



PERGAMON

Applied Geochemistry 15 (2000) 1003–1018

**Applied  
Geochemistry**

www.elsevier.com/locate/apgeochem

# Colloid formation and metal transport through two mixing zones affected by acid mine drainage near Silverton, Colorado

Laurence E. Schemel<sup>a,\*</sup>, Briant A. Kimball<sup>b</sup>, Kenneth E. Bencala<sup>a</sup>

<sup>a</sup>US Geological Survey, Water Resources Division, 345 Middlefield Road, Menlo Park, CA 94025, USA

<sup>b</sup>US Geological Survey, Water Resources Division, 1745 West 1700 South, Salt Lake City, UT 84104, USA

Received 11 March 1999; accepted 17 September 1999

Editorial handling by D.D. Runnells

## Abstract

Stream discharges and concentrations of dissolved and colloidal metals (Al, Ca, Cu, Fe, Mg, Mn, Pb, and Zn), SO<sub>4</sub>, and dissolved silica were measured to identify chemical transformations and determine mass transports through two mixing zones in the Animas River that receive the inflows from Cement and Mineral Creeks. The creeks were the dominant sources of Al, Cu, Fe, and Pb, whereas the upstream Animas River supplied about half of the Zn. With the exception of Fe, which was present in dissolved and colloidal forms, the metals were dissolved in the acidic, high-SO<sub>4</sub> waters of Cement Creek (pH 3.8). Mixing of Cement Creek with the Animas River increased pH to near-neutral values and transformed Al and some additional Fe into colloids which also contained Cu and Pb. Aluminium and Fe colloids had already formed in the mildly acidic conditions in Mineral Creek (pH 6.6) upstream of the confluence with the Animas River. Colloidal Fe continued to form downstream of both mixing zones. The Fe- and Al-rich colloids were important for transport of Cu, Pb, and Zn, which appeared to have sorbed to them. Partitioning of Zn between dissolved and colloidal phases was dependent on pH and colloid concentration. Mass balances showed conservative transports for Ca, Mg, Mn, SO<sub>4</sub>, and dissolved silica through the two mixing zones and small losses (<10%) of colloidal Al, Fe and Zn from the water column. Published by Elsevier Science Ltd.

## 1. Introduction

Oxidation of pyrite (iron sulfide, FeS<sub>2</sub>) and the formation of acidic waters with high Fe and SO<sub>4</sub> concentrations are commonly associated with environments influenced by mineral deposits and debris from mining

and ore processing (e.g., Wentz, 1974). Sulfides of Cu, Mn, Pb, or Zn often are present with pyrite, and oxidation dissolves these metals and can further increase acidity (Rimstidt et al., 1994). Acidic waters produced by this process dissolve minerals containing other metals, such as Al, that are largely insoluble in near-neutral-pH waters. When acidic waters containing dissolved metals flow into streams in which pH is higher, the solubilities of some metal ions, such as Al<sup>3+</sup> and Fe<sup>3+</sup>, are greatly reduced and precipitates form (Stumm and Morgan, 1996). In this type of reactive

\* Corresponding author. Tel.: +1-650-329-4436; fax: +1-650-329-4327.

E-mail address: lschemel@usgs.gov (L.E. Schemel).

confluence, insoluble hydroxides of Al and Fe and similar compounds can form amorphous colloids in the water column and coatings on the stream bed (e.g., Theobald et al., 1963; Chapman et al., 1983; Rampe and Runnells, 1989). Colloidal Al and Fe precipitates and other metals that coprecipitate or adsorb to them, such as Cu, Pb, and Zn, can be transported long distances before they are lost from the water column to the stream bed (Kimball et al., 1995).

Colloidal metals adversely affect habitats and organisms in riverine systems. As colloids aggregate, they fill interstices in the stream bed and reduce the quality of habitat for benthic invertebrates and aquatic plants (e.g., McKnight and Feder, 1984; Malmqvist and Hoffsten, 1999; Niyogi et al. 1999). Colloidal metals accumulated on the stream bed enter the food chain through benthic organisms, which can produce toxic effects when consumed by fish (Woodward et al., 1995; Mayer et al., 1996). In the water column, colloidal Al can be more toxic to fish than the dissolved metal (Witters et al., 1996).

This study examines the transport of dissolved and colloidal metals,  $\text{SO}_4$ , and dissolved silica through two confluences in the upper Animas River system. The upper Animas River drains a caldera near the crest of the San Juan Mountains in SW Colorado. Ring fractures of the caldera are rich in pyrite and in ores that were mined for Au, Ag, Cu, Pb, and Zn for over a century (Varnes, 1963; Luedke and Burbank, 1996; Fetchenier, 1996). The town of Silverton is located

near the southern edge of the caldera where flows from Cement and Mineral Creeks join the Animas River (Fig. 1). These creeks drain areas that contain abundant natural mineral deposits as well as debris left from past mining activities. The last active mine was closed earlier in this decade, and projects to restore the landscape and remediate effects of past mining activities in the river are in progress or being developed. Particular emphasis has been placed on the restoration of habitat for aquatic life in the Animas River (Nimmo et al., 1998; Besser et al., 1998).

Over the last decade the Colorado Department of Public Health and Environment (CDPHE), the US Geological Survey (USGS), and other state and federal agencies have conducted reconnaissance surveys to identify specific areas that contribute to metal loading in the upper Animas River basin. Surveys within the Mineral and Cement Creek drainages have shown significant inputs of metals from many natural and mining-related sources (e.g., Wright and Janik, 1995; Wright, 1997). Evidence of metal loading to the Animas River (ochreous and white deposits on bed and bank materials) is visible at the confluences with Cement and Mineral Creeks and extends at least 60 km downstream from Silverton (Church et al., 1997; Owen, 1997).

Elevations in the study area range from 2800 m at the USGS gaging station on the Animas River below Silverton (AR4) to over 4000 m at the surrounding mountain peaks (Fig. 1). The area typically experiences freezing temperatures and a deep snow pack from late fall to early spring (Keen, 1996). The USGS has measured the flow of the Animas River at and below Silverton and in Cement and Mineral Creeks since October 1991 (Fig. 1). Flow of the Animas River at AR4 for the 1992–1996 water years (October–September) shows large seasonal and interannual variability (USGS 1996; Fig. 2). Spring snowmelt produces maximum flow usually in June, followed by decreasing flow into late summer and fall. Variations in river flow in late summer are typically small and usually related to thunderstorms or weak storm fronts. Mean flow for the 1996 water year ( $6.91 \text{ m}^3/\text{s}$ ), when this study was conducted, was less than the 5-a mean ( $8.18 \text{ m}^3/\text{s}$ ), and the spring peak in flow occurred earlier than in most of the previous years.

The unpublished data base compiled by CDPHE over the last decade and recent work by Church et al. (1997) shows some general relations between metal concentrations and flow in the Animas River below Silverton. Concentrations of many dissolved metals and  $\text{SO}_4$  are highest when flow is low during late summer and early fall. However, high flows associated with snowmelt mobilize colloidal metals and can greatly increase their concentrations. Consequently, total transports of Al, Fe, Zn, Cu, and Pb are highest

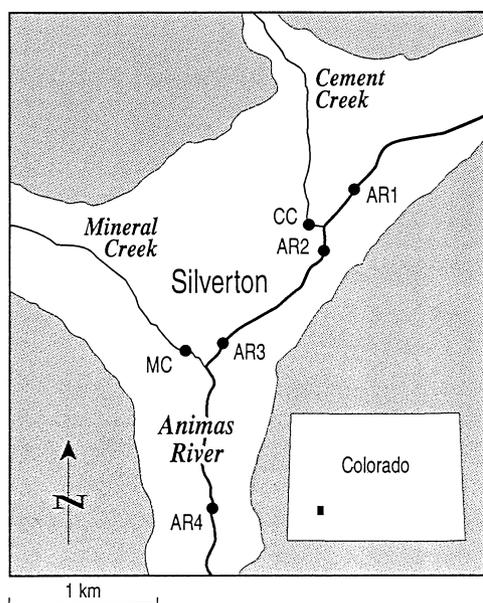


Fig. 1. Locations of sampling sites on Cement and Mineral Creeks and the Animas River near Silverton, Colorado. Site numbers increase downstream in the Animas River.

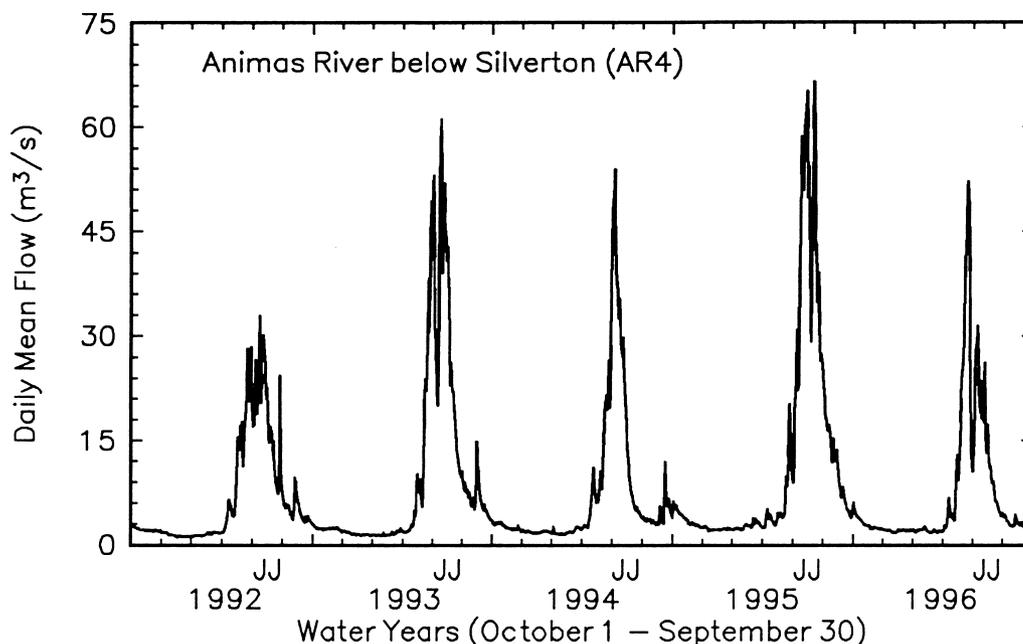


Fig. 2. Daily mean flow ( $\text{m}^3/\text{s}$ ) at the Animas River below Silverton (AR4) gage: 1992–1996 water years. Months of June and July are shown by JJ.

during the high-flow period primarily because of the additional transport of colloidal metals that had been temporarily stored in the streambed over the preceding months of low flow (Church et al., 1997). The study presented here was conducted in September 1996 at low flow so that concentrations of metals were not diluted by snowmelt or influenced by resuspension from the bed. This allowed identification of the processes that form colloids in this reach of the Animas River and facilitated quantitative sampling of the streams to determine mass transports.

## 2. Methodology

Streamflows were measured and water samples were collected at sites in the Animas River (AR1-4), Mineral

Creek (MC), and Cement Creek (CC) during September 1996 (Fig. 1, Table 1). The stream length between AR2 and AR4 is approx. 2.5 km. The AR1, AR4 and MC sites were within 50 m of the USGS gages, whereas the CC site was approximately 1 km downstream from the USGS gage. Fifteen-minute-interval instantaneous values for flow were obtained from the USGS gages to supplement streamflows measured at the six sampling sites.

The distribution of streamflow across a lateral transect was measured at each site so that equal-discharge-increment (EDI) stations could be established (Edwards and Glysson, 1988). Samples collected at each EDI-station were vertically integrated through the water column in order to obtain average concentrations for the segment. The number of EDI stations at each site is shown in Table 1. Samples from the EDI stations in the Animas River upstream of Cement

Table 1  
Measured and USGS-gaged flows ( $Q$ ) in  $\text{m}^3/\text{s}$  during setup of the equal-discharge-increment (EDI) stations, 17–21 September 1996

SITE: SITE CODE (# Stations)	Measured $Q$	Gaged $Q$	Date	Time
Animas River at: AR1 (3)	1.78	1.84	17 September	16:00
Cement Creek: CC (2)	0.48	0.51	18 September	12:45
Animas below CC-I: AR2 (5)	2.27	2.35	18 September	11:30
Animas below CC-II: AR3 (3)	1.98	2.04	19 September	09:20
Mineral Creek: MC (2)	1.64	1.76	19 September	10:15
Animas River below: AR4 (3)	4.16	4.16	21 September	10:30

Creek (AR1) and in Cement Creek (CC) were combined to produce a composite sample for each of these two sites. Both individual EDI samples and composite samples were processed at the other four sites. The polyethylene sample bottles were wrapped in black plastic to exclude light, then transported to the field laboratory for processing within a few hours.

Samples were shaken vigorously before processing in the laboratory. Two unfiltered 125 ml aliquots (total samples) were decanted from each sample carboy. One was acidified with HNO<sub>3</sub> and used for measurements of total metals. Specific conductance and pH were measured on the other aliquot. Each EDI-station sample was filtered through a tangential-flow filtration apparatus (Minitan-S, Millipore Corp.<sup>1</sup>) to provide 0.45 µm and 10k Dalton filtrates. Most of the composite samples were filtered through 0.45 µm filters, then the remaining sample was stored for up to 2 days before the colloids were concentrated using a Pellicon ultrafiltration apparatus (Millipore Corp.) with 10 K Dalton filters. Storage of some samples increased the colloid contents because of oxidation of dissolved Fe. In some cases, a second composite sample (-C2) was processed in the same manner as the EDI samples.

All filtrates and particle concentrates for metal analysis were acidified with HNO<sub>3</sub> (1% final concentration), then allowed to digest for at least 60 days. An unacidified 0.45 µm-filtered sample was collected for analysis of SO<sub>4</sub> by ion chromatography.

Samples for total metals and acidified aliquots of concentrated colloids were pressure filtered before analysis through 0.45 µm capsule filters (Millex-HV SLHV025LS, Millipore Corp.) that had been pre-cleaned with dilute HNO<sub>3</sub> and pre-rinsed with sample. Samples with specific conductance values exceeding about 250 µS/cm were diluted, and others were diluted to bring metal concentrations into the optimum range for analysis. Dilution limited detection of Cu and Pb at some sites.

Concentrations of Al, Ca, Cu, Fe, Mg, Mn, Pb, silicon (referred to here as dissolved silica), and Zn were determined by inductively coupled Ar plasma atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell Ash ICAP 61. Results presented here are mean values for two or more measurements made during different analytical runs. Precision was estimated from a quality control solution measured at least twice during each run. Values were within ±4% of the mean value from all the runs for all analytes.

Samples from both Creeks and the Animas River were examined with a Brookhaven laser-scattering

instrument to estimate particle sizes (J.F. Ranville, Colorado School of Mines, Golden, CO, written communication). Mean particle sizes for all of the samples were less than 0.6 µm, which is within the colloidal size range (Buffle and Leppard, 1995). Colloid concentrations were calculated by subtracting the ultrafiltrate (10 K Dalton) value from the total concentration.

### 3. Results

During the period when water samples were collected in this study (18–21 September 1996; Table 2), flow of the Animas River at AR1 averaged 44% of the flow at AR4, and inflows from Cement and Mineral Creeks averaged 13 and 43% of the flow at AR4, respectively. Fifteen-minute-interval flow data showed that there was good agreement between the total of these three major inflows and flow measured at the gage below Silverton during the 4 days (Fig. 3). The largest variations in flow occurred during the first two days, when a light snow storm passed through the area. Gaged flows and flows measured at the sites when the EDI stations were established agreed within a few percentage points (Table 1).

Specific conductance and pH measurements showed significant differences between the Cement Creek and Mineral Creek confluences. Specific conductance (normalized to 25°C) was 260 µS/cm in the Animas River above Cement Creek (AR1; Table 3). Specific conductance in Cement Creek (CC) was 940 µS/cm, and this inflow increased values downstream in the Animas River to 420 µS/cm at AR3. Inflow from Mineral Creek (MC; 330µS/cm) reduced specific conductance to 380 µS/cm downstream of the confluence at AR4. The pH at AR1 was 7.5 (Table 3). Inflow from Cement Creek, which was pH 3.8, decreased pH at AR3 to 6.9–7.0. Mineral Creek inflow was mildly acidic

Table 2  
Flows (Q) in m<sup>3</sup>/s during collection of samples from the Animas River, Cement Creek, and Mineral Creek, 18–21 September 1996

Site	Code	Date	Time	Q
Animas River	AR1	18 September	09:30	1.78
Animas below CC-I	AR2	18 September	11:30	2.27
Cement Creek	CC	18 September	13:00	0.48
Animas below CC-II	AR3	19 September	10:00	1.98
Animas below CC-II-C2	AR3-C2	21 September	08:30	2.32
Mineral Creek	MC	19 September	11:00	1.64
Mineral Creek-C2	MC-C2	21 September	09:30	1.73
Animas below MC	AR4	21 September	11:30	4.16

<sup>1</sup> Any use of trade, product, or firm names is for descriptive purposes only and does not constitute endorsement by the US Government.

(pH 6.6), and values downstream at AR4 were only slightly lower than those at AR3.

### 3.1. Concentrations of metals

Six metals with concentrations within the optimum analytical ranges for ICP-AES, Al, Ca, Fe, Mg, Mn, and Zn, were selected for the descriptions of concentrations and mass-transport given here. Calcium had the highest concentration among the metals in the river and in the Creeks, with concentrations that were generally an order of magnitude higher than Mg, the metal with the second highest concentrations (Table 3). Comparisons of analytical results from total and filtered samples showed that Al, Fe, and Zn were present in both dissolved and colloidal forms (Fig. 4), whereas Ca, Mg, and Mn were dissolved in the river and both creeks (Table 3). Differences in concentrations between total and filtered samples for Ca, Mg, and Mn were not significant relative to the analytical precision (approx.  $\pm 4\%$ ).

Concentrations of Ca, Mg, and Mn in Cement Creek were about a factor of 3–4 higher than concentrations upstream at AR1 (Table 3). Concentrations of

Mg in Mineral Creek were similar to those at AR3, but lower concentrations of Ca and Mn in Mineral Creek reduced concentrations of these metals at AR4.

Concentrations of Zn in Cement Creek were about twice those at AR1, but concentrations in Mineral Creek were less than those at AR3 (Fig. 4, Table 3). Although variable, most of the Zn was dissolved in both creeks and in the river, as shown by concentrations in the ultrafiltrates that were typically greater than 85% of the total concentrations.

Total concentrations of Al and Fe were very low at AR1 relative to Cement Creek, where they were more concentrated by factors of about 80 and 60, respectively (Fig. 4, Table 3). Consequently, concentrations of Al and Fe were greatly increased downstream in the Animas River, even though the flow from Cement Creek was much less than that at AR1. In the acidic environment of Cement Creek, nearly all of the Al was dissolved, and about half of the Fe was dissolved. At AR2, gradients in concentrations across the channel indicated incomplete mixing of Cement Creek water in the river; however, colloids accounted for most of the Al and a large fraction of the Fe. Farther downstream at AR3, nearly all of the Al and three-quarters of the

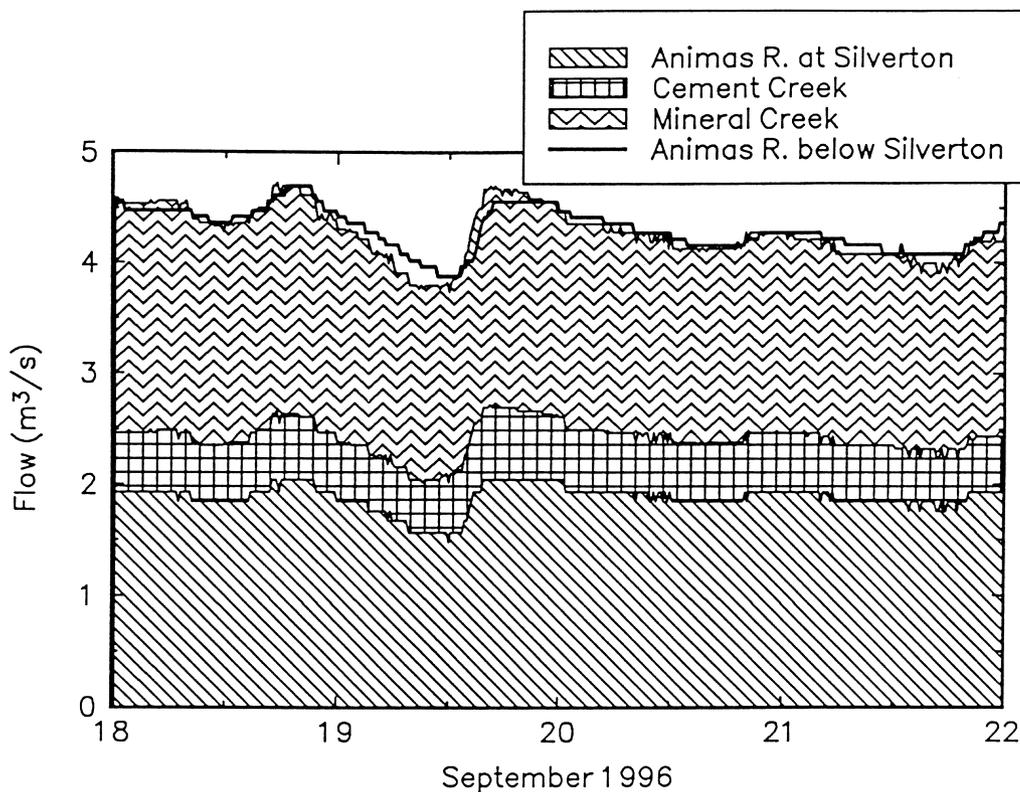


Fig. 3. Total of flows ( $\text{m}^3/\text{s}$ ) at the Animas River at Silverton and Cement and Mineral Creek gages compared to flow at the Animas River below Silverton gage: 18–21 September 1996.

Table 3  
Analytical results for samples collected in the Animas River (AR), Cement Creek (CC), and Mineral Creek (MC)<sup>a</sup>

Sample	Zn	Al	Fe	Mn	Ca	Mg	SpC	pH	Q m <sup>3</sup> /s
18 September 1996									
T AR1-C	6.3	2.4	2.2	13	1080	106	260	7.54	1.78
F AR1-C	6.0	1.5	0.7	13	1070	108	260	7.54	1.78
X AR1-C	5.6	1.3	0.0	12	1020	103	260	7.54	1.78
T CC-C	12	197	135	40	4020	351	940	3.84	0.48
F CC-C	12	193	85	40	4030	351	940	3.84	0.48
X CC-C	12	192	(71)	40	3970	345	940	3.84	0.48
T AR2-1	8.4	83	60	24	2320	214	530	6.20	0.43
F AR2-1	8.3	10	32	24	2290	211	530	6.20	0.43
U AR2-1	(8.1)	8.3	30	24	2310	215	530	6.20	0.43
T AR2-2	7.9	62	44	21	2000	190	470	6.58	0.43
F AR2-2	7.6	2.3	21	22	2030	190	470	6.58	0.43
U AR2-2	7.5	2.6	18	21	2010	191	470	6.58	0.43
T AR2-3	7.5	50	35	20	1820	173	430	6.81	0.43
F AR2-3	7.1	1.0	9.4	20	1870	179	430	6.81	0.43
U AR2-3	6.9	1.1	8.1	20	1850	177	430	6.81	0.43
T AR2-4	7.2	29	21	17	1520	147	360	7.11	0.48
F AR2-4	6.3	1.2	2.0	16	1500	145	360	7.11	0.48
U AR2-4	6.1	0.3	1.5	17	1550	149	360	7.11	0.48
T AR2-5	6.2	6.2	4.7	13	1170	117	280	7.54	0.48
F AR2-5	5.6	1.4	0.1	13	1150	116	280	7.54	0.48
U AR2-5	4.8	2.0	0.1	12	1150	115	280	7.54	0.48
19 September 1996									
T AR3-1	8.6	47	38	19	1740	166	420	6.92	0.65
F AR3-1	8.0	2.0	11.0	20	1780	170	420	6.92	0.65
U AR3-1	7.6	2.1	8.3	20	1780	169	420	6.92	0.65
T AR3-2	8.7	47	37	20	1770	168	420	6.96	0.65
F AR3-2	7.9	1.2	11	19	1740	165	420	6.96	0.65
U AR3-2	7.6	0.4	8.4	19	1730	166	420	6.96	0.65
T AR3-3	8.3	45	36	19	1730	165	420	6.89	0.65
F AR3-3	7.7	2.2	8.7	19	1750	167	420	6.89	0.65
U AR3-3	7.4	2.2	6.4	19	1740	166	420	6.89	0.65
T MC-1	3.4	73	59	4.9	1220	167	330	6.60	0.82
F MC-1	3.1	0.7	28	4.8	1210	166	330	6.60	0.82
U MC-1	3.1	0.2	24	4.9	1230	169	330	6.60	0.82
T MC-2	3.3	69	56	4.8	1220	168	330	6.60	0.82
F MC-2	3.1	0.0	25	4.8	1210	167	330	6.60	0.82
U MC-2	3.0	0.4	22	4.9	1230	169	330	6.60	0.82
21 September 1996									
T MC-C2	4.0	72	49	5.1	1230	170	330	6.53	1.73
F MC-C2	3.8	1.5	23	5.0	1220	171	330	6.53	1.73
U MC-C2	3.7	1.2	19	4.9	1200	167	330	6.53	1.73

Table 3 (continued)

Sample	Zn	Al	Fe	Mn	Ca	Mg	SpC	pH	$Q$ m <sup>3</sup> /s
T AR3-C2	7.4	41	29	18	1670	152	400	6.97	2.32
F AR3-C2	6.9	2.6	14	17	1610	153	400	6.97	2.32
U AR3-C2	5.4	1.1	2.3	17	1570	149	400	6.97	2.32
T AR4-1	5.9	52	35	12	1470	164	380	6.86	1.39
F AR4-1	5.5	0.6	13	12	1490	164	380	6.86	1.39
U AR4-1	5.2	1.2	11	12	1450	163	380	6.86	1.39
T AR4-2	5.8	48	33	12	1440	160	380	6.83	1.39
F AR4-2	5.4	1.0	13	12	1440	159	380	6.83	1.39
U AR4-2	5.3	0.0	11	12	1430	160	380	6.83	1.39
T AR4-3	5.9	49	34	12	1460	161	380	6.96	1.39
F AR4-3	5.3	1.2	9.9	12	1450	158	380	6.96	1.39
U AR4-3	5.1	1.6	8.1	11	1420	159	380	6.96	1.39

<sup>a</sup> Concentrations of metals are micromolar. Specific Conductance (SpC) is  $\mu\text{S}/\text{cm}$  at 25°C. Flow ( $Q$  m<sup>3</sup>/s) is cubic meters per second. The T prefix is for total, unfiltered samples. The F prefix is for 0.45  $\mu\text{m}$  filtrates. The U prefix is for 10k Dalton filtrates from the Minitan system. The X prefix is for 10k Dalton filtrates from the Pellicon system. The -C suffix is for composites of EDI stations. The number suffix is the EDI station number. The two values in parentheses are estimates from other samples.

Fe was colloidal. Concentrations of Al and Fe in Mineral Creek were much lower than the values in Cement Creek, but higher than at AR3. In the slightly acidic environment of Mineral Creek, nearly all of the Al was transported as colloids, and more than half of the Fe was colloidal (Table 3). Downstream at AR4, about two-thirds of the Fe was colloidal, but nearly all of the Al was colloidal.

Effects of mixing and in-stream chemical processes that are evident in the chemical data presented above were visible on the banks and beds of the streams. Iron precipitates coated the bed rocks in both Cement and Mineral Creeks, and white particles from precipitation of Al also had settled in shallow pools in Mineral Creek. Cobbles in the stream bed of the Animas River above the confluence with Cement Creek were not coated with Fe and no Al precipitate was evident. However, the river bed where Cement Creek water mixed with the Animas River (AR2) was coated with white precipitate and the opalescence of the water was visible evidence of the formation of colloids. Farther downstream, ochreous coatings on the stream bed and banks indicated precipitation of Fe. These coatings extended downstream beyond the reach sampled in this study.

Chemical transformations were most evident near AR2, where Cement Creek mixed with the Animas River. Measurements from EDI samples collected across the channel in the mixing zone (AR2) showed the large influence of Cement Creek, with lowest pH values and highest specific conductance values at AR2-1, and values similar to those in the Animas River upstream of the confluence at AR2-5 (Table 3). Similar

cross-channel gradients were seen in the concentrations of metals (Fig. 4). Mass balance calculations from the EDI stations showed that dissolved Al was reduced by over 90%, and that dissolved Fe was lowered to 33% of the total Fe. Similar calculations indicated a small loss of dissolved Zn (<5%), that was mostly due to the low concentration in the ultrafiltrate at AR2-5.

Details of the chemical processes at AR2 were verified by mixing grab samples from Cement Creek and the Animas River (AR1) in varying proportions in the laboratory (Fig. 5). On the mixing diagrams, conservative mixing of a dissolved or colloidal chemical species would result in a linear change between concentrations in the Animas River and Cement Creek (see conservative mixing lines for dissolved Al and colloidal Fe). Aluminium exhibited very large deviations from conservative mixing, whereas deviations for Fe were much smaller. Nearly all of the Al and 59% of the Fe was dissolved in Cement Creek (pH 3.8). The 18% Animas River mixture increased pH to 4.6, resulting in increases in colloids and decreases in dissolved Al and Fe relative to the conservative mixing lines. Precipitation of dissolved Al continued with increasing fractions of Animas River water to 78%, where all the Al was colloidal at pH 6.5 (note that the colloidal Al value lies on the dissolved Al mixing line). However, most of the colloidal Fe had formed by pH 5.3 (37% Animas River water, which was equivalent to 17% of the Fe dissolved in Cement Creek). This is comparable to, but less than, the transformation of an estimated 28% of dissolved Fe indicated by the field data. A mixing diagram for Zn showed conservative mixing for dissolved and colloidal Zn.

### 3.2. Mass transport for metals

Mass transport for the 6 metals were calculated from total concentrations and flow data (Table 4). Transport for dissolved and colloidal forms of Al, Fe, and Zn are shown graphically in Fig. 6. Precision of these estimates was on the order of 5–10% because of

uncertainties in both the analytical measurements and the flow data. Cement Creek and the Animas River each contributed about half of the Mn, Ca, and Mg to their confluence. The Animas River was a larger contributor of Zn, accounting for 66% of the total. As indicated by the concentration data, Cement Creek was the major source of Al (96%) and Fe (94%). In

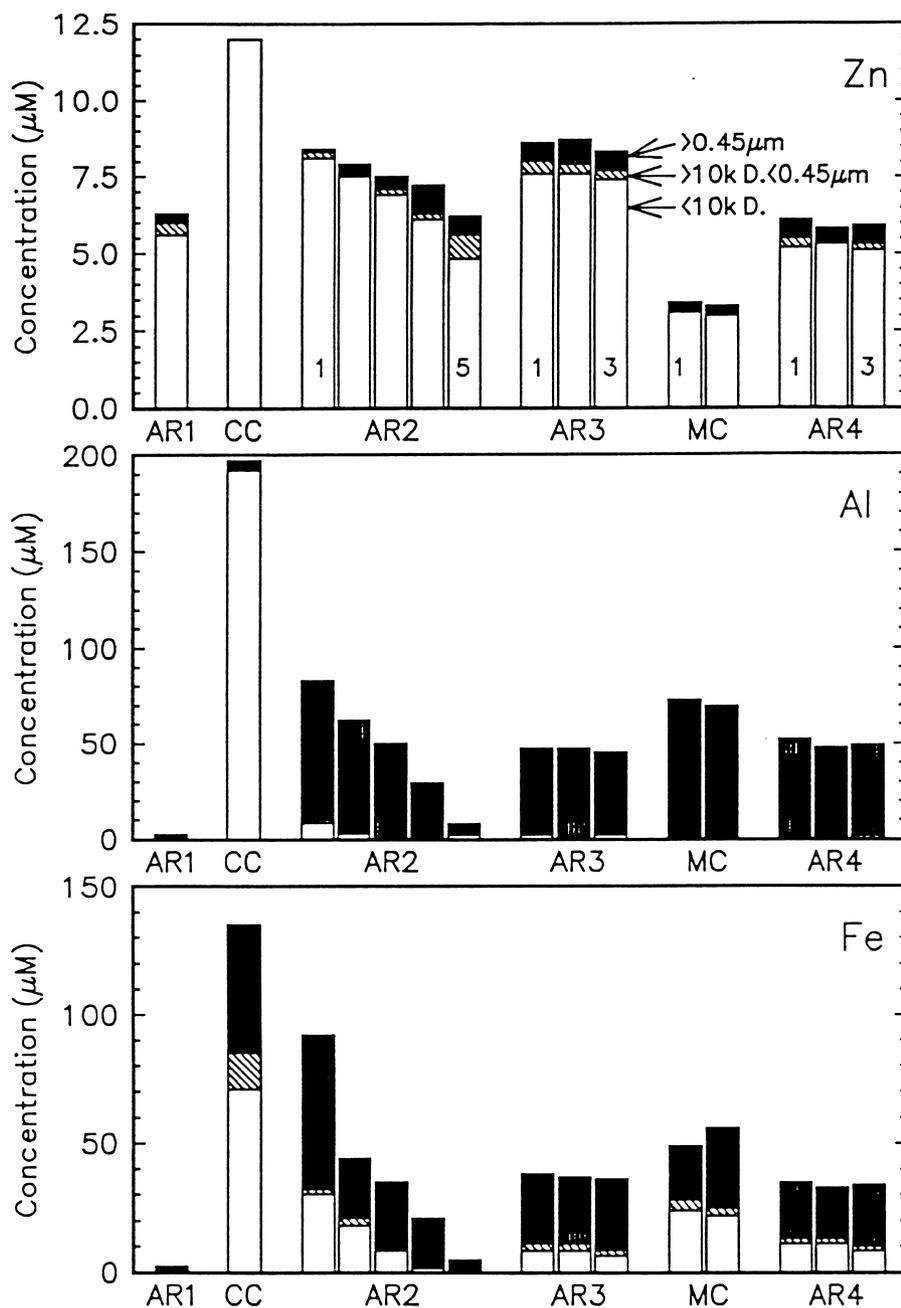


Fig. 4. Concentrations ( $\mu\text{M}$ ) of dissolved (<10k Dalton) and colloidal Zn, Al and Fe for EDI stations at sites on Cement and Mineral Creeks and the Animas River. Site locations are shown in Fig. 1.

the mixing zone below Cement Creek (AR2) total transport of the dissolved metals (Ca, Mn, and Mg) and those present in both dissolved and colloidal forms (Al, Fe, and Zn) agreed within 4% with totals of the inputs from the Animas River and Cement Creek.

Transport at AR3 was measured 3 days later under

similar flow conditions to those when AR2 was sampled (Table 2). The transport values for AR3 were within 5% of the values for AR2. The small losses of Al and Fe were within the estimated errors.

Mass-transport calculations for the confluence with Mineral Creek showed that this creek was a substantial source of metals to the Animas River (Table 4), even

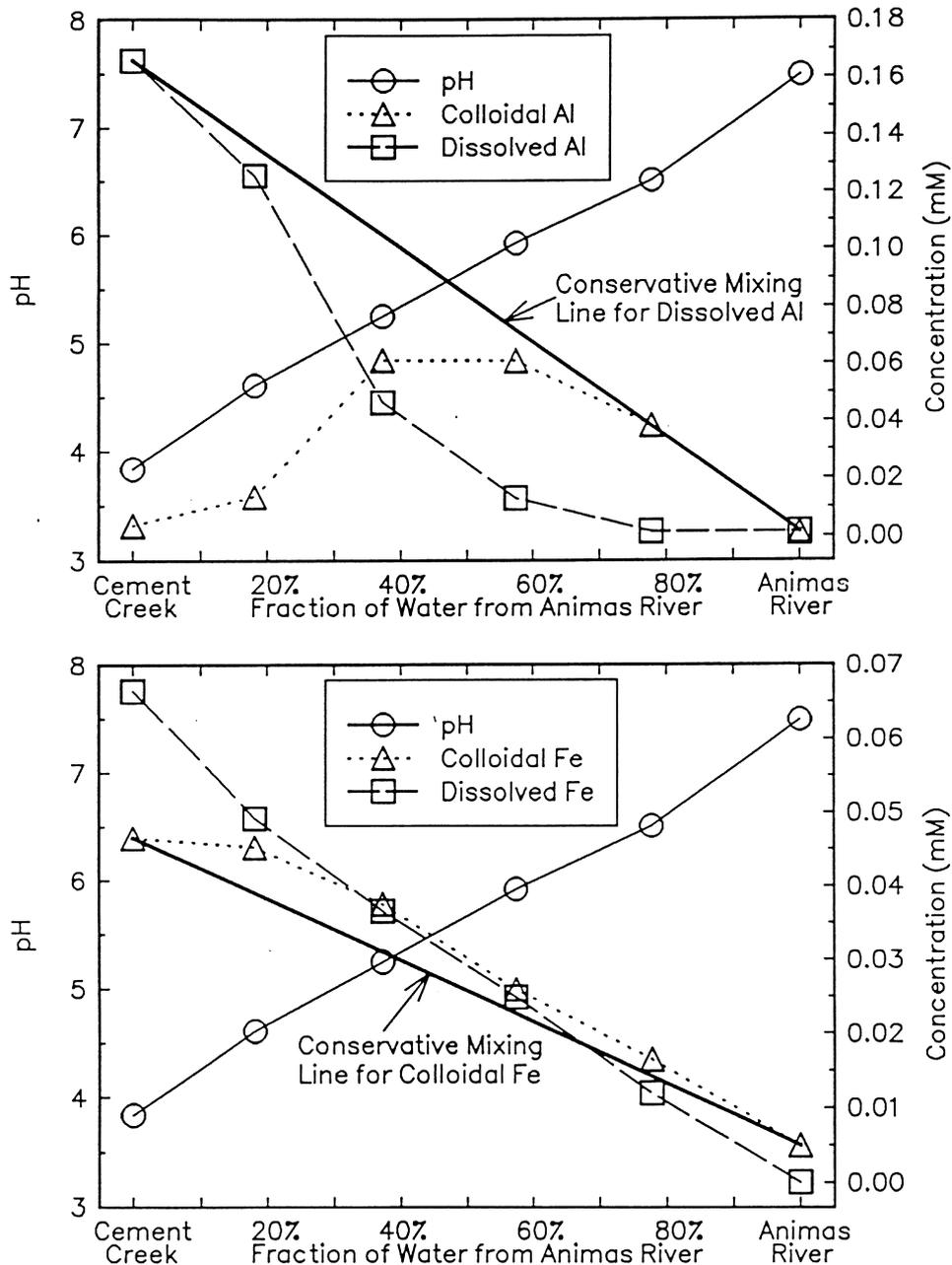


Fig. 5. Diagrams showing pH and concentrations (mM) of dissolved and colloidal Al and Fe from a mixing experiment using water from Cement Creek and the Animas River (AR1).

though it did not greatly change the pH or specific conductance in the river (Table 3). Inflow from Mineral Creek more than doubled transport of total Al and Fe in the Animas River (Fig. 6). The transport of Mg also was nearly doubled, but Mineral Creek accounted for only one-third or less of the total transport of Zn, Ca, and Mn at AR4.

Mass transport for Ca, Mg, Mn, and Zn at AR4 were within 4% of the sum of the transport from AR3 and MC (Table 4). However, transport of total Al and Fe at AR4 showed greater differences. Colloidal Zn, Al, and Fe showed losses of 13, 28 and 68 kg/d, respectively. An equivalent increase in dissolved Zn resulted in no net loss of total Zn (Fig. 6). Small increases in dissolved concentrations also resulted in smaller net losses for Al (29 kg/d) and Fe (55 kg/d), which were equivalent to only 6% and 9% of the colloidal transport, respectively.

Colloidal metals were directly measured in concentrates prepared by de-watering composite samples with the Pellicon filtration system. Aluminium, Fe, and Zn were significantly enriched in the concentrates at all sites except Cement Creek, where Fe was the only metal that was enriched. Calcium, Mg and Mn were not significantly enriched at any of the sites.

With the exception of Cu in Cement Creek (0.6  $\mu\text{M}$ ), ambient concentrations of Cu and Pb were low, <0.2 and <0.08  $\mu\text{M}$ , respectively, and the analytical results often could not be distinguished from values for blanks. However, the concentrates from Mineral Creek and the Animas River sites did show higher values for Cu and Pb. Values from the concentrates were used to calculate ambient concentrations and mass transport of colloidal Cu and Pb (Table 5). Increases in colloidal Cu and Pb between AR1 and AR2 indicate that these metals, which were not associated with colloids in Cement Creek, sorbed to or coprecipitated with colloidal Al and Fe. The dissolved Cu concentration in

Table 4  
Mass transport of metals (kg/day) from total (T) concentrations and flows shown in Table 3

Site-sample	Zn	Al	Fe	Mn	Ca	Mg
18 September 1996						
AR1-C	64	10	19	110	6670	397
CC-C	33	221	314	91	6700	355
Total inputs	97	231	333	201	13370	752
AR2-EDI	94	232	345	199	13500	782
21 September 1996						
AR3-C2	97	222	331	198	13400	742
MC-C2	39	290	409	42	7350	617
Total inputs	136	512	740	240	20750	1360
AR4-EDI	138	483	685	236	21000	1410

Table 5  
Concentrations ( $\mu\text{M}$ ) and mass transports (kg/day) of colloidal Cu and Pb

Site-sample	Cu		Pb	
	( $\mu\text{M}$ )	(kg/d)	( $\mu\text{M}$ )	(kg/d)
18 September 1996				
AR1-C	0.04	0.4	0.013	0.4
AR2-C	0.14	1.7	0.035	1.4
19 September 1996				
AR3-C	0.17	1.8	0.035	1.2
MC-C	0.36	3.2	0.038	1.1
21 September 1996				
AR4-C	0.24	5.4	0.032	2.4

Cement Creek was equivalent to a transport of 1.7 kg/d, which is comparable to the apparent increase of 1.3 kg/d in colloidal Cu shown in Table 5. A Pb concentration of 0.1  $\mu\text{M}$  in Cement Creek would produce the increase in Pb transport that was observed at AR2. Both Cu and Pb were supplied by Mineral Creek in colloidal form. Cement Creek and Mineral Creek supplied similar amounts of Pb, but Mineral Creek was the largest source of Cu (about 60% of the total transport at AR4). Inputs from the upper Animas River (AR1) were much lower than those from the Creeks for both metals.

### 3.3. Sulfate and dissolved silica

Concentrations and mass transport for  $\text{SO}_4$  and dissolved silica are summarized in Table 6. In general, concentrations of  $\text{SO}_4$  were similar to or exceeded those for Ca, the most abundant cation, and were

Table 6  
Concentrations ( $\mu\text{M}$ ) and mass transports (kg/day) of  $\text{SO}_4$  and dissolved silica (as Si)

Site-sample	Sulfate		Dis. silica	
	( $\mu\text{M}$ )	(kg/d)	( $\mu\text{M}$ )	(kg/d)
18 September 1996				
AR1-C	860	12700	114	493
CC-C	4680	18700	456	531
Total inputs		31400		1024
AR2-EDI	1920	31100	190	1047
21 September 1996				
AR3-C2	1800	34600	172	969
MC-C2	1410	20200	182	764
Total inputs		54800		1733
AR4-EDI	1670	57500	179	1808

about an order of magnitude greater than concentrations of dissolved silica. The concentration of  $\text{SO}_4$  in Cement Creek was a factor of 5 times greater than that in the upstream Animas River. Sulfate concentrations in Mineral Creek were only one third the value in Cement Creek and were lower than that at AR3. The concentration of dissolved silica in Cement

Creek was about 4 times higher than that at AR1 and about twice those at the other sites, including Mineral Creek.

Sulfate and dissolved silica transports within the mixing zone downstream of Cement Creek (AR2) were very close to the sum of the upstream Animas River and Cement Creek transports (Table 6). Similarly, at

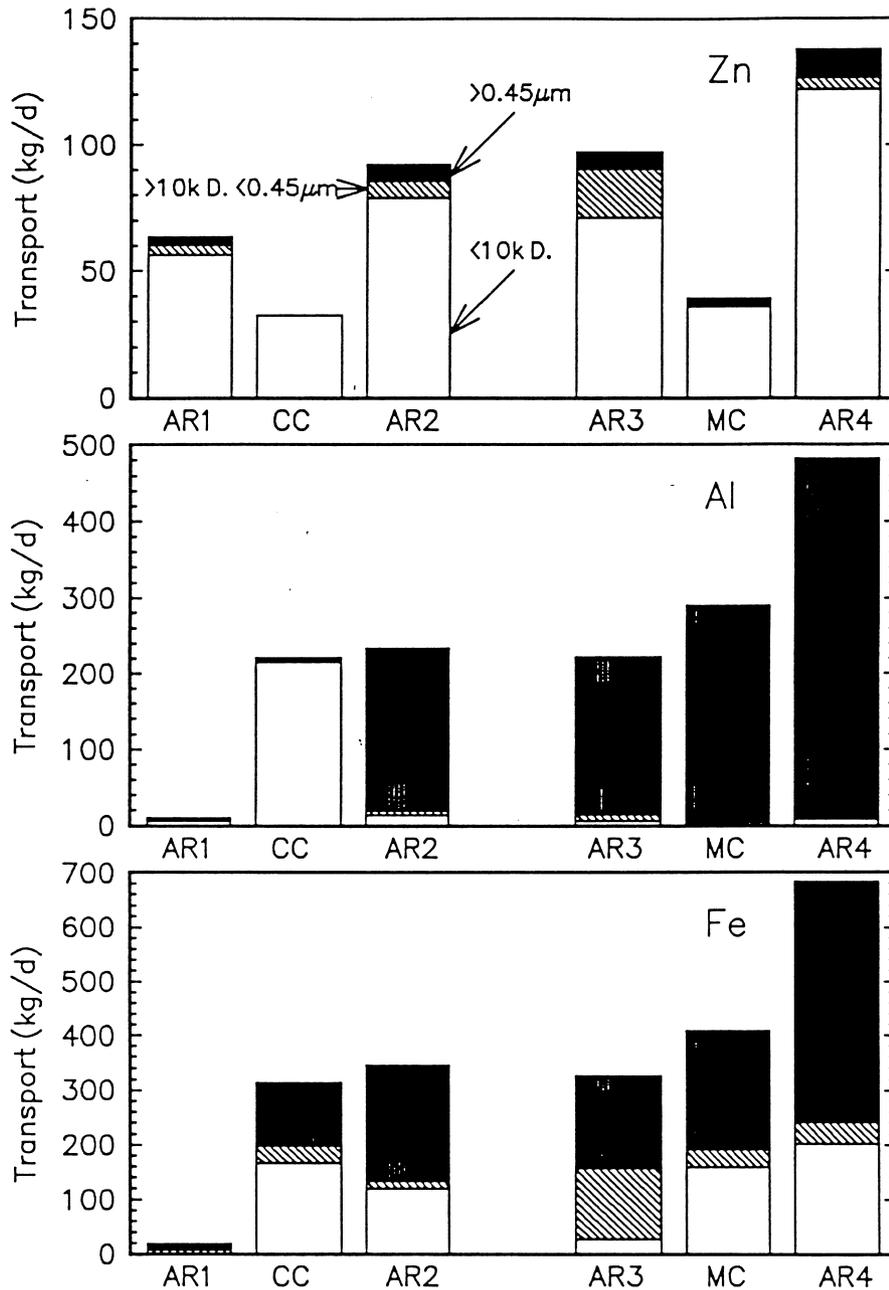


Fig. 6. Transports (kg/day) of dissolved (<10k Dalton) and colloidal Zn, Al, and Fe at sites on Cement and Mineral Creeks and the Animas River. Site locations are shown in Fig. 1.

AR4, small gains of  $\text{SO}_4$  (5%) and dissolved silica (4%) relative to the sum of the transport from AR3 and Mineral Creek were within estimated errors. Therefore,  $\text{SO}_4$  and dissolved silica were conservatively transported through this reach of the river.

#### 4. Discussion

Flow and mass-transport balances showed that the upper Animas River, Cement Creek, and Mineral Creek accounted for most of the flow and chemical transport at AR4 during this study. Monthly average flows are usually highest in June and July, but flow in 1996 was highest in May because of the early spring thaw (Fig. 2). The discharge at AR4 from June through September 1996 was only about 60% of the 1992–1996 average. These characteristics of the 1996 water year indicate that inflows from small gulches and groundwater also were less than normal. During the late summers of relatively wet years, 1993 and 1995, flows in the Animas River below Silverton were 10–12% higher than the sum of the 3 upstream gages. However, flows nearly balanced in summer 1992, which was drier than average and similar to 1996. An additional factor that might have contributed to the agreement of flow and transport balances in this study was that the river was restricted to fewer channels than can be the case when flow is higher.

Good agreement in flows and transports of total Al, Fe, and Zn also were obtained from measurements during a 5-day study in September 1991 (CDPHE data base). Most of the daily results from below Silverton showed only small losses (<15%) of Al and Fe relative to the tributary inputs. However, flow below Silverton increased by a factor of two at the end of the study, and transports of Al and Fe were one-third greater than the tributary inputs. These data indicate that some settled or entrapped colloidal metals can be remobilized in this reach of the river when flow increases during summer storm events. In comparison, the variations in flow during the present study were relatively small.

Many chemical aspects of the mixing of Cement Creek with the Animas River were very different in comparison to Mineral Creek. Specific conductance, pH, and concentrations of  $\text{SO}_4$ , dissolved silica, and many metals in Mineral Creek were similar to those in the Animas River upstream of the confluence. In contrast, pH in Cement Creek was much lower than that in the upstream Animas River, and specific conductance,  $\text{SO}_4$ , dissolved silica, and most metals were much more concentrated in Cement Creek. An important consequence of mixing in the Animas River was that substances dissolved in the low pH (3.8) waters of

Cement Creek experienced a very large increase in pH (>3 units), which substantially decreased the solubility of some metal ions and complexes. This was most evident for Al, which was dissolved in Cement Creek but formed colloidal particles in the mixing zone to AR3 (pH 6.9).

The formation of colloidal  $\text{Al}(\text{OH})_3$  during the neutralization of acidic solutions has been described in many field and laboratory studies (e.g., Nordstrom and Ball (1986) and references therein). With large changes in pH, hydrolysis of Al is a rapid process that produces predominantly amorphous colloids, which slowly aggregate and eventually form microcrystalline gibbsite or other minerals (e.g., Lydersen et al., 1991). Amorphous  $\text{Al}(\text{OH})_3$  begins to form near pH 4.6. The present mixing experiment showed that about 10% of the Al dissolved in Cement Creek had formed particles by pH 4.6 and that nearly all of the Al had formed particles by about pH 6.5 (Fig. 5). This also was similar to observations in the mixing zone at AR2. Aluminum remains relatively insoluble in the range of pH 6–8 in the absence of other complexing ligands (Stumm and Morgan, 1996), which is consistent with concentrations of 2  $\mu\text{M}$  or less at AR1, AR3, and AR4.

Ferrous iron is soluble even at the highest pH values observed in this study, but it is eventually converted to Fe(III) by abiotic and bacteria-mediated oxidation (Singer and Stumm, 1970; Nordstrom, 1982, 1995). Ferric iron is only moderately soluble at the pH of Cement Creek and would be present most likely as amorphous oxyhydroxide colloids at the higher pH values observed in Mineral Creek and the Animas River (Stumm and Morgan, 1996). Precipitation of Fe(III) in Cement Creek was apparent from abundant ochreous coatings on the stream bed and banks, and is consistent with the results showing that about one-half of the Fe transport in Cement Creek was colloidal.

As demonstrated by the mixing experiment, even a relatively small increase in pH upon mixing Cement Creek waters in the Animas River resulted in the rapid precipitation of some dissolved Fe, presumably Fe(III). The higher pH in the Animas River at AR3 and AR4 and in Mineral Creek would favor faster abiotic oxidation of Fe(II), and photoreduction of amorphous Fe(III) oxyhydroxides would be much slower than in more-acidic waters (Waite and Morel, 1984). This coupled with biotic oxidation processes could account for losses of dissolved Fe that were observed in the Animas River downstream from both creeks.

Mineral Creek receives water from acidic tributaries, but pH was only mildly acidic near the confluence with the Animas River during this study. Therefore, reactions and transformations associated with the neutralization of acidic inflows had occurred upstream in the Mineral Creek drainage. Nearly all of the Al and over half of the Fe from Mineral Creek were supplied to

the Animas River as previously formed colloids. Coatings on rocks and aggregates in shallow pools in Mineral Creek indicated the loss of some Al and Fe colloids that could be remobilized by increased flow or decreased pH.

Monthly measurements since 1992 (CDPHE data base) show that pH is typically above 6.5 at the gage on Mineral Creek, but that pH can be substantially lower during low flow. Under these conditions some amorphous Al precipitate could redissolve in Mineral Creek and form colloids when it enters the Animas River. Reversibility of Al precipitation has been demonstrated in mine-affected streams (e.g., Broshears et al., 1996). Decreases in pH also can result in desorption of Cu, Zn, and other metals from amorphous Fe oxyhydroxides (Davis et al. 1991). Measurements at the Cement Creek gage (CDPHE data base) shows that pH is typically low, but can increase above 5.5, indicating that precipitation and dissolution processes could affect the transport of both Al and Fe before flow reaches the Animas River.

Copper, Pb, and Zn appeared to have sorbed (coprecipitated or adsorbed) to the Al and Fe colloids at the Animas River sites downstream from Cement Creek and in Mineral Creek, where pH was near-neutral. In contrast, results from the colloid concentrates showed that Al, Cu, Pb, and Zn were not associated with the

predominantly Fe particles in Cement Creek (pH 3.84). This is consistent with studies that show little sorption of these metals onto amorphous Fe oxyhydroxide below pH 4, and that sorption increases with increasing pH (e.g., Benjamin and Leckie, 1981).

The large increase in pH and the formation of colloidal Al and additional colloidal Fe in the mixing zone near AR2 provided conditions for coprecipitation and adsorption of metals that had been dissolved in Cement Creek. A recent study by Karthikeyan et al. (1997) suggests the importance of both coprecipitation and adsorption in the removal of Cu by Al and Fe hydroxides. Studies of Al and Fe hydroxide sorbents show that Cu and Pb are removed from solution over a lower pH range than Zn (Benjamin and Leckie, 1981; Duker et al., 1995).

Field data from the Animas River downstream from Cement Creek indicated that significant sorption of Zn did not occur until pH exceeded the range where Al and Fe colloids had formed in the mixing zone (Fig. 7). However, colloidal Fe continued to precipitate downstream in the river as Fe(II) was oxidized, which could have removed additional Zn at higher pH. Only 2–4% of the Zn was colloidal at pH values less than 6.6 (Fig. 7). The field data show an increase in the fraction of colloidal Zn with increasing pH at values greater than 6.6 in a manner that indicates pH-dependent

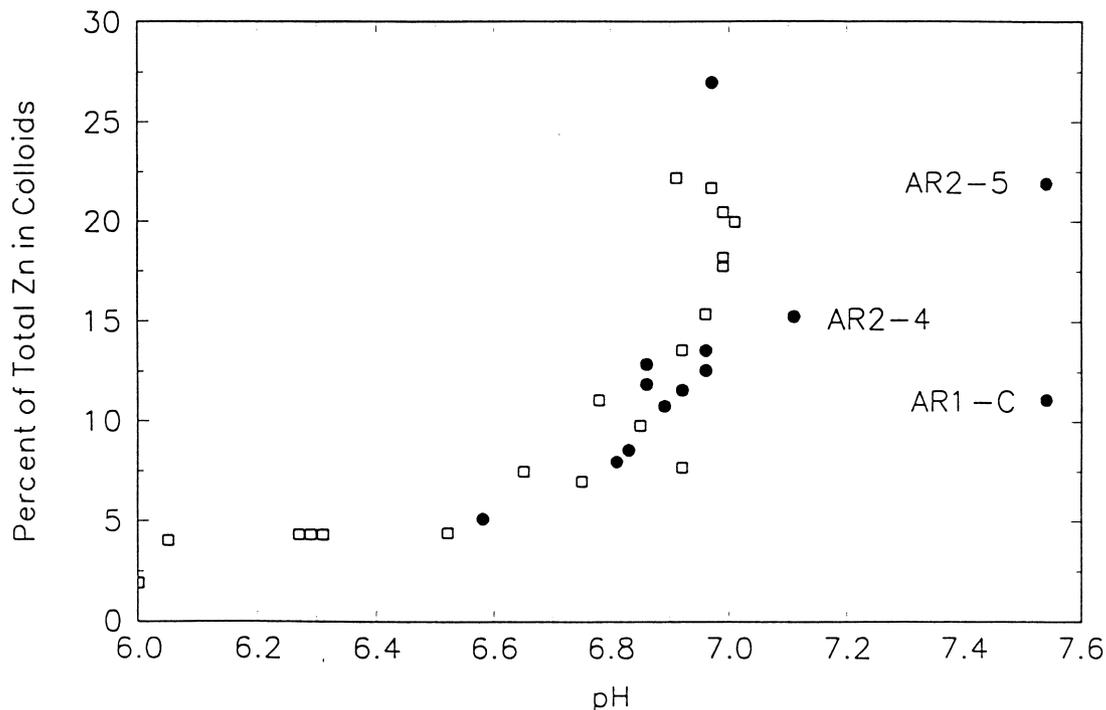


Fig. 7. Percentage of total Zn in colloidal form with respect to pH in the Animas River. Filled circles are data from Table 3; open boxes are unpublished measurements from other dates and locations between AR2 and AR4.

adsorption. The amounts of colloidal Zn in the three samples with pH > 7.1 might be partly explained by differences in the concentrations of colloids. The total concentration of colloidal Al and Fe in the sample from AR1 was only 3  $\mu\text{M}$ , whereas that in the sample from AR2-5 about 9  $\mu\text{M}$ . The total concentrations of Zn and pH were about the same in both of these samples, but the colloidal Zn was about twice as great in the sample from AR2-5. Nearly 30  $\mu\text{M}$  of colloidal Al and Fe were present in the sample from AR2-4, but pH was 7.1. Even though the abundance of colloidal sorbent was greater at AR2-4, colloidal Zn was less at the lower pH. These field data indicate that the pH values in the mixing experiment (highest value 6.5) were too low for appreciable adsorption to be observed.

Colloids formed by acid mine drainage can be more effective sorbents than pure minerals because of the influences of  $\text{SO}_4$  and bacteria during the formation of the precipitates (Webster et al., 1998). However, in the case of the Animas River colloidal Al and Fe coexist in the water column and the interaction of these two sorbents might be an important factor. Zinc appears to sorb preferentially to Fe hydroxide, but the presence of Al hydroxide enhances removal of Zn over systems with Fe hydroxide alone (Anderson and Benjamin, 1990). In general, increases in pH and in the concentrations of Al and Fe colloids appear to be the two major factors that could lead to greater sorption of Zn (Benjamin and Leckie, 1981; Jenne, 1998). Consequently, greater abundance of colloidal Al and Fe during spring runoff could also increase the sorption of Zn.

## 5. Summary and conclusions

Calcium, Mg, Mn,  $\text{SO}_4$  and dissolved silica were conservatively transported through this reach of the Animas River. Aluminium, Fe, and Zn were transported in dissolved and colloidal forms, and small losses of colloids were observed. Measurable concentrations of Cu and Pb were found in colloids collected at all sites except Cement Creek. Cement and Mineral Creeks were the dominant sources of Al, Cu, Fe and Pb, whereas the Animas River upstream of Silverton supplied about half of the Zn. With the exception of Fe, which was present in dissolved and colloidal forms, the metals were dissolved in the acidic waters of Cement Creek. Mixing of Cement Creek with the Animas River increased pH to near-neutral values and transformed Al and some Fe into colloids. Aluminium and about half of the Fe were colloidal in the mildly acidic Mineral Creek. Oxidation of dissolved Fe continued to produce colloidal Fe in the Animas River

downstream from the mixing zones. The colloids in Mineral Creek and the Animas River were effective in sorbing Cu, Pb, and a small fraction of the Zn. Adsorption of Zn in this reach of the river appeared to be limited by pH and the concentration of colloidal Al and Fe during this study.

Small losses of colloids over this reach of the Animas River indicated that colloidal and sorbed metals can be transported long distances downstream. The formation of colloids, the transport of metals involving colloids, and the deposition of colloids are processes that affect the water and stream-bed chemistry and aquatic life in the upper Animas River.

## Acknowledgements

We wish to thank J. M. Evans, M. D. ReMillard, D. M. McKnight, and W. G. Wright for assistance with the field work and R. Gallegos for providing the CDPHE data base. We also thank J. A. Coston, L. Gerner, and T. J. Yager for help with the analytical work and M. H. Cox for technical assistance. Reviews by C. J. Janik, A. F. White, D. D. Runnells, and D. C. Keith are greatly appreciated.

## References

- Anderson, P.R., Benjamin, M.M., 1990. Surface and bulk characteristics of binary oxide suspensions. *Environ. Sci. Technol.* 24, 692–698.
- Benjamin, M.M., Leckie, J.O., 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *J. Colloid Interface Sci.* 79, 209–221.
- Besser, J.M., Brumbaugh, W., Church, S.E., Kimball, B.A., 1998. Metal uptake, transfer, and hazards in the stream food web of the Upper Animas River, Colorado. In: Nimick, D.A., von Guerard, P. (Eds.), *Science for Watershed Decisions on Abandoned Mine Lands: Review of Preliminary Results*, Denver, Colorado, February 4–5, 1998, US Geological Survey Open-file Report 98-297.
- Broshears, R.E., Runkel, R.L., Kimball, B.A., McKnight, D.M., Bencala, K.E., 1996. Reactive solute transport in an acidic stream: Experimental pH increase and simulation of controls on pH, aluminum, and iron. *Environ. Sci. Technol.* 30, 3016–3024.
- Buffle, J., Leppard, G.G., 1995. Characterization of aquatic colloids and macromolecules. 1. Structure and behavior of colloidal material. *Environ. Sci. Technol.* 29, 2169–2184.
- Chapman, B.M., Jones, D.R., Jung, R.F., 1983. Processes controlling metal ion attenuation in acid mine drainage streams. *Geochim. Cosmochim. Acta* 47, 1957–1973.
- Church, S.E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J., Vaughn, R.B., 1997. Source, transport and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado. US Geological Survey Open-File Report 97–151.

- Davis, A., Olsen, R.L., Walker, D.R., 1991. Distribution of metals between water and entrained sediment in streams impacted by acid mine discharge, Clear Creek, Colorado. *Appl. Geochem.* 6, 333–348.
- Duker, A., Ledin, A., Karlsson, S., Allard, B., 1995. Adsorption of zinc on colloidal (hydr)oxides of Si, Al, and Fe in the presence of fulvic acid. *Appl. Geochem.* 10, 197–205.
- Edwards, T.K., Glysson, D.G., 1988. Field methods for measurement of fluvial sediment. US Geological Survey Open-file Report 86-531.
- Fetchenhier, S. 1996. Ore Deposits and Minerals. In: Blair, R. (Ed.), *The Western San Juan Mountains*. Fort Lewis College Foundation, University Press of Colorado, Niwot, Colorado, pp. 80–95.
- Jenne, E.A. 1998. Data analysis, modeling, controlling factors, and related issues. In: Jenne, E.A. (Ed.), *Adsorption of Metals by Geomedia*. Academic Press, San Diego, California, pp. 1–73 (Chapter 1).
- Karthikeyan, K.G., Elliott, H.A., Cannon, F.S., 1997. Adsorption and coprecipitation of copper with hydrous oxides of iron and aluminum. *Environ. Sci. Technol.* 31, 2721–2725.
- Keen, R.A. 1996. Weather and climate. In: Blair, R. (Ed.), *The Western San Juan Mountains*. Fort Lewis College Foundation, University Press of Colorado, Niwot, Colorado, pp. 113–126.
- Kimball, B.A., Callender, E., Axtmann, E.V., 1995. Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, USA. *Appl. Geochem.* 10, 285–306.
- Luedke, R.G., Burbank, W.S., 1996. Preliminary geologic map of the Silverton 7.5 minute quadrangle, San Juan County, Colorado. US Geological Survey Open-File Report 96–275.
- Lydersen, E., Salbu, B., Poleo, A.B.S., Muniz, I.P., 1991. Formation and dissolution kinetics of  $\text{Al}(\text{OH})_3$  (s) in synthetic freshwater solutions. *Water Resour. Res.* 27, 351–357.
- Malmqvist, B., Hoffsten, P., 1999. Influence of drainage from old mine deposits on benthic macroinvertebrate communities in central Swedish streams. *Wat. Res.* 33, 2415–2423.
- Mayer, L.M., Chen, Z., Findlay, R.H., Fang, J., Sampson, S., Self, R.F.L., Jumars, P.A., Quetel, C., Donard, O.F.X., 1996. Bioavailability of sedimentary contaminants subject to deposit-feeder digestion. *Environ. Sci. Technol.* 30, 2641–2645.
- McKnight, D.M., Feder, G.L., 1984. The ecological effect of acid conditions and precipitation of hydrous metal oxides in a Rocky Mountain stream. *Hydrobiol.* 119, 129–138.
- Nimmo, D.W.R., Castle, C.J., Besser, J.M. 1998. A toxicological reconnaissance of the Upper Animas River watershed near Silverton, Colorado. In: Nimick, D.A., von Guerard, P. (Eds.), *Science for Watershed Decisions on Abandoned Mine Lands: Review of Preliminary Results*, Denver, Colorado, February 4–5, 1998. US Geological Survey Open-file Report 98–297, p. 19.
- Niyogi, D.K., McKnight, D.M., Lewis Jr, W.M., 1999. Influences of water and substrate quality for periphyton in a montane stream affected by acid mine drainage. *Limnol. Oceanog.* 44, 804–809.
- Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: Kittrick, J.A., Fanning, D.S., Hossner, L.R. (Eds.), *Acid Sulfate Weathering*, Special Publication #10. Soil Science Society of America, Madison WI, pp. 37–56.
- Nordstrom, D.K., 1995. The rate of ferrous iron oxidation in a stream receiving acid mine effluent. *Selected Papers in Hydrologic Sciences*, US Geological Survey Water Supply Paper 2270, 113–119.
- Nordstrom, D.K., Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. *Science* 232, 54–56.
- Owen, R.J., 1997. Water quality and sources of metal loading to the Upper Animas River Basin. Colorado Department of Public Health and Environment, Water Quality Control Division.
- Rampe, J.J., Runnells, D.D., 1989. Contamination of water and sediment in a desert stream by metals from an abandoned gold mine and mill, Eureka District, Arizona. *Appl. Geochem.* 4, 445–454.
- Rimstidt, J.D., Chermak, J.A., Gagen, P.M. 1994. Rates of reaction of Galena, Sphalerite, Chalcopyrite, and Arsenopyrite with Fe(III) in acidic solutions. In: Alpers, C.N., Blowes, D.W. (Eds.), *Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series 550, American Chemical Society, Washington, DC, pp. 2–13.
- Singer, P.C., Stumm, W., 1970. Acid mine drainage: the rate-determining step. *Science* 167, 1121–1123.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*, 3rd ed. John Wiley and Sons, Inc, New York.
- Theobald Jr, P.K., Lakin, H.W., Hawkins, D.B., 1963. The precipitation of aluminum, iron and manganese at the junction of Deer Creek with the Snake River in Summit County, Colorado. *Geochim. Cosmochim. Acta* 27, 121–132.
- US Geological Survey, 1996. *Water Resources Data for Colorado 1992–1996*, vol. 2, Colorado River Basin, Annual reports. Data are available at URL: <http://water-data.usgs.gov/nwis-w/CO/>.
- Varnes, D.J., 1963. *Geology and ore deposits of the South Silverton mining area, San Juan County, Colorado*. Geol. Surv. Prof. Pap. 378-A.
- Waite, T.D., Morel, F.M.M., 1984. Photoreductive dissolution of colloidal iron oxides in natural waters. *Environ. Sci. Technol.* 18, 860–868.
- Webster, J.G., Swedlund, P.J., Webster, K.S., 1998. Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate. *Environ. Sci. Technol.* 32, 1361–1368.
- Wentz, D.A. 1974. Stream quality in relation to mine drainage in Colorado. In: Hadley, R.F., Snow, D.T. (Eds.), *Water Resource Problems Related to Mining*. American Water Resources Association, Minneapolis, Minnesota, pp. 158–173 Proc. No. 18.
- Witters, H.E., Van Puymbroeck, S., Stouthart, A.J.H.X., Bonga, S.E.W., 1996. Physicochemical changes of aluminium in mixing zones: mortality and physiological disturbances in brown trout. *Environ. Tox. and Chem.* 15, 989–996.
- Woodward, D.F., Farag, A.M., Bergman, H.L., DeLonay,

- A.J., Little, E.E., Smith, C.E., Barrows, F.T., 1995. Metals-contaminated benthic invertebrates in the Clark Fork River, Montana: effects on age-0 brown trout and rainbow trout. *Can. J. Fish. Aquat. Sci.* 52, 1994–2004.
- Wright, W.G., 1997. Natural and mining-related sources of dissolved minerals during low flow in the Upper Animas River Basin, Southwest Colorado, US Geological Survey Fact Sheet FS-148-97.
- Wright, W.G., Janik, C.J., 1995. Naturally occurring and mining-affected dissolved metals in two subbasins of the Upper Animas River Basin, Southwest Colorado, US Geological Survey Fact Sheet FS-243-95.