Cropsy Waste Pile discharges, termination of the land application system by October 30, 1991, the submittal of a waste water discharge plan, and SCMCI's promise of no unpermitted discharges by October 30, 1991. The plan also required waste water from the treatment plant to comply with CPDS effluent limitations by October 30, 1991. In addition, the agreement required the company to submit a surface water management plan identifying point source surface discharges, storm water point source discharges, and nonpoint source discharges to state waters. The agencies required that quantity and quality of storm water runoff be monitored and that the company develop a best management practices plan for storm water discharges that would comply with state and federal regulations. In addition, SCMCI was required to develop a Revised Water Sampling Protocol for surface and groundwater monitoring, to be submitted by June 3, 1991. *See* 1991 Settlement Agreement Compliance Plan (July 1, 1991) (on file with the DMG).

[116] Knight Piesold & Co., *supra* note 9, at 39-40.

[117] Knight Piesold & Co., *supra* note 9, at 41.

[118] The company employees who operated the environmental systems and who stayed on their jobs with no assurance of pay while the company's management apparently tried to maximize its leverage under bankruptcy law deserve a note of acknowledgement.

[119] *The Mine That Killed a River*, Denv. Post, Jan. 3, 1993, at 2D; Mark Obmascik, *Bankrupt Mine Costly to EPA*, Denv. Post, Dec. 24, 1992, at 1B; Mark Obmascik, *Taxpayers Get $15 Million Shaft in Summitville Mine Fiasco*, Denv. Post, Dec. 12, 1992, at 1B.

Analysis

In retrospect, Summitville's permit should have prohibited winter construction of the liner. Beyond that, the DMG clearly should have required the operation to shut down in June 1986, when the leak was first detected. The failure to do this put regulators in a bind. When the DMG eventually concluded that both the primary and secondary liners were failing to contain the cyanide solution, it could have ordered that no more cyanide be added to the circuit, but the company would still have had to operate the circulation pumps to protect the groundwater. The regulators' rationale for choosing not to exercise this option may have been that, because it was necessary for the circuit to operate, the best could be made of a bad situation by allowing continued gold recovery, which would provide the company with a source of revenue for environmental protection and allow workers to continue their employment. The decision to allow the operation to continue placed regulators in the defensive position of "damage control."

The fact that SCMCI's performance bond was inadequate fatally weakened regulators' bargaining position in dealing with the company. The bond alone was inadequate to complete reclamation.

Some of the problems at Summitville also arose from the company's failure to report accidents and spills to the DMG in a timely manner. Problems were discovered weeks, sometimes months, after they had occurred, making reclamation more expensive. Regulations requiring notice to the DMG could have partially remedied this problem.[120]

Generally, failure to regulate more effectively can, in part, be blamed on less than adequate statutory authority. The Mined Land Reclamation Act as it existed in 1984 failed to provide sufficient authority to MLRB to deny a permit and failed to include any emergency reporting requirements that would have held SCMCI responsible for contacting the DMG following cyanide spills or other environmentally harmful occurrences.[121]

An additional factor contributing to Summitville's problems was the perceived lack of political support for the regulatory program, concretely demonstrated by the legislature's 50 percent reduction of the "Minerals Program" budget in 1987.[122] This substantial reduction of the program's funding acted as a catalyst in the Summitville disaster.

Bonding

Adequate bonding may be the most important single element of the Colorado Mined Land Reclamation Act program. Deficiencies in the Act's bonding requirements became evident soon after Summitville declared bankruptcy in December 1992. While the MLRB had increased the company's bonding requirement several times during the life of the mine,[123] it was soon clear that the amount was inadequate to remedy the environmental damage at the site. Part of the bond's inadequacy was due to the fact that the MLRB, as required by law, accepted a "salvage credit bond" of $913,000, secured by on-site mining equipment, which later proved to be nearly valueless, subject to prior county tax liens, and needed at the site for environmental control.[124] In addition, the bond originally calculated at the time the permit was approved did not include the estimated cost of heap detoxification or water treatment.

It may not have been possible to bond adequately for the cleanup necessary at the Summitville site. Bonds prescribed by the MLRB are based on the estimated cost of reclamation. The Act requires the MLRB to determine the amount and duration of financial warranties based on the nature, extent, and duration of the proposed mining operation and the magnitude, type, and estimated cost of planned reclamation.[125] Absent from the factors that may be considered for reclamation bonds is the possibility and potential effect of an unpredictable disaster.[126] Even the most careful and comprehensive analysis of Summitville's permit application would not have produced a bond figure sufficient to cover ultimate costs of the unanticipated problems. This is not to exonerate the DMG. The fact is that in 1984 bonds were not set with the precision and detail used to calculate bonds today. Summitville's bond

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[120] Colo. Rev. Stat. §34-32-121.5 (1991), amended by Act of June 3, 1993 S.B. 93-247 (1993) now contains this requirement.

[121] *Id.*

[122] Legislative Overview, *supra* note 102.

[123] Summitville's original bond was for $1,304,509. In addition to the $913,801 submitted in the form of salvage credit on August 24, 1989, the company also submitted $5,000,000 as part of the amended settlement agreement on June 21, 1992. Of this, $2,500,000 was put into a special account, to be released following the completion of summer 1992 reclamation activities. This was later released to the company. At the time the mine declared bankruptcy, the bond stood at $4,718,310--well below the estimated $170,000,000 cleanup cost now projected by EPA. *See* Knight Piesold & Co., *supra* note 9, at 41-42.

[124] Colo. Rev. Stat. §34-32-117(a)(VIII) (1991). Colo. Rev. Stat. §34-32-117(c) (1991), *amended by* Act of June 3, 1993, S.B. 93-247 (1993), allows the MLRB to refuse to accept financial warranties under specified conditions. Summitville's salvage credit bond would have met these conditions. The amended statute eliminates the predicament caused by Summitville's salvage credit bond in realizing a security interest in the mining operation's water treatment plant: if the DMG sold the plant, necessary water treatment would stop; if it did not sell the plant, the security interest would have no value.

[125] Colo. Rev. Stat. §34-32-117(4) (1991).

[126] *Id.*

was inadequate to pay for even the anticipated costs of reclamation.

The inadequate bond value forced regulators to enter into long and tedious negotiations with the company instead of simply forfeiting the bond and closing the mine.[127] Regulators lacked the leverage and flexibility that an option to forfeit on an adequate bond would have provided.[128]

SCMCI's abrupt bankruptcy and inadequate bond point to inadequacies in the 1984 regulations. The Colorado Mined Land Reclamation Act places full legal liability for the ultimate cost of reclamation on the operator.[129] The bond is the DMG's principal protection from an operator's insolvency. If the operation becomes insolvent, recovery is limited to the value of the bond; the Act does not provide for recovery from other company assets or from the company's owners or officers.[130] The Act differs in this way from the Colorado Surface Mining Control and Reclamation Act[131] and the federal Surface Mining Control and Reclamation Act,[132] which explicitly provides for the personal liability of persons controlling the operator for the reclamation costs.[133]

POST-BANKRUPTCY: ENVIRONMENTAL CONDITIONS AND FUTURE RECOMMENDATIONS

Environmental Damages

Following SCMCI's bankruptcy, government agencies, with almost no warning, inherited a complex site with enormous problems. They began a difficult battle during one of the worst winters in many years. By the time EPA assumed control of the mine site[134] under its emergency authority following the company's bankruptcy, the liquid in the heap had far exceeded its anticipated level[135] and was threatening to overflow with the anticipated spring melt off. During spring runoff, the heap had the potential for discharging heavily contaminated liquids at the rate of 300 gpm. Currently, EPA is working to treat and contain four major sources of contaminated water on-site: (1) the heap leach pad, where an accumulation of metals and cyanide, continues to collect; (2) the French drain; (3) the Reynolds Adit; and (4) the acidic Cropsy Waste Pile.[136]

Summitville's legacy also includes millions of tons of acid-bearing, metal-heavy waste rock that continue to release toxins into ground and surface water sources. The Cropsy Waste Pile, located in violation of the Mined Land Reclamation Permit, contains six million tons of sulfide-rich waste rock and continues to contaminate surrounding waters. To limit discharges from this source, up until July 1994, effluent from the Cropsy was being diverted to the heap pad, once again increasing the liquid in the heap. The site also has smaller waste rock dumps, which are sources of acid rock drainage. None were being controlled or treated until EPA began its emergency response action.

Excavation of the open pit exposed considerable acid-bearing rock, and the progression of the pit design from a terraced configuration, over which most surface water flowed, to an open pit configuration, into which most surface water infiltrates, has increased the collection of precipitation and infiltration inside the pit.[137] The addition of waste and oxygen to the ores generates sulfuric acid and releases heavy metals. This material found its way into, and eventually drained out of, the historic Reynolds Adit.

Since assuming control of the site, EPA has spent over $10.8 million on monitoring. During the winter, EPA was spending an average of $30,000 a day to prevent heap overflow. Overall costs during the winter totalled $3.5 million dollars.[138] It is estimated that cleanup could cost up to $120 million.[139] The immediate project of moving the six-million ton Cropsy Waste Pile to an acceptable location is in itself an enormous engineering task, costing $17.7 million to date and not yet completly capped.

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[127] *Id.* §34-32-118.

[128] *Id.* §§34-32-118, -124.

[129] *Id.* §34-32-117.

[130] *Id.* §34-32-117.

[131] Colorado Surface Caol Mining Reclamation Act, §34-33-101 (1993).

[132] 30 U.S.C. §§1201-1328, ELR Stat. SMCRA §§101-908.

[133] See Regulations of the Colorado Mined Land Reclamation Board for Coal Mining, Rule 2.03.4 and Rule 5.04.7 (1994).

[134] SCMCI filed for Chapter 7 bankruptcy liquidation in federal court on December 1, 1992. EPA assumed control of the mine site on December 16, 1992. *See* Knight Piesold & Co., *supra* note 9, at 22.

[135] At its high point in the spring of 1993, the heap contained 200 million gallons of cyanide solution, and was five feet from overflowing, with the fluid level rising. Some computer projections were predicting overflow by the last week of May. Telephone interview with Hays Griswold, On-Scene Coordinator, Denver, Colorado, EPA (Oct. 8, 1993).

[136] Summitville Mine Removal Action, Site Summary 4 (1993) (on file with the DMG).

[137] Telephone Interview with Harry Posey, *supra* note 118.

[138] Danielson & McNamara, *supra* note 40, at 41.

[139] Telephone interview with Hays Griswold, *supra* note 142.

The Superfund listing of Summitville has triggered a rash of litigation. Galactic, its officers, other mining companies whose only involvement in Summitville may have been core drilling or sampling, landowners, engineering consultants, and others are girding for battle over their relative responsibilities for on-site conditions. For EPA, state regulators, lawyers, potential criminal defendants, and the various mining companies' land and mineral owners who will be PRPs at this site, Summitville will continue for a long time.

This is one of the costliest failures in the recent history of the mining industry. However, the cleanup cost is likely to be dwarfed by the increased price industry will pay in the form of more stringent regulation and public distrust.

Public Land Law

While the blame for the failures of Summitville can be placed at least partially on the inadequacies of state regulations, the mine's failure also demonstrates the weaknesses in existing federal laws governing mining activity. Among these laws is the General Mining Law of 1872 (the 1872 Mining Law), which regulates mining activity on public lands. The 1872 Mining Law grants an individual the right to prospect on public land, to locate a mining claim, and to mine the claim.[140] Drafted to encourage exploration and extraction on public lands, the Act requires no royalty and carries no bonding or reclamation requirements, though some such requirements are now imposed under the Federal Land Policy and Management Act.[141] The public lands are open to any interested prospector.[142]

While only 21 acres of the project site are currently administered by the Forest Service, most of the private land was originally public land that only became private under the 1872 Mining Law, and the Forest Service did precious little to use any leverage it did have to ensure resource protection.

The National Environmental Policy Act (NEPA)[143] partially mitigates the 1872 Mining Law's "open door policy." Under NEPA, the Forest Service must conduct an environmental assessment (EA)[144] to determine whether a proposed action on public land is a major federal action significantly affecting the quality of the human environment.[145] If it is, the Service must prepare a full environmental impact statement (EIS). Less damaging alternatives must be considered.

Nevertheless, 1872 Mining Law, as interpreted by complacent land management agencies, severely curtails NEPA's effect. In completing its EA and issuing a "finding of no significant impact" on the Summitville project, the Alamosa District of the Rio Grande National Forest argued that it had approved the mine's operating plan because it had no legal alternative. The District wrote: "The no action alternative would be in violation of the 1872 General Mining Law which allows for exploration and development of minerals on public domain lands. This alternative would also deny information about the nation's mineral reserves."[146]

While it must be kept in mind that the Forest Service approval extended only to use of its 21 acres and various associated road rights-of-way, the idea that this project has "no significant impact" defies logic. The 1872 Mining Law can render the EA/EIS process relatively meaningless.

In an ideal world, it should not matter whether the acid drainage at Summitville came from Galactic's operations, operations during the 1930s, or operations during the 1890s. Funds should be spent to maximize environmental cleanup, not resolve legal fine points. At Summitville, a small fortune has already been spent trying to allocate liability.[147]

Inactive or abandoned hardrock mines are a significant problem in the United States today. It has been estimated that there are 557,650 hardrock and abandoned mine sites in this nation and that the cost of cleaning them up will range from $32.7 billion to $71.5 billion.[148] The current federal, state, and private funds spent to reclaim such sites do not address the magnitude of this problem.[149]

1993 AMENDMENTS TO THE COLORADO MINED LAND RECLAMATION ACT

Following the Summitville bankruptcy, an awareness of the serious deficiencies in current legislation led lawmakers and members of the DMG and MLRB to draft legislative and subsequent rule and regulation revisions. The 1993 amendments to the Mined Land Reclamation Act (MLRA)[150] and 1994 revisions to the Mineral Rules

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[140] 30 U.S.C. §22 (1993).

[141] 43 U.S.C. §§1701-1784, ELR Stat. FLPMA §§102-603.

[142] 30 U.S.C. §22 (1993).

[143] 42 U.S.C. §§ 4321-4370d, ELR Stat. NEPA §§2-209.

[144] 22 C.F.R. §161.8(b) (1993).

[145] *Id.* §161.8(a).

[146] U.S. Forest Service, Alamosa Ranger District, Summitville Project, Summitville Consolidated Mining Co. Inc., Environmental Assessment (Dec. 14, 1984).

[147] This does not imply that a very hard look at the responsibility of Galactic and its management is not in order.

[148] Mineral Policy Ctr., Burden of Gilt 4 (June 1993).

[149] *Id.* at 32-33.

[150] Colo. Rev. Stat. §34-32-101 to -127 (1991), *amended by* Act

and Regulations of the Colorado Mined Land Reclamation Board[151] recognize the scale and hazards of modern chemical mining by creating a new class of permits for operations that (1) use toxic or acidic chemicals or (2) expose or disturb acid- or toxic-forming materials as a result of the mining operation.[152] The amendments require operators of these mines to meet more stringent permitting standards and to develop environmental protection plans.[153] This is an explicit recognition that reclamation and environmental protection must be integrated into mining operations throughout the life of the mine, not just after mining has ceased. Amendments to the MLRA grant the MLRB the right to deny a permit if there are serious or unresolved public health or environmental concerns.[154]

The revised Act and Rules also strengthen the baseline data requirements. Pursuant to C.R.S. § 34-32-116.5, Rules 6.4.19(9) and (11) require groundwater and surface water quality data, respectively, to be "collected during five (5) successive calendar quarters or as specified by the Division to adequately characterize baseline data" within two miles down gradient of the affected land. This requirement may prove to be beneficial to all players in the mining industry.

The revised MLRA also sets forth emergency reporting requirements, which require a company to report any accidents immediately.[155] It allows the MLRB to extend the permit application review period by 60 days for complex operations.[156]

The amendments to the MLRA also strengthen the MLRB's bonding authority by allowing it to reject bonding vehicles (such as real estate) that often prove inadequate or difficult to administer, by abolishing the "salvage credit" bond, and by granting the MLRB discretion to accept or reject letters of credit.[157] In addition, the amended Act creates an emergency response fund that use donated monies to address reclamation problems requiring immediate attention.[158] As an additional safeguard, the amended Act increases permit and annual fees to reflect better the cost of permitting and inspecting mining facilities.[159] This has allowed a staffing increase at the DMG, which now has 17 professional staff members to monitor the state's 1,935 non-coal mines.[160]

CONCLUSION

Environmental problems in the domestic mining industry are not a relic of the distant past. They can and will happen any time that effective regulatory programs are not maintained.

The environmental tragedy of Summitville cannot be blamed on one party alone. A certain number of completely unscrupulous operators have always existed in the mining industry.[161] Part of the job of regulators and citizen groups is to anticipate this factor of skills and charlatans and present them from creating Summitvilles. The company should have complied strictly with applicable regulations. The company's consultants should have monitored the mine's technical problems more closely and expressed their reservations more clearly. State administrators should have acted more decisively when there was still time. Legislators should have supported a more effective regulatory program.[162] The public should have participated more diligently in the approval process. Blaming Summitville on an irresponsible promoter--despite the ample justification there may be for this--misses a vital point. The mining industry has long been a haven for wild promotions, and an effective regulatory scheme must take this into account.[163]

Federal, state and local environmental organizations should learn at least one important lesson from Summitville: an environmental presence in the decision-making process may help avert many future catastrophes. It is easy to raise funds after a disaster, but raising money for, and public interest in, preventing such a disaster before it happens is more important.

The MLRB repeatedly sees dozens or even hundreds of citizens protesting the construction or operation of quarries near their homes. While these quarries may pose

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of June 3, 1993, S.B. 93-247 (1993). The authors played some role in drafting and negotiating the amendments.

[151] Mineral Rules and Regulations, 2 Colo. Code Regs. § 407-1 (April, 1994).

[152] Colo. Rev. Stat. §34-32-103(3.5) (1993).

[153] *Id.* §34-32-112.5.

[154] *Id.* §34-32-115.

[155] *Id.* §34-32-121.5.

[156] *Id.* §34-32-115(2).

[157] *Id.* §34-32-117.

[158] *Id.* §34-32-122.

[159] *Id.* §34-32-127.

[160] Report of the State Auditor, Preliminary Draft, DMG Minerals Program, Performance Audit (Nov. 1993).

[161] While we have no desire to offend anyone in the mining industry, it is true that Mark Twain wrote over 100 years ago that "a mine is a hole in the ground owned by a liar."

[162] The fact that the reforms in the 1993 amendments passed both houses of the legislature unanimously may be an indication that the problem of political support for the state regulatory program is behind us, at least for the moment.

[163] It has, after all, been 80 years since George Graham Rice wrote *My Adventures With Your Money* (1913).

environmental problems, the magnitude of these problems is often nowhere comparable to the magnitude of the problems created by a project with the scale and complexity of Summitville. The MLRB often receives no public comment, or only minimal comment, on massive chemical mining projects because the impact of these projects on citizens' interests seems remote.[164] This is a major challenge for environmental groups in the 1990s.

The Summitville situation also creates a challenge for state and federal legislators. Statutes encouraging agency skepticism in the permitting process, such as by authorizing extended review or permit denials, can help discourage operations that create excessive environmental risks. In addition, coordination between agencies at the beginning of the permitting process can help lessen misunderstanding and encourage cooperation while generating important baseline data. In the case of the CWA, federal or state requirements for baseline data from supposed nondischarge facilities would minimize problems should discharges occur later.

The benefits of domestic environmental protection are limited unless there is also increased international cooperation. Without unified efforts, environmental enforcement in the United States will only export the problem.[165]

If the United States is to achieve the twin goals of maintaining a viable domestic mining industry and preventing the kind of environmental tragedy represented by Summitville, we must realize that no one except the irresponsible fringe element of the mining industry is benefitted by weak regulatory programs or lax enforcement. Certainly, the events at Summitville have led to a nationwide push for better environmental regulation. This is going to cost the mining industry a lot of money.

Just as clearly, some of the proposals that have been advanced are ill-considered, and would achieve limited environmental benefits while imposing enormous costs on the mining industry. The industry itself would be much better off if it had thrown its powerful political weight behind maintenance of a reasonable, balanced, and adequately funded program in Colorado. The law-abiding mining industry will pay an enormous share of the price at Summitville, as will downstream farmers and recreationists, taxpayers, local government, and others. We are a long way from having "solved" the problems of environmental regulation on a domestic U.S. level, much less on an international basis.

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[164] A new high altitude heap leach project five times the size of Summitville was just approved by the MLRB. One individual citizen--and no organizations--appeared to comment on the application. *See supra* notes 57-61 and accompanying text.

[165] For example, the promoter who created Galactic Resources and developed the Summitville project, Robert Friedland, has turned his attention to gold mines outside North America. Vivian Danielson, *Friedland Strong Supporter of Guiana Shield Gold Rush*, N. Miner, Mar. 29, 1993, at B1. He is currently promoting a cyanide heap leach operation in the Kilometer 88 gold district along the border between Venezuela and Guyana. Friedland has recently obtained a series of Canadian court gag orders to restrain Canadian news media from, inter alia, reporting about his involvement in the Summitville environmental problems. Penelope Purdy, *Coloradans Pierced Censors' Veil to Fax the Facts to Our Canadian Friends*, Denv. Post, Sept. 20, 1993, at B7.

IS SUMMITVILLE REALLY UNIQUE?

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ABSTRACT

The Summitville Mine Superfund Site burst onto the national scene when the mining venture's Canadian owners abruptly declared bankruptcy in December 1992. They left 160 million gallons of cyanide-contaminated, metals-laden water within five feet of overtopping the containing dike. In a winter which had already experienced 170 percent of normal snowfall, the sudden catastrophic release of this water to the Alamosa watershed during spring snowmelt seemed certain. At a time of proposed reform for the hard-rock Mining Law of 1872, the Summitville disaster was heralded as the "poster child" to enact reform legislation.

As more information about the Summitville Mine is acquired and environmental issues at other mining sites are becoming apparent, it becomes less certain that Summitville is a unique situation. A detailed history of the Summitville Mine Site and the response actions undertaken by the Environmental Protection Agency in conjunction with the State of Colorado are presented in the following discussion. A brief evaluation of the environmental concerns presented by Summitville and other mining sites is then offered for consideration in answering the question, "Is Summitville really unique?"

INTRODUCTION

Gold in the Summitville Mine area of Rio Grande County, Colorado was first discovered in Wightman Gulch in 1870 (E&E, 1993). Three years later, a load deposit was found and open cut mine workings were established on South Mountain by 1875. Construction of the Reynolds Adit was initiated in 1897 to provide drainage to what is still the central portion of the current Summitville Mine Superfund Site. Thus, the Summitville Mining District was begun and mining of gold, silver, and copper continued intermittently until 1992.

SITE BACKGROUND/DESCRIPTION

Mining History

With the completion of the Reynolds Adit in 1906 (Knight Piesold, 1993) came observations that the water exiting the Adit was acidic in nature. A significant find of high grade gold ore in 1926 (ECC, 1994a & b; MK and EPA, 1994) resulted in the creation of additional adits to dewater the growing number of underground mine workings. These adits discharged acid mine drainage (AMD) directly to the Wightman Fork stream bordering the Summitville Site until they were captured for treatment in an interim treatment system in 1992.

In addition to the adits, approximately 550 acres of South Mountain terrain was heavily altered due to the surface and underground mining activities since 1870 (ECC, 1994a & b). These activities have included placer mining, open cut workings, construction of underground tunnels and shafts, processing mills, construction of a tailings pond, several extensive exploration and underground rehabilitation programs, disposal of waste materials, and open pit mining. These various disturbances have resulted in the exposure of highly mineralized, sulfide-containing rock to both oxygen and moisture which results in the generation of additional acid mine drainage from the Summitville Site.

The most dramatic change in surface topography occurred during mining of low-grade gold ore located within the area of the historic underground workings. This included the excavation of a 100-acre open pit, construction of a heap leach pile, and placement of several overburden and waste ore dumps. The mine pit itself was hydraulically connected to the adit drainage system via the remaining underground workings. The pit then acted as a catchment basin for snow and rain and funneled the resultant water directly through an underlying pyritic ore body. Overall, water quality in the

Wightman Fork deteriorated and metal levels increased as much as five times their pre-1988 levels (SCMCI, 1992).

Site Characteristics

As with many metal mines, the Summitville Minesite is located at a high elevation (average elevation of 11,500 feet) near the headwaters of one or more streams (Alamosa and Rio Grande Rivers). It is located within the San Juan Mountain Range of the Rocky Mountains approximately 25 miles south of Del Norte, Colorado and two miles east of the Continental Divide (see Site Map in Roeber and others, this volume). The Site is located in the Rio Grande Drainage Basin and is drained by the Wightman Fork and Cropsy Creek streams. Wightman Fork enters the Alamosa River approximately 4.5 miles downstream from the Wightman Fork - Cropsy Creek confluence on the northeastern edge of the Site.

Winters at Summitville are harsh and characterized by heavy snowfalls. Most of the annual 55 inches of precipitation occurs as snow though afternoon thunderstorms are common during the summer (ECC, 1994 a & b; MK and EPA, 1994). The Summitville "construction season" occurs during the relatively snow-free months of May through October of each year. Any Site activities after October have generally required a significant amount of snow removal to gain access and carefully considered winter protection for equipment and materials.

Summitville Consolidated Mining Company, Incorporated (SCMCI) Operations

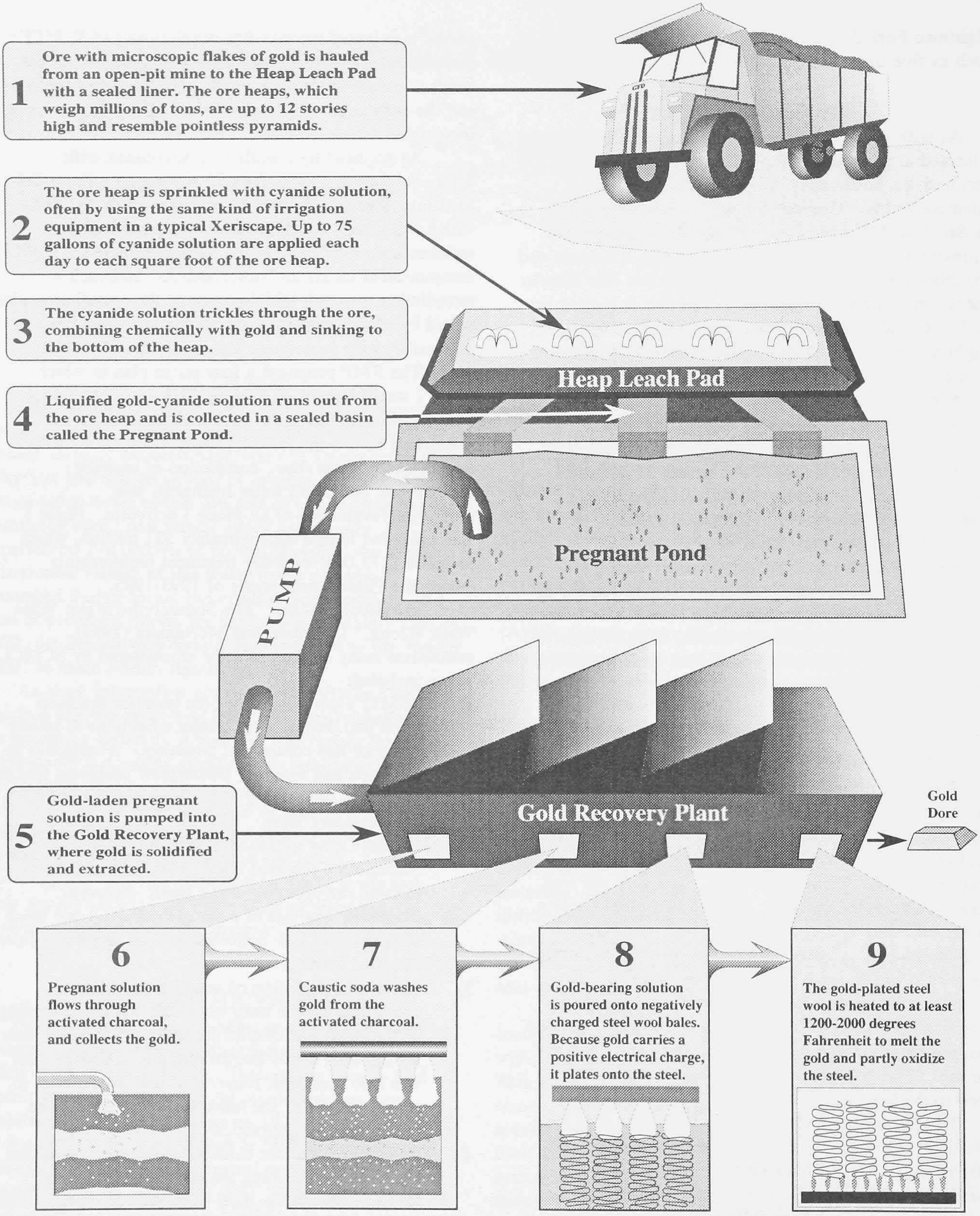
The most recent operations at Summitville were conducted by the Summitville Consolidated Mining Company, Incorporated (SCMCI) in which the low-grade gold reserves were developed as a large tonnage, open pit heap leach mine during 1984-1992. The gold ore was excavated from the open pit, crushed and placed onto a constructed clay-and-synthetic-lined pad (see Figure 1). A dilute sodium cyanide solution was percolated through the heaped ore to leach the gold to the cyanide. The resultant solution was removed from the heap and the gold extracted with activated carbon. The gold was then stripped from the carbon and melted into gold "buttons" for sale. The gold-free cyanide solution was recycled back to the heap leach pile.

The Summitville Mine was the first large gold heap leaching project proposed in Colorado (Danielson and McNamara, 1993). This relatively new technology seemed to offer economic recovery of gold from low-grade ore but had not been fully evaluated in a high altitude, high precipitation environment with severe climatic conditions. In the 1984 regulatory climate which was friendly to the mining industry, the Summitville Mine permit was issued prior to full development of SCMCI's reclamation plan. Other problems related to the severe weather conditions and financial concerns soon developed, and the path to environmental failure of the mine became inevitable.

As required by a settlement agreement with Colorado State agencies, SCMCI developed a Remedial Measures Plan (RMP) dated November 1992 (SCMCI) which evaluated various technology alternatives for reclamation/remediation of the Summitville Site. SCMCI recommended taking an "observational" approach to remediation in which initial phases of the remediation plan would be implemented and the results evaluated prior to proceeding with subsequent phases of the reclamation plan. The RMP proposed a four phase plan in which Phase I would consist of plugging the Reynolds Adit, decommissioning the heap leach pad, installation of subsurface diversions for the Cropsy Waste Pile and Beaver Mud Dump areas, completion of ongoing reclamation, continued water treatment, and monitoring/evaluation of all Phase I activities. Phase I was estimated to cost approximately $21 million, which included $273,000 for water treatment requirements during the Phase I time frame of 1993-1995.

In a report entitled "The Summitville Mine: What Went Wrong," Danielson and McNamara (1993) summarize many of the problems encountered by SCMCI. These included:

1) SCMCI's construction of the liner for the heap leach pad during harsh winter conditions to satisfy financial and contractual pressures. Avalanches in the leach pad area and freeze/thaw problems lead to stretching and tearing of the liner and washout of the secondary liner.
2) Six days after initiation of leaching operations, Summitville reported a leak of cyanide solution through the upper synthetic liner. Eventual laboratory analysis of a sample collected one week after the first leak indicated that the secondary liner was also leaking.
3) Gross miscalculation of actual water balance conditions for the heap led to the continued loading of the leach pad despite the leaks in the upper liner. By the time it was known that the secondary liner was also breached, removal of the ore material to attempt repair of the leaks was considered to be "economically impractical."
4) The incorrect water balance calculations were also the basis for pumping the contaminated water leaking through the liner back onto the heap. The calculations indicated that the heap would still be in a negative water balance condition. Unfortunately, just the opposite was true and the heap began



1 Ore with microscopic flakes of gold is hauled from an open-pit mine to the Heap Leach Pad with a sealed liner. The ore heaps, which weigh millions of tons, are up to 12 stories high and resemble pointless pyramids.

2 The ore heap is sprinkled with cyanide solution, often by using the same kind of irrigation equipment in a typical Xeriscape. Up to 75 gallons of cyanide solution are applied each day to each square foot of the ore heap.

3 The cyanide solution trickles through the ore, combining chemically with gold and sinking to the bottom of the heap.

4 Liquified gold-cyanide solution runs out from the ore heap and is collected in a sealed basin called the Pregnant Pond.

5 Gold-laden pregnant solution is pumped into the Gold Recovery Plant, where gold is solidified and extracted.

6 Pregnant solution flows through activated charcoal, and collects the gold.

7 Caustic soda washes gold from the activated charcoal.

8 Gold-bearing solution is poured onto negatively charged steel wool bales. Because gold carries a positive electrical charge, it plates onto the steel.

9 The gold-plated steel wool is heated to at least 1200-2000 degrees Fahrenheit to melt the gold and partly oxidize the steel.

Figure 1. The Summitville heap leaching, gold mining process (modified from Society of Mining Engineers, Inc.).

accumulating contaminated water which could not be discharged to nearby streams without treatment.

Danielson and McNamara also discuss concerns about Colorado's capability to deal with the continuing problems at Summitville. While bonds are not required as insurance against accidents, the Summitville bond was not sufficient to even address expected reclamation costs. However, the more obvious concern was that Colorado had no emergency response capability. Such a capability would allow a state agency to intervene in a site problem before it becomes so severe that Federal assistance is required.

Shortly after submitting the RMP, SCMCI informed Colorado state officials of their intent to declare bankruptcy. SCMCI also notified Colorado that the heap was within 2-5 feet of overtopping its primary dike and snowpack - which would later become spring snowmelt - was well above normal levels.

GOVERNMENTAL RESPONSE

Superfund Involvement

At the State of Colorado's request, the Environmental Protection Agency's (EPA) Superfund program took over operations of the three Summitville water treatment plants on 16 December 1992. During the first nine months of EPA's operations, efforts were directed primarily at stabilizing the site and increasing treatment capabilities such that effluent water quality was improved to dischargeable limits. Two other Emergency Response removal actions to address the Reynolds Adit system and the Cropsy Waste Pile were initiated in October 1993. This work has continued into 1994 and documents regarding additional work for the heap leach pad, site-wide reclamation, and continued water treatment and Cropsy efforts were issued for public comment in August 1994.

Water Treatment Operations

Initially, EPA's primary objective at the Summitville site was to decrease water levels within the heap leach pile so it would not overtop its dike and release cyanide-contaminated, metals-laden water to the Alamosa watershed. To accomplish this task, each of the water treatment processes was carefully evaluated and then modified to increase treatment capacity. Sitewide treatment capacity was approximately tripled and stoichiometric chemical consumption decreased by one-third.

In April 1994, water treatment in the Portable Interim Treatment System (PITS) was terminated due to the successful plugging of the Reynolds Adit. The PITS was reinstituted in October 1994 to treat water encountered during excavation of the Cleveland Cliffs Tailings Pond as part of the Cropsy Waste Pile Removal Action. Once the Pond excavation is complete, the PITS will again be mothballed until needed for specific areas of treatment.

Reynolds Adit System

The 1993 Engineering Evaluation/Cost Analysis (E&E) estimated copper loadings from the Reynolds Adit to Wightman Fork to be 143,000 pounds per year, or approximately 44.5 percent of the potential copper loadings attributed to the entire site. This understanding of relative source loadings led to the issuance of a Request for Proposals in February 1993 for the purpose of plugging the Reynolds Adit system. A contract was awarded on 4 October 1993 and work began on 22 November 1993. After extensive technical considerations, only the Reynolds and Chandler Adits were ultimately plugged. The Dexter Adit was found to terminate approximately 450 feet from its intersection with the Reynolds (ECC, 1994) so no plug was needed.

Upon completion of the Reynolds plug, there was an immediate decrease in flow and a 65 percent reduction in copper concentrations from the Site overall. Copper loadings directly attributed to the Reynolds Adit were decreased by 97 percent.

On 25 May 1994, the Chandler Adit was discovered to be discharging high volumes of water from porous/ fractured rock surrounding the plug. The leak was initially estimated at 340 gallons per minute (gpm) and peaked at 725 gpm in June 1994 with high concentrations of metals and low pH (ECC, 1994). However, this new contaminant source produced less flow and less copper concentrations than experienced from the Reynolds Adit system during the previous year. Work to fortify the Chandler plug was initiated in late 1994 and plug performance will be closely monitored through the 1995 spring runoff season.

Cropsy Waste Pile Removal Action

The intent of the Cropsy work was to remove the waste materials from their location in former drainage basins. As mentioned earlier, it is known that waste material which contains sulfide ores will generate AMD if placed near a water/moisture source unless it can be adequately isolated. Unfortunately, using naturally occurring drainage valleys - such as Summitville's Cropsy Creek and Wightman Fork streams - has, historically, been a very common practice for disposing of mine wastes throughout the industry.

This removal action included the Cropsy Waste Pile, Cleveland Cliffs Tailings Pond, Beaver Mud Dump, and Mine Pits. The selected remedy for these areas of the site was consolidation of the various waste piles within the Mine Pits. Because this work would require more than one construction season to complete, the design and actual construction were phased. Phase I work was initiated on 1 October 1993 and concluded in February 1994. During this time, approximately 927,000 cubic yards of the Cropsy Waste Pile was placed in the Mine Pits. The waste materials were isolated from ground water by lining the surface of the Mine Pits with impermeable material identified on-site. A protective layer of lime kiln dust was placed on the liner prior to placement of the waste materials to neutralize any AMD generated during this work.

Phase II work was initiated in August 1994. The Cropsy Waste Pile was completed in November 1994 and the Cleveland Cliffs/Beaver Mud Dump were expected to be completed in December 1994. Phase II will have moved an additional 3.5 million cubic yards of waste material to the Mine Pits.

Focused Feasibility Studies (FFS)

Four Focused Feasibility Studies (FFS) were issued to the public in August 1994. The Cropsy and Water Treatment FFSs provided a summary of available historical information and a detailed update for these two on-going removal actions. The FFSs are required documentation for obtaining 1995 remedial EPA funding. Essentially these two FFSs proposed to continue the Cropsy work and Water Treatment with little change in scope or direction.

The third FFS evaluated alternatives for detoxification and closure of the heap leach pad. Of the final alternatives, it was determined that biotreatment to destroy the cyanide accompanied with dewatering of the heap followed by contouring and capping provided the best overall long-term protection of human health and the environment.

The final FFS addressed stabilization of non-point source areas to control erosion and AMD generation. Because Summitville is located in a remote location, the number of alternatives which survived the initial screening processes were limited. Consideration of standard reclamation practices for mining sites also indicated that the most economic alternative for Site reclamation would be revegetation which utilizes on-site topsoil. Unfortunately, the on-site topsoil is in poor condition and will require amendment(s) as well as careful management to establish adequate growth under the harsh Summitville climate.

Cleanup Costs

Despite the success of the Emergency response work to protect the Alamosa watershed, the cost for the Summitville project can be startling even for a Superfund site. In July of 1993, EPA projected stabilization costs at Summitville to be approximately $120 million. As of 31 December 1994, approximately $50.2 million will have been spent in only two years. Of this, $30.3 million is attributed solely to water treatment requirements. An additional $18.8 million was expended for Phases I and II of the Cropsy removal and $1.1 million for plugging of the Reynolds and Chandler Adits. The State of Colorado has voluntarily contributed 10 percent of the costs associated with Phase I and II of the completed Cropsy work. All additional work proposed will require a similar commitment from Colorado as each action is implemented.

The four FFSs provide estimates for each of the proposed remediation alternatives. Water treatment is estimated at $26.9 million over the next five years of operation, if required. Phase III of the Cropsy work will require an additional $24.1 million and includes a potential nine more years of treating the underground seeps as they "flush" any contaminants which have infiltrated the soils/bedrock underlying the Cropsy Waste Pile and/or Cleveland Cliffs and Beaver Mud Dump areas. Closure of the heap leach pile will cost approximately $18.9 million and includes treatment of any residual contamination for an additional 3-4 years after the cyanide destruction is complete. The Reclamation work is envisioned to require approximately 5-10 years to complete at a cost of $11.7 million.

This proposed work represents a total of $63.7 million anticipated to be spent within the next five-year time frame. When added to the costs already incurred at Summitville, this brings the total estimated costs for the project to $113.9 million.

State Response

Both the Colorado Department of Public Health and Environment (CDPHE) and the Colorado Department of Natural Resources, Division of Minerals and Geology (DMG) participated in and concurred with the technical development of all actions taken to date including the cleanup remedies proposed within the FFSs. As discussed previously, the State has also agreed to provide a voluntary cost share towards payment of the Cropsy removal action work.

In addition, the Colorado Division of Minerals and Geology initiated a formal rule making process to amend the Colorado Mined Land Reclamation Act under Senate Bill 93-247. The amendments addressed many of the conclusions and recommendations regarding problems experienced during SCMCI's operations which were formalized in the Danielson and McNamara report (1993). These amendments became effective 1 July 1993. Major highlights of these amendments are listed below (DMG, 1994).

1) A new class of mining operation was developed for metal mining operations that use toxic or hazardous materials, or produce or disturb acid or toxic forming materials.

2) An environmental protection plan for designated operations would be required so that greater protection of the environment would occur during the time a mine is actually operating.
3) Requires certification at critical construction phases so that problems can be addressed while they are still manageable.
4) Allows for a 60 day extension to the permit review period for complex operations.
5) Increases the State's bonding authority.
6) Creates a mitigation fund and provides an expedited process for immediate intervention in emergency concerns.

SUMMITVILLE UNIQUE?

But is the Summitville Mine Site really so unique that it warrants all of the media attention and focus regarding reform of the 1872 Mining Law? The presence of another mining site in Colorado or the U.S. is certainly not unique. Nor is the fact that the site produced gold or that it is currently on the Superfund National Priorities List. Further, Summitville is not located at the headwaters of a national treasure as is proposed by Noranda/Crown Butte at the Henderson Mountain just 2.5 miles from the northeastern corner of Yellowstone National Park.

However, Summitville is the first of the modern, heap leaching gold mines to be abandoned and require cleanup under the Superfund program. This type of gold mine did not begin operating until the 1980's, well after enactment of all major environmental legislation. Certainly the passage of the National Environmental Protection Act and Clean Air Act in 1970, the Clean Water Act in 1972, and the Mined Land Reclamation Act should have prevented such a near disaster. Further, SCMCI was able to effect these dramatic changes in only six years. However, this short time span is perhaps not so surprising considering that a modern heap leaching operation must mine as much as 190 tons of ore and overburden - such as the Newmont gold quarry near Elko, Nevada (Obmascik, 1993) - to extract one single ounce of microscopic gold.

For EPA and Colorado, the Summitville Site is a potential black hole for funding. All of the other mining sites within EPA's Superfund program address a watershed which has already been destroyed by historic mining activities. As a result, there is no expense associated with preventing the destruction of a watershed. For Summitville, EPA has expended approximately $15 million dollars per year for water treatment operations during 1993 - 1994 to prevent any further degradation of the Alamosa watershed. This cost has been decreased to $13 million for the 1995 year based on Removal actions taken during 1993 and 1994.

Questions

But even with the cleanup activities conducted to date and the increased efficiencies related to water treatment, the monetary investment for EPA and Colorado will continue to be enormous. As a result, many of the unanswerable questions are being asked. Is the estimated $120 million too much to clean up Summitville? Are these "few fish" really worth restoring? Why not just write-off the Watershed? Shouldn't we really prioritize our funding for sites which can document human health risk? What guarantee do you have that any of this will work?

For all these questions, there are not currently answers. However, it is interesting to hear communities, regulated industry, and management from EPA and Colorado ask for a guarantee that a cleanup will work before allowing EPA to proceed with a proposed remedy. Generally, this guarantee requires the conduct of additional studies to try to determine the perfect solution to a given problem. With regard to Summitville, each additional day spent studying the problem is another day of having to fund water treatment.

However, it seems that the time to ask many of the questions above is before a mine is permitted. Certainly it is difficult to know if you have successfully restored a mined area if a proper baseline study of soils, ground water, surface water, and revegetation needs has not been conducted. Mining permits require reclamation upon completion of mining activities, however, the permit requestor is not asked to conduct laboratory studies beforehand to "guarantee" that they actually can achieve the promised reclamation.

This has recently been the focus of concern at the Kerr Coal Mine near Walden, Colorado. Kerr has spent $8 million refilling the pits to a "valley configuration." But this reclamation approach is being challenged because it does not return the land to its exact pre-mining conditions (Finley, 1994). Kerr officials estimate that the proposed reshaping will cost an additional $3.5 million to achieve and could put them out of business. Of course once the mining has been completed, it is difficult to require perfect restoration from a private company which lacks the necessary funds to do so. It is impossible if the reclamation requires a technical understanding which does not exist, such as restoring vegetation which supports a wildlife habitat at high elevations.

For particularly challenging sites such as Summitville, it is essential that informed decisions be made upfront. Any studies to support the promised reclamation need to be done before any mining begins. Actual funding for the agreed upon reclamation should be held in escrow, accumulating as the mining progresses, so that funding issues do not compromise the "guaranteed" reclamation. If a particular resource such as coal must be developed to meet national needs, then any potential environmental degradation must be agreed to beforehand and not overlooked because private industry "thinks" it can be minimized. It is here that the regulating entities must decide if those "few fish" are worth saving.

At sites where the mined resource is a luxury commodity - such as gold at Summitville and elsewhere, environmental legislation seems clear that any degradation of human health or the environment is too great. If the necessary studies and guarantees are too costly or technically infeasible, then resource recovery should wait until a better recovery technology becomes available and leave recovery to the future generations of miners.

It is estimated that SCMCI recovered approximately 280,000 ounces of gold. At a November 1993 price of $350 per ounce, this translates into $98 million in gross revenues - $22 million less than EPA's estimated costs for stabilization activities. Had the appropriate studies and guarantees been required before applying for a permit, SCMCI may have convinced themselves and regulators that this was a project which should be avoided.

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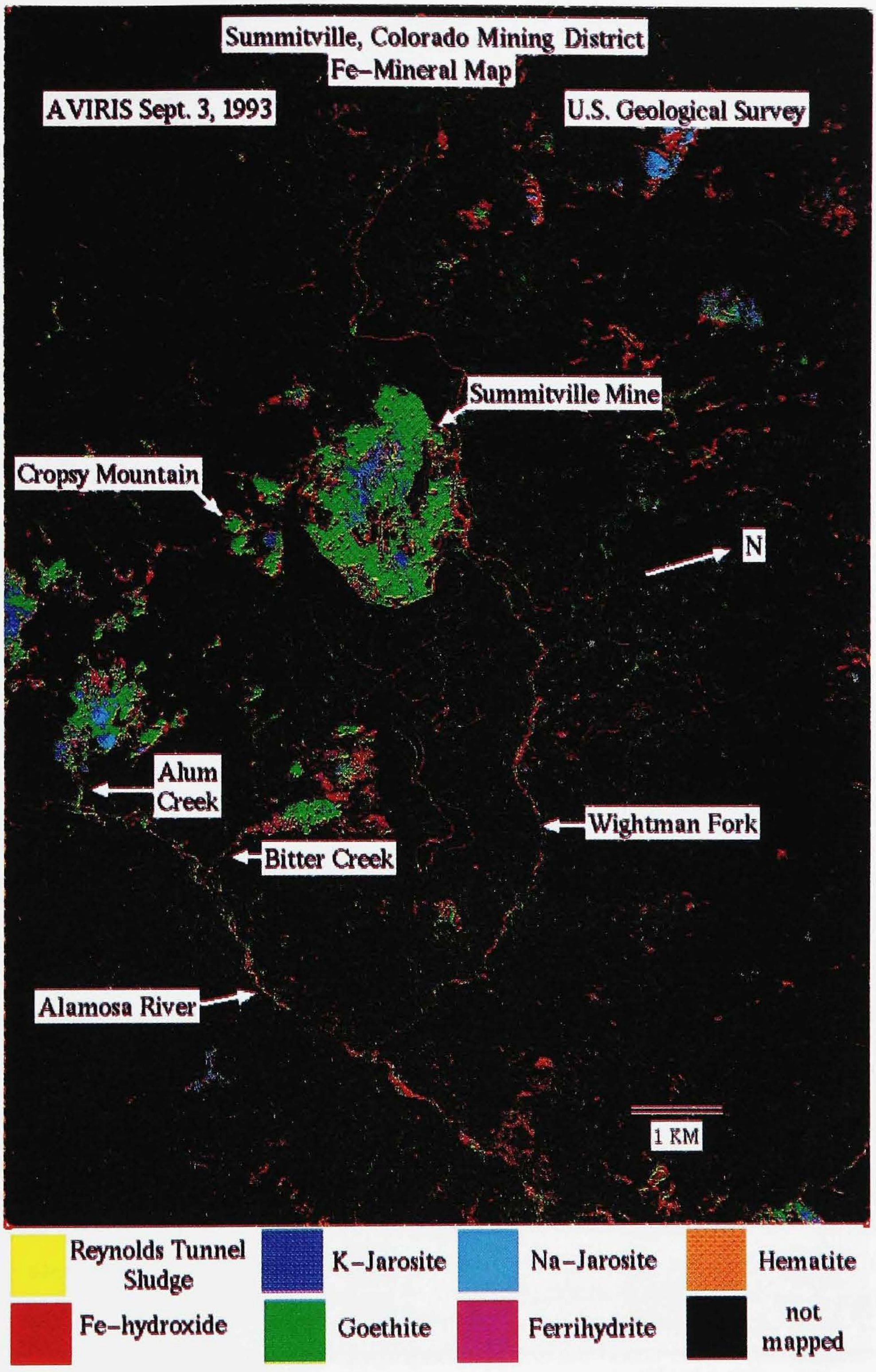


Figure 1. AVIRIS image of the Summitville mine and surrounding area showing the distribution of minerals having Fe-absorption features. The image covers an area from approximately 37° 27' 30"N to 37° 22' 30"N latitude, 106° 30'W to 106° 37'30"W longitude.

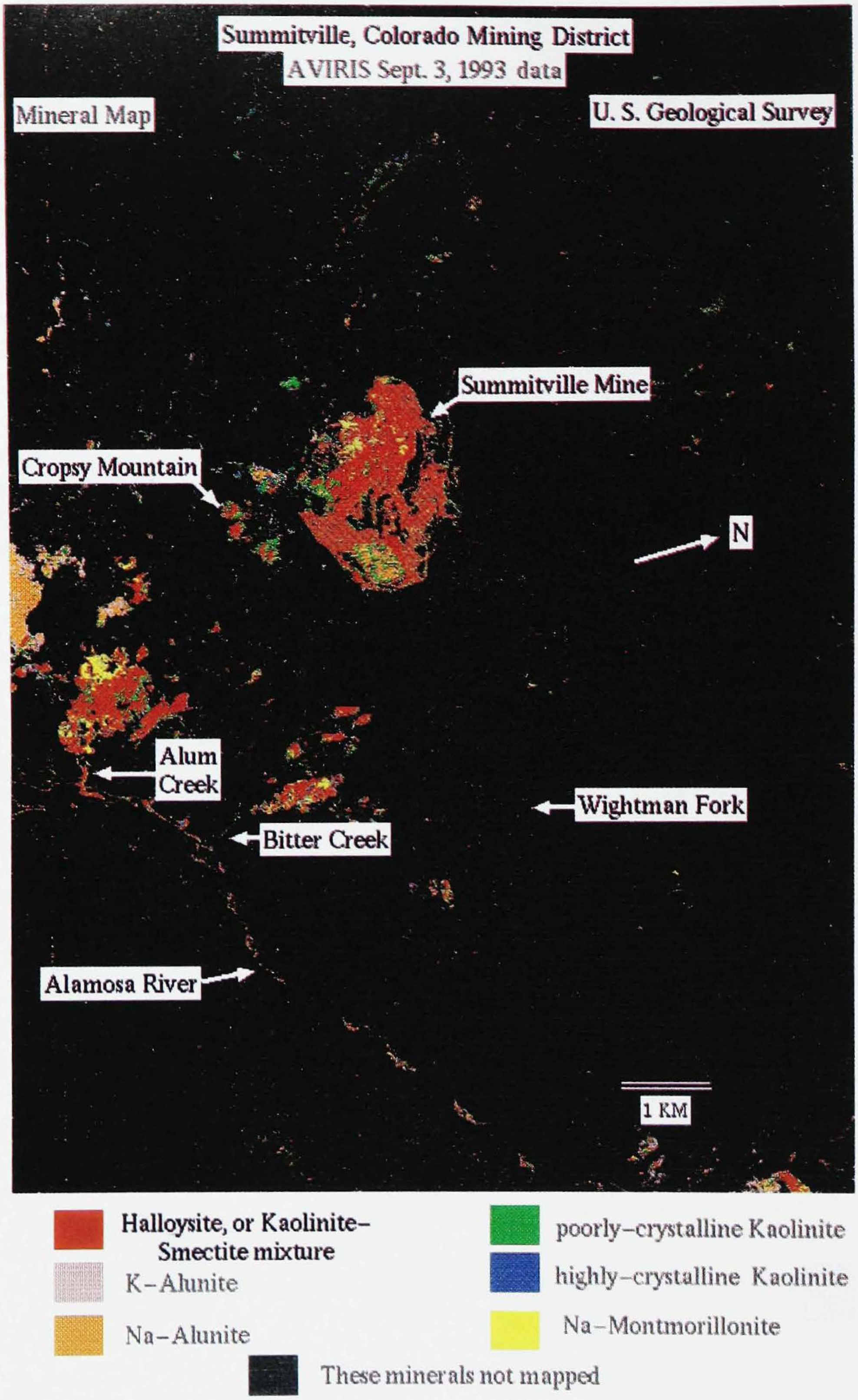


Figure 2 . AVIRIS image of the Summitville mine and surrounding area showing the distribution of minerals having absoprtion features in the 2.0 μm-2.4 μm wavelength region. The image covers an area from approximately 37° 27' 30"N to 37° 22' 30"N latitude, 106° 30'W to 106° 37'30"W longitude.

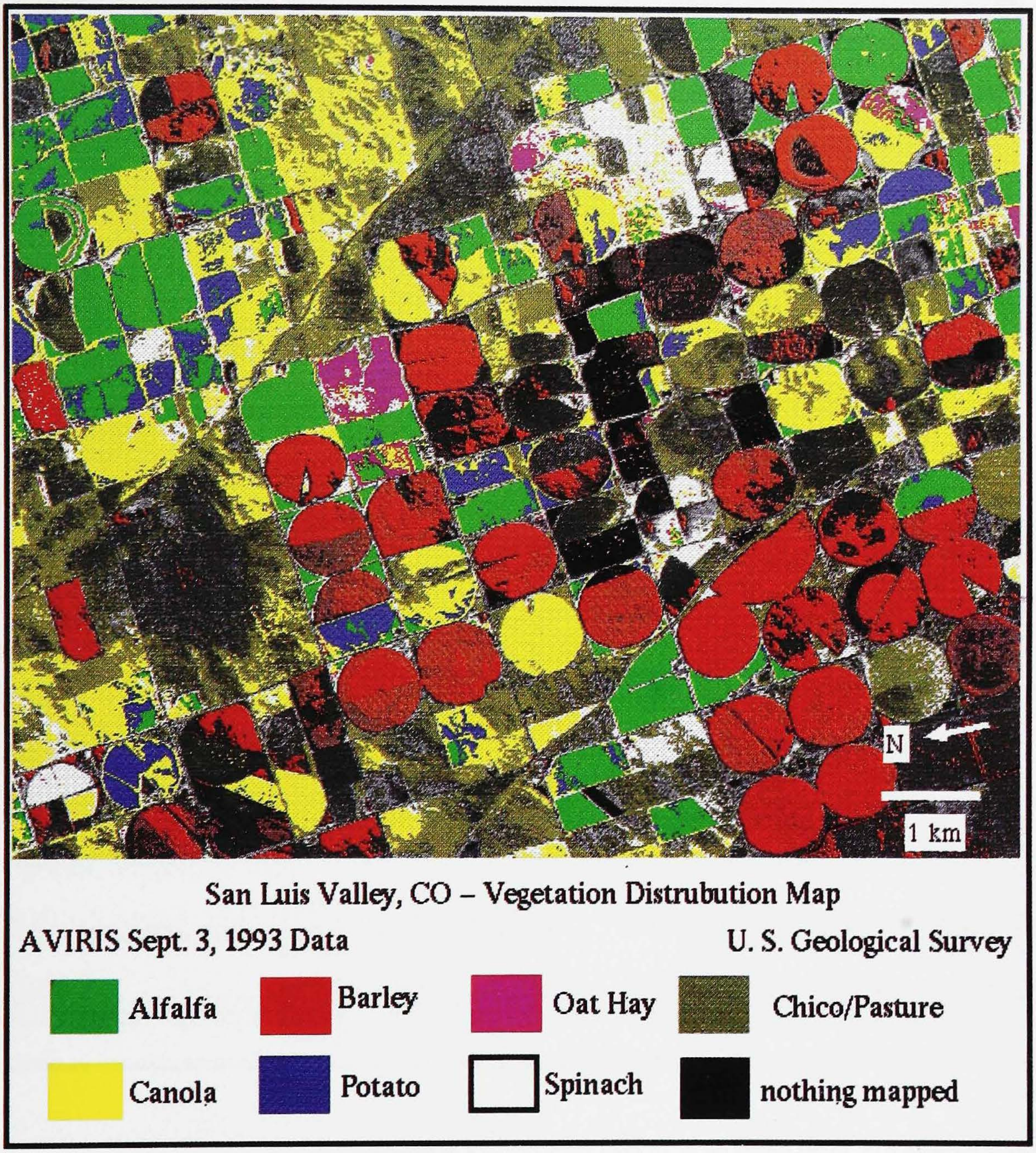


Figure 3. The tricorder analysis of vegetation species. See text.

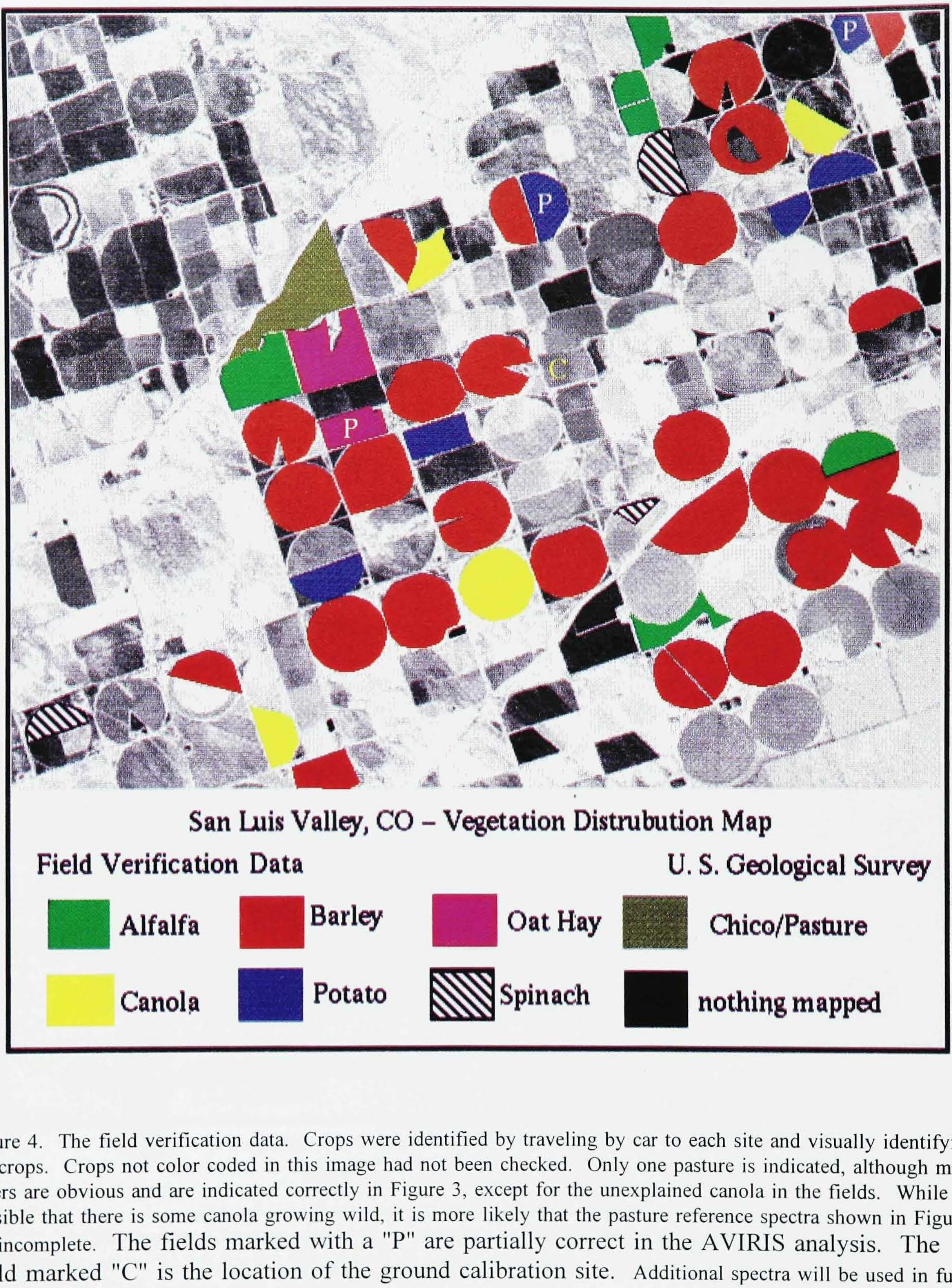


Figure 4. The field verification data. Crops were identified by traveling by car to each site and visually identifying the crops. Crops not color coded in this image had not been checked. Only one pasture is indicated, although many others are obvious and are indicated correctly in Figure 3, except for the unexplained canola in the fields. While it is possible that there is some canola growing wild, it is more likely that the pasture reference spectra shown in Figure 1 are incomplete. The fields marked with a "P" are partially correct in the AVIRIS analysis. The Field marked "C" is the location of the ground calibration site. Additional spectra will be used in future mapping studies.

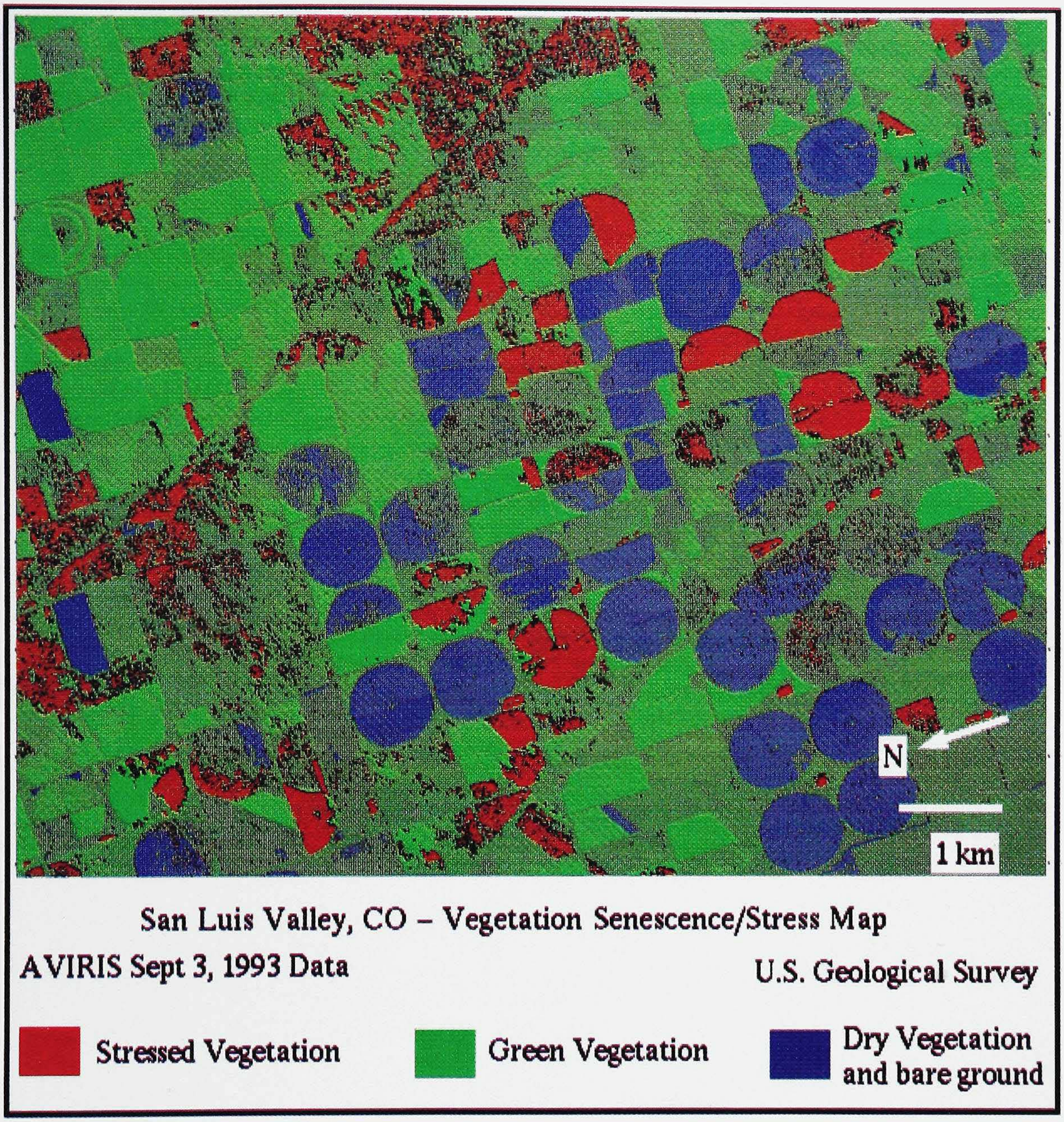
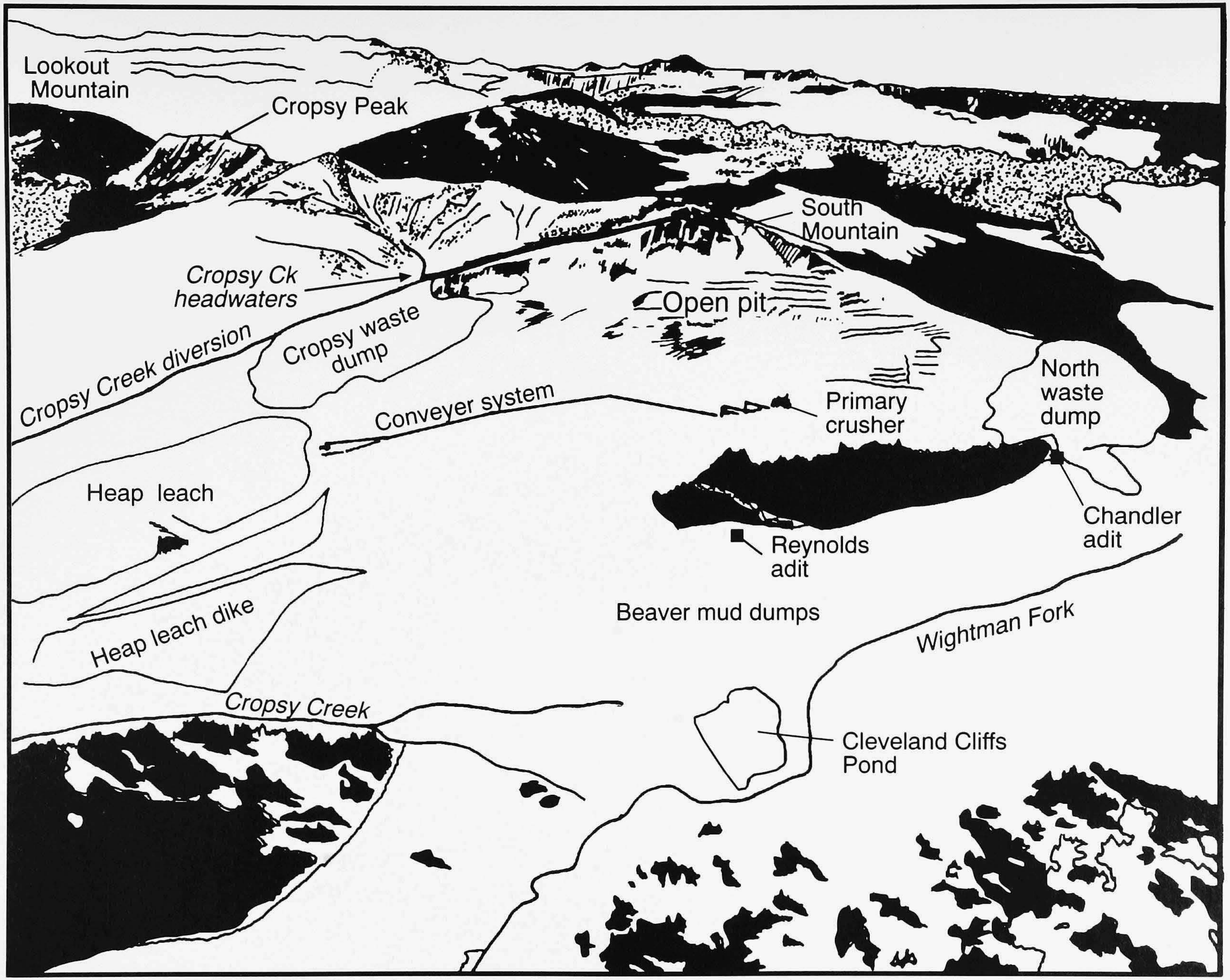


Figure 5. The vegetation senescence/stress anomaly map

Photograph of Summitville region, October 4, 1991 by IntraSearch, Inc.



Line drawing of Summitville region photograph by Richard Walker