ACID MINE DRAINAGE; STREAMBED SORPTION OF COPPER,CADMIUM AND ZINC

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ABSTRACT

St. Kevin Gulch, a sub-alpine Colorado stream heavily contaminated with acid
mine drainage is the site of this investigation attempting to determine the
factors that control the transport of copper, cadmium and zinc contaminants.
Monthly samples of stream water and streambed sediments for the period May-
October, 1988 provide an extensive chemical and physical characterization of
the system. Preliminary sorption studies and dialysis bag experiments in 1988
indicate that iron oxyhydroxides are precipitated with chemical, not biological
control, and that such precipitates may be controlling the uptake of trace
metals by the sediments. Careful laboratory studies for samples collected in
1989, along with equilibrium computer modeling confirms that iron
oxyhydroxides alone can account for the sorption behavior of copper and zinc.
Other factors apparently control the sorption of cadmium. These results imply
that pH perturbations may be effective in remediation attempts for acid-mine-
drainage contaminated streams.

INTRODUCTION

The Rocky Mountains are scattered with thousands of abandoned mine workings, many of which discharge acidic waters. These acidic waters, which frequently contain high concentrations of heavy metals, often have adverse effects on the quality and ecology of waters receiving the effluent.

Acid mine drainage (AMD) arises from the leaching and subsequent oxidation of sulfide minerals. The ferrous iron released by the leaching processes undergoes oxidation, hydrolysis and precipitation as iron oxyhydroxides. These iron precipitates generally have large surface areas and provide a large number of sites for sorption of metals and/or natural organic matter.

Sorption processes have been suggested as important controls of trace metal concentrations in natural waters. Few studies, however, have been reported that compare sorption experiments in well-defined media to sorption in natural systems. Johnson (1986) found the sorption of Cu and Zn onto particulates in a system contaminated by AMD to be pH-dependent and in general agreement with laboratory studies of trace metal sorption onto amorphous iron oxyhydroxides. Tessier, et al. (1985) reported fairly good agreement between field and laboratory experiments for the partitioning of Cd, Ni, and Zn between pore waters and oxic lake sediments.

Adsorption properties of a material are controlled by the surface properties of the material. Coatings and sorption by counterions and/or organic material can alter the original surface properties. Such alteration is often manifest by a change in the surface charge of the material. AMD often contains high concentrations of sulfate. Brady et al.(1986) found that sorption of sulfate onto oxyhydroxides can result in destabilization of colloidal sols produced by ferric iron hydrolysis. They reported that the sulfate concentration in the initial hydrolysis solution can have a dramatic effect on the mineralogy and proportions of the phases produced. Newton and Liss (1987) found that overall surface charge of oxide/hydroxide phases is generally controlled in natural waters by organic coatings, but that the phases themselves may control when there is insufficient organic matter to fully coat the particles.

Another consideration in the control of trace metal concentrations in AMD is the role of microorganisms. Previous research has shown that several microbial isolates from acidic coal mining discharges in the Eastern United States have a remarkable ability to attenuate metals (Dugan, 1970). Bacterial surfaces contain sites, especially carboxyl and phosphoryl groups, that can bind metals. Also, microbial production of extracellular polymers can result in significant metal complexation (Beveridge and Fyfe, 1985). Ferris et al. (1988) found that binding of iron by bacterial cells is an important factor in the fossilization of microorganisms. LaBerge (1973) also reported iron in association with fossil microbes.

This study focuses on St. Kevin Gulch, a small sub-alpine stream located seven kilometers northwest of Leadville, Colorado (Figure 1). The stream receives acidic, metal-rich tailings effluent, which produces elevated concentrations of sulfate and several metals, including iron, manganese, aluminum, zinc, copper, and cadmium (McKnight et al., 1988). Extensive investigations of St. Kevin Gulch are part of a larger study of AMD contaminated streams being conducted by the Water Resources and Geologic Divisions of the U. S. Geological Survey, Denver, Colorado. The Colorado School of Mines has participated in these studies through participation by several faculty and graduate students, supported in part by the Colorado Water Resources Research Institute. The work reported herein represents the results of this support to the principal investigator and the doctoral degree research of Kathleen S. Smith and James F. Ranville.

OBJECTIVES

The objectives of this study are part of the overall goal of developing a comprehensive understanding of the factors that determine the transport of trace metals in AMD-contaminated streams. This will, in turn, enable effective remediation programs to be developed to counteract the deleterious effects of AMD on Colorado's natural waters. Specifically, this research was designed to test the hypothesis that organic coatings and/or microbially-mediated processes control the sorption of trace metals, especially copper and cadmium, to streambed materials in St. Kevin Gulch. The alternatives to this hypothesis include control by iron oxyhydroxide particles, by counteranions sorbed to such particles, or by co-precipitated phases such as aluminum hydroxides. To test the above hypothesis, the following sub-objectives were formulated:

1. To characterize streambed materials in St. Kevin Gulch as to their elemental composition, morphology, and bacterial constituents.
2. To determine the partitioning of copper and cadmium between streambed material and stream water as a function of pH, noting variations within the course of the stream and with season.
3. To determine the relative influences of elemental composition, organic matter, bacterial composition, and particulate surface charge on copper and cadmium accumulation by streambed materials.
4. To develop computer-model simulations of copper and cadmium sorption onto synthetic iron hydroxides for conditions in St. Kevin Gulch and compare these with field metal-partitioning data.
5. Based on the results of this and associated studies, to develop guidelines which can be used in the formulation of plans to remediate the effects of AMD from St. Kevin Gulch and similar streams on Colorado's natural waters.

EXPERIMENTAL METHODS

Prior to the initiation of this research, a series of sample sites were selected along St. Kevin Gulch (Figure 1). SK-11 is a site far above the main influent of AMD, but still shows indications of contamination by AMD. Just above site SK-20, a significant, year-round stream of AMD enters St. Kevin Gulch from a large repository of mine dump/mill tailings. Just below SK-20 a tributary stream, Single Mill Gulch, enters St. Kevin Gulch. This stream, though it also passes through extensive mining territory, appears to be much less influenced by AMD. Site SMG is along Single Mill Gulch just above its confluence with St. Kevin Gulch. Site SK-25 is on St. Kevin Gulch, just below this confluence. Several other sites, SK-35, SK-49, and SK-700 were selected at intervals along St. Kevin Gulch below SK-25. All sites are shown on Figure 1. Most of the results in this report refer to three sites, SK-20, SK-25, and SK-49.

Procedures for the sampling and chemical characterization of the stream water and streambed sediments were also developed in earlier work and are summarized in Appendices I and II of this report. Methods for electrophoretic mobility determinations of particle surface charge are summarized in Appendix III. Appendix I also outlines the methods used for determinations of the pH dependent sorption of copper and cadmium to the streambed sediments. Scanning-electron microscopic determinations of morphology and particle sizes (Appendix III) are also summarized elsewhere and will not be repeated here. Field determinations of stream pH, conductivity, and temperature were made in situ using standard techniques.

Microbiological investigations, which were originally to be an important part of this project, were set aside during the phase of the investigations covered by this report. When it became clear that the iron oxyhydroxides control the attenuation of metals in the system as a whole, extensive work with microbes was obviated. Limited work with microbes included attempts to obtain bacterial counts in the streambed material and several experiments with dialysis bags which confirmed that precipitation of iron oxyhydroxides in the stream was largely chemically, rather than biologically controlled (Smith, et al., 1989).

Samples were collected at approximately monthly intervals during the summers of 1988 and 1989. For each sampling, field determinations of pH, conductivity, and temperature were made, and samples of the streambed material and stream water were collected for later experiments and stored at 4° C. Since the streambed material had the form of a floc attached to rocks and pebbles, it was given the name "floc" in this project.

Computer modelling of the sorption of copper and cadmium onto St. Kevin Gulch sediments was conducted using the MINTEQA2 computer code, obtained from the Athens Environmental Research Laboratory of the U.S. Environmental Protection Agency (for a copy, write to Dr. David Brown, USEPA-ERL, College Station Road, Athens, GA 30613). The pre-release version of the program used in this study is based on the surface complexation model for sorption of metals onto amorphous iron oxyhydroxide (ferrihydrite) developed by Dr. David Dzombak (Dzombak, 1986). The inputs to the model include stream chemical data and the percentage of amorphous iron in the sediments. It assumes that metal sorption is controlled exclusively by ferrihydrite and associated stream components.

RESULTS AND DISCUSSION

The data collected for the 1988 sampling season included field and laboratory data for stream water characteristics and extensive analyses of the streambed sediments (floc). The field stream water data is summarized in Table I and illustrated according to temporal and spatial variations in Figures 2-11. Figure 12 shows the stream discharge at SK-25 during the 1988 sampling season.

The stream pH shows a substantial lowering at SK-20 due to the input of the acid mine drainage just above that site. This lowering is counteracted somewhat by the influx of water from SMG just above site SK-25, and changes slowly toward slightly lower pH's as the course of the stream progresses, due primarily to continued precipitation of iron oxyhydroxides (Figure 2). Temporal variations in pH (Figure 3) are relatively minor at all sites.

Conductivity variations show similar trends, with increases due to influx of mine drainage (SK-20) counteracted by the addition of low-conductivity water from SMG, and relative minor spatial variations over the remainder of the sample range (Figure 4). Temporal variations show the effects of diminished flow as the season progresses (Figure 5).

Dissolved organic carbon (DOC) contents of the stream water samples are generally quite low (0.5-1.4 mg C/L), with the exception of the SK-11 site, far upstream of the mine tailings influx, which showed one abnormally high DOC in the early spring, presumably due to the influence of terrestrial runoff water. Spatial variations, shown in Figure 6, also show the effects of the addition SMG, which also has a relatively high DOC in the spring and early summer. Temporal variations in DOC at sites other than SMG show a gradual diminishing trend as the season progresses and the influence of surface runoff decreases (Figure 7).

Sulfate, the dominant anion in the system, also varies in a predictable manner. The influx of the high-sulfate mine drainage shows up at SK-20 and is diluted before SK-25 by the influx of low-sulfate water from SMG (Figure 8). Sulfate concentrations increase as the season progresses due to the generally lower flow conditions and the concomitant increase of the even-flowing mine drainage on the stream sulfate levels (Figure 9).

Table I. 1988 field data for St. Kevin Gulch, Shingle Mill Gulch, and the mine effluent. Collection sites are shown in Figure 1.

1988 field data from St. Kevin Gulch.

Date	Site	pH	Cond.	Temp.
5.18	11	6.40	34	3.5
5.18	20	3.75	185	4.0
5.18	25	4.25	140	5.5
5.18	49	4.10	143	3.5
6.03	11	4.20	78	8.5
6.03	20	3.85	200	10.0
6.03	25	4.30	145	9.5
6.03	49	4.25	115	8.5
6.21	11	4.70	75	8.5
6.21	20	3.90	225	11.5
6.21	25	4.55	110	11.0
6.21	35	4.40	140	7.5
6.21	49	4.40	95	--
6.21	700	4.43	160	8.0
7.08	11	4.20	180	12.0
7.08	20	3.65	400	12.5
7.08	25	4.22	195	9.5
7.08	35	4.10	195	11.5
7.08	49	4.05	195	14.5
7.08	700	4.10	190	15.5
7.26	11	3.98	255	7.5
7.26	20	3.52	440	9.5
7.26	25	3.85	280	8.5
7.26	35	3.75	320	7.5
7.26	49	3.80	290	9.5
7.26	700	3.75	320	12.0
8.10	11	4.05	235	8.0
8.10	20	3.38	535	12.0
8.10	25	3.78	300	12.0
8.10	49	3.72	310	8.0
8.24	11	3.72	360	8.0
8.24	20	3.30	710	14.5
8.24	25	3.65	425	12.5
8.24	35	3.60	420	9.0
8.24	49	3.60	400	9.0
9.13	11	3.95	330	3.5
9.13	20	3.50	580	5.5
9.13	25	3.82	380	4.5
9.13	35	3.69	385	--
9.13	49	3.60	380	6.5
10.07	11	4.15	270	3.0
10.07	20	3.60	530	4.5
10.07	25	3.91	335	5.0
10.07	35	3.77	420	4.0
10.07	49	3.74	420	3.5

1988 field data from Shingle Mill Gulch.

Date	Site	pH	Cond.	Temp.
5.18	SMG	6.80	42	4.5
6.03	SMG	6.75	25	8.5
6.21	SMG	6.60	28	8.5
7.08	SMG	6.48	64	7.0
7.26	SMG	6.40	68	8.0
8.10	SMG	6.10	140	11.0
8.24	SMG	6.18	240	11.0
9.13	SMG	6.10	300	5.5
10.07	SMG	6.09	235	4.5

1988 field data from the mine effluent.

Date	Site	pH	Cond.	Temp.
5.18	MD	2.78	1800	4.0
6.03	MD	2.80	2100	8.5
6.21	MD	2.70	2300	12.0
7.08	MD	2.82	2800	9.5
7.26	MD	2.70	2400	9.5
8.10	MD	2.62	2200	15.5
8.24	MD	2.70	2400	13.0
9.13	MD	2.82	2450	6.0
10.07	MD	2.95	2000	7.5

Total (includes suspended particulates) and dissolved (0.1 micrometer filtered) iron shows spatial variations also dominated by the influx of the high iron content of the mine drainage and the dilution by the lower iron water from SMG (Figures 10a and 10b). As the stream flows, iron contents are diminished downstream by precipitation of iron oxyhydroxides. Iron contents at the upstream sites generally increase as the season progresses due to lower flow conditions and the relatively higher influence of the mine drainage (Figure 11). At the lower sampling point (SK-49), seasonal variations in iron are much less dramatic, as precipitation buffers the effect of the mine drainage influx. SK-11, far upstream of the mine drainage, shows a similar lack of seasonal variations.

Analyses of stream waters for a variety of trace constituents were also performed on the 1988 samples. Presentation of spatial and temporal variations in each of these parameters, however, is probably more data than would be useful for the purposes of this report. In general, these variations are not significant beyond the influences of the influx of the mine drainage and SMG. The average values for selected trace constituents for St. Kevin Gulch during the 1988 sampling season are shown below. The numbers represent the averages and standard deviations for 93 separate analyses of the sites and sampling dates. All concentrations are in milligrams of metal per liter of 0.1 micrometer filtered stream water.

Aluminum	1.61	+/- 0.15
Calcium	32.22	+/- 1.38
Cadmium	0.018	+/- 0.008
Copper	0.527	+/- 0.025
Manganese	8.99	+/- 0.30
Lead	0.025	+/- 0.029
Zinc	4.54	+/- 0.20

Analyses of the streambed material samples (floc) collected during the 1988 field season included elemental analyses, electrophoretic mobility determinations and morphological and particle-size characterizations. The complete elemental analyses are given in Tables 2 and 3 of Appendix II. The floc is everywhere dominated by iron. At sites SK-20 and 25, its composition is between 35 and 45 percent by dry weight iron. As one progresses downstream and later in the season from these sites, the iron percentage drops, mostly due to the increasing proportion of carbon from increasing amounts of algal growth which is visually evident in the floc samples. The iron content decreases to as low as 10-15% at site SK-700.

The organic carbon content of the floc samples is illustrated in Figures 13 and 14. Figure 13 illustrates the general increase in organic carbon below SK-20. Temporal variations, Figure 14, are less dramatic, except the marked increase at the downstream site (SK-49) as the season progresses. Note the very high organic carbon contents in all samples, from about 2% at SK-20, to as high as 14% at SK-49. Also note, that if the iron is assumed to be present as $Fe(OH)_3$ and the organic carbon as CH_2O, these two elements account for a very high percentage (ca. 95%) of the streambed sediment material.

The electrophoretic mobility of the floc material is summarized in Figures 15 and 16. If the surface of the floc particles would be dominated by amorphous iron oxyhydroxide material, as might be expected from the elemental analyses, the mobility, and the related surface charge, of the floc would be expected to be quite positive at the pH's of the stream. The mobilities are actually zero or only slightly positive for SK-20 and 25, and slightly negative for SK-49 throughout the sampling season. Site SK-11, far above the influx of the mine drainage, shows consistently negative mobilities. The reason for these results is not entirely known, though alterations in surface properties of iron oxyhydroxides by sorption of anions or organic matter could produce the alterations observed.

Variations in the trace metal concentrations in the streambed material are illustrated for copper, zinc, lead and arsenic in Figures 17-20 respectively. Cadmium was near or below detection limit for most of the floc samples. Copper, Figure 17, is highest at SK-11, lowest at SK-20, just below the mine drainage, and increases slightly below this point in the stream. Zinc, Figure 18, shows less regular variations, with dramatically increased values at site SK-49 as the season progresses. Lead, Figure 19, shows trends similar to copper. Arsenic, on the other hand, shows quite different variations, with very high levels at SK-20 dominating the patterns (Figure 20).

One possible explanation for the variations in the trace metal concentrations of the streambed sediments is the variation in the pH of the stream water. As the pH is increased, a greater fraction of a given metal might be expected to be associated with the sediment, due to its increasingly negative surface charge. Only one sampling date, May 18, 1988, showed sufficient variation in stream pH to test this idea. The results are shown for copper, lead and zinc in Figure 21. Copper and lead show the expected increase in the sediments as the pH increases, indicating the possibility that pH controls the sorption of these metals. Zinc, however, shows quite a different trend, probably due in part to the influx of sediments from SMG, which have very high zinc levels (site SK-25, pH = 4.25).

The morphology and particle size analyses of the floc samples by scanning electron microscopy are described in Appendix III. The floc material appears to be dominated by aggregates of very small (ca. 0.040 micrometers) spheroids. The particle sizes of these aggregates increases as one progresses downstream from site SK-25, with a concomitant decrease of measured surface areas (measured by single-point N_2 adsorption, BET) from about 170 m^2/g at SK-25 to less than 50 at SK-700.

Within the framework established by the above results, which provide an extensive characterization of the aqueous and sediment components of St. Kevin Gulch and its tributaries, investigations into the factors controlling the transport of the trace metals copper, cadmium and zinc in this stream also were begun in the summer of 1988. Streamside experiments investigating the distribution of these trace metals between the aqueous and sediment phases as a function of pH were conducted. The results of these preliminary trials were not conclusive due to the difficulty in controlling sediment concentrations in

these streamside studies. They strongly suggested, however, that sorption by iron oxyhydroxides could account for the observed distributions of these trace metals between the aqueous and solid phases.

Another possibility which was considered was that iron bacteria strongly influenced the precipitation of iron and trace metals from the stream water. A series of experiments with dialysis bags, however, provided strong evidence that abiotic chemical processes control the precipitation reactions in St. Kevin Gulch (Smith, et al., 1989). Thus, it was decided to first investigate the control of trace metal distributions by sorption to iron oxyhydroxides by conducting carefully controlled laboratory experiments with samples to be collected during the 1989 field season.

During the summer and fall of 1989, a sampling and analysis program similar to that conducted in 1988 was initiated. The results from these investigations are not completely available at the time of this report, but in general, the stream water and floc characteristics were not substantially different from the 1988 samples.

For the samples collected on July 18, 1989, however, a careful series of laboratory sorption studies were conducted. Floc and stream waters from sites SK-20, 25, and 49 were collected and analyzed. The results of these analyses are shown in Tables II and III. Then, using samples of stream water and floc from each of these three sites, pH-dependent metal-partitioning batch experiments were performed. The floc/water ratios were adjusted to be the same (2.9 g/L) for all three sites. The floc suspensions were dispensed into a series of bottles and the pH raised using NaOH to obtain a range of pH's between ambient and about 7.0. The pH-adjusted suspensions sat at room temperature for four hours with occasional shaking. Then, a portion of each suspension was filtered using a 0.1 micrometer nitrocellulose filter and saved for analyses of metals by ICP-AES and flameless atomic absorption. The pH was measured in the remaining contents of the bottles.

The flocs from the three sites represent different iron-to-carbon ratios. SK-20, 25, and 49 had 38, 41, and 24% iron by weight respectively. The carbon content at the three sites was 3.6, 5.4, and 8.8% respectively.

Sorption isotherms (percent metal sorbed vs. pH) were developed for copper, cadmium and zinc at the three sites. These isotherms are shown as the experimental points on Figures 22-24 respectively.

Then, the sorption reactions at the three sites were modeled using the water-equilibrium program MINTEQA2 (Felmy, et al.,1985; Brown and Allison, 1987) coupled with the MIT Diffuse-Layer Sorption Model (Dzombak, 1986). (We acknowledge Dr. Nicholas Loux, USEPA, for providing us with a pre-release version of this sorption model package). The floc iron content at the three sites was put into the model as amorphous iron oxyhydroxide. In this model, amorphous iron oxyhydroxide is assumed to be the only sorbent material present in the system. The actual stream water chemistry at each site was also provided as input to the program and provides the data by which the program

Table II. Elemental chemistry of St. Kevin Gulch streambed sediment,
July 18, 1989.

Constituent	Site SK-20	Site SK-25	Site SK-49
Fe (%)	38	41	24
C (%)	3.6	5.4	8.8
Al (%)	0.67	0.51	4.5
Si (%)	0.5	0.3	2
P (%)	0.31	0.27	0.30
K (%)	0.2	0.1	1.4
Mg (%)	0.05	0.03	0.30
Na (%)	0.04	0.03	0.33
Ca (%)	0.03	0.03	0.22
Ti (%)	0.02	0.01	0.10
Zn (ppm)	243	306	2479
Pb (ppm)	132	182	560
Th (ppm)	130	149	156
Mn (ppm)	106	97	537
As (ppm)	72	52	59
Cu (ppm)	57	107	201
Ag (ppm)	15	14	63
Ba (ppm)	43	21	224
Cd (ppm)	<4	<4	16
Ce (ppm)	15	14	100
Co (ppm)	4	4	7
Cr (ppm)	17	19	47
Ga (ppm)	<8	8	18
La (ppm)	10	7	46
Li (ppm)	<4	<4	15
Mo (ppm)	4	9	8
Nd (ppm)	12	17	64
Ni (ppm)	<4	<4	11
Sc (ppm)	<4	<4	8
Sr (ppm)	12	7	68
V (ppm)	<4	<4	28
Y (ppm)	<4	<4	19

Table III. Elemental chemistry of St. Kevin Gulch stream water,
July 18, 1989 (as mg/L; unfiltered).

Constituent	Site SK-20	Site SK-25	Site SK-49
Ca	18	12	13
Zn	13	7.4	8.0
Si	7.7	6.8	7.1
Fe	7.5	3.1	1.2
Mn	7.4	4.0	3.9
Mg	6.7	4.5	4.6
Al	4.1	2.4	2.7
Na	2.8	2.8	2.9
K	0.5	0.5	0.8
Cu	0.308	0.163	0.160
Cd	0.074	0.042	0.045
SO_4^{2-}	176	88	91
pH	3.58	3.96	4.03

computes the speciation, sorption and precipitation reactions expected at each site. The pH was then fixed at 0.5 pH intervals from 3.5 to 7.0 and the model was allowed to predict water equilibrium and sorption reactions. A sample of the output for water phase speciation and aqueous plus sorbed speciation for site SK-20 is illustrated in Tables IV and V, respectively. It should be noted that undersaturation with respect to trace-metal hydroxide precipitates was indicated by the model predictions.

Thus model sorption isotherms which assume only amorphous iron oxyhydroxide sorption processes were developed for each site. The resulting isotherms are shown for copper, cadmium and zinc as the solid-line curves in Figures 22-24, respectively. Excellent agreement was obtained between the model predictions and the experimental data for copper. Good agreement was obtained for zinc. The computer simulation underestimated the sorption of cadmium compared with the experimental results.

Since the agreement is so good between the experimental data and the model, the indications are that organic matter is not very important in the partitioning of copper and zinc in St. Kevin Gulch. The pH-dependent sorption reactions can be modeled successfully with only amorphous iron oxyhydroxides as the sorbent material. Hence, transport of aqueous copper and zinc can be predicted using currently-available sorption models.

Work is in progress to determine the factors which control cadmium sorption and why the large fraction of organic carbon in the floc does not appear to significantly scavenge copper and zinc in St. Kevin Gulch. Additional work also focuses on the mechanisms which control the sorption and transport of these trace metals by suspended solids (as opposed to streambed materials) in St. Kevin Gulch.

The results of this phase of the study of streams impacted by acid-mine drainage suggest that pH changes and iron particulates in the streambed can be used to alter the transport of trace metals. This study, along with work in progress should provide a solid basis from which methods for the removal of harmful levels of trace metals from such streams can be developed.

Table IV. MINTEQA2 aqueous speciation for major cations in unfiltered SK-20 stream water (see Table III for composition) with no sorbent material present and MINTEQA2 aqueous speciation of the same water at three higher fixed pH values. Iron and aluminum were allowed to precipitate as ferrihydrite and $Al(OH)_{3(am)}$. This table lists the remaining aqueous species as percent of the total aqueous species for that element.

| | Stream Water | Fixed-pH Runs | | |
pH =	3.58	4.5	5.5	6.5
Iron:				
Fe^{3+}	3.4 %	--	--	--
$FeOH^{2+}$	22.0	7.8	--	--
$Fe(OH)_2^+$	59.4	92.1	98.8	96.4
$Fe(OH)_3^0$	--	--	--	3.4
$FeSO_4^+$	12.8	--	--	--
$FeH_2PO_4^{2+}$	1.8	--	--	--
Aluminum:				
Al^{3+}	61.6	79.4	9.8	--
$AlOH^{2+}$	--	14.1	17.5	--
$Al(OH)_2^+$	--	4.1	51.3	19.5
$Al(OH)_3^0$	--	--	19.3	72.9
$Al(OH)_4^-$	--	--	--	6.9
$AlSO_4^+$	34.8	2.2	1.8	--
$Al(SO_4)_2^-$	3.0	--	--	--
Calcium:				
Ca^{2+}	86.8	99.3	95.8	89.9
$CaSO_4^0$	13.2	--	4.1	9.8
Magnesium:				
Mg^{2+}	88.2	99.4	96.4	91.2
$MgSO_4^0$	11.8	--	3.6	8.7
Manganese:				
Mn^{2+}	88.7	99.4	96.4	91.3
$MnSO_4^0$	11.3	--	3.6	8.7

Table V. MINTEQA2 aqueous speciation of unfiltered SK-20 stream water (see Table III for composition) with no sorbent material present and MINTEQA2 speciation of the same water at three fixed pH values with sorbent material present. This table lists both aqueous and sorbed species as percent of the total aqueous and sorbed species for that element. The "=FeO(h)" refers to high-energy sorption sites and the "=FeO(l)" refers to low-energy sorption sites.

|	No Sorption Stream Water	Fixed-pH Sorption Runs		
pH =	3.58	4.5	5.5	6.5
Sulfate:				
SO_4^{2-}	86.9	3.0	18.9	50.5
HSO_4^-	1.1	--	--	--
$AlSO_4^+$	2.9	--	--	--
$CaSO_4^0$	3.2	--	--	2.4
$MgSO_4^0$	1.8	--	--	1.3
$ZnSO_4^0$	1.7	--	--	--
$=Fe(h)SO_4^-$	--	1.8	--	--
$=Fe(l)SO_4^-$	--	77.4	46.1	12.1
$=FeO(l)HSO_4^{2-}$	--	16.8	32.3	32.9
Zinc:				
Zn^{2+}	84.8	97.1	56.7	7.3
$ZnSO_4^0$	15.0	--	2.8	--
$=FeO(h)Zn^+$	--	2.0	35.4	49.5
$=FeO(l)Zn^+$	--	--	5.1	42.2
Copper:				
Cu^{2+}	86.5	33.7	1.2	--
$CuSO_4^0$	13.5	--	--	--
$=FeO(h)Cu^+$	--	53.3	57.0	18.6
$=FeO(l)Cu^+$	--	12.8	41.7	81.3
Cadmium:				
Cd^{2+}	81.7	98.4	79.9	26.3
$CdSO_4^0$	18.0	--	4.9	4.1
$=FeO(h)Cd^+$	--	--	14.3	51.0
$=FeO(l)Cd^+$	--	--	--	18.5

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FIGURES

Figure 1. Sampling localities along St. Kevin Gulch and Shingle Mill Gulch, Lake County, Colorado.

Figure 2. Spatial variation in field-measured pH in St. Kevin Gulch for 1988.

Figure 3. Temporal variation in field-measured pH in St. Kevin and Shingle Mill Gulches for 1988.

Figure 4. Spatial variation in field-measured conductivity in St. Kevin Gulch for 1988.

Figure 5. Temporal variation in field-measured conductivity in St. Kevin and Shingle Mill Gulches for 1988.

Figure 6. Spatial variation in dissolved organic carbon concentration in St. Kevin Gulch for 1988.

Figure 7. Temporal variation in dissolved organic carbon concentration in St. Kevin and Shingle Mill Gulches for 1988.

Figure 8. Spatial variation in sulfate concentration in St. Kevin Gulch for 1988.

Figure 9. Temporal variation in sulfate concentration in St. Kevin Gulch for 1988.

Figure 10a. Spatial variation in dissolved iron in St. Kevin Gulch for 1988.

Figure 10b. Spatial variation in total iron in St. Kevin Gulch for 1988.

Figure 11. Temporal variation in total and dissolved iron in St. Kevin Gulch for 1988.

Figure 12. Discharge in St. Kevin Gulch at site SK-25 for 1988.

Figure 13. Spatial variation in carbon content of floc in St. Kevin Gulch for 1988.

Figure 14. Temporal variation in carbon content of floc in St. Kevin Gulch for 1988.

Figure 15. Spatial variation in electrophoretic mobility of floc in St. Kevin Gulch for 1988.

Figure 16. Temporal variation in electrophoretic mobility of floc in St. Kevin Gulch for 1988.

Figure 17. Concentration of copper in St. Kevin Gulch streambed sediment for 1988.

Figure 18. Concentration of zinc in St. Kevin Gulch streambed sediment for 1988.

Figure 1

Figure 2

Spatial variation in field measured pH in St. Kevin
Gulch for 1988.

Figure 3

Temporal variation in field measured pH in St. Kevin and Shingle Mill Gulches for 1988.

Figure 4

Spatial variation in field measured conductivity in St. Kevin Gulch for 1988.

Figure 5

Temporal variation in field measured conductivity
in St. Kevin and Shingle Mill Gulches for 1988.

Figure 6

Spatial variation in dissolved organic carbon concentration in St. Kevin Gulch for 1988.

Figure 7

Temporal variation in dissolved organic carbon
concentration in St. Kevin and Shingle Mill Gulches.

Figure 8

Spatial variation in sulfate concentration in St. Kevin Gulch for 1988.

Figure 9

Temporal variation in sulfate concentration
in St. Kevin Gulch for 1988.

Spatial variation in dissolved Iron (0.1 μm filter) in St. Kevin Gulch for 1988.
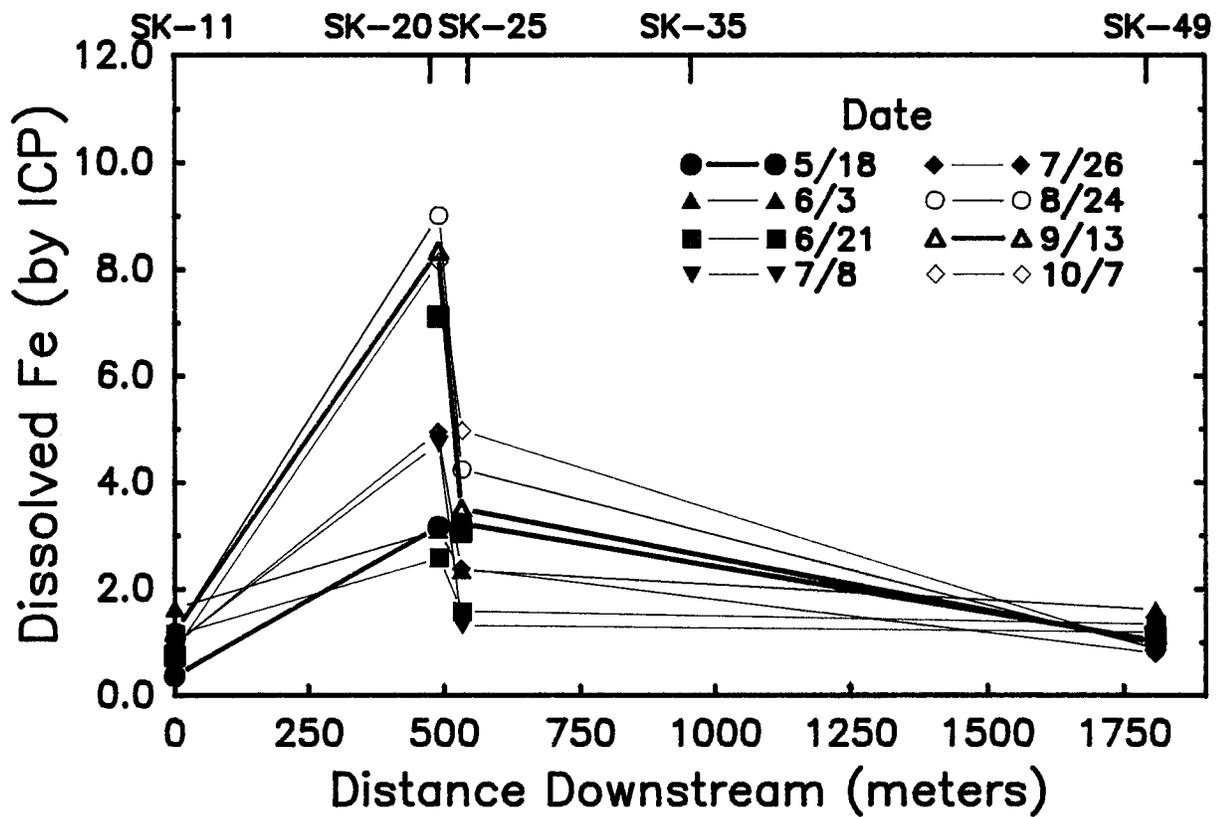
Spatial variation in total Iron in St. Kevin Gulch for 1988.
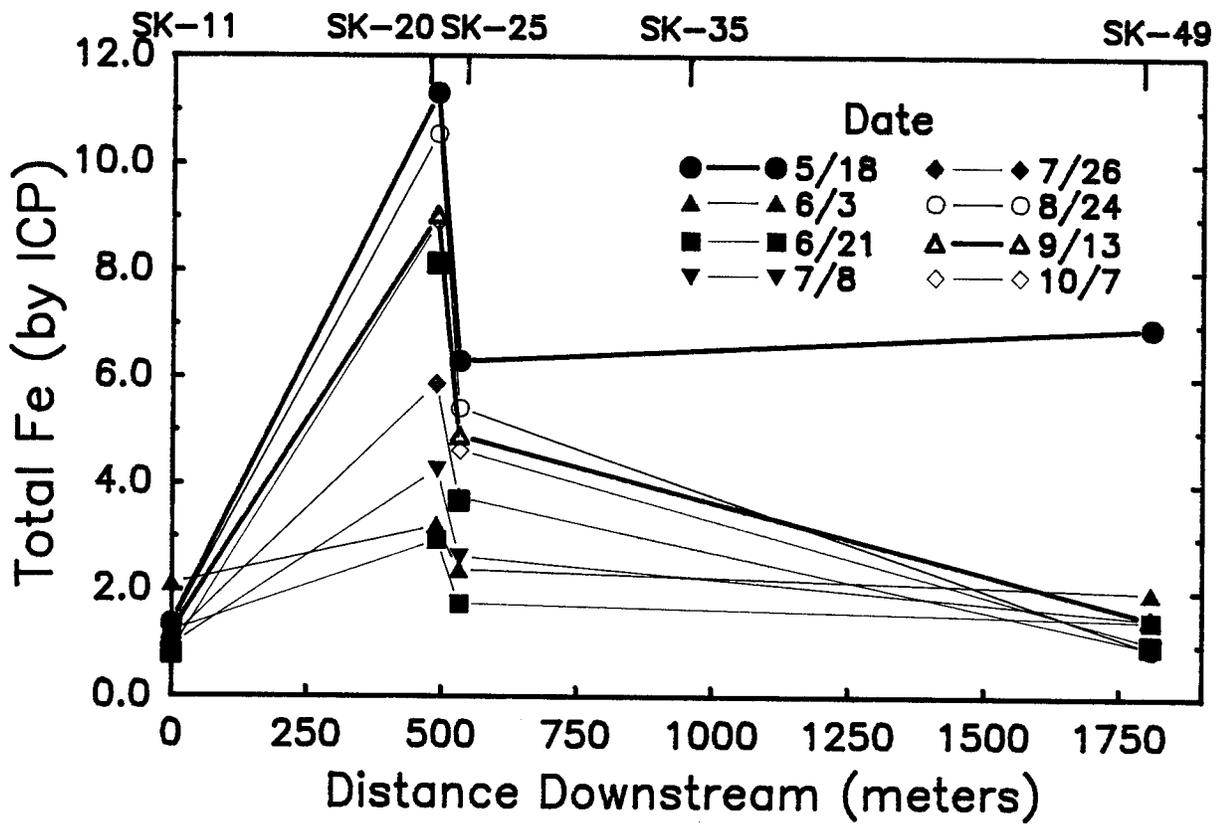
Figure 11

Temporal variation in total (filled symbols) and dissolved (open symbols) Fe in St. Kevin Gulch for 1988.
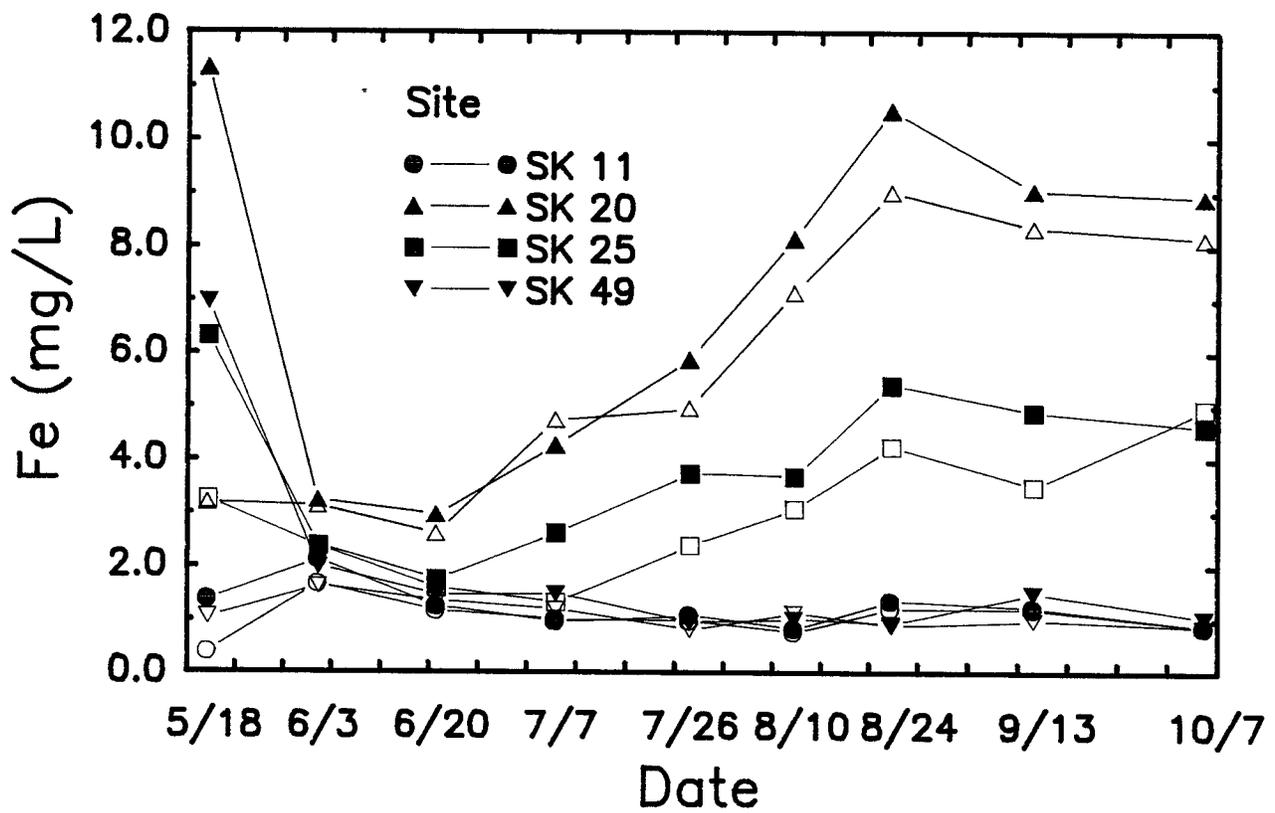
Figure 12

Discharge in St. kevin Gulch at SK-25, 1988.
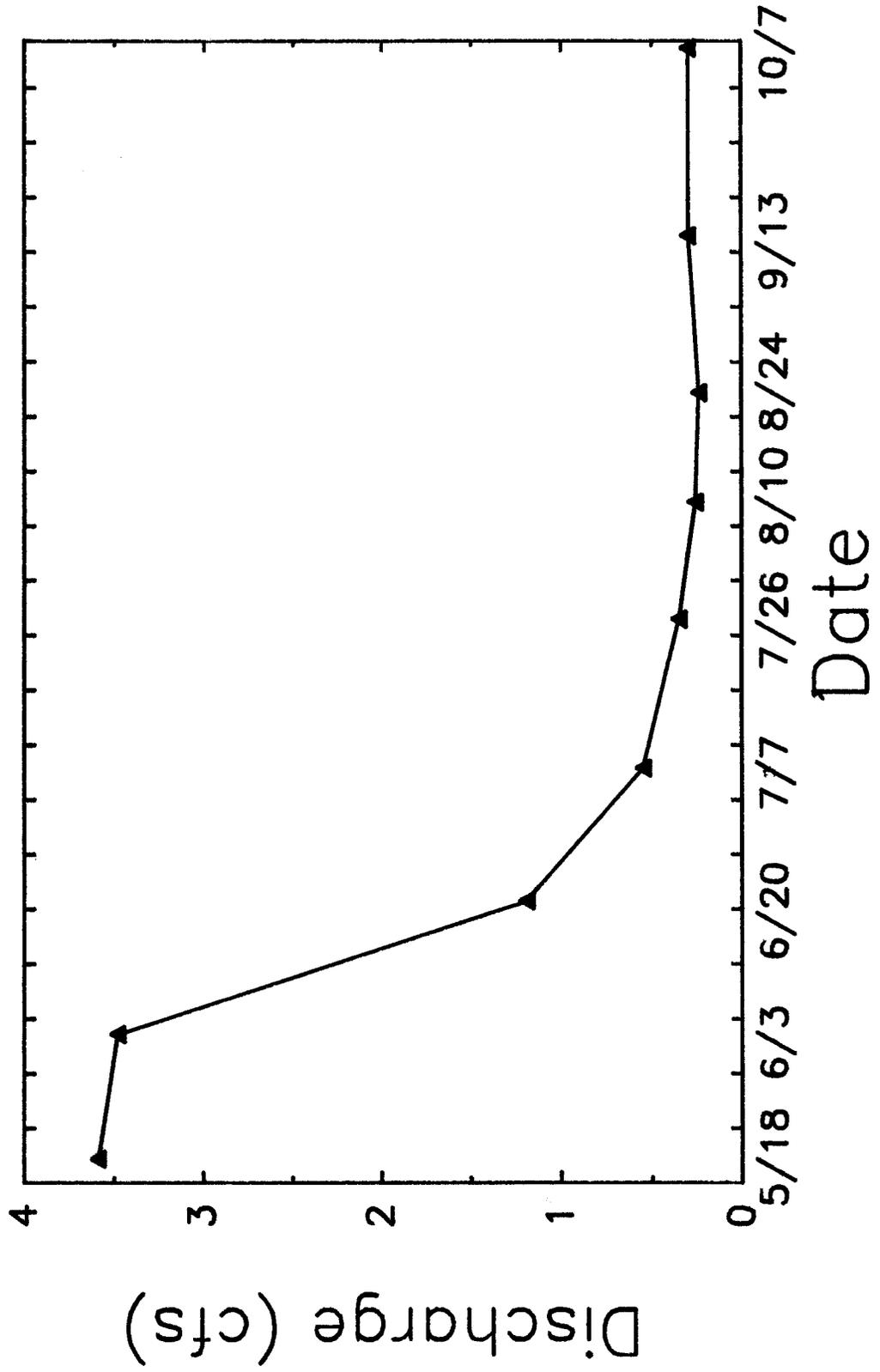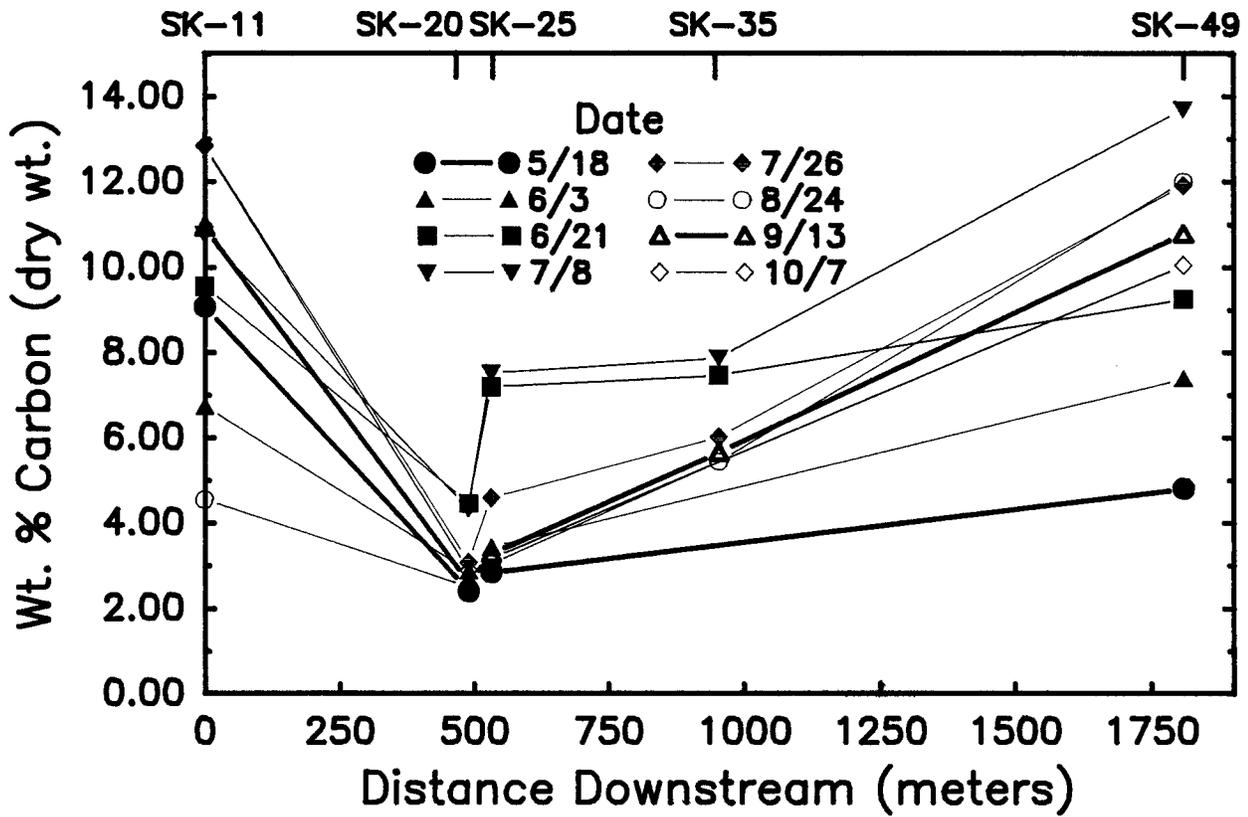
Figure 13

Spatial variation in carbon content of floc in St. Kevin Gulch for 1988.

Figure 14

Temporal variation in carbon content of floc in
St. Kevin Gulch for 1988.

Figure 15

Spatial variation in electrophoretic mobility of floc in St. Kevin Gulch for 1988.

Figure 16

Temporal variation in electrophoretic mobility of floc in St. Kevin Gulch for 1988.

Site
- ●——● SK-11
- ▲——▲ SK-20
- ■——■ SK-25
- ▼——▼ SK-49

mobility (μm/sec/volt/cm)

Date

Figure 17

St. Kevin Gulch Streambed Sediment

Cu

Legend:
- ○ 5/18
- ● 6/3
- ◁ 6/21
- ▽ 7/26
- ▽ 8/24
- ◇ 10/7

Parts per Million Cu

1988 Sample Site

Figure 18

St. Kevin Gulch Streambed Sediment

Zn

5/18
6/3
6/21
7/26
8/24
10/7

Parts per Million Zn

1988 Sample Site

Figure 19

St. Kevin Gulch Streambed Sediment

Pb

1988 Sample Site

Parts per Million Pb

Legend:
- ○ 5/18
- ● 6/3
- ◁ 6/21
- ▽ 7/26
- ▽ 8/24
- ◇ 10/7

Figure 20

St. Kevin Gulch Streambed Sediment

5/18
6/3
6/21
7/26
8/24
10/7

As

Parts per Million As

1988 Sample Site

Figure 21
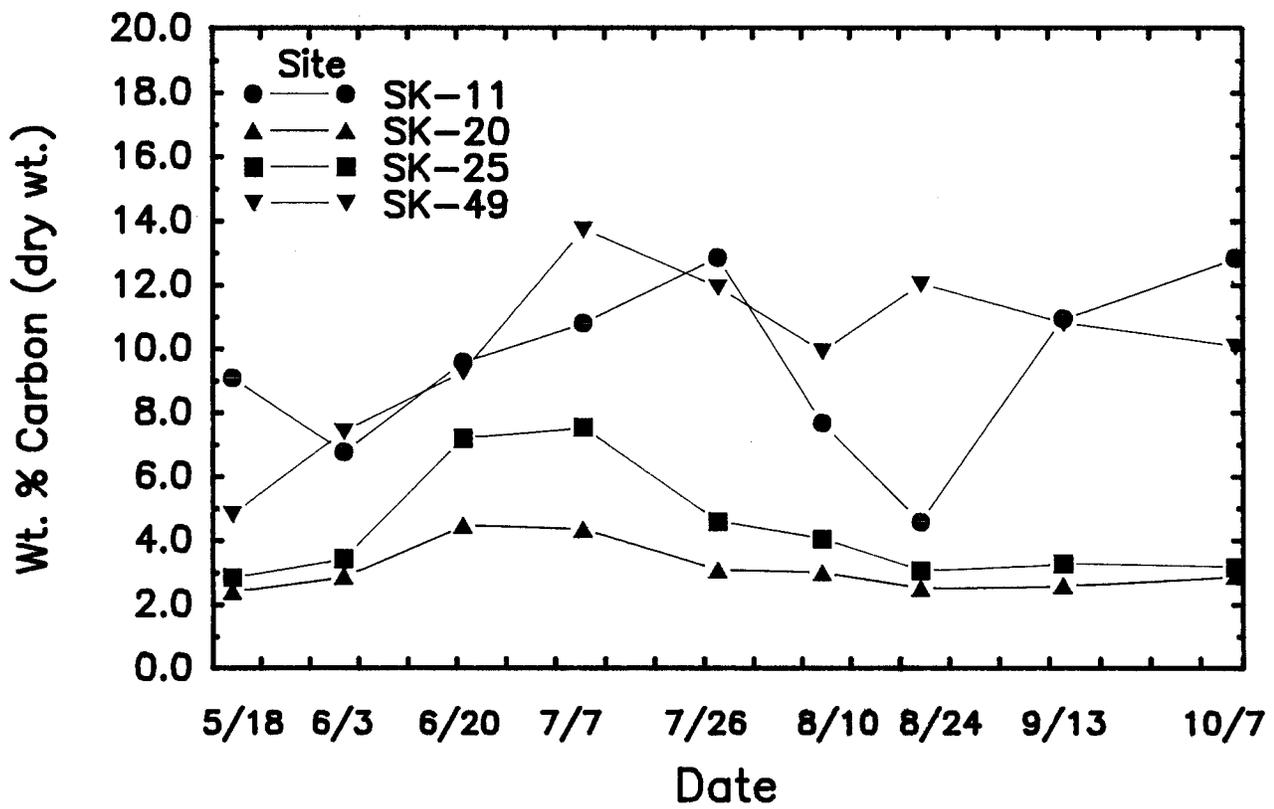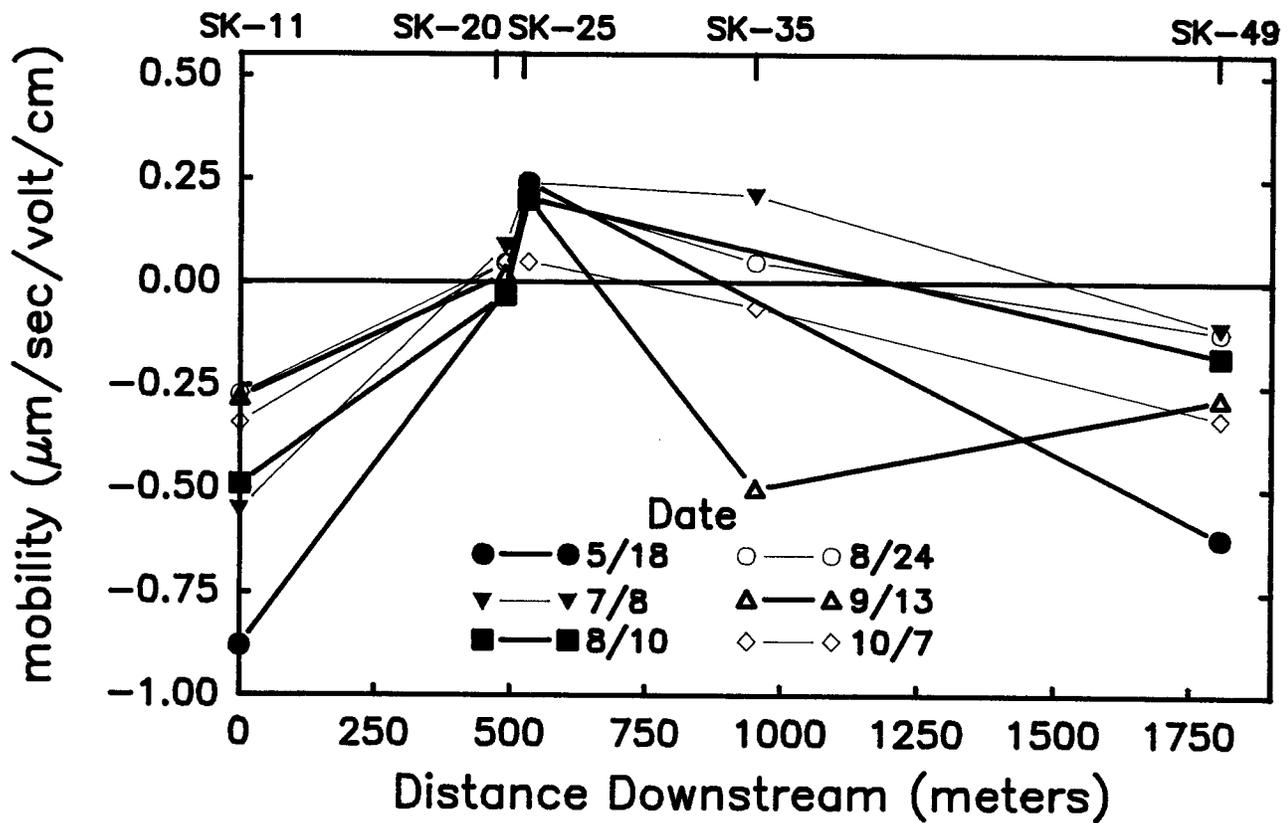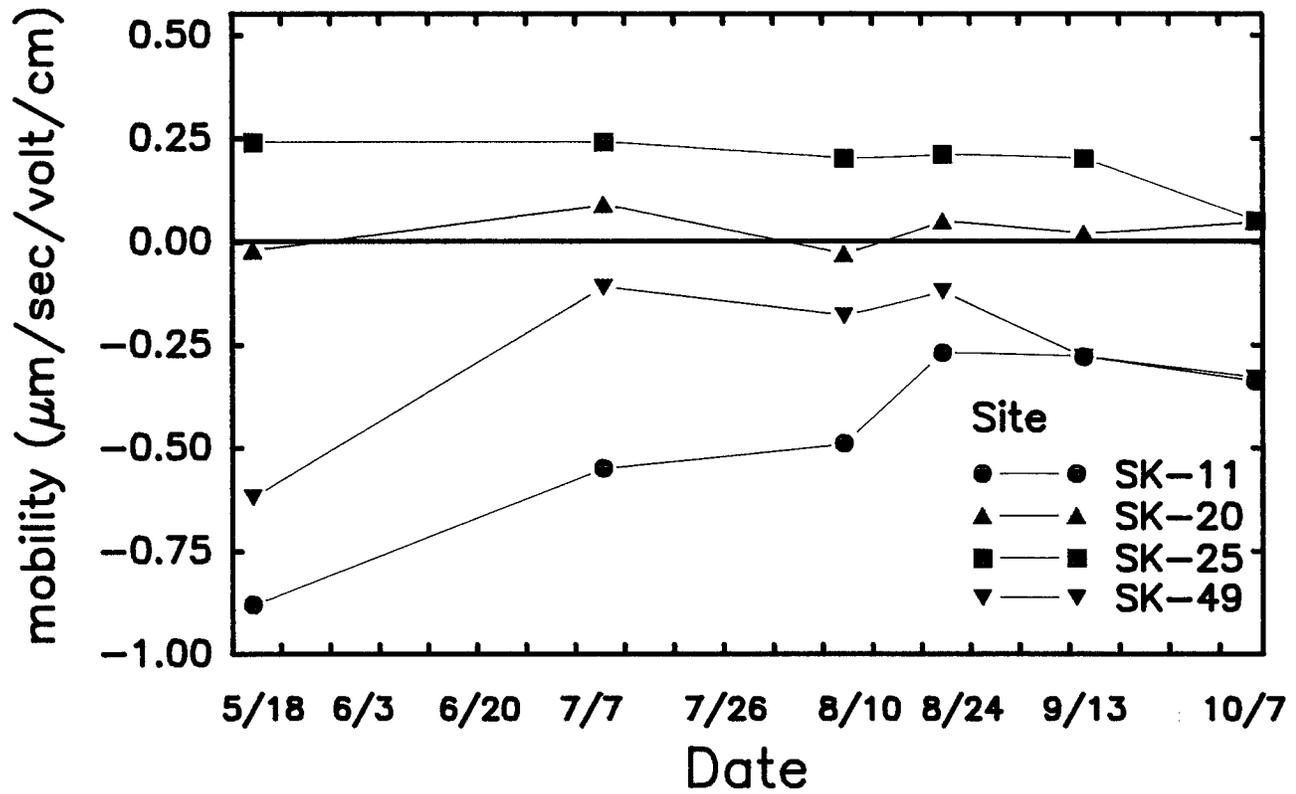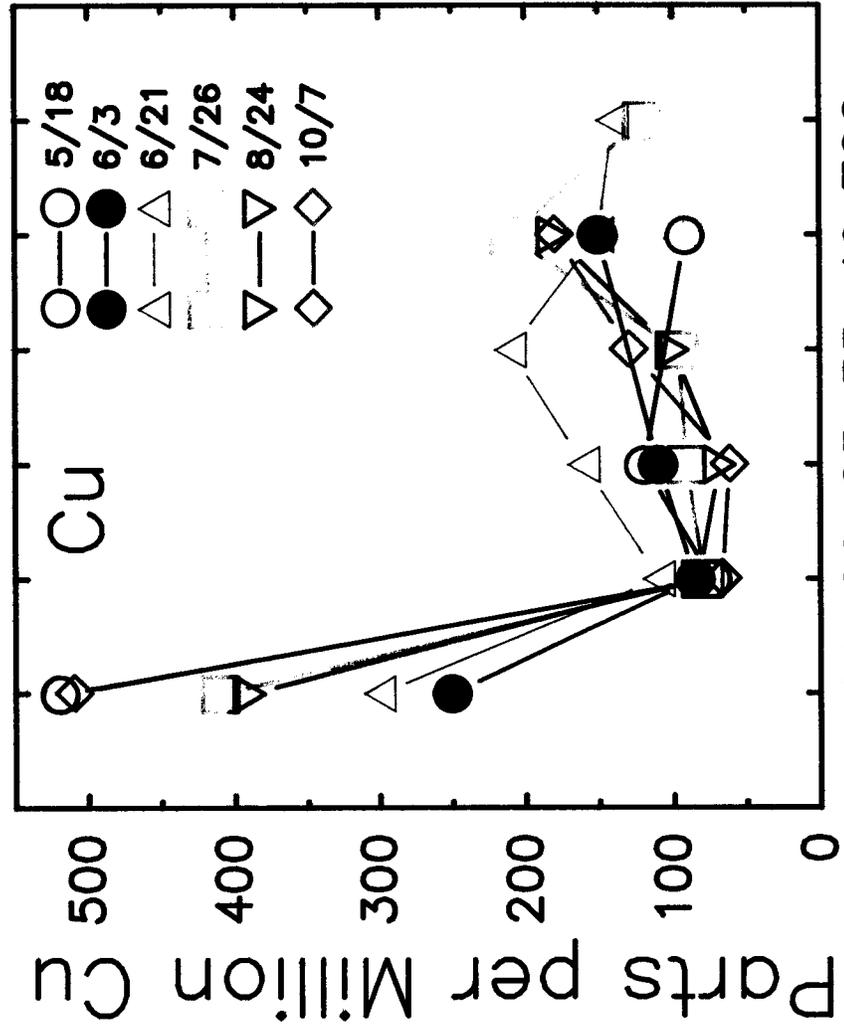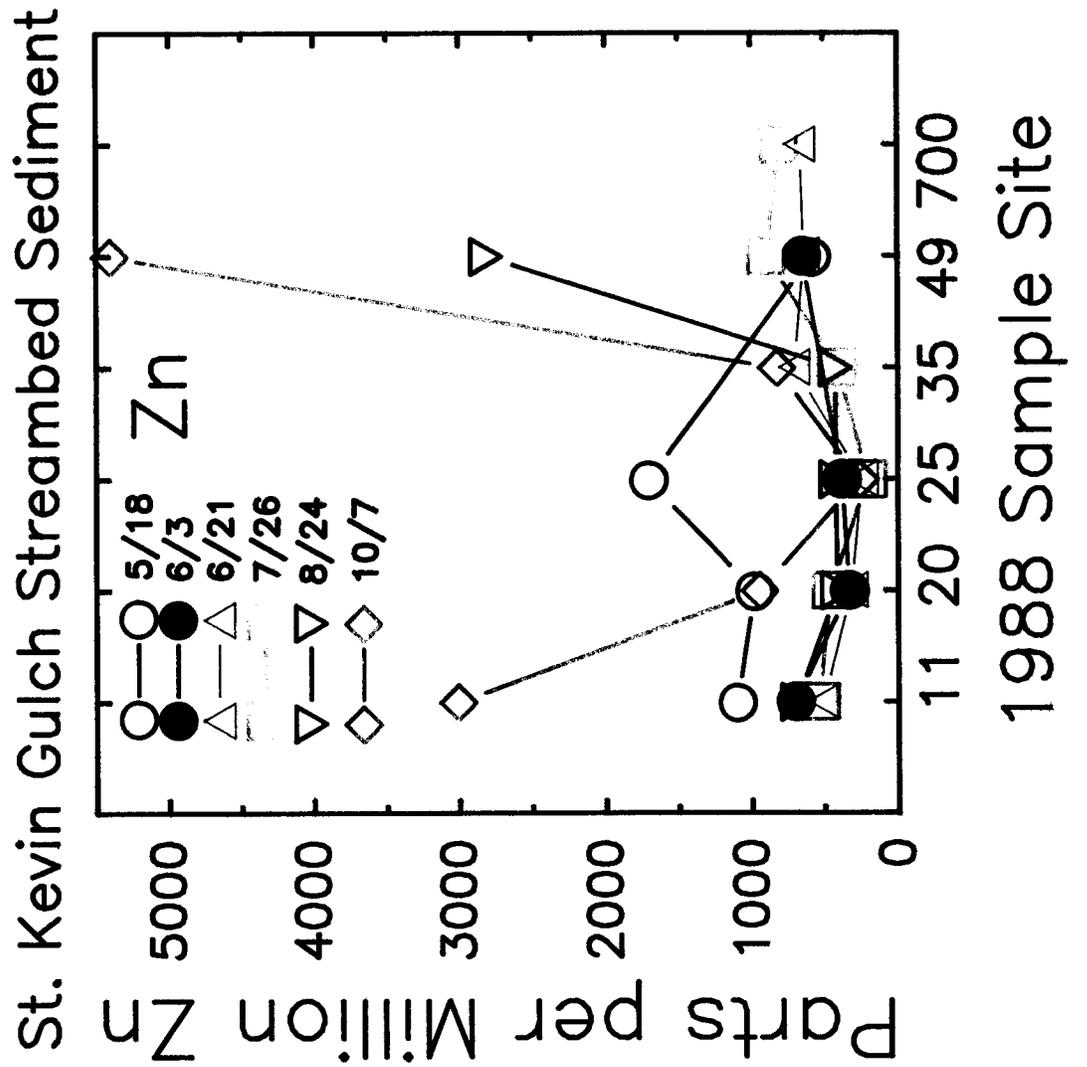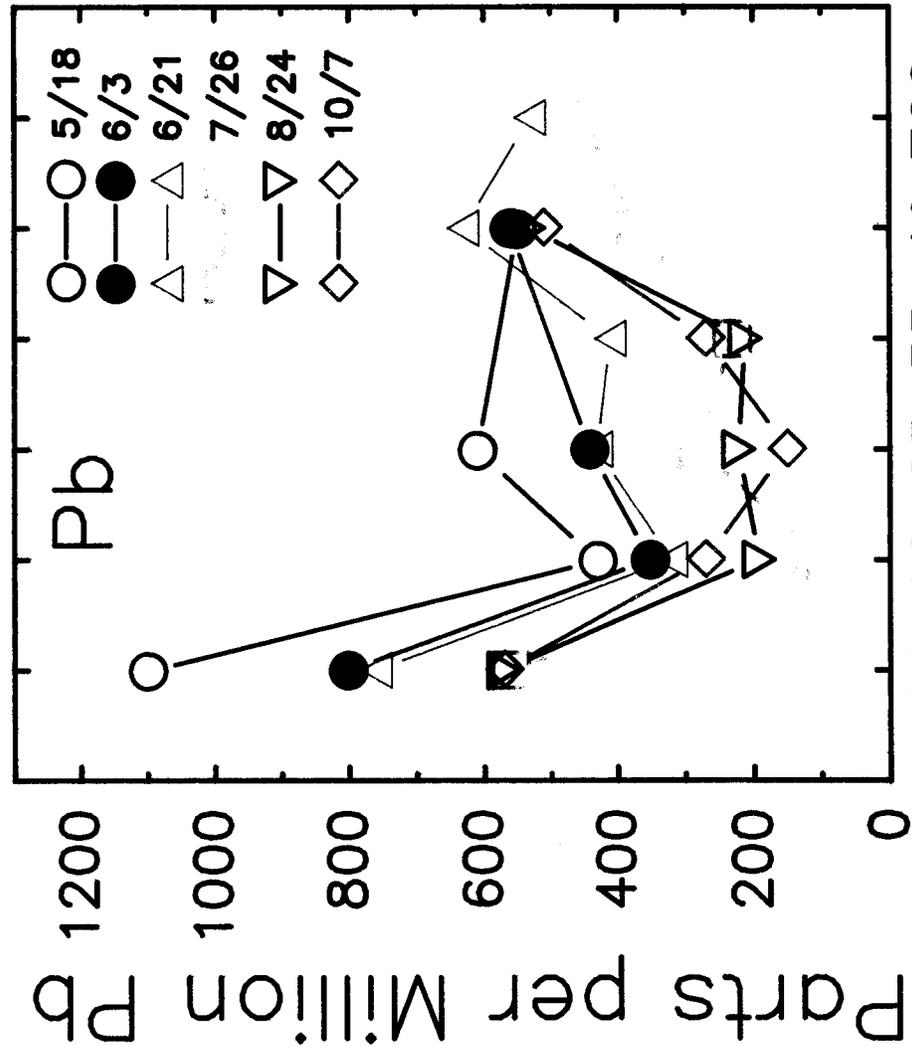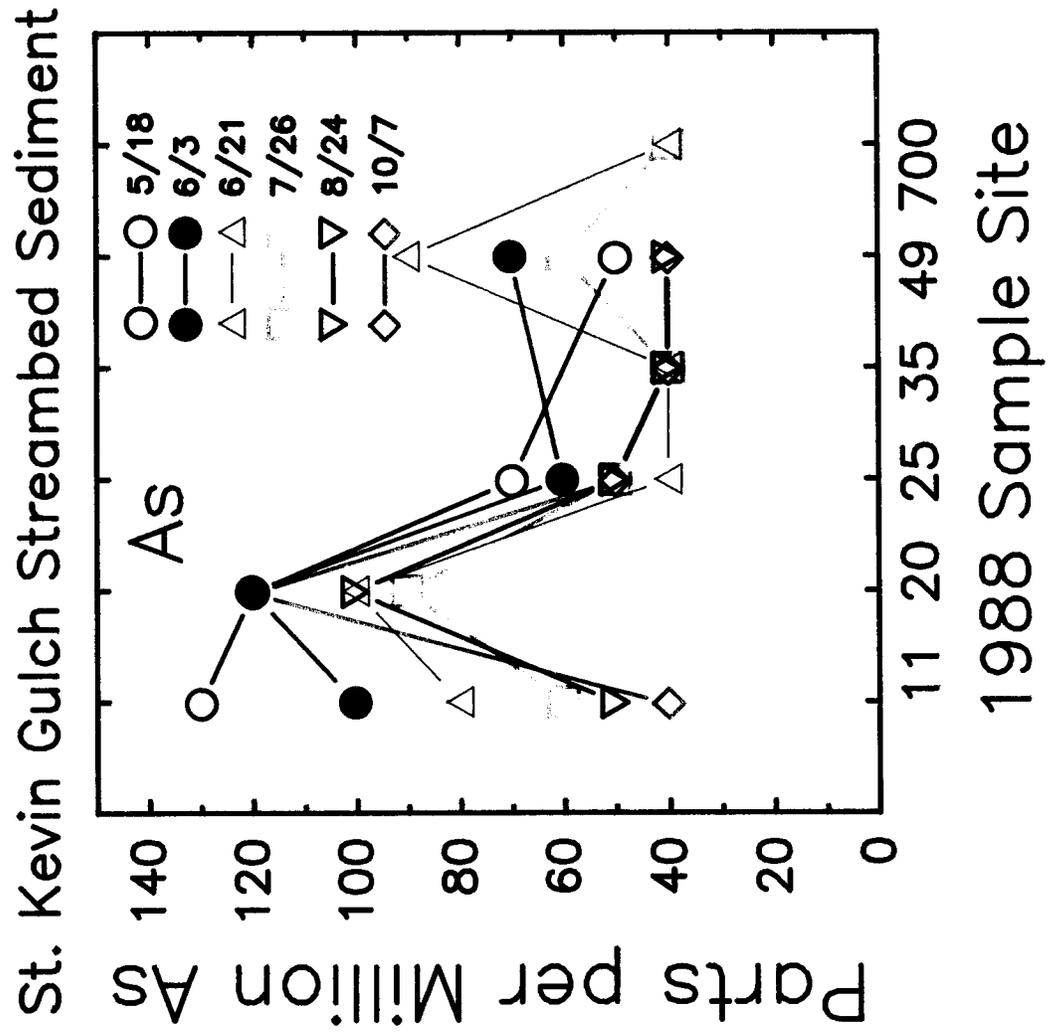
St. Kevin Gulch Streambed Sediment
May 18, 1988
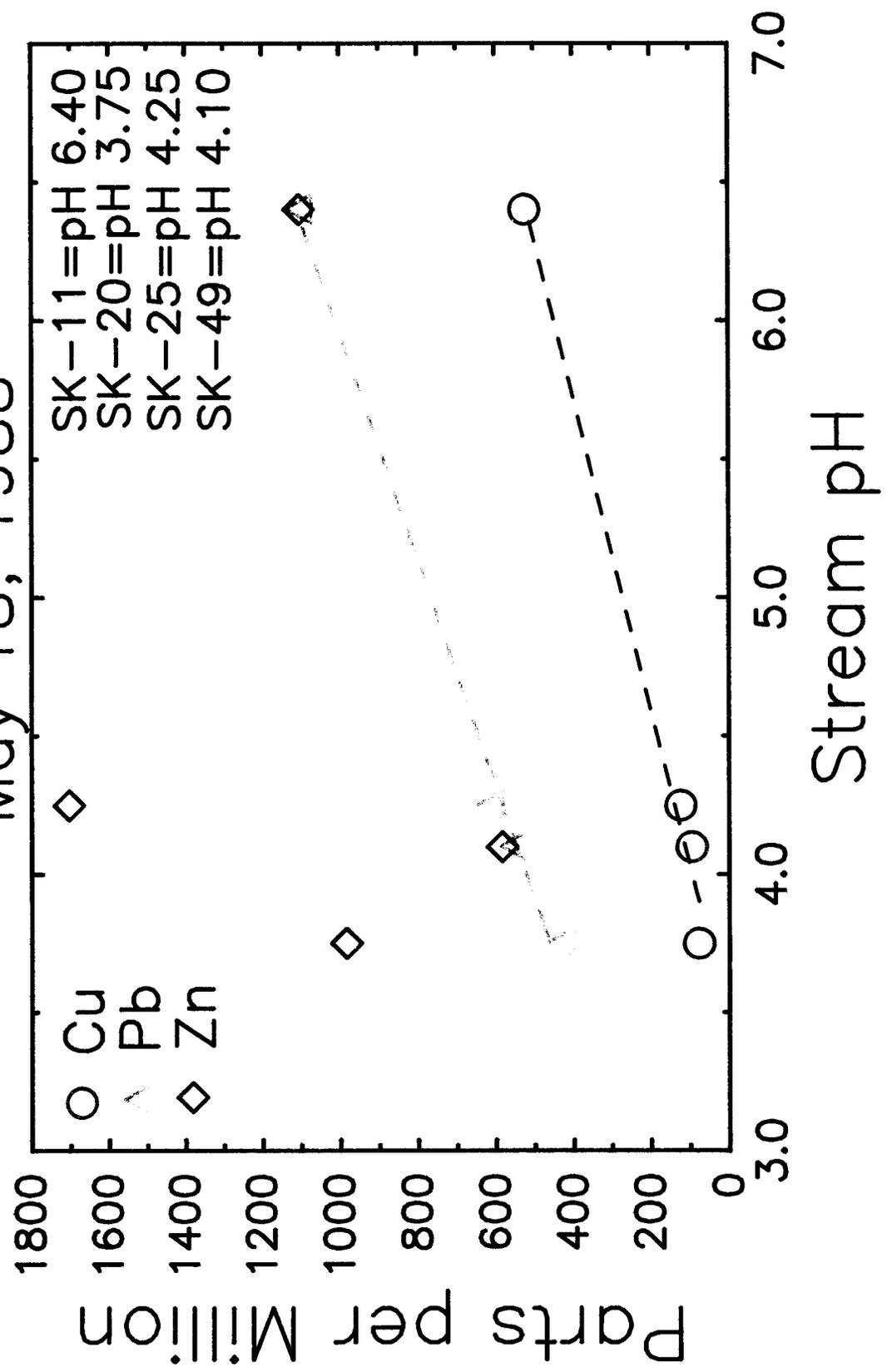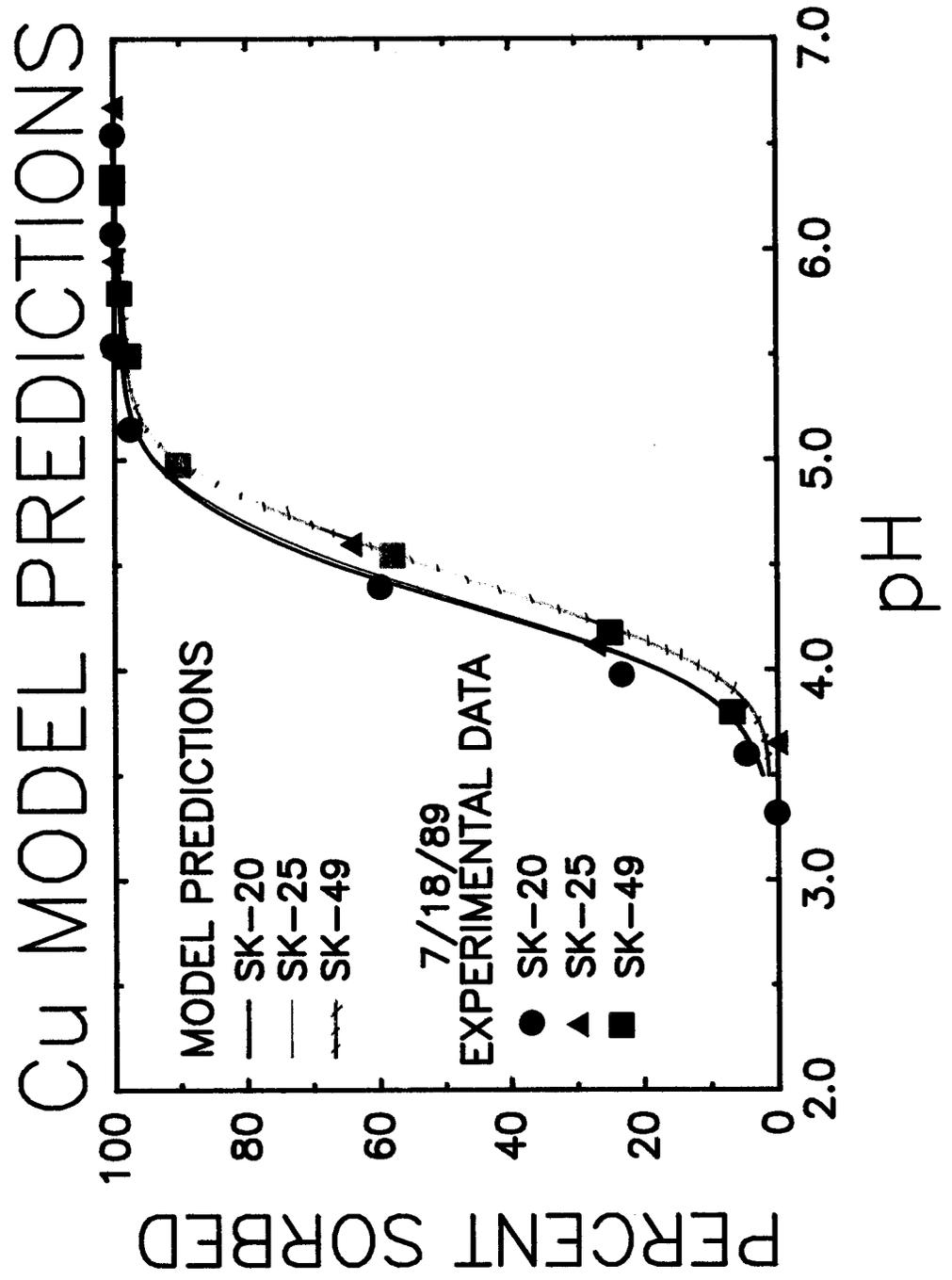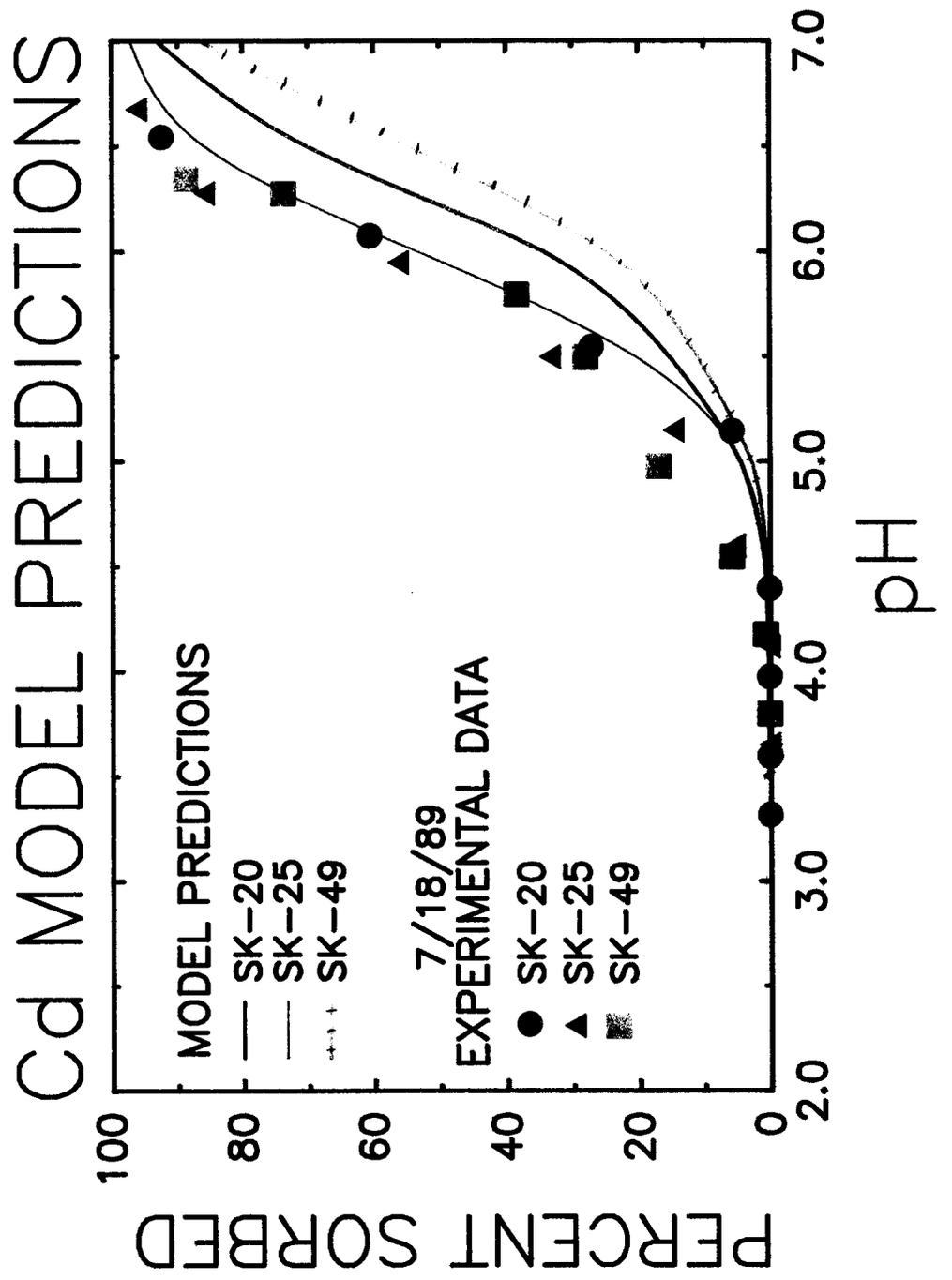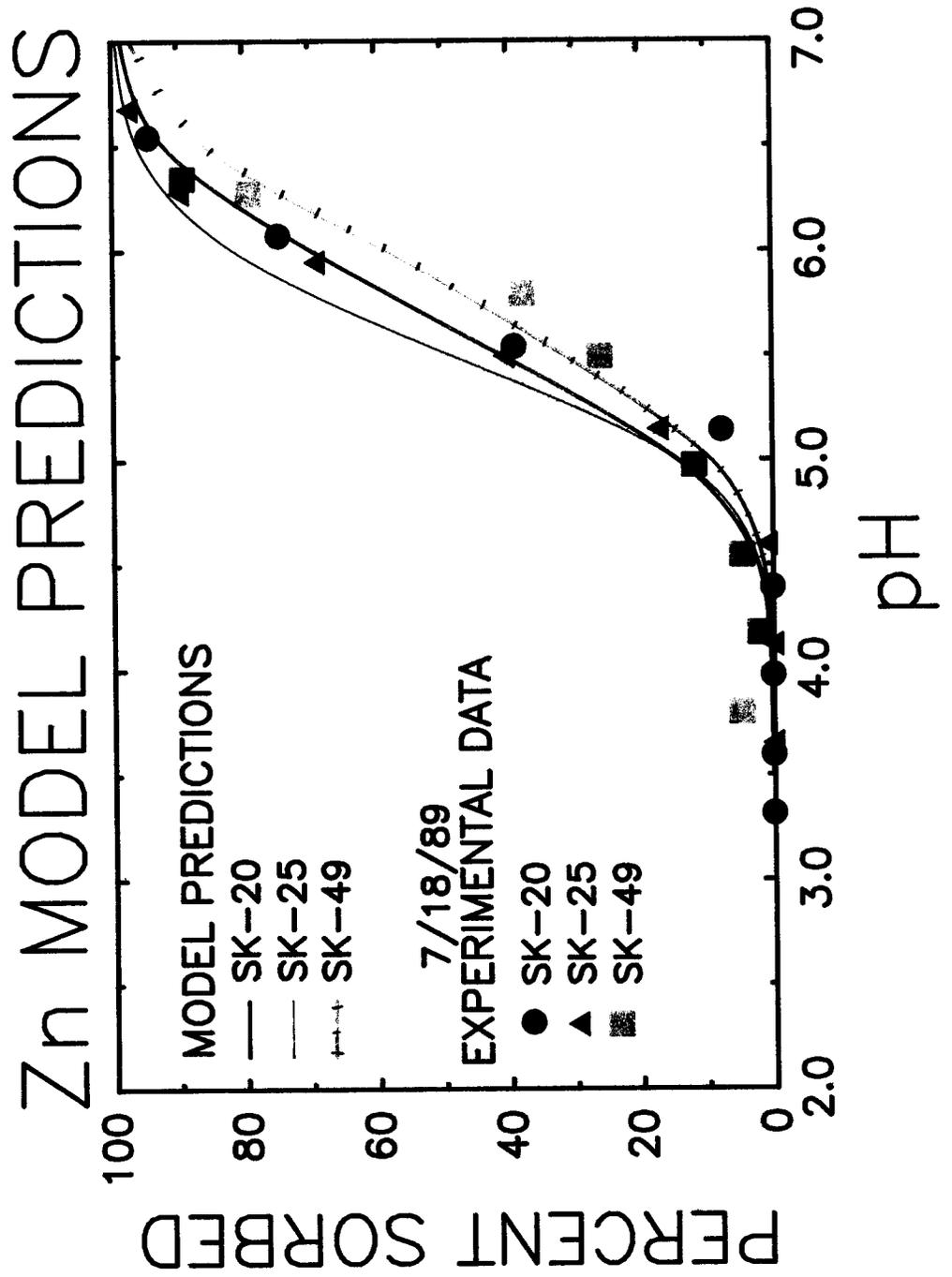
SK-11=pH 6.40
SK-20=pH 3.75
SK-25=pH 4.25
SK-49=pH 4.10

○ Cu
  Pb
◇ Zn

Stream pH

Parts per Million

Figure 22

Cu MODEL PREDICTIONS

Figure 23

Cd MODEL PREDICTIONS

Figure 24

Zn MODEL PREDICTIONS

PARTITIONING OF METALS BETWEEN WATER AND FLOCCULATED BED MATERIAL IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE NEAR LEADVILLE, COLORADO

By Kathleen S. Smith[1,2], Donald L. Macalady[2], and Paul H. Briggs[1]

ABSTRACT

Onsite metal-partitioning studies were performed in August 1987 using mixtures of flocculated iron oxyhydroxide material (floc) and streamwater collected from St. Kevin Gulch, a central Colorado mountain stream contaminated by acid mine drainage. The pH was varied between ambient (about 3.5) and 6 by the addition of NaHCO3 to aliquots of unfiltered streamwater and floc/streamwater mixtures. Iron and aluminum aqueous concentrations seem to be controlled primarily by solubility reactions, whereas zinc, manganese, copper, and cadmium concentrations are controlled by sorption reactions. The sorption reactions are pH dependent, with a sorption edge between pH 5 and 6 for zinc, and between pH 3.5 and 4.5 for copper. Cadmium does not appear to have a well-defined sorption edge up to pH 6, and the manganese concentration gradually decreases over the pH range tested. Flocculated iron oxyhydroxide material does not seem to be an effective sink for trace metals in St. Kevin Gulch at the ambient pH of about 3.5. Although pH-dependent solubility and sorption reactions drive metal partitioning to the solid phase at higher pH, aqueous concentrations of manganese, zinc, and cadmium at pH 6 are still significant.

INTRODUCTION

Acid mine drainage is a potential threat to the quality and ecology of receiving waters. Treatment of these metal-rich waters is hampered by a lack of understanding of the processes that control metal mobility in acidic systems. A detailed understanding of this metal chemistry is necessary if successful mitigation procedures are to be adopted.

This paper describes research that examined metal partitioning between flocculated iron oxyhydroxide(s) (floc) and streamwater in an acid mine drainage system. Jenne (1968) emphasized the importance of amorphous hydrous iron oxides in the sorption of metals in natural systems. It has been reported that hydrous iron oxides have a high affinity for the binding of copper (Cu), cadmium (Cd), and zinc (Zn) (Benjamin and Leckie, 1981). Tessier and others (1985) found the sorption of trace metals onto low-pH, iron oxyhydroxide-rich lake sediments to be greater than predicted by simple models. Controls on metal-partitioning processes may be significant in the determination of metal transport in aquatic systems affected by acid mine drainage.

St. Kevin Gulch is a small subalpine stream located 7 km (kilometers) northwest of Leadville, Colo. (fig. B–24). St. Kevin Gulch receives acidic, metal-rich tailings effluent, which produces elevated concentrations of sulfate and several metals including iron (Fe), manganese (Mn), aluminum (Al), Zn, Cu, and Cd (McKnight and others, 1988).

The questions considered in this paper include: (1) Is the floc that coats streambed pebbles in St. Kevin Gulch an important sink for metals? (2) How does metal partitioning between streamwater and floc change as the pH of the stream changes?

An onsite metal-partitioning study was performed with unfiltered streamwaters and floc/streamwater mixtures collected from St. Kevin Gulch in early August 1987. The pH was varied in these experiments, and the corresponding equilibrated aqueous metal concentrations were determined. The experiments were designed to simulate seasonal pH changes and pH changes encountered at confluences of acidic waters with nonacidic waters.

EXPERIMENTAL METHODS

Experiments were performed to determine the time period for rapid-step sorption reactions

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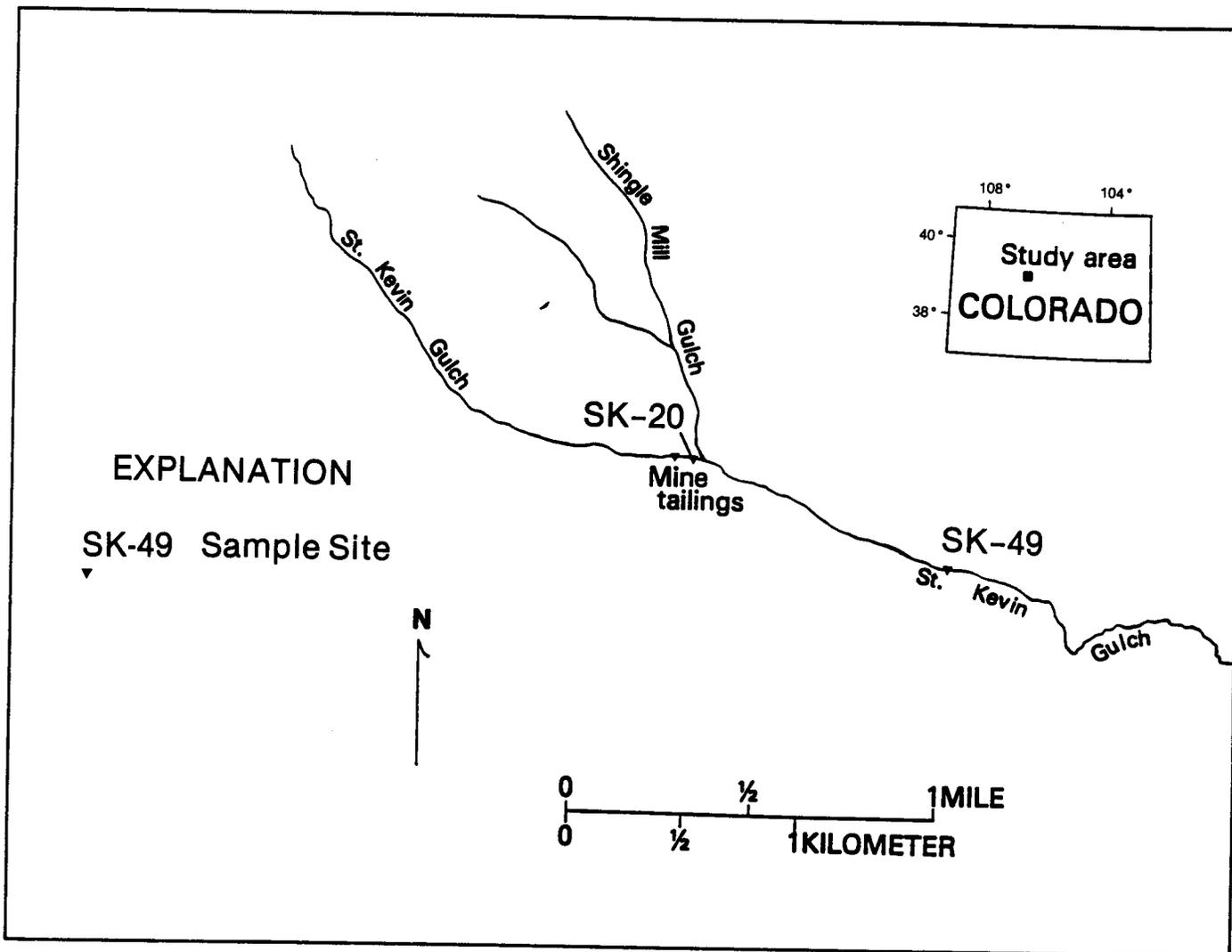
Figure B-24.—Sampling sites along St. Kevin Gulch (from McKnight and others, 1988).

to reach completion. Floc was collected from St. Kevin Gulch sites SK–20 and SK–49 (fig. B–24) by agitating floc-coated streambed pebbles in a closed polyethylene container to obtain a floc/streamwater mixture. Enough 0.5 M NaHCO₃ was added to these floc suspensions to raise the pH to 6. Aliquots of the mixture were removed and filtered at various time intervals over a 1-day period. Analyses of these aliquots indicated that a time period of 2 hours was adequate for rapid-step sorption reactions to reach completion.

Metal-partitioning experiments were conducted with unfiltered streamwaters and floc/streamwater mixtures collected from sites SK–20 and SK–49 (fig. B–24). A 40-mL (milliliter) subsample of each suspension was titrated to determine the amount of base necessary to raise the pH to 6. Forty-mL aliquots of unfiltered streamwaters and floc/streamwater mixtures were pipetted into a series of 60-mL polyethylene bottles. The pH of the aliquots was adjusted to several values between ambient (about 3.5) and 6 using either 0.1 M or 0.5 M NaHCO₃. The contents of the bottles were equilibrated at streamwater temperature with occasional shaking for 2 hours after which final pH values were determined and aliquots were filtered through 0.1-μm

102

(micrometer) nitrocellulose filters. The filtrates were collected for analysis.

Most metal concentrations in the filtrates were determined using inductively coupled plasma-atomic emission spectrometry (ICP–AES) (Lichte and others, 1987). Flameless atomic-absorption spectrometry (AAS-graphite furnace) was used to measure Cu and Cd (Perkin-Elmer, 1977).

RESULTS AND DISCUSSION

Rates of Cu and Cd sorption at pH 6 onto floc from sites SK–20 and SK–49 are illustrated in figures B–25a and B–25b. These data show initially very rapid sorption followed by a less well-defined, much slower sorption process. Results from both sites exhibit a slight decrease in the amount of sorption between the initial rapid step and the slower step. On the basis of these data, a time period of 2 hours was deemed adequate for the rapid sorption step to reach completion and

was chosen as the equilibration time for metal-partitioning experiments.

In the metal-partitioning experiments, the floc suspension from site SK–20 contained 5.7 g/L (grams per liter) solid floc, and that from site SK–49 contained 7.0 g/L. Surface area of the floc is about 150 m^2/g (square meters per gram) at site SK–20, and 50 m^2/g at site SK–49 (Ranville and others, 1989, this Proceedings). As a consequence, the suspension from site SK–20 contained about 2.4 times more sites than that from site SK–49. Figures B–26a and B–26b illustrate titration curves of equal volumes of floc suspensions using NaHCO3. About 2.5 times more moles of NaHCO3 per unit volume of suspension were required to obtain a pH of 6 in the floc suspension from site SK–20 than in the floc suspension from site SK–49.

Results of the partitioning studies are summarized in figures B–27a, B–27b, B–28a, and
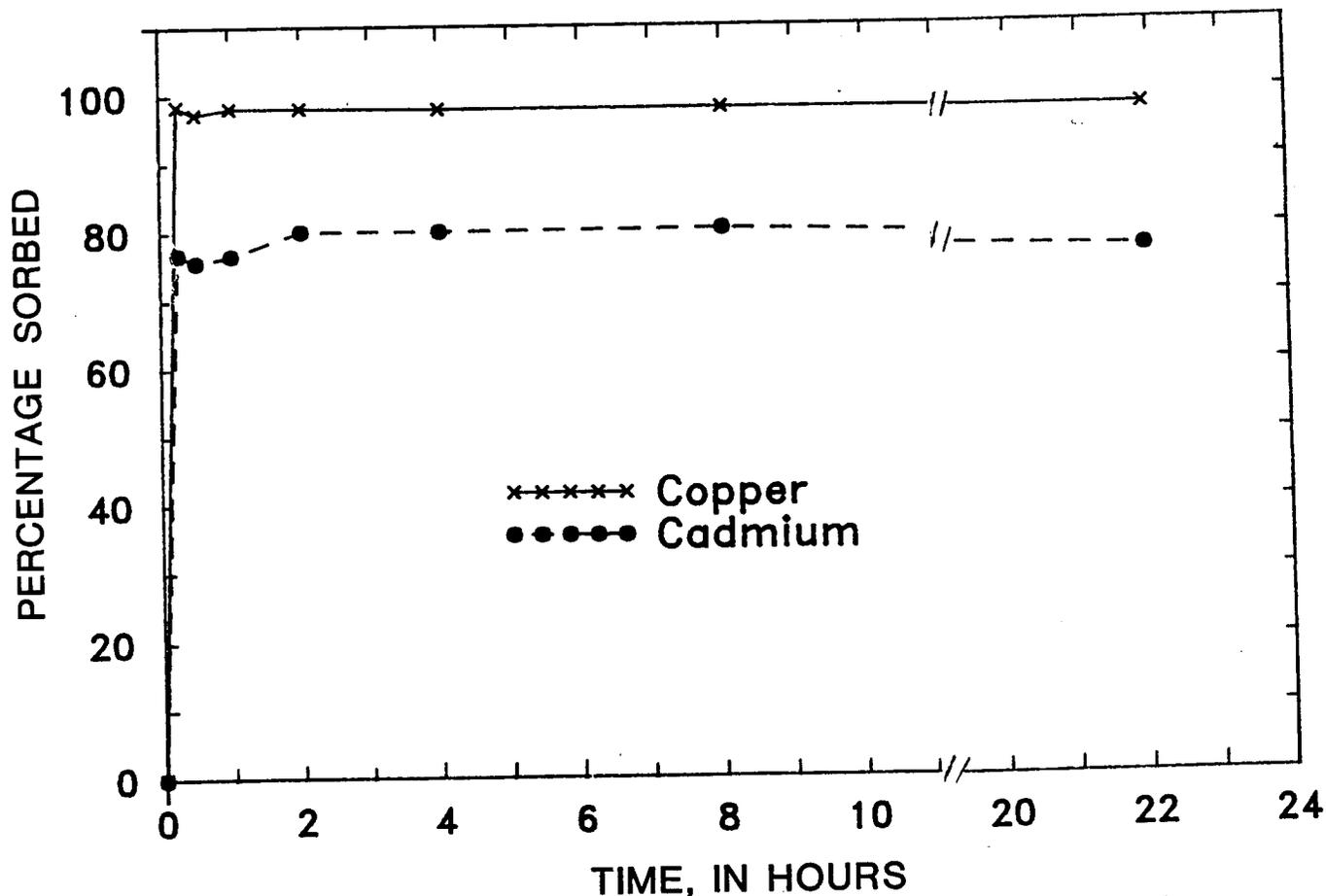
Figure B-25a. — Rates of copper and cadmium sorption at pH 6 onto floc collected from site SK–20.

B–28b. Four bars are shown for each species. The far-left bar represents the species concentration in pH-unaltered unfiltered streamwater collected at the time of floc suspension collection, the middle-left is the species concentration in a pH-unaltered floc-suspension aliquot, the middle-right is the species concentration in an unfiltered streamwater aliquot adjusted to the highest pH measured, and the far-right is the species concentration in a floc-suspension aliquot adjusted to the highest pH measured. These data show that aqueous Fe and Al concentrations in the floc/streamwater mixtures are below the limits of detection of 0.06 ppm (parts per million) and 2 ppm, respectively, at pH 6. The aluminum concentration drops to below detection by pH 4 at both sites whereas the Fe concentration drops to below detection at pH 4 for site SK–49 and at pH 5.9 for site SK–20. Decrease in aqueous Fe concentration between the pH-unaltered unfiltered streamwater and the pH-unaltered floc/streamwater mixture from site SK–20 points to active loss of Fe from the aqueous phase and indicates disequilibrium of Fe at that site. A slight pH decrease was noted in the pH-unaltered mixture. Comparison of results from pH alteration of unfiltered streamwaters with those from pH alteration of floc suspensions reveals that Fe and Al aqueous concentrations are primarily controlled by solubility reactions.

Zn, Mn, Cu, and Cd concentrations appear to be controlled by sorption reactions. The sorption edge is between pH 5 and 6 for Zn, and between pH 3.5 and 4.5 for Cu. Cadmium does not appear to have a well-defined sorption edge up to pH 6, and Mn exhibits a gradual concentration decrease over the pH range tested. This pH-dependent sorption behavior is in agreement with generally accepted trends observed in laboratory studies on simple amorphous iron oxyhydroxide
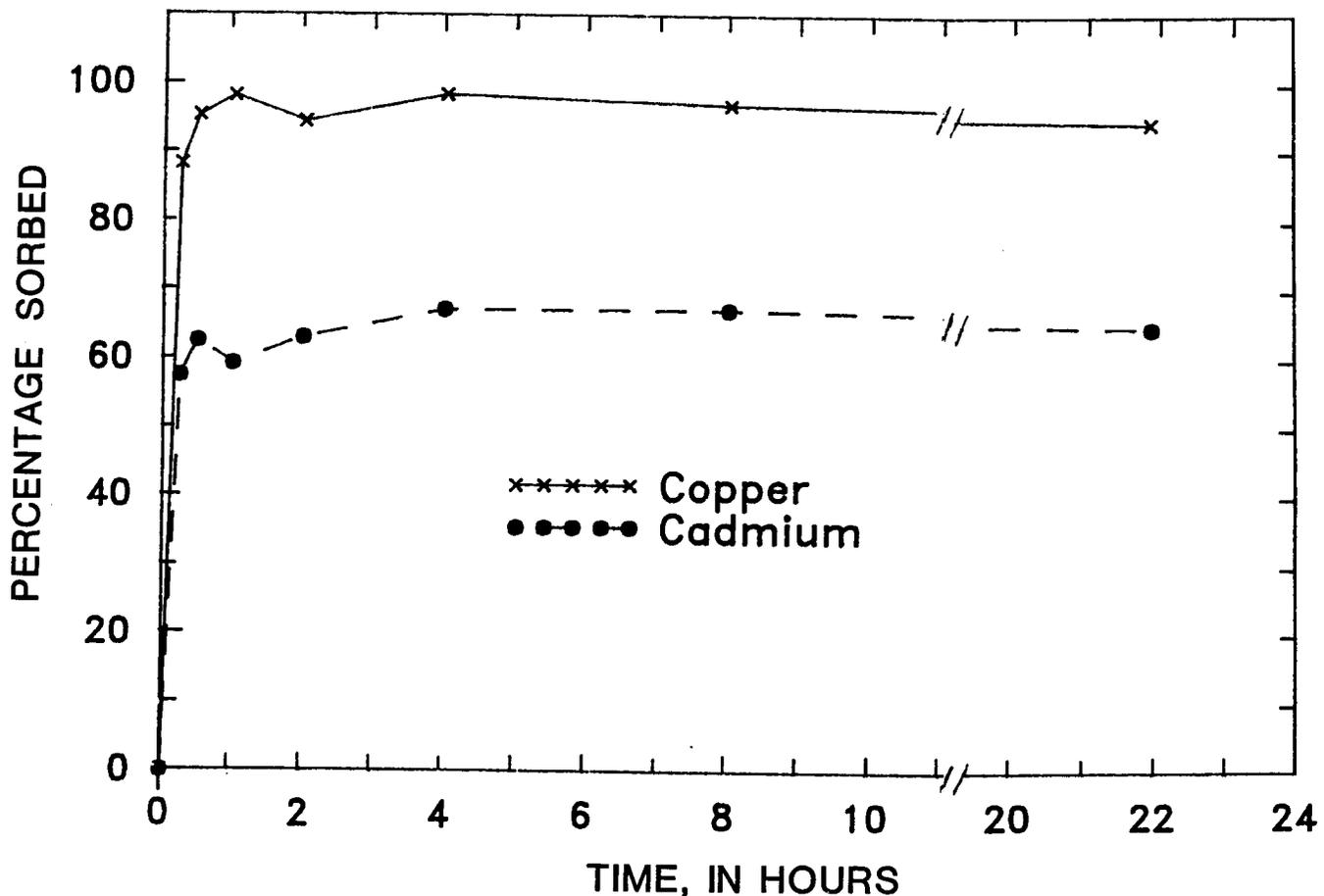
Figure B-25b.—Rates of copper and cadmium sorption at pH 6 onto floc collected from site SK–49.
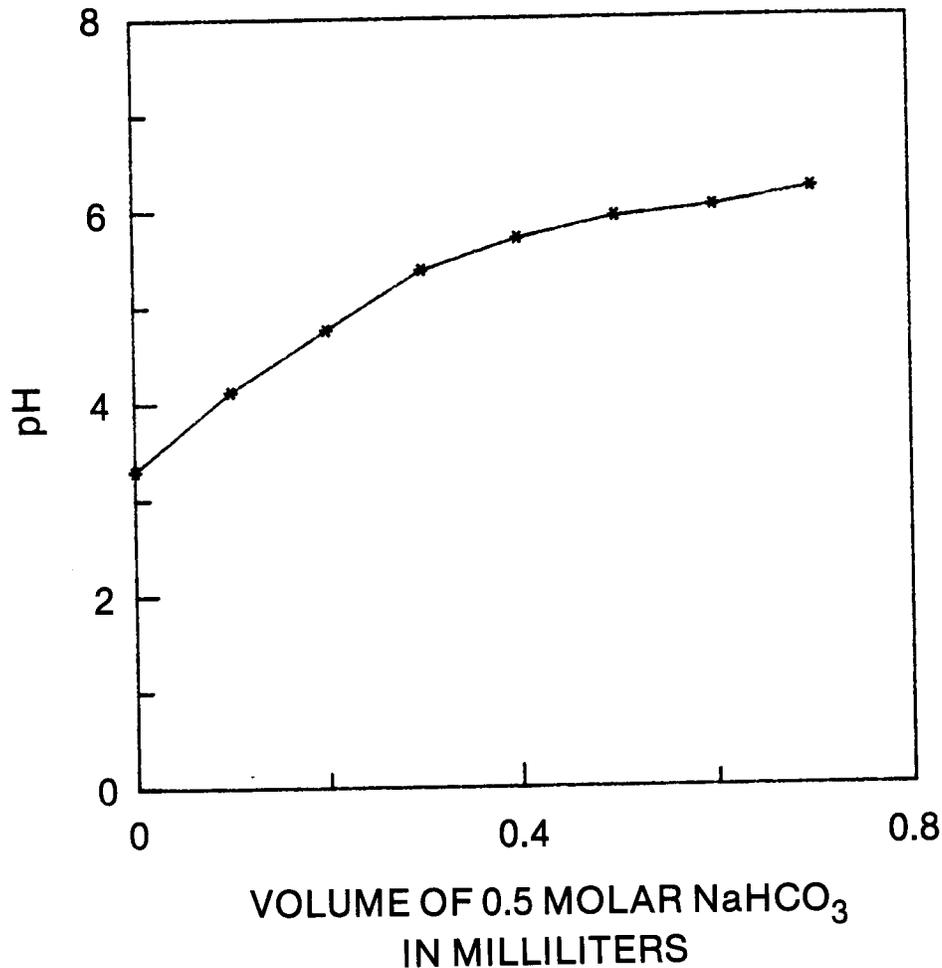
Figure B-26a. — Titration curve for floc suspension collected from site SK-20.

systems (for example see Benjamin and Leckie, 1981).

Conclusions regarding partitioning trends are consistent with data from Shingle Mill Gulch (fig. B-24), a tributary of St. Kevin Gulch with higher pH (6.5). Shingle Mill Gulch has much lower aqueous metal concentrations and, with the exception of Fe, higher solid-phase metal concentrations than does St. Kevin Gulch. These data are discussed in detail by Ranville and others, 1989 (this Proceedings), and indicate that metal partitioning has been driven toward the solid phase in Shingle Mill Gulch.

Adsorption properties of a material are controlled by the surface properties of that material. Coatings and sorption of counterions (for example, sulfate) and/or organics can alter the original surface properties, especially surface charge. Data presented by Ranville and others, 1989 (this Proceedings), illustrate that St. Kevin Gulch floc has a near-neutral surface charge, indicating modifications of the floc surface. Planned research toward understanding the processes that control surface charge will improve understanding of sorption mechanisms and metal-partitioning reactions.

SUMMARY

Results from this study indicate that the flocculated iron oxyhydroxide material that coats streambed pebbles in St. Kevin Gulch is not an effective sink for trace metals at the ambient pH (about 3.5). Floc/water metal partitioning increases as the pH increases, but aqueous concentrations of several metals at pH 6 are still significant.
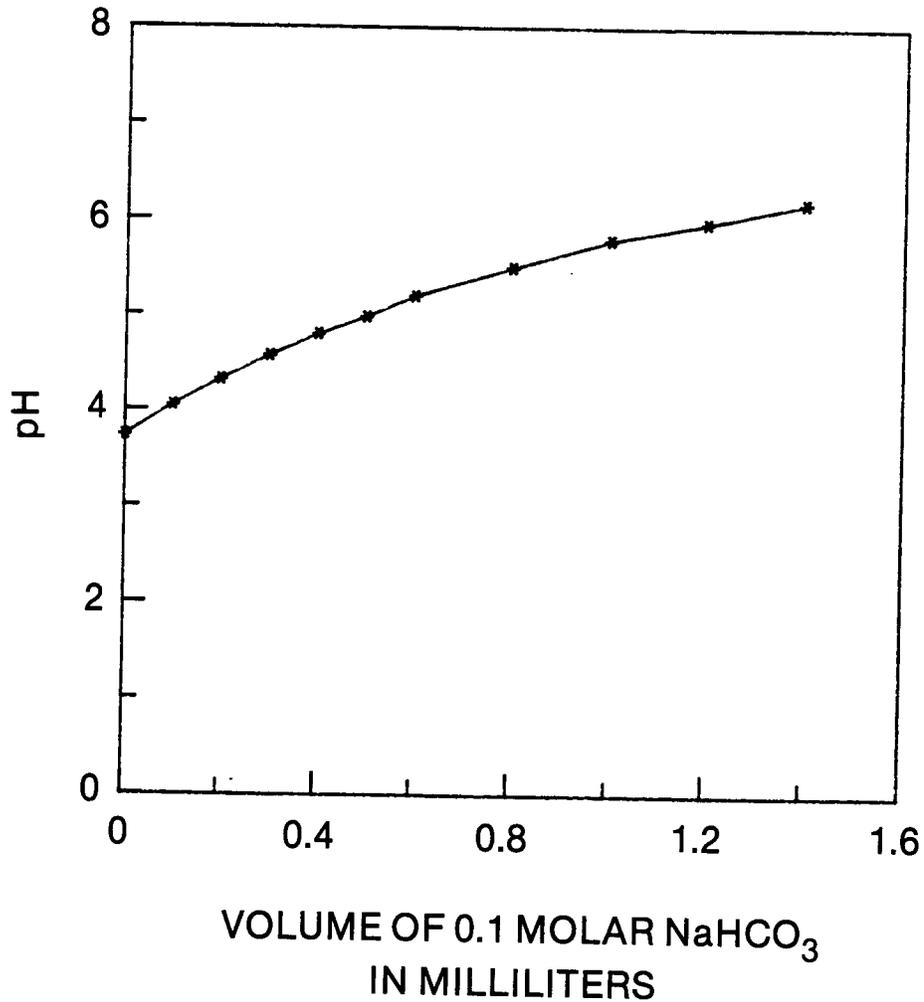
Figure B-26b. — Titration curve for floc suspension collected from site SK–49.

106
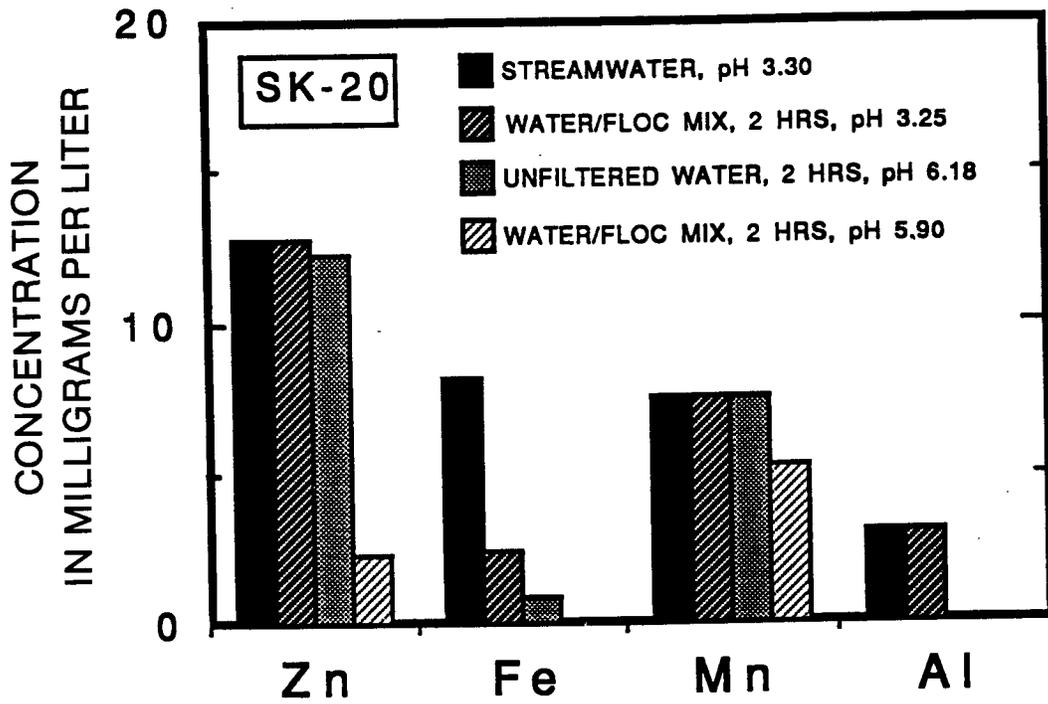
Figure B-27a. — Metal-partitioning for zinc (Zn), iron (Fe), manganese (Mn), and aluminum (Al) at site SK-20.
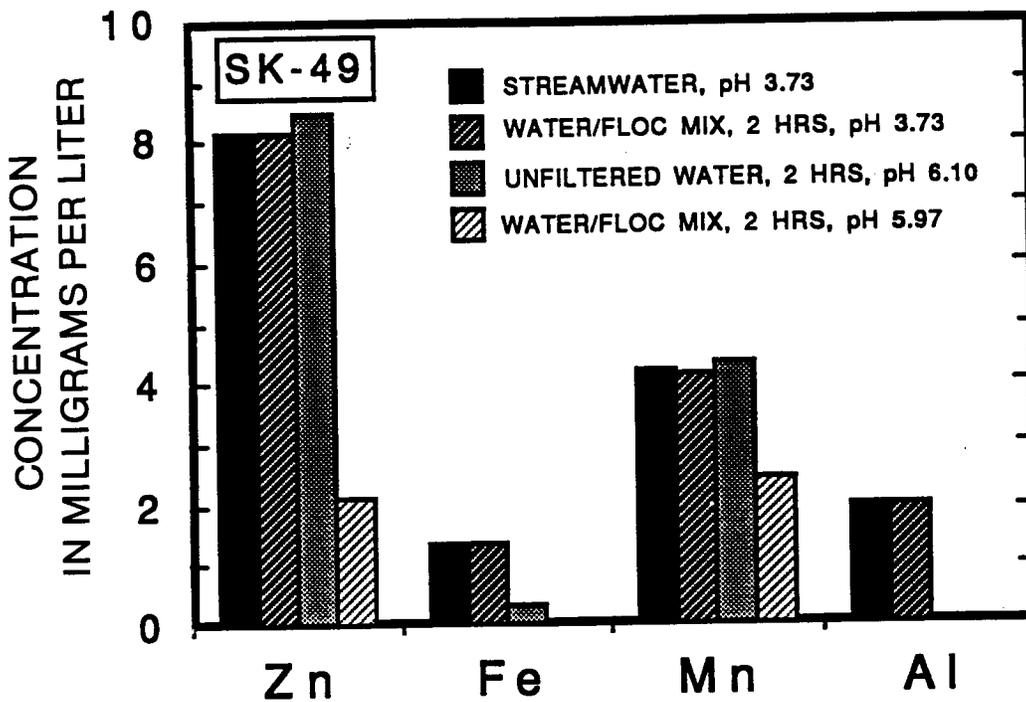
Figure B-27b. — Metal-partitioning for zinc (Zn), iron (Fe), manganese (Mn), and aluminum (Al) at site SK-49.
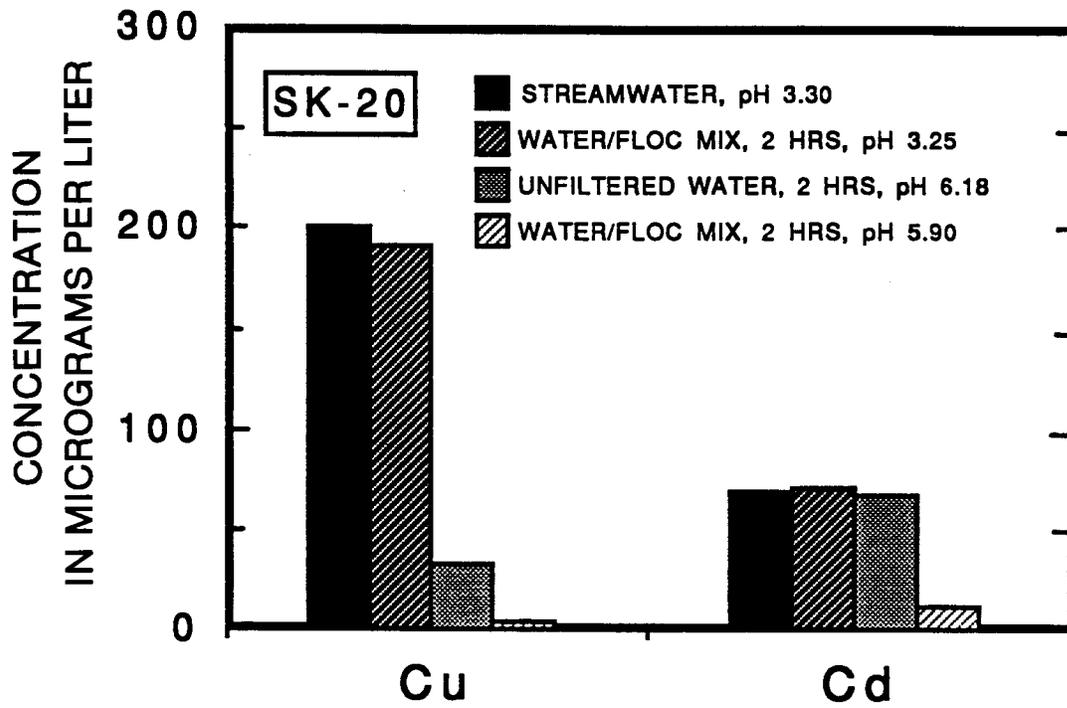
Figure B-28a.—Metal-partitioning for copper (Cu) and cadmium (Cd) at site SK-20.
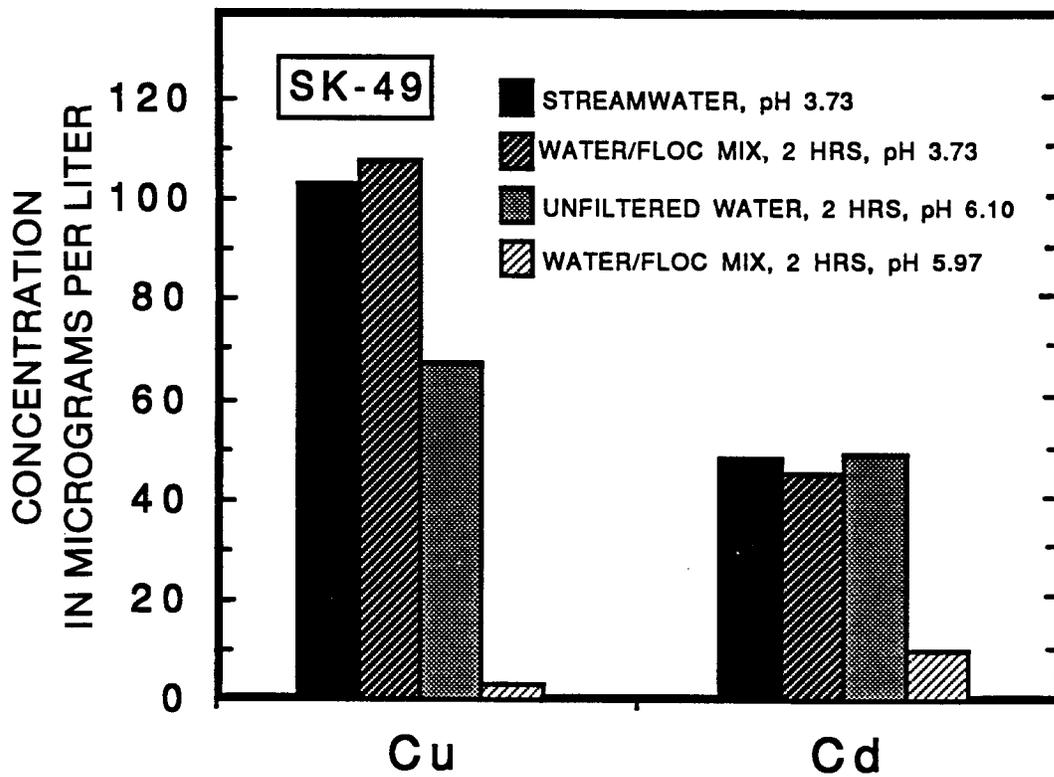
Figure B-28b.—Metal-partitioning for copper (Cu) and cadmium (Cd) at site SK-49.

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U.S. GEOLOGICAL SURVEY TOXIC SUBSTANCES HYDROLOGY PROGRAM--PROCEEDINGS OF THE TECHNICAL MEETING, PHOENIX, ARIZONA, SEPTEMBER 26-30, 1988

By Gail E. Mallard and Stephen E. Ragone, editors

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Water-Resources Investigations Report 88-4220

Reston, Virginia
1989

DEPARTMENT OF THE INTERIOR

MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

APPENDIX II: Composition of bed sediment from two streams contaminated by acid-mine drainage, St. Kevin Gulch and Shingle Mill Gulch, Lake County, Colorado

CONTENTS

TABLES

TABLES, cont.

INTRODUCTION

Between May and October, 1988, we collected nine suites of streambed-sediment samples from sites along St. Kevin Gulch and Shingle Mill Gulch, Lake County, Colorado (fig. 1). St. Kevin Gulch, a small subalpine mountain stream, is a tributary of Tennessee Creek and is located 7 km northwest of Leadville, Colorado. St. Kevin Gulch receives acidic (pH 2.8) metal-rich discharge from an abandoned mine-dump/mill-tailings area (labeled "Tailings" in fig. 1). St. Kevin Gulch also receives some metal-rich contamination from mine workings upstream of the tailings discharge. Downstream from the tailings discharge the pH of St. Kevin Gulch ranges between 3.3 and 4.6. The streambed material consists of rocks and pebbles coated with iron-rich hydrous oxides (floc). The ore in the area is silver sulfide veins in quartz-biotite-feldspar schist and gneiss (McKnight et al., 1988). The vegetation in the area is a pine and spruce forest.

Shingle Mill Gulch enters St. Kevin Gulch downstream from the tailings discharge (fig. 1). Although Shingle Mill Gulch flows through an abandoned mine-dump area, its pH ranges between 6.1 and 6.8. The bed of Shingle Mill Gulch is covered with plant-like material that traps and retains sediment.

The objective of this report is to present elemental analyses of streambed sediments from both St. Kevin Gulch and its tributary, Shingle Mill Gulch.

METHODS OF STUDY
Sample Collection

We collected samples at six sites along St. Kevin Gulch and one site on Shingle Mill Gulch (fig. 1). In St. Kevin Gulch we collected the iron-rich floc that coated streambed rocks and pebbles by placing the rocks and pebbles inside a one-quart plastic container. The rocks and pebbles were shaken with stream water and the floc/stream-water slurry was decanted into a 1-gallon polyethylene jug. This procedure was repeated several times until the one-gallon jug was filled. Each sample represents a composite of streambed floc within about a 12-foot by 4-foot area. Duplicate gallon jugs of floc were collected at selected sites to test the variation of this collection method. The floc/stream-water slurry in each of the 1-gallon jugs was shaken and dispensed into several smaller polyethylene and glass containers to be saved for a variety of analyses. The polyethylene containers were new and untreated. The glass containers had been washed in soap and water and heated at 400 C overnight. The glass containers were equipped with teflon-lined caps.

In Shingle Mill Gulch, the streambed consisted of plant material that had trapped and retained sediments. This plant material was gently washed in stream water and the trapped sediments were removed from the plant material. The resulting sediment/stream-water slurry was treated as was descibed for the St. Kevin Gulch floc.

The pH of the stream water was determined in the field using an Orion Model 401 Specific Ion Meter and a Ross combination pH electrode. The pH meter was standardized using pH 4 and pH 7 buffers.

Sample Preparation

Bed-sediment/stream-water slurries were allowed to settle overnight. The next day the clarified water was decanted off and the sediments were allowed to air-dry. Air-dried sediments in polyethylene containers were hand ground using a mortar and pestle. The mortar and pestle were cleaned in-between samples with fine-grained silica sand, and wiped out with deionized water and Kimwipes. These samples were then weighed, digested, and analyzed for elemental chemistry. Air-dried sediments in glass containers were disaggregated inside the container using a teflon-coated spatula. These samples were then analyzed for carbon content.

Sample Analysis

Atomic emission spectrometry method

We analyzed the streambed-sediment samples for 40 elements using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Lichte and others, 1987). The samples were digested in a mixture of nitric, hydrochloric, perchloric, and hydrofluoric acids. This digestion procedure vaporizes silicon and boron (Lichte and others, 1987). The precision of most determinations with this technique is about 5 to 10% relative standard deviation (Lichte and others, 1987). The elements analyzed and their lower limits of detection are listed in table 1.

Spectrographic method for silicon

We analyzed for silicon using a semiquantitative, direct-current arc emission spectrographic method (Grimes and Marranzino, 1968). Spectrographic results were obtained by visual comparison of spectra derived from the sample against spectra obtained from standards made from pure oxide. The limits of determination for silicon ranged from 10% to 0.001%. Standard concentrations are geometrically spaced over any given order of magnitude of concentration as follows: 10, 5, 2, 1, and so forth.

Table 1. Detection limits for elements analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Element	Detection Limit	Element	Detection Limit
Al (%)	0.01	Ag (ppm)	4
Ca (%)	0.01	As (ppm)	20
Fe (%)	0.01	Au (ppm)	16
K (%)	0.1	Ba (ppm)	2
Mg (%)	0.01	Be (ppm)	2
Na (%)	0.01	Bi (ppm)	20
P (%)	0.01	Cd (ppm)	4
Ti (%)	0.01	Ce (ppm)	8
		Co (ppm)	2
		Cr (ppm)	2
		Cu (ppm)	2
		Eu (ppm)	4
		Ga (ppm)	8
		Ho (ppm)	8
		La (ppm)	4
		Li (ppm)	4
		Mn (ppm)	8
		Mo (ppm)	4
		Nb (ppm)	8
		Nd (ppm)	8
		Ni (ppm)	4
		Pb (ppm)	8
		Sc (ppm)	4
		Sn (ppm)	20
		Sr (ppm)	4
		Ta (ppm)	80
		Th (ppm)	8
		U (ppm)	200
		V (ppm)	4
		Y (ppm)	4
		Yb (ppm)	2
		Zn (ppm)	4

Samples whose concentrations are estimated to fall between those values are assigned values of 7, 3, 1.5, and so forth. The precision of the analytical method is approximately plus or minus one reporting interval at the 83 percent confidence level and plus or minus two reporting intervals at the 96 percent confidence level (Motooka and Grimes, 1976).

Combustion/coulometric method for carbon

We analyzed for total carbon using a Coulometrics, Inc. Model 5011 Coulometer with a Model 5120 Total Carbon Combustion Apparatus. Approximately 100 mg of sediment was combusted at 900 C for 6 minutes. The evolved carbon dioxide was titrated in a coulometric cell to determine the amount of carbon present in the sample (Lee and Macalady, 1989). For a similar procedure, Lee and Macalady (1989) calculated a relative standard deviation of 2.78% for 15 replicate measurements of a sediment containing about 1.20% total carbon. In St. Kevin Gulch, total carbon results are assumed to represent organic carbon due to the low pH of the stream water.

RESULTS

Elemental Composition of Streambed Material

Tables 2 and 3 list the results of analyses of streambed-sediment samples from St. Kevin Gulch and Shingle Mill Gulch, respectively. Also listed are the stream-water pH values measured in the field at the time of sediment collection. The data are arranged so that column 1 contains the USGS-assigned site numbers. These numbers correspond to the site numbers shown on the site location map (fig. 1). A "D" after the site number indicates that the sample is an analytical duplicate, and a "X" after the site number indicates that the sample is a field duplicate. Column 2 contains the dates the samples were collected during the 1988 field season. The number before the period refers to the month and the number after the period refers to the day. Column 3 lists the stream-water pH values at the time of sample collection. Column 4 contains total carbon data obtained using a combustion/coulometric method. Column 5 contains silicon data obtained using a semi-quantitative spectrographic method. The remaining columns list elemental data obtained using atomic emission spectrometry (ICP-AES). If an element was below the limit of detection, a "less than" symbol (<) was entered in the tables in front of the lower limit of detection. If an element was observed but was above the highest reporting value, a "greater than" symbol (>) was entered in the tables in front of the upper limit of determination. These "less-than" and "greater-than" values will be referred to as qualified values. The ICP-AES determinations for Eu, Ho, Sn, Ta, and U in St. Kevin Gulch streambed sediment, and for Bi, Ho, Sn, Ta, and U in Shingle Mill Gulch streambed sediment were all below the limit of detection listed in table 1; consequently, the columns for these elements have been deleted from tables 2 and 3.

Table 2. Results of elemental analysis of streambed-sediment samples and stream-water pH measurements, St. Kevin Gulch, Colorado.

Site No.	Date	pH	C(%)	Si(%)	Al(%)	Ca(%)	Fe(%)	K(%)	Mg(%)	Na(%)	P(%)
SK-11	5.18	6.40	9.1	2	5.4	0.15	21	1.8	0.36	0.26	0.20
SK-11D	5.18			2	5.4	0.15	21	1.8	0.36	0.25	0.20
SK-20	5.18	3.75	2.4	1	2.2	0.07	35	0.9	0.22	0.18	0.33
SK-20D	5.18			2	2.2	0.07	34	0.9	0.22	0.19	0.33
SK-25	5.18	4.25	2.8	0.7	2.7	0.06	34	1.0	0.19	0.18	0.24
SK-49	5.18	4.10	4.8	3	5.8	0.18	14	2.8	0.30	0.62	0.20
SK-49D	5.18			3	5.9	0.17	15	2.8	0.32	0.62	0.20
SK-11	6.03	4.20	6.7	>10	5.3	0.13	20	2.1	0.37	0.35	0.16
SK-20	6.03	3.85	2.9	5	1.5	0.03	36	0.6	0.12	0.09	0.36
SK-25	6.03	4.30	4.1	1.5	2.6	0.06	32	1.0	0.16	0.22	0.23
SK-25X	6.03		2.8	10	3.4	0.09	27	1.3	0.22	0.30	0.21
SK-25XD	6.03			10	3.5	0.09	29	1.4	0.22	0.31	0.22
SK-49	6.03	4.25	7.4	>10	4.6	0.13	21	1.8	0.30	0.33	0.26
SK-11	6.21	4.70	9.6	2	3.8	0.12	24	1.4	0.31	0.26	0.15
SK-20	6.21	3.90	4.4	1	0.94	0.03	39	0.3	0.08	0.05	0.33
SK-25	6.21	4.55	7.2	0.3	0.97	0.04	40	0.3	0.05	0.06	0.23
SK-35	6.21	4.40	7.5	2	3.0	0.09	29	1.2	0.17	0.22	0.21
SK-49	6.21	4.40	9.3	5	4.8	0.11	21	1.8	0.31	0.26	0.27
SK-700	6.21	4.43	6.1	2	5.7	0.19	13	2.7	0.32	0.50	0.24
SK-700X	6.21		4.7	5	6.6	0.28	9.8	2.8	0.46	0.63	0.20
SK-11	7.08	4.20	11	2	3.0	0.13	24	1.0	0.21	0.27	0.13
SK-20	7.08	3.65	3.1	0.5	0.62	0.04	43	0.2	0.05	0.04	0.33
SK-20D	7.08			0.7	0.61	0.04	41	0.2	0.05	0.04	0.32
SK-25	7.08	4.22	7.5	0.3	0.78	0.07	41	0.2	0.06	0.04	0.21
SK-35	7.08	4.10	7.9	0.5	1.7	0.17	36	0.4	0.09	0.10	0.19
SK-49	7.08	4.05	13	2	2.9	0.15	25	1.0	0.20	0.23	0.33
SK-49X	7.08		14	1	3.0	0.14	25	1.1	0.24	0.24	0.34
SK-700	7.08	4.10	6.2	10	6.6	0.23	10	2.3	0.51	0.62	0.24
SK-11	7.26	3.98	13	5	1.8	0.08	30	0.5	0.11	0.11	0.20
SK-20	7.26	3.52	3.0	0.5	0.29	0.05	41	< 0.1	0.04	0.02	0.33
SK-25	7.26	3.85	4.6	0.7	0.52	0.02	42	0.2	0.03	0.03	0.25
SK-25D	7.26			0.7	0.51	0.02	42	0.2	0.03	0.03	0.25
SK-35	7.26	3.75	6.0	0.7	0.68	0.03	40	0.2	0.04	0.04	0.23
SK-49	7.26	3.80	12	10	3.4	0.16	21	1.2	0.23	0.27	0.40
SK-700	7.26	3.75	6.4	>10	5.1	0.18	14	2.0	0.33	0.50	0.25
SK-11	8.10	4.05	7.6	5	5.9	0.17	15	2.1	0.47	0.45	0.18
SK-20	8.10	3.38	2.5	0.3	0.44	< 0.01	44	0.1	0.03	0.02	0.37
SK-25	8.10	3.78	4.0	0.5	0.86	0.03	41	0.3	0.06	0.08	0.25
SK-25D	8.10			1	0.86	0.03	40	0.3	0.06	0.08	0.24
SK-49	8.10	3.72	9.9	5	4.7	0.12	20	1.6	0.35	0.27	0.28
SK-11	8.24	3.72	4.5	2	3.3	0.10	24	1.0	0.23	0.16	0.23
SK-20	8.24	3.30	2.9	0.3	0.76	0.04	41	0.3	0.06	0.05	0.35
SK-20D	8.24			0.5	0.80	0.04	41	0.3	0.06	0.05	0.35
SK-20X	8.24		2.4	1	0.78	0.02	45	0.3	0.06	0.04	0.44
SK-25	8.24	3.65	3.0	0.5	0.54	0.02	42	0.2	0.04	0.03	0.25
SK-35	8.24	3.60	5.4	0.5	1.1	0.04	39	0.4	0.07	0.06	0.23
SK-49	8.24	3.60	12	2	4.2	0.13	21	1.4	0.31	0.21	0.28
SK-11	9.13	3.95	11	2	3.0	0.18	23	1	0.27	0.15	0.23
SK-20	9.13	3.50	2.8	0.7	0.82	0.03	44	0.3	0.06	0.05	0.47
SK-25	9.13	3.82	3.3	0.5	0.52	0.03	45	0.2	0.04	0.04	0.28
SK-35	9.13	3.69	6.0	1.5	1.1	0.05	38	0.4	0.08	0.07	0.36
SK-35X	9.13		5.3	1.5	4.1	0.42	25	1.2	0.29	0.34	0.22
SK-49	9.13	3.60	11	7	5.1	0.24	17	1.8	0.39	0.28	0.26
SK-11	10.07	4.15	13	10	3.1	0.17	22	1	0.26	0.20	0.27

Table 2. Continued.

Site No.	Date	pH	C(%)	Si(%)	Al(%)	Ca(%)	Fe(%)	K(%)	Mg(%)	Na(%)	P(%)
SK-20	10.07	3.60	2.9	5	1.3	0.08	39	0.5	0.11	0.08	0.44
SK-25	10.07	3.91	3.2	2	0.48	0.02	43	0.2	0.03	0.03	0.25
SK-25D	10.07			1	0.48	0.02	42	0.2	0.03	0.03	0.25
SK-35	10.07	3.77	7.3	1.5	1.9	0.1	32	0.7	0.14	0.15	0.28
SK-49	10.07	3.74	10	>10	4.2	0.26	20	1.6	0.30	0.35	0.24

Table 2. Continued.

Site No.	Date	Ti(%)	Mn(ppm)	Ag(ppm)	As(ppm)	Ba(ppm)	Be(ppm)	Bi(ppm)	Cd(ppm)	Ce(ppm)	Co(ppm)
SK-11	5.18	0.10	810	60	130	240	2	< 20	9	180	13
SK-11D	5.18	0.12	820	61	130	240	3	< 20	9	150	13
SK-20	5.18	0.07	360	20	120	130	< 2	30	6	36	6
SK-20D	5.18	0.08	430	20	110	130	< 2	30	6	39	5
SK-25	5.18	0.06	2000	22	70	260	< 2	20	11	48	11
SK-49	5.18	0.12	380	35	50	330	< 2	< 20	< 4	140	4
SK-49D	5.18	0.14	400	35	60	320	< 2	< 20	< 4	140	4
SK-11	6.03	0.11	530	43	100	250	< 2	< 20	< 4	130	8
SK-20	6.03	0.05	240	18	120	98	< 2	< 20	< 4	27	5
SK-25	6.03	0.06	280	19	60	150	< 2	20	< 4	57	4
SK-25X	6.03	0.08	330	21	60	190	< 2	20	< 4	81	5
SK-25XD	6.03	0.08	340	24	60	200	< 2	< 20	< 4	89	4
SK-49	6.03	0.11	410	42	70	240	< 2	20	< 4	93	4
SK-11	6.21	0.09	420	40	80	200	< 2	20	< 4	110	6
SK-20	6.21	0.03	170	12	100	51	< 2	20	< 4	20	4
SK-25	6.21	0.02	250	8	40	48	< 2	20	< 4	31	5
SK-35	6.21	0.06	290	37	40	160	< 2	< 20	< 4	72	5
SK-49	6.21	0.11	250	45	90	190	< 2	< 20	< 4	100	4
SK-700	6.21	0.13	1100	26	40	380	< 2	< 20	< 4	150	7
SK-700X	6.21	0.19	970	28	30	470	< 2	< 20	< 4	130	7
SK-11	7.08	0.09	270	25	50	200	< 2	20	< 4	98	5
SK-20	7.08	0.02	200	14	90	37	< 2	30	< 4	15	4
SK-20D	7.08	0.01	200	14	90	36	< 2	30	< 4	11	5
SK-25	7.08	0.01	290	10	40	34	< 2	20	< 4	27	5
SK-35	7.08	0.05	330	30	30	130	< 2	20	5	53	5
SK-49	7.08	0.07	360	76	50	150	< 2	< 20	4	90	4
SK-49X	7.08	0.07	310	77	50	180	< 2	< 20	< 4	80	5
SK-700	7.08	0.22	600	38	40	440	< 2	< 20	< 4	170	7
SK-11	7.26	0.04	200	37	60	110	< 2	20	< 4	55	4
SK-20	7.26	< 0.01	280	11	90	16	< 2	30	< 4	< 8	5
SK-25	7.26	0.01	170	11	50	24	< 2	30	< 4	19	4
SK-25D	7.26	0.01	180	11	50	26	< 2	30	< 4	14	4
SK-35	7.26	0.02	120	35	40	35	< 2	20	< 4	22	3
SK-49	7.26	0.07	280	120	60	160	< 2	< 20	< 4	83	4
SK-700	7.26	0.17	260	58	40	390	< 2	< 20	< 4	180	5
SK-11	8.10	0.19	340	42	60	340	< 2	< 20	4	98	8
SK-20	8.10	0.01	72	14	110	24	< 2	30	< 4	< 8	4
SK-25	8.10	0.02	130	14	50	77	< 2	30	< 4	23	4
SK-25D	8.10	0.02	140	14	50	66	< 2	20	< 4	26	5
SK-49	8.10	0.11	240	91	50	220	< 2	< 20	6	96	5
SK-11	8.24	0.08	300	66	50	150	< 2	< 20	< 4	74	5
SK-20	8.24	0.02	180	18	100	52	< 2	30	< 4	18	4
SK-20D	8.24	0.02	250	18	100	57	< 2	20	< 4	16	4
SK-20X	8.24	0.02	110	24	120	49	< 2	30	< 4	15	5
SK-25	8.24	0.01	120	13	50	65	< 2	30	< 4	13	4
SK-35	8.24	0.02	160	43	40	50	< 2	< 20	< 4	23	4
SK-49	8.24	0.08	370	91	40	180	< 2	< 20	16	71	6
SK-11	9.13	0.07	600	73	50	160	< 2	< 20	15	64	12
SK-20	9.13	0.02	230	23	130	53	< 2	30	< 4	14	4
SK-25	9.13	0.01	130	14	60	36	< 2	20	< 4	15	4
SK-35	9.13	0.03	170	87	60	59	< 2	20	< 4	25	5
SK-35X	9.13	0.16	690	45	50	400	2	< 20	26	92	10
SK-49	9.13	0.12	840	94	30	260	< 2	< 20	25	90	10
SK-11	10.07	0.07	370	71	40	170	< 2	< 20	20	64	9

Table 2. Continued.

Site No.	Date	Ti(%)	Mn(ppm)	Ag(ppm)	As(ppm)	Ba(ppm)	Be(ppm)	Bi(ppm)	Cd(ppm)	Ce(ppm)	Co(ppm)
SK-20	10.07	0.04	360	27	120	85	< 2	30	< 4	25	5
SK-25	10.07	0.01	94	14	50	29	< 2	20	< 4	11	4
SK-25D	10.07	0.01	94	15	50	30	< 2	20	< 4	11	4
SK-35	10.07	0.05	270	60	40	120	< 2	20	< 4	43	5
SK-49	10.07	0.09	880	90	40	260	< 2	< 20	28	100	9

Table 2. Continued.

Site No.	Date	Cr(ppm)	Cu(ppm)	Ga(ppm)	La(ppm)	Li(ppm)	Mo(ppm)	Nb(ppm)	Nd(ppm)	Ni(ppm)	Pb(ppm)
SK-11	5.18	70	520	15	77	13	7	< 8	110	12	1100
SK-11D	5.18	70	510	15	65	13	7	9	96	12	1100
SK-20	5.18	26	74	11	17	10	< 4	< 8	20	7	430
SK-20D	5.18	25	73	12	18	10	< 4	< 8	21	8	430
SK-25	5.18	25	120	14	19	12	8	< 8	30	6	610
SK-49	5.18	27	92	20	61	17	4	10	74	8	550
SK-49D	5.18	28	91	16	64	17	5	11	71	9	550
SK-11	6.03	62	250	17	56	16	7	< 8	75	11	800
SK-20	6.03	19	85	10	11	6	< 4	< 8	13	4	350
SK-25	6.03	20	110	12	25	8	8	< 8	32	< 4	440
SK-25X	6.03	24	110	12	35	12	7	< 8	42	5	500
SK-25XD	6.03	24	110	15	38	12	8	< 8	47	6	470
SK-49	6.03	35	150	16	40	16	8	< 8	55	10	560
SK-11	6.21	72	300	16	44	13	8	< 8	69	12	760
SK-20	6.21	19	110	10	8	5	< 4	< 8	10	< 4	320
SK-25	6.21	28	160	9	11	< 4	18	< 8	25	< 4	430
SK-35	6.21	36	210	13	30	10	8	< 8	49	8	410
SK-49	6.21	42	150	15	41	15	9	< 8	59	9	630
SK-700	6.21	36	140	17	67	18	7	10	82	10	530
SK-700X	6.21	47	140	20	56	27	5	9	70	13	550
SK-11	7.08	63	300	12	40	11	9	< 8	62	9	650
SK-20	7.08	12	130	9	6	< 4	< 4	< 8	10	< 4	170
SK-20D	7.08	13	120	9	6	< 4	< 4	< 8	11	< 4	180
SK-25	7.08	29	130	< 8	9	< 4	13	< 8	24	< 4	480
SK-35	7.08	37	290	< 8	21	< 4	10	< 8	39	6	430
SK-49	7.08	42	190	12	34	11	14	< 8	64	8	530
SK-49X	7.08	47	170	14	32	12	14	< 8	62	10	460
SK-700	7.08	51	130	21	75	31	6	12	96	14	570
SK-11	7.26	74	410	10	24	5	13	< 8	44	6	560
SK-20	7.26	12	79	< 8	< 4	< 4	< 4	< 8	< 8	< 4	93
SK-25	7.26	22	91	9	6	< 4	12	< 8	19	< 4	280
SK-25D	7.26	21	93	8	5	< 4	12	< 8	17	< 4	250
SK-35	7.26	26	96	< 8	8	< 4	9	< 8	14	< 4	230
SK-49	7.26	46	210	16	33	12	16	< 8	58	8	370
SK-700	7.26	42	120	17	79	21	9	11	95	9	450
SK-11	8.10	77	250	17	42	22	7	11	60	18	680
SK-20	8.10	11	77	< 8	< 4	< 4	< 4	< 8	< 8	< 4	110
SK-25	8.10	19	77	8	10	< 4	10	< 8	15	< 4	240
SK-25D	8.10	20	73	8	10	< 4	10	< 8	13	< 4	260
SK-49	8.10	43	130	17	40	18	10	< 8	55	12	590
SK-11	8.24	79	390	12	32	11	12	< 8	48	10	570
SK-20	8.24	13	83	< 8	7	16	< 4	< 8	10	< 4	190
SK-20D	8.24	13	89	< 8	8	15	< 4	< 8	9	< 4	190
SK-20X	8.24	12	64	9	7	9	< 4	< 8	< 8	< 4	200
SK-25	8.24	17	68	9	< 4	7	8	< 8	10	< 4	220
SK-35	8.24	21	100	8	10	10	6	< 8	14	< 4	210
SK-49	8.24	37	180	14	31	30	9	< 8	44	12	530
SK-11	9.13	86	410	12	30	10	11	< 8	44	26	630
SK-20	9.13	14	96	9	6	< 4	< 4	< 8	10	< 4	190
SK-25	9.13	18	90	9	5	< 4	7	< 8	11	< 4	170
SK-35	9.13	24	110	11	10	5	9	< 8	14	4	200
SK-35X	9.13	36	230	16	40	15	6	10	48	21	390
SK-49	9.13	44	190	18	39	20	7	8	55	23	580
SK-11	10.07	81	510	11	29	11	9	10	44	23	570

Table 2. Continued.

Site No.	Date	Cr(ppm)	Cu(ppm)	Ga(ppm)	La(ppm)	Li(ppm)	Mo(ppm)	Nb(ppm)	Nd(ppm)	Ni(ppm)	Pb(ppm)
SK-20	10.07	15	67	9	12	6	< 4	< 8	12	5	270
SK-25	10.07	15	62	< 8	4	< 4	7	< 8	< 8	< 4	150
SK-25D	10.07	14	57	< 8	4	< 4	6	< 8	12	< 4	140
SK-35	10.07	24	130	< 8	21	7	8	< 8	29	5	270
SK-49	10.07	34	180	15	45	14	6	< 8	55	17	510

Table 2. Continued.

Site No.	Date	Sc(ppm)	Sr(ppm)	Th(ppm)	V(ppm)	Y(ppm)	Yb(ppm)	Zn(ppm)
SK-11	5.18	14	120	94	32	33	4	1100
SK-11D	5.18	14	130	80	32	28	3	1200
SK-20	5.18	< 4	33	77	25	< 4	< 2	980
SK-20D	5.18	< 4	36	76	25	< 4	< 2	950
SK-25	5.18	< 4	26	120	21	5	< 2	1700
SK-49	5.18	6	79	95	28	14	< 2	580
SK-49D	5.18	6	85	100	29	14	< 2	660
SK-11	6.03	10	100	89	34	15	< 2	690
SK-20	6.03	< 4	22	97	20	< 4	< 2	320
SK-25	6.03	< 4	43	130	17	5	< 2	370
SK-25X	6.03	< 4	46	110	24	8	< 2	510
SK-25XD	6.03	< 4	48	110	24	9	< 2	540
SK-49	6.03	6	76	120	30	13	< 2	640
SK-11	6.21	10	56	100	28	17	2	500
SK-20	6.21	< 4	17	140	14	< 4	< 2	310
SK-25	6.21	< 4	9	150	9	4	< 2	240
SK-35	6.21	5	34	130	18	10	< 2	700
SK-49	6.21	7	84	140	32	15	< 2	630
SK-700	6.21	7	68	100	34	19	< 2	660
SK-700X	6.21	9	90	80	45	21	< 2	760
SK-11	7.08	9	56	100	21	15	2	550
SK-20	7.08	< 4	15	120	10	< 4	< 2	420
SK-20D	7.08	< 4	15	120	11	< 4	< 2	420
SK-25	7.08	< 4	9	170	7	< 4	< 2	600
SK-35	7.08	< 4	27	150	50	16	2	990
SK-49	7.08	7	39	190	24	19	3	910
SK-49X	7.08	8	36	200	26	15	2	780
SK-700	7.08	10	90	110	51	24	2	820
SK-11	7.26	9	24	130	16	14	2	530
SK-20	7.26	< 4	7	130	8	< 4	< 2	450
SK-25	7.26	< 4	6	200	7	< 4	< 2	200
SK-25D	7.26	< 4	6	190	6	< 4	< 2	190
SK-35	7.26	< 4	9	190	9	< 4	< 2	400
SK-49	7.26	10	49	290	26	17	< 2	890
SK-700	7.26	9	76	180	36	21	< 2	800
SK-11	8.10	12	82	84	44	16	< 2	850
SK-20	8.10	< 4	10	100	10	< 4	< 2	260
SK-25	8.10	< 4	10	180	8	< 4	< 2	290
SK-25D	8.10	< 4	10	180	9	< 4	< 2	290
SK-49	8.10	8	53	190	34	14	< 2	910
SK-11	8.24	10	43	120	26	16	< 2	680
SK-20	8.24	< 4	15	100	11	< 4	< 2	400
SK-20D	8.24	< 4	17	100	11	< 4	< 2	410
SK-20X	8.24	< 4	17	91	13	< 4	< 2	700
SK-25	8.24	< 4	7	170	7	< 4	< 2	410
SK-35	8.24	< 4	12	150	8	< 4	< 2	410
SK-49	8.24	7	42	170	29	15	< 2	2800
SK-11	9.13	10	41	120	25	13	< 2	2700
SK-20	9.13	< 4	15	110	14	< 4	< 2	940
SK-25	9.13	< 4	8	170	11	< 4	< 2	440
SK-35	9.13	< 4	14	180	14	< 4	< 2	730
SK-35X	9.13	6	85	110	54	21	< 2	4300
SK-49	9.13	9	58	170	36	16	< 2	5100
SK-11	10.07	10	39	120	26	16	< 2	3000

Table 2. Continued.

Site No.	Date	Sc(ppm)	Sr(ppm)	Th(ppm)	V(ppm)	Y(ppm)	Yb(ppm)	Zn(ppm)
SK-20	10.07	< 4	28	81	16	< 4	< 2	940
SK-25	10.07	< 4	9	140	7	< 4	< 2	250
SK-25D	10.07	< 4	8	140	7	< 4	< 2	240
SK-35	10.07	< 4	28	130	14	< 4	< 2	820
SK-49	10.07	7	58	150	28	16	< 2	5400

Table 3. Results of elemental analysis of streambed-sediment samples and stream-water pH measurements, Shingle Mill Gulch, Colorado.

Site No.	Date	pH	C(%)	Si(%)	Al(%)	Ca(%)	Fe(%)	K(%)	Mg(%)	Na(%)	P(%)
SMG	5.18	6.80	9.5	5	8.2	0.39	6.5	1.1	0.29	0.25	0.44
SMG	6.03	6.75	7.8	3	7.3	0.50	6.1	1.6	0.39	0.42	0.39
SMG	6.21	6.60	9.3	10	7.1	0.54	5.7	1.7	0.43	0.46	0.38
SMGD	6.21			7	7.2	0.54	5.8	1.8	0.44	0.47	0.38
SMG	7.08	6.48	8.6	2	7.4	0.55	6.4	1.6	0.42	0.41	0.45
SMG	7.26	6.40	9.3	7	7.2	0.47	6.3	1.5	0.37	0.37	0.45
SMGX	7.26			2	7.2	0.50	6.2	1.6	0.40	0.41	0.43
SMGXD	7.26			2	7.2	0.51	6.1	1.6	0.40	0.41	0.43
SMG	8.24	6.18	5.4	3	7.0	0.42	6.6	1.8	0.41	0.49	0.36
SMG	9.13	6.10	8.4	10	7.3	0.40	6.2	1.7	0.39	0.44	0.36
SMG	10.07	6.09	9.9	7	7.5	0.32	6.8	1.4	0.34	0.36	0.37
SMGD	10.07			10	7.5	0.32	6.8	1.4	0.34	0.37	0.37

Table 3. Continued.

Site No.	Date	Ti(%)	Mn(ppm)	Ag(ppm)	As(ppm)	Ba(ppm)	Be(ppm)	Cd(ppm)	Ce(ppm)	Co(ppm)	Cr(ppm)
SMG	5.18	0.09	43000	16	30	540	18	160	250	91	28
SMG	6.03	0.15	55000	13	30	780	13	220	220	100	32
SMG	6.21	0.17	36000	13	30	700	11	160	180	58	34
SMGD	6.21	0.17	37000	13	30	720	11	160	180	59	33
SMG	7.08	0.16	40000	14	40	720	13	170	200	74	33
SMG	7.26	0.13	49000	13	30	690	14	190	220	86	31
SMGX	7.26	0.16	49000	14	30	750	12	200	220	92	33
SMGXD	7.26	0.15	48000	14	30	730	12	190	210	88	32
SMG	8.24	0.16	39000	13	40	800	11	140	190	71	34
SMG	9.13	0.16	41000	14	30	680	12	140	200	78	33
SMG	10.07	0.13	42000	14	30	640	12	130	210	87	32
SMGD	10.07	0.14	42000	15	40	640	13	130	220	87	32

Table 3. Continued.

Site No.	Date	Cu(ppm)	Eu(ppm)	Ga(ppm)	La(ppm)	Li(ppm)	Mo(ppm)	Nb(ppm)	Nd(ppm)	Ni(ppm)	Pb(ppm)
SMG	5.18	1200	7	< 8	110	24	12	< 8	150	42	770
SMG	6.03	840	5	10	99	31	16	< 8	120	71	610
SMG	6.21	620	< 4	16	84	33	12	10	100	50	560
SMGD	6.21	630	< 4	16	85	33	11	10	110	50	560
SMG	7.08	720	4	12	88	32	12	8	110	54	570
SMG	7.26	810	5	13	100	30	14	< 8	130	62	680
SMGX	7.26	770	5	10	97	32	14	9	120	65	590
SMGXD	7.26	750	4	12	95	31	14	9	120	63	590
SMG	8.24	650	4	14	86	32	13	8	110	55	530
SMG	9.13	770	5	13	91	36	12	< 8	120	53	640
SMG	10.07	830	5	< 8	91	32	14	< 8	120	47	690
SMGD	10.07	830	5	11	91	32	14	< 8	130	46	690

Table 3. Continued.

Site No.	Date	Sc(ppm)	Sr(ppm)	Th(ppm)	V(ppm)	Y(ppm)	Yb(ppm)	Zn(ppm)
SMG	5.18	7	54	45	27	150	10	10000
SMG	6.03	7	74	47	33	110	7	14000
SMG	6.21	7	81	40	38	90	6	8900
SMGD	6.21	7	83	42	39	91	6	9000
SMG	7.08	7	76	43	38	100	6	11000
SMG	7.26	7	67	45	33	120	7	12000
SMGX	7.26	7	74	47	35	110	6	13000
SMGXD	7.26	7	74	48	35	110	7	12000
SMG	8.24	7	69	44	37	90	6	8500
SMG	9.13	7	65	44	35	100	7	8500
SMG	10.07	7	53	40	31	110	8	7400
SMGD	10.07	7	53	45	32	110	7	7500

Ranges, Means, and Precision of Data

Table 4 lists the ranges and means of analytical values for all elements in St. Kevin Gulch that had greater than 40 out of 45 valid values (those that are not qualified values). The value for Mn in St. Kevin Gulch Site SK-25 on May 18 is probably due to flushing of Shingle Mill Gulch sediment, which is very high in Mn, into St. Kevin Gulch. Table 5 lists the ranges and means of analytical values for all elements in Shingle Mill Gulch that had at least 7 out of 8 valid values. These basic statistics do not include field or analytical duplicates.

In St. Kevin Gulch the pH generally decreased from mid June to mid August and increased slightly during September and October. With the exception of the May 18 samples, the range of spatial pH differences in St. Kevin Gulch was always less than one pH unit for a given sampling date. In Shingle Mill Gulch the pH gradually decreased throughout the field season. The pH ranged from 6.80 in May to 6.09 in October.

The average relative deviation from the mean (rd_m) for 12 pairs of analytical duplicates and six pairs of field duplicates is given in table 6. The rd_m was calculated using the following formula (Skoog and West, 1976):

$$rd_m = \frac{|Mean - Duplicate|}{Mean} \times 100 \quad Where: \quad Mean = \frac{Sample + Duplicate}{2}$$

Samples with qualified analytical values were not included in the computations. The rd_m for analytical duplicates analyzed by ICP-AES averaged 2.7% and the rd_m for field duplicates analyzed by ICP-AES averaged 12.2%. Many of the large deviations for the field duplicates occurred for elements associated with detrital minerals (e.g. clays, micas, feldspars). Zinc, Ni, Ag, Co, and Mn also have large deviations in the field duplicates.

Table 4. Ranges and means of selected elements in streambed sediment, St. Kevin Gulch, Colorado.

Element	Minimum	Maximum	Mean	Valid (of 45)
C (%)	2.4	13	6.7	45
Si (%)	0.3	10	3	41
Al (%)	0.29	6.6	2.7	45
Ca (%)	0.01	0.26	0.10	44
Fe (%)	10	45	30	45
K (%)	0.1	2.8	1.0	44
Mg (%)	0.03	0.51	0.19	45
Na (%)	0.02	0.62	0.19	45
P (%)	0.13	0.47	0.27	45
Ti (%)	0.01	0.22	0.07	44
Mn (ppm)	72	2000	371	45
Ag (ppm)	8	120	41	45
As (ppm)	30	130	65	45
Ba (ppm)	16	440	152	45
Ce (ppm)	8	180	64	43
Co (ppm)	3	13	6	45
Cr (ppm)	11	86	37	45
Cu (ppm)	62	520	174	45
La (ppm)	4	79	27	42
Nd (ppm)	8	110	40	42
Pb (ppm)	93	1100	436	45
Sr (ppm)	6	120	39	45
Th (ppm)	77	290	137	45
V (ppm)	7	51	22	45
Zn (ppm)	200	5400	985	45

Table 5. Ranges and means of selected elements in streambed sediment, Shingle Mill Gulch, Colorado.

Element	Minimum	Maximum	Mean	Valid (of 8)
C (%)	5.4	9.9	8.5	8
Si (%)	2	10	6	8
Al (%)	7.0	8.2	7.4	8
Ca (%)	0.32	0.55	0.45	8
Fe (%)	5.7	6.8	6.3	8
K (%)	1.1	1.8	1.6	8
Mg (%)	0.29	0.43	0.38	8
Na (%)	0.25	0.49	0.40	8
P (%)	0.36	0.45	0.40	8
Ti (%)	0.09	0.17	0.14	8
Mn (ppm)	36000	55000	43130	8
Ag (ppm)	13	16	14	8
As (ppm)	30	40	33	8
Ba (ppm)	540	800	694	8
Be (ppm)	11	18	13	8
Cd (ppm)	130	220	164	8
Ce (ppm)	180	250	209	8
Co (ppm)	58	100	81	8
Cr (ppm)	28	34	32	8
Cu (ppm)	620	1200	805	8
Eu (ppm)	4	7	5	7
La (ppm)	84	110	94	8
Li (ppm)	24	36	31	8
Mo (ppm)	12	16	13	8
Nd (ppm)	100	150	120	8
Ni (ppm)	42	71	54	8
Pb (ppm)	530	770	631	8
Sc (ppm)	7	7	7	8
Sr (ppm)	53	81	67	8
Th (ppm)	40	47	44	8
V (ppm)	27	38	34	8
Y (ppm)	90	150	109	8
Yb (ppm)	6	10	7	8
Zn (ppm)	7400	14000	10040	8

Table 6. Average relative deviation from the mean for 12 pairs of analytical duplicates and six pairs of field duplicates.

Element	Analytical Duplicates	Field Duplicates
Si	14.9 %	44.2 %
Al	0.6	12.3
Ca	0.3	24.4
Fe	1.1	7.0
K	0.6	11.6
Mg	0.3	15.5
Na	0.7	17.8
P	0.4	8.4
Ti	4.6	18.5
Mn	3.1	16.5
Ag	1.2	10.0
As	2.5	4.6
Ba	2.2	17.8
Be	10.7	7.7
Bi	5.0	0.0
Cd	0.4	2.6
Ce	5.0	14.4
Co	3.4	11.0
Cr	1.6	8.1
Cu	1.6	9.5
Eu	5.6	0.0
Ga	4.3	12.3
La	2.7	13.7
Li	1.3	19.0
Mo	3.3	9.3
Nb	2.4	5.3
Nd	4.4	22.2
Ni	3.1	27.5
Pb	1.5	9.9
Sc	0.0	4.8
Sr	2.1	17.0
Th	2.0	8.0
V	1.9	16.1
Y	2.4	8.8
Yb	9.5	13.8
Zn	2.1	21.1

The precision of the carbon data was determined separately. The average standard deviation of samples analyzed during the same day was 0.26% for 21 pairs of duplicates. The average standard deviation for duplicate samples analyzed on different days was 0.66% for 25 analyses. The average standard deviation of the field duplicates was 0.51%.

Correlations between Variables

Table 7 lists correlation coefficients for all elements in St. Kevin Gulch that had greater than 40 out of 45 valid analytical values. These correlation coefficients do not include field or analytical duplicates. Iron is highly negatively correlated with elements associated with detrital minerals and Pb. Carbon is most highly correlated with Ag and Cr, Mn is most highly correlated with Co, and the stream pH is most highly correlated with Pb.

Table 8 lists correlation coefficients for all elements in Shingle Mill Gulch that had at least 7 out of 8 valid analytical values. Iron is most negatively correlated with Ca and Sr. Carbon is most negatively correlated with Ba, As, Na, and K, and most positively correlated with Pb. Manganese is most highly correlated with Co, Mo, Zn, and Cd, and the stream pH is most highly correlated with Cd.

Table 7. Correlation coefficients between selected variables, St. Kevin Gulch, Colorado.

	Al	pH	C	Si	Ca	Fe	K	Mg	Na	P	Ti	Mn	Ag	As	Ba
Al	1.00	.41	.48	.64	.84	-.97	.98	.97	.93	-.40	.95	.45	.51	-.18	.94
pH	.41	1.00	.30	.05	.26	-.34	.38	.36	.30	-.49	.29	.34	.00	.09	.34
C	.48	.30	1.00	.43	.64	-.60	.38	.49	.33	-.34	.37	.11	.71	-.43	.35
Si	.64	.05	.43	1.00	.66	-.68	.60	.66	.62	-.05	.65	.17	.53	-.11	.62
Ca	.84	.26	.64	.66	1.00	-.89	.80	.84	.80	-.33	.80	.44	.64	-.37	.82
Fe	-.97	-.34	-.60	-.68	-.89	1.00	-.94	-.95	-.91	.40	-.92	-.40	-.61	.29	-.92
K	.98	.38	.38	.60	.80	-.94	1.00	.92	.96	-.38	.91	.46	.43	-.16	.94
Mg	.97	.36	.49	.66	.84	-.95	.92	1.00	.88	-.36	.95	.44	.54	-.13	.91
Na	.93	.30	.33	.62	.80	-.91	.96	.88	1.00	-.37	.93	.39	.36	-.24	.96
P	-.40	-.49	-.34	-.05	-.33	.40	-.38	-.36	-.37	1.00	-.35	-.21	.04	.51	-.40
Ti	.95	.29	.37	.65	.80	-.92	.91	.95	.93	-.35	1.00	.37	.41	-.18	.95
Mn	.45	.34	.11	.17	.44	-.40	.46	.44	.39	-.21	.37	1.00	.17	-.04	.55
Ag	.51	.00	.71	.53	.64	-.61	.43	.54	.36	.04	.41	.17	1.00	-.31	.38
As	-.18	.09	-.43	-.11	-.37	.29	-.16	-.13	-.24	.51	-.18	-.04	-.31	1.00	-.24
Ba	.94	.34	.35	.62	.82	-.92	.94	.91	.96	-.40	.95	.55	.38	-.24	1.00
Ce	.93	.54	.47	.59	.80	-.92	.92	.88	.91	-.45	.89	.40	.43	-.17	.91
Co	.49	.48	.32	.26	.56	-.46	.43	.57	.32	-.29	.41	.73	.35	.02	.49
Cr	.60	.43	.70	.42	.60	-.68	.49	.66	.44	-.54	.56	.21	.48	-.20	.51
Cu	.37	.54	.66	.25	.46	-.45	.26	.40	.18	-.44	.28	.19	.40	-.10	.27
La	.94	.52	.45	.60	.81	-.92	.92	.88	.91	-.44	.89	.41	.43	-.16	.92
Nd	.91	.59	.56	.57	.81	-.91	.88	.86	.86	-.49	.86	.39	.47	-.20	.87
Pb	.79	.72	.59	.40	.65	-.76	.71	.79	.61	-.59	.68	.50	.38	-.03	.69
Sr	.94	.56	.41	.62	.75	-.88	.91	.91	.85	-.39	.88	.37	.41	.04	.85
Th	-.18	-.23	.30	.07	-.03	.09	-.22	-.20	-.18	.14	-.21	-.21	.42	-.49	-.21
V	.86	.30	.44	.59	.83	-.83	.79	.87	.78	-.31	.88	.39	.46	-.15	.84
Zn	.36	-.06	.47	.42	.64	-.40	.30	.42	.23	-.04	.27	.47	.60	-.26	.33

Table 7. Continued.

	Ce	Co	Cr	Cu	La	Nd	Pb	Sr	Th	V	Zn
Al	.93	.49	.60	.37	.94	.91	.79	.94	-.18	.86	.36
pH	.54	.48	.43	.54	.52	.59	.72	.56	-.23	.30	-.06
C	.47	.32	.70	.66	.45	.56	.59	.41	.30	.44	.47
Si	.59	.26	.42	.25	.60	.57	.40	.62	.07	.59	.42
Ca	.80	.56	.60	.46	.81	.81	.65	.75	-.03	.83	.64
Fe	-.92	-.46	-.68	-.45	-.92	-.91	-.76	-.88	.09	-.83	-.40
K	.92	.43	.49	.26	.92	.88	.71	.91	-.22	.79	.30
Mg	.88	.57	.66	.40	.88	.86	.79	.91	-.20	.87	.42
Na	.91	.32	.44	.18	.91	.86	.61	.85	-.18	.78	.23
P	-.45	-.29	-.54	-.44	-.44	-.49	-.59	-.39	.14	-.31	-.04
Ti	.89	.41	.56	.28	.89	.86	.68	.88	-.21	.88	.27
Mn	.40	.73	.21	.19	.41	.39	.50	.37	-.21	.39	.47
Ag	.43	.35	.48	.40	.43	.47	.38	.41	.42	.46	.60
As	-.17	.02	-.20	-.10	-.16	-.20	-.03	.04	-.49	-.15	-.26
Ba	.91	.49	.51	.27	.92	.87	.69	.85	-.21	.84	.33
Ce	1.00	.45	.59	.42	1.00	.99	.78	.93	-.14	.79	.22
Co	.45	1.00	.54	.57	.46	.47	.66	.49	-.29	.46	.63
Cr	.59	.54	1.00	.89	.59	.67	.79	.59	-.15	.58	.28
Cu	.42	.57	.89	1.00	.41	.52	.70	.43	-.16	.40	.30
La	1.00	.46	.59	.41	1.00	.98	.77	.93	-.17	.79	.24
Nd	.99	.47	.67	.52	.98	1.00	.83	.92	-.10	.79	.23
Pb	.78	.66	.79	.70	.77	.83	1.00	.82	-.26	.68	.30
Sr	.93	.49	.59	.43	.93	.92	.82	1.00	-.28	.80	.23
Th	-.14	-.29	-.15	-.16	-.17	-.10	-.26	-.28	1.00	-.17	.07
V	.79	.46	.58	.40	.79	.79	.68	.80	-.17	1.00	.35
Zn	.22	.63	.28	.30	.24	.23	.30	.23	.07	.35	1.00

Table 8. Correlation coefficients between selected variables, Shingle Mill Gulch, Colorado.

	pH	C	Si	Al	Ca	Fe	K	Mg	Na	P	Ti	Mn	Ag	As	Ba
pH	1.00	.21	-.29	.43	.52	-.45	-.42	-.18	-.40	.54	-.33	.36	.25	-.21	-.19
C	.21	1.00	.48	.50	-.10	-.11	-.63	-.45	-.64	.40	-.45	.03	.41	-.66	-.75
Si	-.29	.48	1.00	-.13	-.20	-.43	.07	.00	.07	-.35	.11	-.32	-.05	-.66	-.35
Al	.43	.50	-.13	1.00	-.39	.35	-.93	-.86	-.92	.44	-.86	.09	.95	-.29	-.85
Ca	.52	-.10	-.20	-.39	1.00	-.71	.42	.69	.39	.37	.53	.04	-.44	.28	.46
Fe	-.45	-.11	-.43	.35	-.71	1.00	-.38	-.53	-.38	.04	-.48	-.00	.39	.32	-.22
K	-.42	-.63	.07	-.93	.42	-.38	1.00	.92	.99	-.53	.95	-.22	-.81	.42	.87
Mg	-.18	-.45	.00	-.86	.69	-.53	.92	1.00	.92	-.28	.97	-.26	-.78	.47	.81
Na	-.40	-.64	.07	-.92	.39	-.38	.99	.92	1.00	-.59	.95	-.25	-.82	.41	.87
P	.54	.40	-.35	.44	.37	.04	-.53	-.28	-.59	1.00	-.48	.26	.35	.08	-.36
Ti	-.33	-.45	.11	-.86	.53	-.48	.95	.97	.95	-.48	1.00	-.29	-.75	.38	.79
Mn	.36	.03	-.32	.09	.04	-.00	-.22	-.26	-.25	.26	-.29	1.00	-.15	-.37	.16
Ag	.25	.41	-.05	.95	-.44	.39	-.81	-.78	-.82	.35	-.75	-.15	1.00	-.15	-.85
As	-.21	-.66	-.66	-.29	.28	.32	.42	.47	.41	.08	.38	-.37	-.15	1.00	.50
Ba	-.19	-.75	-.35	-.85	.46	-.22	.87	.81	.87	-.36	.79	.16	-.85	.50	1.00
Be	.59	.40	-.22	.89	-.17	.22	-.89	-.80	-.91	.69	-.89	.32	.79	-.27	-.72
Cd	.69	.01	-.36	-.06	.61	-.44	-.03	.11	-.06	.47	-.02	.80	-.29	-.18	.30
Ce	.47	.36	-.25	.83	-.36	.36	-.88	-.88	-.90	.54	-.92	.57	.68	-.39	-.63
Co	.26	.16	-.35	.50	-.36	.38	-.57	-.65	-.58	.25	-.62	.86	.30	-.38	-.21
Cr	-.49	-.48	.12	-.88	.36	-.31	.94	.91	.96	-.58	.97	-.40	-.76	.43	.77
Cu	.46	.41	-.14	.94	-.44	.34	-.93	-.93	-.93	.44	-.94	.35	.84	-.41	-.77
Eu	.39	.43	.04	.89	-.51	.27	-.88	-.93	-.89	.32	-.92	.33	.80	-.54	-.79
La	.54	.34	-.17	.76	-.27	.20	-.82	-.83	-.85	.54	-.88	.61	.60	-.47	-.59
Li	-.65	-.24	.38	-.77	.14	-.28	.84	.74	.82	-.62	.87	-.26	-.63	.14	.57
Mo	.12	-.12	-.31	-.21	-.05	.08	.02	-.06	.04	-.10	-.05	.85	-.45	-.26	.41
Nd	.31	.34	-.09	.82	-.48	.39	-.86	-.92	-.89	.47	-.94	.42	.73	-.41	-.71
Ni	.14	-.37	-.31	-.55	.46	-.31	.46	.44	.43	.02	.39	.75	-.70	.02	.74
Pb	.19	.66	.19	.82	-.58	.35	-.91	-.95	-.93	.38	-.92	.31	.73	-.63	-.87
Sr	.26	-.31	-.07	-.67	.92	-.75	.72	.90	.71	.00	.79	-.07	-.67	.32	.69
Th	.39	-.37	-.47	.16	.12	.00	-.11	-.19	-.16	.31	-.26	.74	.06	.00	.19
V	-.27	-.45	.01	-.82	.64	-.43	.90	.98	.89	-.25	.94	-.42	-.69	.57	.73
Y	.49	.48	-.12	.88	-.36	.31	-.94	-.91	-.96	.58	-.97	.40	.76	-.43	-.77
Yb	.30	.48	.04	.92	-.62	.40	-.93	-.98	-.92	.26	-.94	.22	.84	-.51	-.85
Zn	.66	-.04	-.47	.00	.57	-.32	-.07	.07	-.11	.54	-.07	.82	-.21	-.08	.29

Table 8. Continued.

	Be	Cd	Ce	Co	Cr	Cu	Eu	La	Li	Mo	Nd	Ni	Pb	Sr
pH	.59	.69	.47	.26	-.49	.46	.39	.54	-.65	.12	.31	.14	.19	.26
C	.40	.01	.36	.16	-.48	.41	.43	.34	-.24	-.12	.34	-.37	.66	-.31
Si	-.22	-.36	-.25	-.35	.12	-.14	.04	-.17	.38	-.31	-.09	-.31	.19	-.07
Al	.89	-.06	.83	.50	-.88	.94	.89	.76	-.77	-.21	.82	-.55	.82	-.67
Ca	-.17	.61	-.36	-.36	.36	-.44	-.51	-.27	.14	-.05	-.48	.46	-.58	.92
Fe	.22	-.44	.36	.38	-.31	.34	.27	.20	-.28	.08	.39	-.31	.35	-.75
K	-.89	-.03	-.88	-.57	.94	-.93	-.88	-.82	.84	.02	-.86	.46	-.91	.72
Mg	-.80	.11	-.88	-.65	.91	-.93	-.93	-.83	.74	-.06	-.92	.44	-.95	.90
Na	-.91	-.06	-.90	-.58	.96	-.93	-.89	-.85	.82	.04	-.89	.43	-.93	.71
P	.69	.47	.54	.25	-.58	.44	.32	.54	-.62	-.10	.47	.02	.38	.00
Ti	-.89	-.02	-.92	-.62	.97	-.94	-.92	-.88	.87	-.05	-.94	.39	-.92	.79
Mn	.32	.80	.57	.86	-.40	.35	.33	.61	-.26	.85	.42	.75	.31	-.07
Ag	.79	-.29	.68	.30	-.76	.84	.80	.60	-.63	-.45	.73	-.70	.73	-.67
As	-.27	-.18	-.39	-.38	.43	-.41	-.54	-.47	.14	-.26	-.41	.02	-.63	.32
Ba	-.72	.30	-.63	-.21	.77	-.77	-.79	-.59	.57	.41	-.71	.74	-.87	.69
Be	1.00	.25	.93	.57	-.96	.94	.89	.92	-.89	-.09	.92	-.27	.80	-.51
Cd	.25	1.00	.32	.48	-.21	.12	.07	.41	-.25	.61	.13	.78	-.02	.44
Ce	.93	.32	1.00	.82	-.97	.96	.92	.98	-.83	.23	.96	-.09	.87	-.64
Co	.57	.48	.82	1.00	-.67	.69	.65	.78	-.47	.68	.70	.35	.63	-.52
Cr	-.96	-.21	-.97	-.67	1.00	-.97	-.95	-.96	.87	-.06	-.96	.27	-.91	.66
Cu	.94	.12	.96	.69	-.97	1.00	.98	.93	-.83	.02	.95	-.33	.89	-.71
Eu	.89	.07	.92	.65	-.95	.98	1.00	.92	-.75	.01	.95	-.33	.92	-.73
La	.92	.41	.98	.78	-.96	.93	.92	1.00	-.81	.24	.95	-.00	.84	-.55
Li	-.89	-.25	-.83	-.47	.87	-.83	-.75	-.81	1.00	-.04	-.78	.26	-.64	.44
Mo	-.09	.61	.23	.68	-.06	.02	.01	.24	-.04	1.00	.06	.75	.04	-.01
Nd	.92	.13	.96	.70	-.96	.95	.95	.95	-.78	.06	1.00	-.22	.91	-.74
Ni	-.27	.78	-.09	.35	.27	-.33	-.33	-.00	.26	.75	-.22	1.00	-.37	.51
Pb	.80	-.02	.87	.63	-.91	.89	.92	.84	-.64	.04	.91	-.37	1.00	-.81
Sr	-.51	.44	-.64	-.52	.66	-.71	-.73	-.55	.44	-.01	-.74	.51	-.81	1.00
Th	.46	.66	.55	.65	-.40	.40	.38	.62	-.34	.42	.50	.60	.17	.00
V	-.79	-.05	-.92	-.75	.92	-.93	-.94	-.88	.73	-.23	-.92	.28	-.94	.83
Y	.96	.21	.97	.67	-1.00	.97	.95	.96	-.87	.06	.96	-.27	.91	-.66
Yb	.84	-.08	.88	.61	-.92	.96	.97	.84	-.75	-.01	.91	-.47	.93	-.83
Zn	.33	.98	.39	.54	-.26	.18	.11	.46	-.28	.58	.20	.78	.01	.38

Table 8. Continued.

	Th	V	Y	Yb	Zn
pH	.39	-.27	.49	.30	.66
C	-.37	-.45	.48	.48	-.04
Si	-.47	.01	-.12	.04	-.47
Al	.16	-.82	.88	.92	.00
Ca	.12	.64	-.36	-.62	.57
Fe	.00	-.43	.31	.40	-.32
K	-.11	.90	-.94	-.93	-.07
Mg	-.19	.98	-.91	-.98	.07
Na	-.16	.89	-.96	-.92	-.11
P	.31	-.25	.58	.26	.54
Ti	-.26	.94	-.97	-.94	-.07
Mn	.74	-.42	.40	.22	.82
Ag	.06	-.69	.76	.84	-.21
As	.00	.57	-.43	-.51	-.08
Ba	.19	.73	-.77	-.85	.29
Be	.46	-.79	.96	.84	.33
Cd	.66	-.05	.21	-.08	.98
Ce	.55	-.92	.97	.88	.39
Co	.65	-.75	.67	.61	.54
Cr	-.40	.92	-1.00	-.92	-.26
Cu	.40	-.93	.97	.96	.18
Eu	.38	-.94	.95	.97	.11
La	.62	-.88	.96	.84	.46
Li	-.34	.73	-.87	-.75	-.28
Mo	.42	-.23	.06	-.01	.58
Nd	.50	-.92	.96	.91	.20
Ni	.60	.28	-.27	-.47	.78
Pb	.17	-.94	.91	.93	.01
Sr	.00	.83	-.66	-.83	.38
Th	1.00	-.29	.40	.19	.75
V	-.29	1.00	-.92	-.97	-.08
Y	.40	-.92	1.00	.92	.26
Yb	.19	-.97	.92	1.00	-.05
Zn	.75	-.08	.26	-.05	1.00

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COLLOIDAL PROPERTIES OF FLOCCULATED BED MATERIAL IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

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ABSTRACT

A suite of samples of flocculated iron oxyhydroxide material (floc) was collected along St. Kevin Gulch, a central Colorado metal-rich stream (pH less than 3.8) contaminated by acid mine drainage. Iron is the predominant metal in the floc, with minor amounts of aluminum, zinc, and manganese, and trace amounts of lead, copper, and cadmium. Scanning electron microscopy reveals that the floc is composed of aggregates, generally greater than 1 micrometer in size, of uniformly sized 0.04 micrometer spheroids. Large values of surface area, on the order of 150 square meters per gram, were measured. Electrophoretic mobility measurements, made using a light-scattering technique, indicated a near-neutral charge in the shear plane. Formation of these flocs from iron oxyhydroxide colloids in the stream is consistent with the near-zero charge implied by their electrophoretic mobility. The mechanism(s) of formation of these apparently monodisperse colloids, the physical chemistry responsible for the surface charge neutralization, and the importance of the floc aggregates in metal partitioning in St. Kevin Gulch are under investigation.

INTRODUCTION

St. Kevin Gulch, located 7 km (kilometers) northwest of Leadville, Colo., is a small subalpine stream contaminated by acidic drainage from abandoned mines and mill tailings (McKnight and others, 1988). As a result, the streamwater is acidic (pH less than 3.8) and contains elevated concentrations of sulfate, iron (Fe), aluminum (Al), manganese (Mn), zinc (Zn), and several other trace metals.

Streambed materials in St. Kevin Gulch, as in most streams contaminated by acid mine drainage (AMD), are heavily coated with yellow to orange red precipitates of hydrous Fe oxides. The importance of Fe oxyhydroxides in the removal of dissolved metals by sorption and/or coprecipitation has been extensively examined in laboratory studies (Davis and Leckie, 1978; Benjamin and Leckie, 1981) and field investigations (Jenne, 1968; Robinson, 1981; Lion and others, 1982; Singh and Subramian, 1984; Johnson, 1986). The ability of such material to scavenge metals from solution is strongly controlled by its surface properties—its charge, area, and adsorption site density.

These surface properties, especially charge, also strongly affect the transport of colloidal Fe oxyhydroxides in surface waters. Charge repulsion caused by the electrostatic charge on the particle surfaces is a major mechanism for maintaining the particles in suspension. The development of surface charge on oxides is a result of acid-base reactions on the surface and is therefore strongly pH-dependent. For most Fe oxyhydroxides, the zero point of charge (ZPC) is approximately pH = 6 to 9 (Parks, 1965). At a pH less than the ZPC, the surface is positively charged. At a pH greater than the ZPC, a negative surface charge is expected. When electrophoresis is used to measure surface charge, the point of zero net surface charge is called the isoelectric point (IEP).

Adsorption of organic matter onto particle surfaces has been widely recognized as the major factor in producing a ubiquitous net negative surface charge on particles in natural waters (Hunter and Liss, 1979; Tipping and Cooke, 1982). A study of the Carnon River, England, has shown that, in an AMD contaminated stream with chemistry similar to St. Kevin Gulch, insufficient organic matter to completely coat the Fe oxyhydroxide particles has resulted in positively charged particles (Newton and Liss, 1987).

The goal of this study is to improve an understanding of the role of Fe oxyhydroxide surface chemistry in the transport of Fe and trace

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metals in AMD affected streams. This paper reports the results of a preliminary reconnaissance study of Fe oxyhydroxide surface chemistry at St. Kevin Gulch, performed in August 1987.

EXPERIMENTAL METHODS

Four samples of the flocculated material coating the streambed rocks in St. Kevin Gulch were collected in August 1987. The sampling sites were SK-20, SK-25, SK-37, and SK-700 (fig. B-29). This material was yellow to orange red. The floc upstream from the confluence of Shingle Mill Gulch was redder than the floc downstream of the confluence. The floc formed a loosely held coating, the thickness of which differed among the sites, being thickest at site
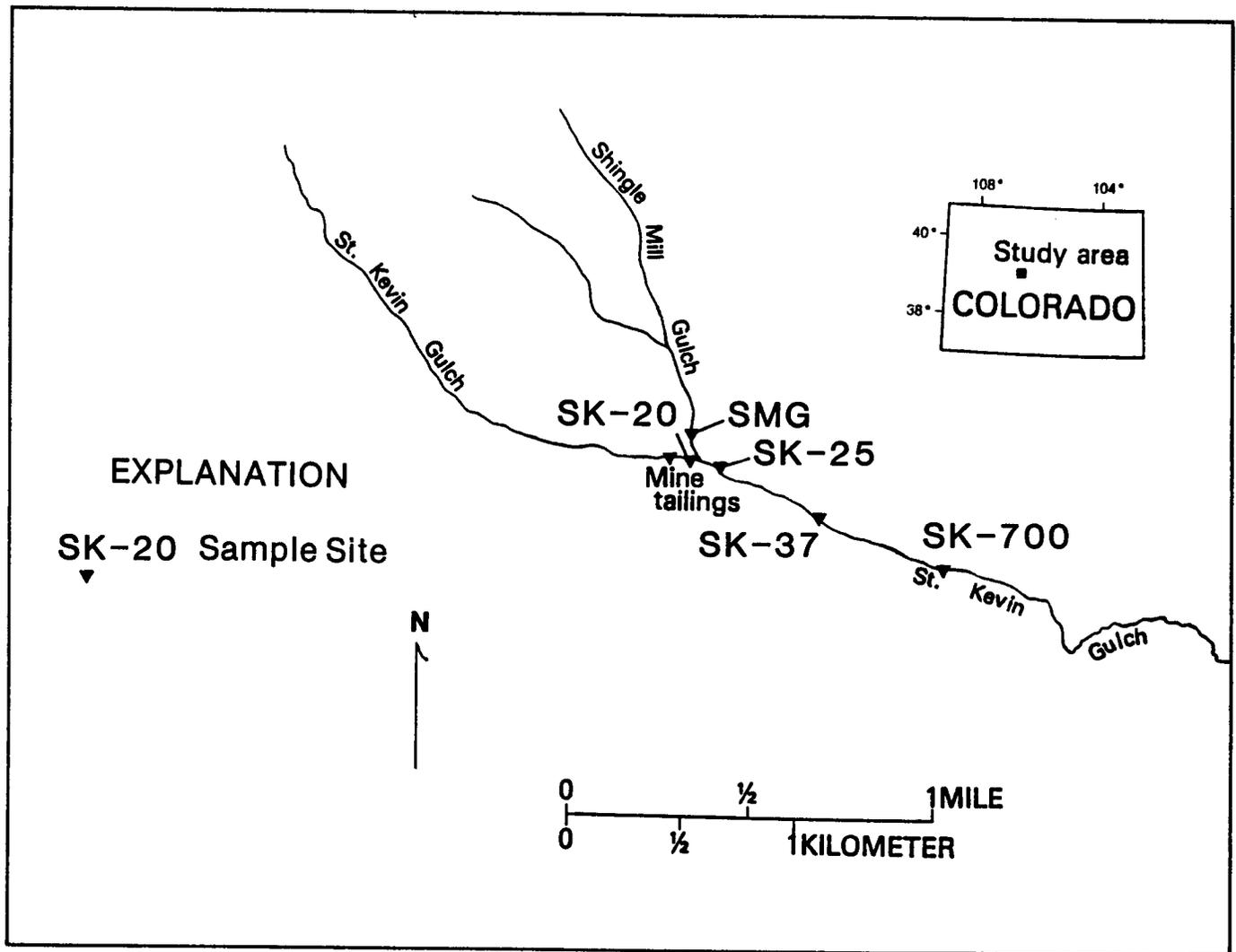
Figure B-29.—Sample-collection locations along St. Kevin Gulch and Shingle Mill Gulch (modified from McKnight and others, 1988, fig. 1).

SK–25. A sediment sample also was collected from Shingle Mill Gulch, a tributary with higher pH and lower dissolved metal concentrations than that of St. Kevin Gulch. This sample was brownish gray and appeared to be clay-rich. Sample materials from St. Kevin Gulch were obtained by collecting streambed pebbles and agitating them with streamwater in a polyethylene bottle. The Shingle Mill Gulch sample was obtained by agitating moss in a similar manner. The resulting concentrated suspensions were transferred to sterile borosilicate glass bottles and kept refrigerated prior to analysis. Measurements of pH and stream temperature were made at the time of sample collection. Dissolved organic carbon analyses were attempted but were unsuccessful because of sample contamination.

Quantitative chemical analysis was performed on a cold nitric acid digestate of air-dried sample using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Percent carbon was measured on air-dried samples by combustion of the sample followed by coulometric titration of the evolved CO_2. Surface area was measured using a single-point N_2 adsorption (BET) technique.

Particle size and morphology were investigated with scanning electron microscopy (SEM). Qualitative chemistry was obtained by energy dispersive X-ray analysis (EDAX). SEM and EDAX analyses were performed on the fine fraction of material obtained by agitating the sample in native streamwater, allowing the suspension to settle for 30 minutes, then filtering a small volume of the supernatant liquid through a 0.1 μm (micrometer) Nucleopore[3] filter.

The surface charge, more properly the electrophoretic mobility, of the fine fraction dispersed in the streamwater was measured using a laser electrophoretic light-scattering technique (ELS). This method involves the measurement of the frequency shift in the light scattered by charged particles moving under the influence of an electric field (Rees, 1987). The magnitude of this shift is proportional to the particle velocity under an applied potential and is a measure of the charge on the region of the double layer known as the shear plane. The shear plane can be defined as the plane that separates solvent molecules and adsorbed ions that drift with the particle under

the influence of an applied field from solvent molecules and ions that remain immobile under the field. Some knowledge of the nature of the adsorbed ions in the double layer is necessary to translate electrophoretic mobilities to surface charge values, which are usually determined by potentiometric titration.

RESULTS

Figure B–30a shows the low values and small variation of pH in St. Kevin Gulch. The pH of Shingle Mill Gulch (6.5)· is considerably higher than that of St. Kevin Gulch. Inflow of this stream results in a slight increase in the pH of St. Kevin Gulch.

The chemical composition of the St. Kevin Gulch floc and Shingle Mill Gulch sediment, as determined by ICP-AES, is shown in table B–6. Fe is the predominant metal in St. Kevin Gulch floc. The percentage of Fe in the floc is greatest in the sample collected at site SK–25 (just below the confluence with Shingle Mill Gulch) and less in the sample from site SK–20 (above the confluence with Shingle Mill Gulch and immediately below the tailings inflows) and in samples from progressively downstream sites (SK–37 and SK–700). The high Fe content of the floc is in agreement with the dominance of various forms of Fe oxyhydroxides (Fitzpatrick, 1989, this Proceedings). The floc also contains minor amounts of Al, Zn, and Mn. Trace amounts of lead (Pb), copper (Cu), and cadmium (Cd) are present. Concentrations of Al, Mn, and Zn in the floc generally increase downstream. The Shingle Mill Gulch floc sample contains a much lower Fe concentration and higher concentrations of Al, Mn, and Zn than do the St. Kevin Gulch samples. This higher trace-metal content in the Shingle Mill Gulch may reflect increased efficiency of metal scavenging by the streambed materials at higher pH (Smith and others, 1989, this Proceedings). Figure B–30b presents the results of organic carbon analysis of the floc. The percentage of organic carbon is low (less than 1 percent) in the floc and increases downstream. The Shingle Mill Gulch sample is higher in organic carbon. Possible explanations for this increase may be the incorporation of dissolved organic matter into the floc or an increase in the ratio

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[3]The use of brand names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table B-6.—*Elemental chemistry of the nitric acid soluble fraction of St. Kevin Gulch floc and Shingle Mill Gulch sediment*

[−, below detection; %, weight percent; ppm, milligrams per kilogram]

Con-stit-uent[1]	St. Kevin Gulch				Shingle Mill Gulch
	SK-20	SK-25	SK-37	SK-700	SMG
Fe (%)	37.9	43.3	32.8	28.0	10.6
Al (%)	.6	1.1	1.3	1.6	6.8
Mn (%)	.05	.08	2.20	.15	4.80
Zn (%)	.08	.15	.28	.38	2.33
Cu (ppm)	78	136	197	192	993
Pb (ppm)	−	−	575	−	975
Cd (ppm)	35	63	48	50	170

[1]Fe, iron; Al, aluminum; Mn, manganese; Zn, zinc; Cu, copper; Pb, lead; Cd, cadmium.

of organic-matter production to metal precipitation.

The results of the N_2 BET adsorption are shown in figure B–30c. St. Kevin Gulch floc has a large surface area of 50 to 170 m^2/g (square meters per gram). There is a slight increase in surface area at site SK–25 followed by a general decrease in downstream samples. The surface area computed from the observed particle diameter, assuming a spherical shape, is 40 m^2/g. Surface area computed from the unit cell size of 160 angstroms determined for SK–25 floc by Fitzpatrick (1989, this Proceedings) gives a value of 110 m^2/g, a value that is in somewhat better agreement with the BET results than the 40 m^2/g computed value.

Electrophoretic mobility results, shown in figure B–30d, indicate a near-neutral surface charge in the shear plane for all St. Kevin Gulch samples. The sample from Shingle Mill Gulch on the other hand, exhibited a large negative electrophoretic mobility (-1.3 micron centimeter/second volt), indicating negatively charged surfaces.

Direct observation by SEM indicates that the fine fraction of the iron-rich floc is present as 1 to 10 μm aggregates composed of very small, uniformly sized spheroids (0.040 ± 0.008 μm). This is the predominant morphology in samples SK–20 and SK–25. An example of this morphology is shown in figure B–31. SEM examination of the larger fraction, which settled after 30 minutes, showed the presence of aggregates larger than 10 μm also composed of very small spheroids. Similar aggregates are visible in the downstream samples, but they are mixed with other particle types. The sample from Shingle Mill Gulch does not display particles with this characteristic morphology.

DISCUSSION

St. Kevin Gulch floc has a near-zero electrophoretic mobility despite an ambient stream pH well below the expected ZPC for Fe oxyhydroxides. This indicates either incorporation of low-ZPC materials or adsorption of anions at the double layer. Possible anionic species responsible for surface-charge neutralization include sulfate and/or organic matter. The determination of the species responsible for this charge neutralization will be attempted during the 1988 field season. Interpretation of metal partitioning results may be facilitated by this knowledge.

Particle size, determined by SEM, is quite small (0.040 ± 0.008 μm for SK–25) and is expressed in the large measured surface areas (approximately 150 m^2/g). Decrease in surface area per gram downstream could result from increase in the proportions of larger detrital minerals or recrystallization of the Fe floc. A possible consequence of this decrease in surface area may be a general loss of surface adsorption sites downstream.

The formation of these flocs from Fe oxyhydroxide colloids in the stream is consistent with the near-zero charge implied by their electro-

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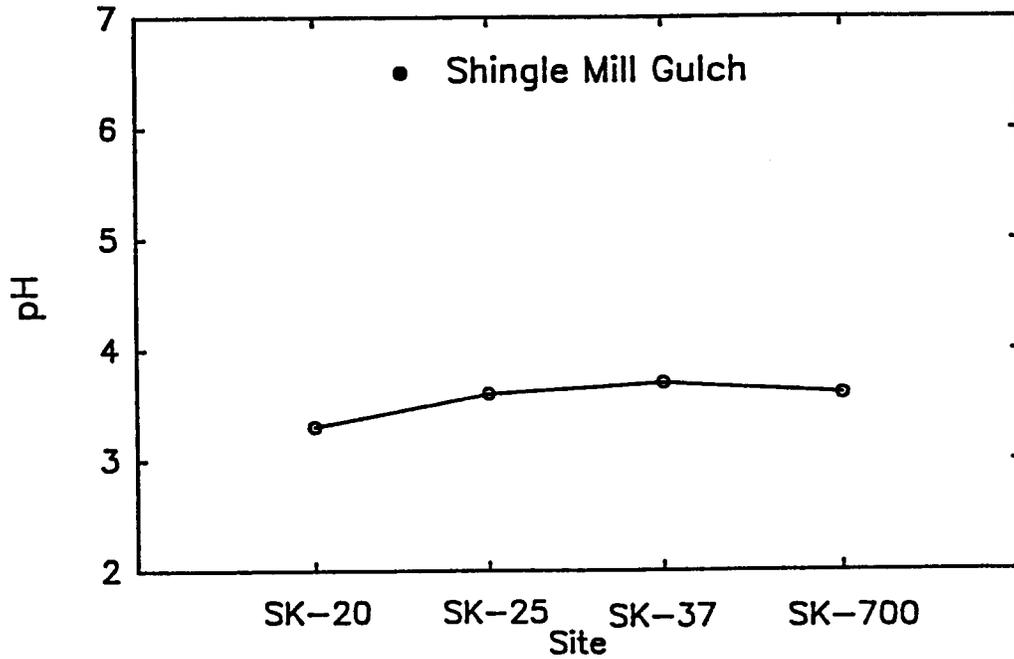
Figure B-30a. — Field-measured pH values in St. Kevin Gulch and Shingle Mill Gulch.
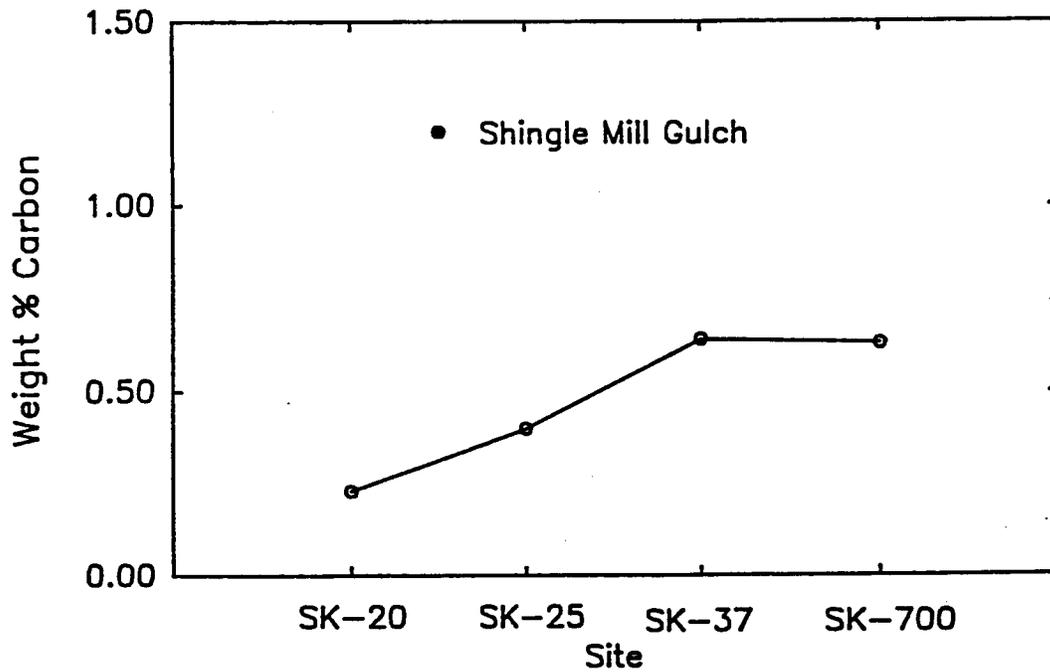
Figure B-30b. — Carbon content of St. Kevin Gulch floc and Shingle Mill Gulch sediment.

115
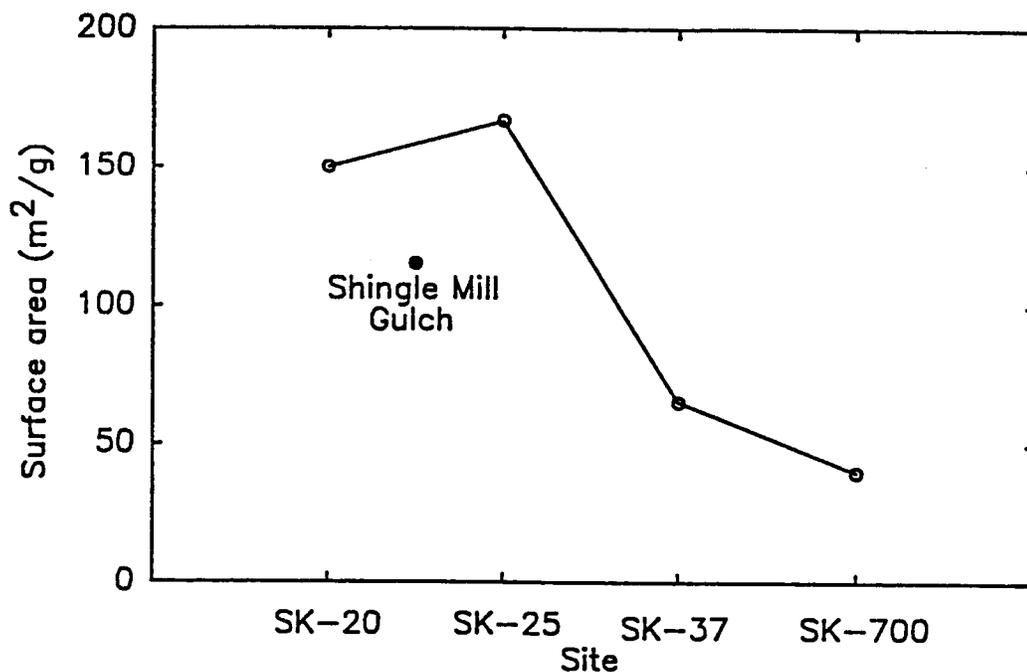
Figure B-30c. — Single-point N_2 adsorption (BET) surface areas of St. Kevin Gulch floc and Shingle Mill Gulch sediment.
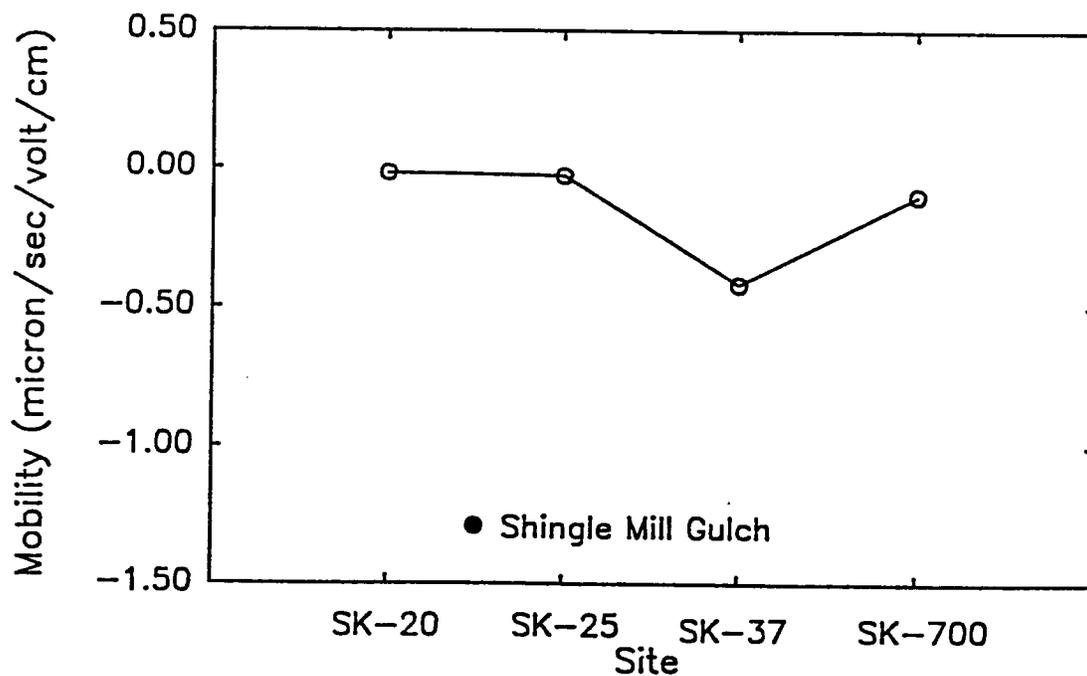

Figure B-30d. — Electrophoretic mobilities of St. Kevin Gulch floc and Shingle Mill Gulch sediment.

0   **400 NANOMETERS**
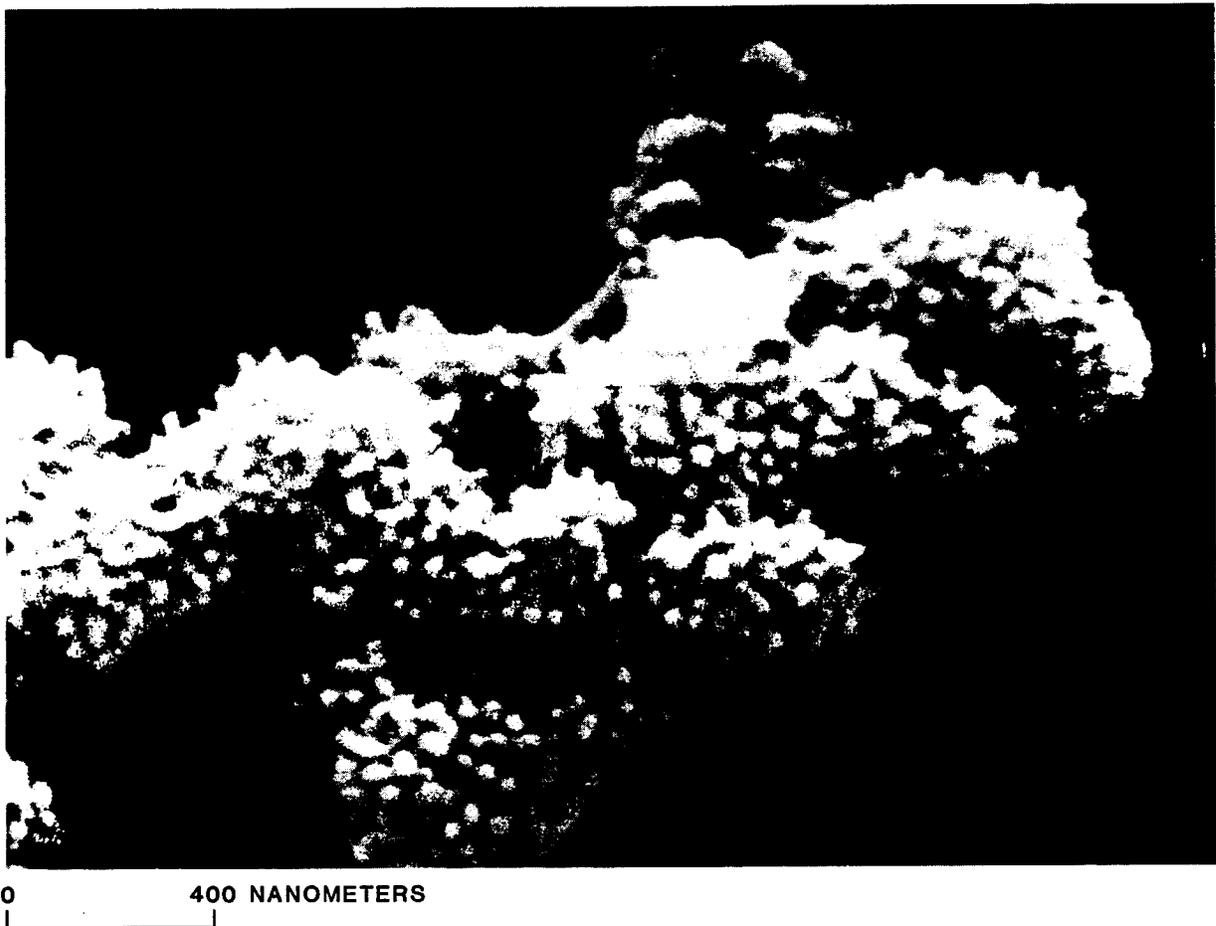
Figure B-31.—SEM photomicrograph of a typical aggregate collected at site SK-25.

phoretic mobility. Such flocculation may be an important process for Fe removal from the stream.

Under the pH conditions (less than 3.8) of St. Kevin Gulch, the floc does not appear to effectively scavenge trace metals (Smith and others, 1989, this Proceedings). Shingle Mill Gulch sediment contains higher concentrations of the minor (Al, Mn, and Zn) and trace (Cu, Pb, and Cd) metals than St. Kevin Gulch floc, perhaps as a consequence of the high pH, high carbon content and/or mineralogy of the Shingle Mill Gulch sediments.

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117

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