Chapter 17

Transport and Natural Attenuation of Cu, Zn, As, and Fe in the Acid Mine Drainage of Leviathan and Bryant Creeks

Jenny G. Webster[1], D. Kirk Nordstrom[2], and Kathleen S. Smith[3]

[1]Institute of Environmental Health and Forensic Science, P.O. Box 92021, Auckland, New Zealand
[2]U.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303
[3]U.S. Geological Survey, MS 973, Denver Federal Center, Denver, CO 80225

The Leviathan and Bryant Creek (LBC) drainage system, on the border of California and Nevada, flows through overburden and waste from a former open-pit sulfur mine. The drainage contains acid mine waters with high concentrations of several trace elements, including Cu, Zn, and As, derived from oxidative weathering of sulfides in the wastes and altered bedrock. In June and October, 1982, the mainstream and tributary flows of the LBC drainage were measured and the waters sampled and analyzed for major and trace elements. Empirical mass flow and metal attenuation rates were determined, and chemical models were used to examine mechanisms of trace element removal during downstream transport. In June the flow in the mainstream was 2-5 times greater than in October, and with higher contributions from the acid mine effluent. Seasonal variations in the attenuation rates of Cu, Zn, and As were directly related to this increase in acid mine-effluent production, and to the consequent increase in the acidity of the mainstream drainage. Although As concentrations immediately below the mine site were high in June, As was readily removed from solution by adsorption onto an assumed iron(III) oxyhydroxysulfate precipitate, whereas Cu was incompletely adsorbed and Zn remained unaffected by adsorption. In October, the smaller discharge of acidic LBC drainage waters were more readily diluted (and neutralized) by other regional tributaries. Arsenic concentrations remained low, and both Cu and Zn were removed from solution by adsorption onto iron(III) oxyhydroxysulfate in the lower regions of the LBC drainage system.

Leviathan and Mountaineer Creeks are major tributaries of Bryant Creek, near Markleeville in Alpine County, California. Bryant Creek crosses the border of

In Environmental Geochemistry of Sulfide Oxidation; Alpers, C., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1993.

California to join with the East Fork Carson River in Nevada (Figure 1). Although Mountaineer Creek flows through an area disturbed by roads, revegetation projects and waste piles, it contains uncontaminated waters whereas Leviathan Creek is significantly contaminated by seepage from the waste dumps of the Leviathan copper-sulfur mine and from an unstable landslide to the north of the Leviathan mine open pit. Prior to remediation activities in 1984, contaminated drainage from the open pit also reached Leviathan Creek. Consequently, the waters of Leviathan Creek had become acidic and contained anomalously high concentrations of sulfate and trace elements, including As, Co, Cr, Cu, Fe, Mn, Ni, and Zn. Trout kills and cattle deaths, observed by local ranchers and caretakers of the local fish hatchery, have been attributed to the contaminated stream waters.

In June and October of 1982 hydrologic and water quality data were collected for the Leviathan and Bryant Creek (LBC) drainage basin as part of a pollution abatement project undertaken by the California Regional Water Quality Control Board. Trace metal concentrations from the study by Ball and Nordstrom (1) have been used, together with auxiliary data from a previous study (2), to examine attenuation processes for Cu, As, and Zn from the site of drainage contamination to the junction of Bryant Creek with the East Fork Carson River (ca. 20 km). These three metals were chosen because their geochemical behavior was expected to be quite different, ranging from strongly reactive for arsenic to strongly non-reactive for zinc. Mass flows (mol/s) and mass balances have been calculated for each metal, and the chemical speciation and adsorption models, WATEQ4F and MINTEQA2, respectively, have been used to interpret the geochemical behavior of these metals and their attenuation in the LBC drainage.

Many previous studies of trace-metal attenuation have been based on trace-metal concentrations in a river system (e.g., 3), rather than on trace-metal mass flow, hence certain terms used in this study need to be clearly defined. "Attenuation" is defined here as a decrease in concentration, density or some other measurable quantity over a specified distance. "Chemical attenuation" relates to the mass loss of a dissolved constituent from a flowing body of water by hydrobiogeochemical processes such as oxidation, reduction, hydrolysis, gas exchange, mineral precipitation, adsorption, storage in hydrologic "dead zones", and biological uptake. Dilution at tributary confluences does not affect the mass flow or attenuation of a metal. The "chemical attenuation rate," referred to later in the text, is the mass loss of a dissolved constituent over a unit distance per unit time (μmol/km/s has been used here).

Methods

Sampling and Analytical Techniques. Revised chemical analyses are given by Ball and Nordstrom (1) for the samples taken in June and October 1982, from the sites shown on Figure 1. Temperature, pH, Eh, and specific conductance were determined on site. Water samples were filtered on site through 0.1 μm, 142 mm-diameter membranes in a pre-cleaned acrylic plastic filter assembly. Samples for Fe determinations were acidified with 4 mL of ultrapure HCl per 500 mL sample, and samples for other trace and major metals were acidified with 2 mL of ultrapure

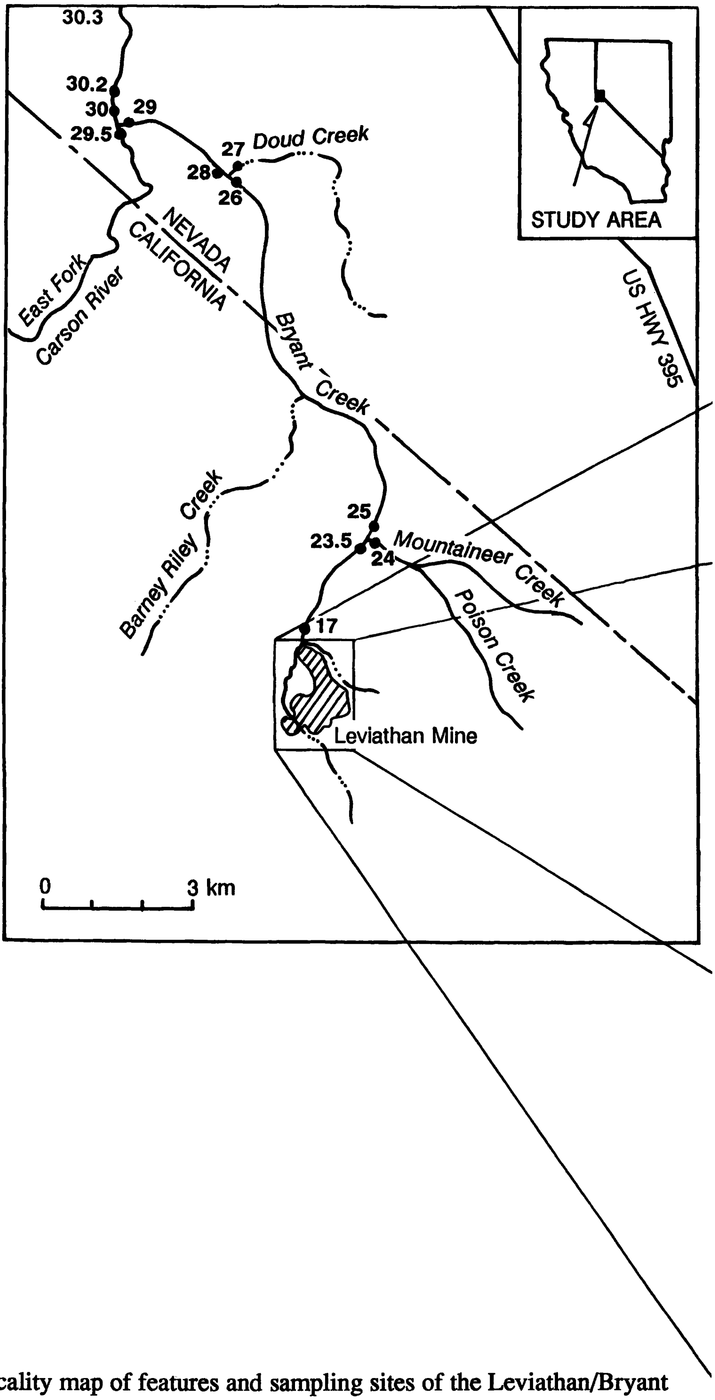

Figure 1. Locality map of features and sampling sites of the Leviathan/Bryant Creek drainage system.

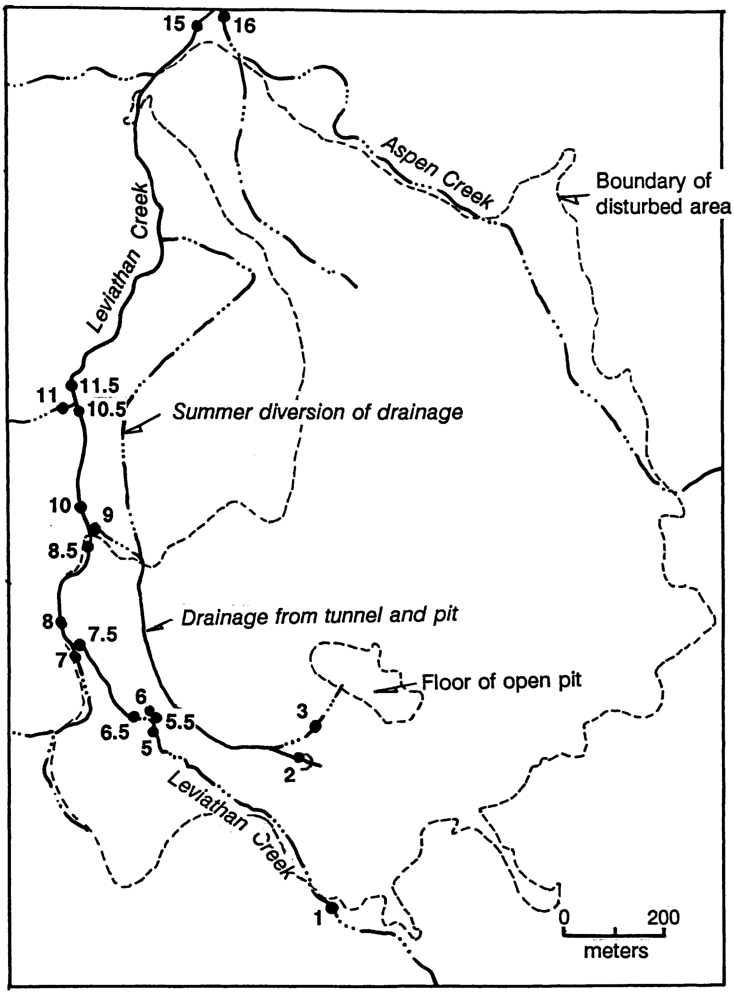

Figure 1. Continued.

HNO_3 per 250 mL sample. Metal analyses were done by simultaneous multielement atomic emission spectrometry (both by direct-current and inductively-coupled plasma techniques), flame and graphite furnace atomic absorption techniques and by ferrozine colorimetry for ferrous ion determinations. Sulfate determinations were made using ion chromatography. Sampling and analytical techniques are described in more detail by Ball and Nordstrom (1, and written communication). The analytical and physical data used in this study are shown in Table I. As these analyses had previously been subjected to a critical review process a few alterations to the revised data set were necessary (see Appendix).

Flow Rates. Stream discharges were determined by conventional procedures using a pygmy flow meter over a measured cross sectional area of the stream. The discharges of main and tributary drainages must be known and must be consistent to do useful mass-balance calculations for each component across and between confluences. During an initial attempt to balance SO_4 across confluences, shortcomings in the accuracy of some of the measured discharge data became evident. The most conservative ions occurring at concentrations high enough to be easily detected after dilution are SO_4, Li, Ca, and Mg so these ions were used to establish consistent discharge values. If the mass balance of each ion was significantly improved by a reasonable change in the discharge rate and if this change was compatible with adjacent discharge rates in the drainage, then the new value was adopted for inclusion in Table I (revised flow rates allow the mass balance of conservative ions to within 10% across each confluence). Only in a few cases did this result in major revision of the original discharge value (see Appendix).

June discharges ranged from 25 to 240 L/s for the main drainage compared to 3 to 110 L/s for the October discharges. Discharges and pH values are plotted in Figure 2a for June and in Figure 2b for October. In June, summer diversion of the open-pit drainage caused an increase in discharge between sites 11.5 and 15. An unsampled tributary and seepage from the toe of the landslide also contributed to the mainstream flow near the confluence of Aspen and Leviathan Creeks. The theoretical discharge for these seeps and surface flows and for Barney Riley Creek, which meets Bryant Creek between the confluences with Mountaineer and Doud Creek, can be calculated but their effect on trace-metal concentrations in the LBC drainage can not be quantified because there were no samples taken in the vicinity of these confluences.

Computational Methods. The computer codes WATEQ4F (4) and MINTEQA2 (5) were used with the analytical data to evaluate the main mechanisms of trace-metal removal. WATEQ4F calculates the distribution of aqueous species in solution based on thermodynamic data and the assumption of equilibrium. WATEQ4F also calculates a 'free' metal-ion concentration and saturation indices $\log(IAP/K_{sp})$ for mineral phases. A summary of the computational methods and data used in WATEQ4F is given by Ball and Nordstrom (4).

Adsorption modelling was performed with MINTEQA2 (5), using the Generalized Double-Layer Sorption Model. Details of this adsorption model, which

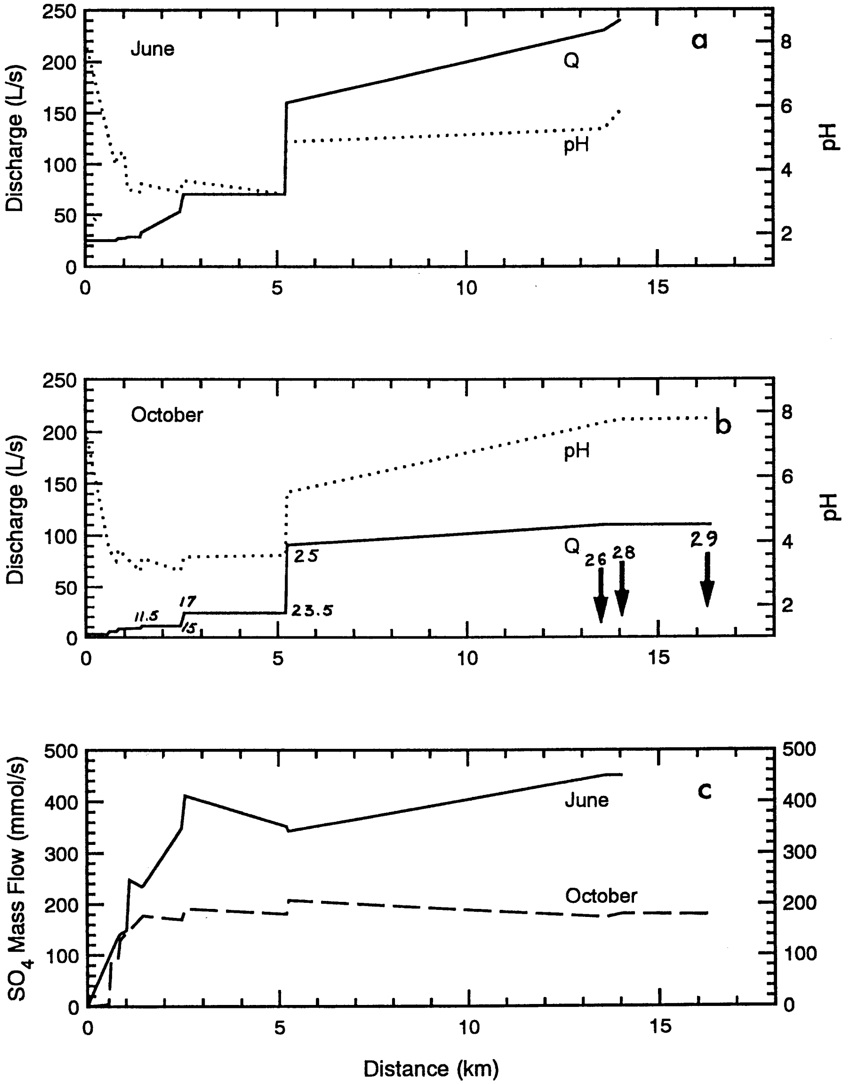

Figure 2. a. Variation in discharge and pH with distance downstream for the sampling of June 14-17, 1982. b. Variation in discharge and pH with distance downstream for the sampling of October 4-6, 1982. Numbers inside diagram box refer to site locations found in Figure 1. c. Mass flow for dissolved sulfate with distance downstream for both June 1982 and October 1982 sampling.

Table I. **Chemical analyses (mg/L) and physical parameters (discharge, Q, in L/s; temperature in °C; Eh in volts) for the Leviathan and Bryant Creeks**

Site No.	Q	Temp.	pH	Eh	SO_4	Al	As	Cu	Fe^{II}	Fe^{TOT}	Mn	Zn
June, 1982:												
1	25	12.5	8.10	.380	5.3	.018	.004	.0015	.0076	.0088	.0187	.0001
7	2	18	6.85	.238	276	.038	.002	.0005	6.03	6.38	2.13	.0182
7.5	25	18	4.18	.488	517	21.7	.008	.18	90.0	91.1	3.87	.137
8	27	18	4.50	.471	504	16.0	.005	.165	77.8	80.0	3.85	.155
8.5	27	18	4.58	.461	530	15.0	.007	.153	79.4	81.3	4.31	.146
9	1.5	18	2.10	.601	5730	355	27	5.43	1070	1210	15.4	1.29
10	28.5	18	3.40	.591	833	39.9	1.5	.447	142	150	5.05	.205
10.5	28.5	18.5	3.32	.622	790	37.5	1.2	.348	123	141	5.25	.192
11	4.5	13.5	8.00	.384	57.2	.195	.005	.002	.0081	.0091	.0247	.0013
11.5	33	18	3.58	.612	686	32.2	1.0	.261	103	117	4.31	.147
15	53	14.5	3.31	.644	631	28.8	.45	.260	66.6	83.3	3.84	.136
16	17	13	7.98	.304	283	.109	.003	.012	.0177	.0207	1.26	<.0001
17	70	14	3.68	.628	564	20.5	.35	.231	47.9	55.7	3.06	.109
23.5	70	19.5	3.25	.689	483	19.8	.018	.231	9.01	18.4	3.04	.100
24	90	12.5	8.85	.379	1.89	.01	.002	.001	.0086	.0099	.0052	.0001
25	160	16	4.90	.692	206	5.06	.01	.093	4.44	4.72	1.26	.0429
26	230	21	5.30	.398	188	.73	.003	.0555	5.12	5.52	1.04	.0327
27	8.5	17.5	8.41	.340	38.9	.007	.003	.002	.0236	.0242	.0115	.0002
28	240	20	5.88	.338	180	.202	.003	.0385	4.84	5.17	.961	.0335
29	71	23	5.50	.392	189	.048	.002	.0445	4.29	4.59	.957	.0331

Table I. (continued): Chemical analyses (mg/L) and physical parameters (discharge, Q, in L/s; temperature in °C; Eh in volts) for the Leviathan and Bryant Creeks

Site No.	Q	Temp.	pH	Eh	SO_4	Al	As	Cu	Fe^{II}	Fe^{TOT}	Mn	Zn
Oct., 1982:												
1	3.1	6	7.50	.279	7.21	.029	.0007	≤.0005	.0005	.0041	.0085	.0046
5	3	8.2	5.08	.437	143	2.13	.001	.026	11.1	11.4	.775	.0346
5.5/6	2.7	7.9	3.13	.546	2850	106	.48	.398	616	625	22.6	.694
6.5	5.7	7.8	3.78	.547	1450	51.0	.023	.192	278	280	11.1	.332
7	2.5	14.3	6.00	.263	1200	.45	.006	<.0005	37.6	38.1	11.4	.051
7.5	5.7	11.5	3.43	.574	1570	55.6	.032	.209	299	308	12.0	.383
8	8.2	12	3.78	.555	1520	46.9	.019	.196	264	266	12.6	.32
10.5	9	9.1	3.10	.612	1870	58.1	.032	.224	254	277	15.2	.385
11	2	4	7.15	.463	130	.016	.001	.0005	.0053	.0127	.0109	.0003
11.5	11	6	3.52	.607	1550	47.8	.032	.213	215	233	12.7	.332
15	11	7	3.11	.658	1480	45.0	.019	.202	112	174	11.8	.307
16	14	11.9	7.62	.235	245	.088	.005	.0015	.0045	.0123	.95	.0015
17	24	7.8	3.55	---	764	18.8	.012	.101	45.6	56.2	5.53	.125
23.5	24	8.3	3.60	.662	723	19.9	.011	.108	23.6	35.5	5.48	.129
24	67	7	8.20	.344	1.26	.01	.003	.002	.0059	.011	.0052	.0001
25	91	7	5.53	.370	219	.62	.004	.0175	6.94	7	1.57	.0388
26	110	12.7	7.69	.404	152	.036	.002	.002	.0018	.0091	1.04	.0019
27	5.7	12.2	8.20	.439	44.7	.009	.003	.0015	.0155	.0389	.0075	.0006
28	110	13.5	7.78	.394	158	.107	.003	.0015	.0013	.0033	.928	.0017
29	110	14	7.80	.423	156	.14	.003	.0015	.0019	.0066	.923	.0032

is a surface complexation model, and the accompanying set of internally consistent surface complexation constants for adsorption onto hydrous iron oxide are given by Dzombak and Morel (6). The properties for hydrous Fe oxide used in this study are the same as those used in (6) to determine the surface complexation constants. For modelling purposes, it is assumed that the suspended Fe particulate is the sole adsorbent and is present as hydrous Fe oxide. Calculations for binding site concentrations and total amorphous Fe concentrations are based on these assumptions. MINTEQA2 was used to calculate trace-metal adsorption onto Fe oxide over selected intervals of the LBC drainage, using upstream water chemistry and downstream pH.

The suspended material (> 0.10 μm) was not measured or analyzed in the water samples on which this study is based. An estimate of the amount of freshly precipitated, suspended Fe particulates was made for each interval of the LBC drainage, using the difference in mass flow of dissolved Fe. The decrease in the mass of soluble iron is assumed equal to the mass of suspended particulate iron. This estimate provides a concentration and a mass flow of particulate iron. It is then assumed that the particulate iron has the same properties (surface area, i.e. 600 m^2/g, and adsorption site density) as those of freshly precipitated hydrous oxide described by Dzombak and Morel (6). Two site densities are used, 0.005 mol/mol Fe for the high-affinity site densities and 0.20 mol/mol Fe for the low-affinity site densities. A further assumption is that the iron from the mass balance results is used as $Fe_2O_3 \cdot H_2O$ with a formula weight of 89 g/mol Fe (6). A comparison of the Fe content of the suspended load, for the few sites which were previously sampled simultaneously (2), suggests that this method provides a reasonable approximation to the concentrations of suspended Fe particulate in the river. Variation of the total concentration of Fe-rich particulates or the equilibrium pH (using upstream rather than downstream pH values) in the MINTEQA2 model does not affect greatly the qualitative outcome of these results.

Results: Trace-Metal Attenuation

Stream Description. Iron-rich, brown-to-orange precipitates were particularly evident on the stream bed in the tributary entering the LBC drainage in three locations: at site 7, near the confluence of Mountaineer Creek, and near the confluence with the East Fork Carson River. During periods of high rainfall the LBC mainstream becomes turbid and appears to carry a high concentration of suspended Fe(III) precipitate. Often the stream-bed precipitates are mixed with white precipitates of Al hydroxysulfates, particularly below the Mountaineer Creek confluence. Analyses of the mixed Al- and Fe-bearing precipitates from the LBC stream bed downstream from Mountaineer Creek indicated that the precipitate contained 1-24 wt% Fe. Analyses of bed sediments in this region of the drainage (at sites 17, 25, and 26, collected in May 1983; 2) are consistent, identifying an Al-rich sediment with < 1 wt% Fe.

Sites of trace-metal removal from solution. Partitioning of metals between the dissolved and solid phases can be identified by mass-flow calculations for Cu, As, Zn, and Fe at each sampling site on the main drainage. The mainstream mass flow of a metal will not decrease as a result of dilution of the mainstream at a confluence, but will decrease if the metal is removed from solution by precipitation or adsorption, or increase if the mainstream mixes with a metal-rich tributary. The sulfate mass flow only increases from acid mine water inflows and then remains constant (Figure 2c). The mass flow of each metal (in mmol/s and μmol/s) is shown as a function of distance from site 1 in Figure 3a-d. An average error of 10% in the discharge rates and 5% in the analyses has been assumed, giving a total error of 15% in the metal mass flow shown.

Iron and Arsenic. In June 1982, the As and Fe content of the LBC drainage increased dramatically between site 5 and site 10 (Figure 3a-b), where the mainstream is contaminated mainly by drainage from the open pit (site 9). The mainstream also appeared to have been contaminated by Fe over this interval by the tributary at site 7 and by seepage from waste dumps near sites 5 and 6.5. On the other hand, the As present at site 10 was derived solely from the surficial tunnel drainage entering LBC drainage at site 9 and was attenuated to background levels similar to those upstream from the Leviathan mine site, above site 23.5 just above the Mountaineer Creek confluence (Figure 3b).

Iron was removed from solution between site 10 and 10.5, but replaced between site 11.5 and 15. This recharge may have been caused by input from the summer diversion of the open-pit drainage as shown in Figure 1 and/or seepage into the stream from the landslide which occurs in the northwest area of the disturbed ground surrounding the mine. A similar input can be seen for SO_4, Cu, and Zn in this section of the drainage. As the groundwaters in the toe of the landslide have generally low concentrations of Cu, As, and Zn (2), it seems likely that the open-pit drainage diversion caused the observed increase in Fe mass flow between sites 11.5 and 15. More than 80% of the dissolved Fe present at site 15, just upstream from the Aspen Creek confluence, was removed before site 25, just below the Mountaineer Creek confluence. However, there also appears to have been an increase in Fe mass flow below site 25 (Figure 3a), similar to that noted for SO_4 mass flow. This increase may have been due to either the photoreduction of Fe(III) in the flat, exposed section of the drainage (7), or to the oxidation of pyrite aggregates carried through the faster sections of the drainage. Pyrite oxidation is more likely because it explains the coincident increase in both Fe and SO_4 mass flows observed in this region of the LBC drainage.

In October, 1982, the mass flow of Fe was less than that of June, but showed a similar trend within the drainage. Leviathan Creek was contaminated primarily by seepage from waste dumps (e.g., at sites 5.5 and 6) and not by surficial flow from the open pit in October. Approximately 75% of the dissolved Fe present at site 11.5 was removed upstream from the Mountaineer Creek confluence, and the remaining 25% was removed between the confluences with Mountaineer and Doud Creeks. The As mass flow was low (Figure 3b; note the different vertical scales for June and October As mass flow) and although variations are apparent, there is over 100% variability on repeat analyses and between different analytical techniques for As concentrations < 0.01 mg/L (1). In October

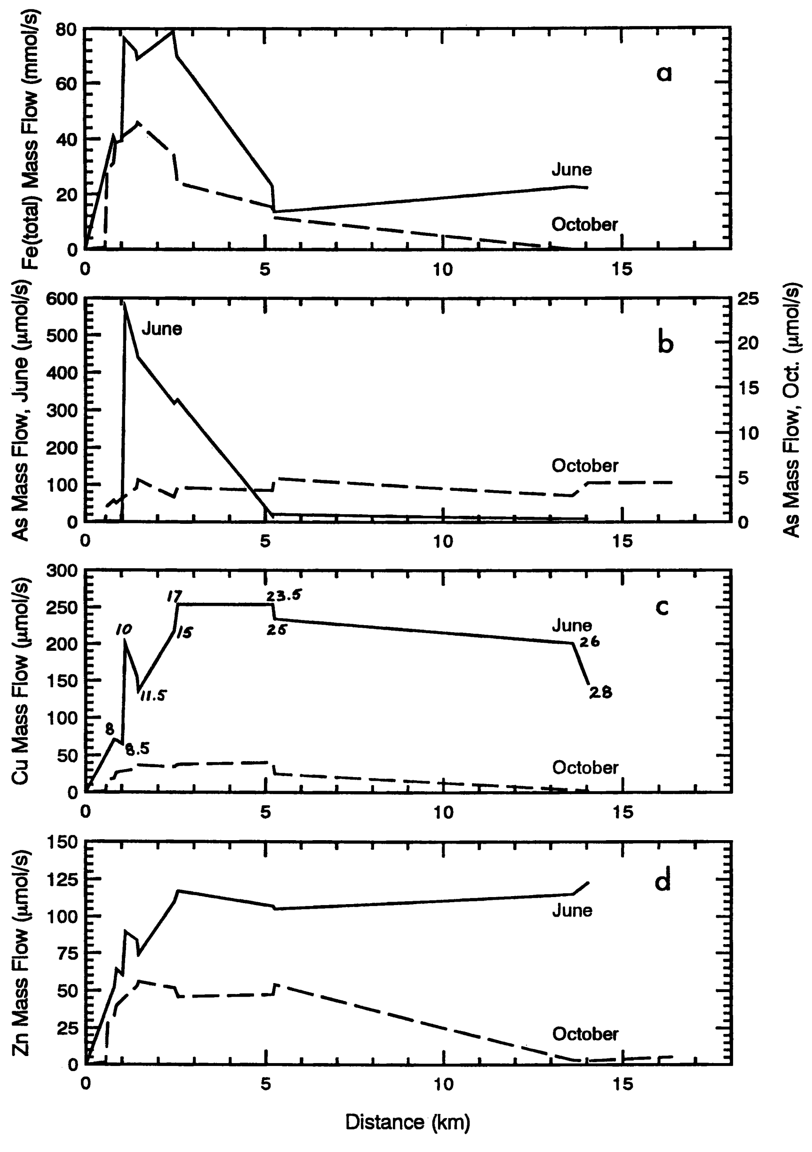

Figure 3. a. Mass flow for total dissolved iron with distance downstream, June and October 1982. The discharge and mass flow at site 29 for June have been omitted because summer diversion of this water for irrigation greatly decreases the discharges. b. Mass flow for dissolved arsenic with distance downstream where the mass flow for June is shown on left-hand scale and the mass flow for October is shown on the right-hand scale. c. Mass flow for dissolved copper with distance downstream, June and October 1982. Numbers inside diagram box refer to site locations found in Figure 1. d. Mass flow for dissolved zinc with distance downstream, June and October 1982.

mainstream As concentrations ranged from 0.0007 to 0.032 mg/L, so there is considerable analytical error which is further propagated by the mass flow calculations. In both June and October, As and Fe were primarily removed between confluence points, even at low pH.

Copper and Zinc. In June the mass flows of Cu and Zn were similar to that of Fe above the Aspen Creek confluence (Figure 3c and 3d, above site 17). For example, a small amount of the dissolved Cu and Zn appears to have been removed from solution between sites 10 and 10.5, immediately after the input of open-pit effluent at site 9. This effect is more significant for Cu (22% removed) than for Zn (6.3%), as the latter is within the calculation error. Like Fe, Cu and Zn mass flows increased between site 11.5 and 15, where seepage from the landslide and the diverted drainage from the open pit found their way into the LBC mainstream. However, Cu and Zn were not removed from solution between the Aspen Creek and Mountaineer Creek confluences (sites 17 to 25). Although approximately 42% of the dissolved Cu present at site 15 was removed further downstream, between Mountaineer and Doud Creek (sites 25 to 28), Cu and Zn mass flows remained high in the lower drainage region. At site 29, Cu and Zn concentrations were respectively 30 and 330 times those of the uncontaminated LBC drainage at site 1.

In October the Cu and Zn mass flows were significantly less than those of June, and had decreased to near background levels by the Doud Creek confluence (site 26). Of the Cu and Zn introduced by contamination of the LBC mainstream at the mine site, 92% of the dissolved Cu was removed between sites 23.5 and 26, and 94% of the dissolved Zn between sites 25 and 26. In both June and October, therefore, Cu and Zn failed to show significant attenuation in waters of $\mathrm{pH} < 5$. At $\mathrm{pH} > 5$ Cu and Zn were partially removed from solution, mainly between confluence points.

Chemical Attenuation Rates. It is evident that Fe, As, Cu, and Zn were each removed from solution over different intervals of the LBC drainage, and at different rates. When the drainage is arbitrarily divided into two intervals, from the mine site (site 10) to Mountaineer Creek confluence (site 23.5) and from the Mountaineer Creek confluence to site 28, attenuation rates can be calculated for Fe, Cu, As, and Zn for these intervals (see Table II).

Between the mine site and Mountaineer Creek, the attenuation rate of Fe was higher in June than in October, reflecting the greater quantities of Fe reaching the LBC drainage from the mine site in June. In June, Fe was removed from solution over this interval at more than 100 times the rate of attenuation downstream from the Mountaineer Creek confluence. Arsenic had the highest attenuation rate of the three metals (As, Cu, and Zn) between the mine site and Mountaineer Creek confluence. There was a net increase in the mass flow of Cu over this interval in both June and October, and a net increase in the mass flow of Zn in June. Downstream from the Mountaineer Creek confluence, both Cu and Zn were removed from solution at a similar, low rate of attenuation in October, and Cu was removed at a higher rate in June.

Table II. Chemical attenuation rates (μmol/km/s) for trace metals in the LBC drainage system

Site Interval	Length (km)	As (J)	Cu (J)	Cu (O)	Zn (J)	Zn (O)	Fe (J)	Fe (O)
10.5-23.5	3.79	116	+	+	+	1.5	12900	7750
23.5-28	8.85	0.8	12.3	4.4	+	5.0	95	1720

'+'indicates a net increase in the mass flux of a metal between these sites; 'J' and 'O' represent June and October.

Chemical Modelling. The analytical data in Table I has been used with the geochemical speciation models WATEQ4F (4) and MINTEQA2 (5) to indicate whether mineral-phase precipitation or adsorption processes were limiting trace-metal concentrations in the LBC drainage in 1982.

Iron. Ferrihydrite ($Fe(OH)_3$) saturation indices computed by WATEQ4F show saturation or slight supersaturation for all samples. Supersaturation with respect to jarosite is also indicated for waters of the upper drainage (pH < 6). The solubility-limiting mineral phase for Fe may be deduced from plots of the free Fe^{3+} activity against pH (8). For waters of pH > 7, such as the uncontaminated LBC drainage and LBC drainage near and after the East Fork Carson River confluence, log a_{Fe3+} plotted against pH has a slope of -3.0, suggesting equilibrium with ferrihydrite. In the waters of pH < 6, however, a slope of -2.3 is observed. This slope is inconsistent with that expected for waters at equilibrium with ferrihydrite, goethite, or jarosite.

It has been proposed (9) that a poorly crystalline oxyhydroxysulfate of Fe (unit cell formula of $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$ or $Fe_{16}O_{16}(OH)_{10}(SO_4)_3$ is a primary component of the Fe-rich precipitates formed in acid-sulfate mine waters of pH 2.5 to 4. However, if Fe^{III} is in equilibrium with a phase of either stoichiometry, slopes of -2.8 or -2.6 respectively may be expected. A slope of -2.3 appears to be consistent with a more sulfate-rich iron oxyhydroxide: $Fe_{16}O_{16}(OH)_5(SO_4)_{5.5}$ which may also be written as the iron oxyhydroxsulfate: $Fe(OH)_{2.3}(SO_4)_{0.35}$. Similar problems have been experienced characterizing orange amorphous precipitates from an acid mine drainage in the West Shasta mining district in California (10), which have been described as either a mixture of jarosite [$KFe_3(SO_4)_2(OH)_6$] and ferric hydroxide or ferric hydroxide with adsorbed sulfate.

Arsenic. There appears to be a close correlation between the removal of As and Fe from solution in the LBC drainage, although any stoichiometric relationship between the quantities of Fe and As removed from solution is obscured by the abundance of Fe. All saturation indices for scorodite ($FeAsO_4 \cdot 2H_2O$) show undersaturation. An alternative mechanism for As attenuation is the adsorption and (or) coprecipitation of As with the suspended or stream-bed iron phases. The adsorptive capacity of a ferrihydrite or ferric oxyhydroxysulfate phase is high for both As(III) and As(V), even at a pH as low as 4 (11). Arsenic in the oxidized, acid mine effluent will be predominantly present as As(V), which is adsorbed more strongly at lower pH where it exists as an anionic complex. Adsorption onto the surface of suspended particulate Fe can account for the observed removal of As, for both June and October, based on MINTEQA2 results shown in Table III. In June, the amount of As actually removed over most intervals in the upper drainage is less than that predicted by MINTEQA2. This may be due to the sulfate-rich nature of the adsorbent or perhaps to the lack of time in the fast-flowing stream. Also, the As/Fe weight ratio of the stream-bed sediment is 0.25 to 0.15 at sites 17, 25, and 26 (2), and is significantly higher than the similar ratio for As/Fe removed from solution which is 0.04 between sites 10 and 17. Therefore, As may also be adsorbed by existing stream-bed precipitate.

Table III: Metal adsorbed over specific intervals in the LBC drainage, expressed as a percentage of the upstream metal mass flow

	Site Interval	pH	Fe (mg/L)[#]	As (m)[§]	As (c)[§]	Cu (m)[§]	Cu (c)[§]	Zn (m)[§]	Zn (c)[§]
June:	10-10.5	3.4-3.3	9	31	20	0	22	0	6
	11.5-15	3.6-3.3	9	33	28	0	-	0	-
	17-23.5	3.7-3.3	37	70	95	0	-	0	8
	23.5-25	3.3-4.9	7	59	-[*]	4	8	0	2
	25-26	4.9-5.3	7	84	57[*]	21	14	0	-
Oct:	11.5-15	3.5-3.1	59	70	41[*]	0	5	0	8
	23.5-25	3.6-5.5	8	77	-[*]	33	39	0	-
	25-26	5.5-7.7	7	99	40[*]	97	86	77	94

[#] 'Fe' is the amount of Fe precipitated, calculated as the difference in mass flow (mg/sec) over the interval, divided by upstream discharge (L/sec).

[§] Adsorption predicted using the MINTEQA2 model is shown as (m) and the calculated percentage decrease in the mass flow of the metal as (c). '-' indicates that metal load has increased or remained unchanged over the interval.

[*] The uncertainties in the analyses for these samples cause a high degree of error in these values.

Copper and Zinc. All of the LBC drainage waters were undersaturated with respect to the Cu and Zn sulfate and hydroxysulfate salts such as antlerite ($Cu_3(SO_4)(OH)_4$), brochantite ($Cu_4(SO_4)(OH)_6$) and goslarite ($ZnSO_4 \cdot 7H_2O$), which potentially could precipitate from the sulfate-rich mine waters. Saturation with respect to tenorite (CuO), malachite ($Cu_2(OH)_2CO_3$), zincite (ZnO) and $Zn(OH)_2$ was approached in the waters of pH > 7. Tenorite and zincite are phases unlikely to form in this environment, however phases such as malachite, hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) may form; unfortunately the thermodynamic and kinetic data are not available to evaluate adequately their role in metal attenuation. For the waters of the LBC drainage with pH < 6 neither WATEQ4F saturation indices nor free-ion activities can be used to identify a likely Cu- or Zn-bearing precipitate.

Although the attenuation trends for Cu and Zn in the LBC drainage are not as clearly defined as for Fe and As, the removal of dissolved Cu and Zn in the lower drainage (23.5 to 26) in October is consistent with adsorption onto hydrous Fe oxide (Table III). Likewise, the removal of dissolved Cu over the same interval in June is very likely to have been due to adsorption processes. Because Cu is adsorbed more readily onto hydrous Fe-oxides than Zn at pH < 6 (6,12), Cu was removed preferentially between sites 23.5 to 25 in October and sites 25 and 26 in June 1982, while Zn remained in solution. A further increase in pH, as occurred between sites 25 and 26 in October, would have been required for Zn adsorption.

Summary and Discussion

A geochemical model is proposed to explain trace-metal attenuation in a mountainous stream receiving acid mine drainage, based on the precipitation of a ferric oxyhydroxysulfate and consequent trace-metal attenuation by adsorption onto this particulate phase. The model can account for variations in trace-metal concentration, both with distance from the mine site and with seasonal changes in drainage flow and acidity. Adsorption onto suspended ferric oxyhydroxysulfate appears to be the major mechanism regulating the concentrations of As, Cu, and Zn downstream from the mine site in the LBC drainage system. In June 1982, when the concentrations of As, Cu, and Zn in the mainstream were high, close to the mine site, all the dissolved As was adsorbed onto Fe particulates within 5 km of the mine site. Although a fraction of the dissolved Cu similarly was adsorbed further downstream, between Mountaineer and Doud Creeks, the Cu and Zn concentrations remained high in the lower drainage and may have contaminated the East Fork Carson River at this time of year. In October 1982, As concentrations in the LBC drainage were not increased significantly by seepage from the mine site, and dissolved Cu and Zn were removed effectively by adsorption between the Mountaineer and Doud Creek confluences.

Seasonal differences in metal attenuation were caused by increased discharge from the mine site during the spring and early summer months. This increased As concentrations in the LBC, because the surficial drainage from the open pit of the Leviathan Mine had high As concentrations. The elevated mine-site discharge also increased the acidity of the lower drainage (below Mountaineer Creek). The LBC drainage between Mountaineer Creek and Doud Creek (pH = 4.5 to 5.3) was considerably more acid in June than in October (pH = 5.5 to 7.7). Because Zn is not adsorbed as readily onto the surface of Fe-oxide as copper at pH < 6 (6,12), Zn remained in solution in the lower drainage in June, but was adsorbed in October. Similar controls have been reported for Cu and Zn concentrations in other rivers and estuarine waters receiving acid mine drainage. Cu and Zn concentrations in the Canon River and Restrongnet Creek in England, for example, also were interpreted to be controlled by binding to amorphous Fe oxyhydroxides (13); a process which is pH-dependent and consistent with laboratory studies.

There are other factors which may affect trace metal attenuation in the LBC drainage which have not been considered here. For example, the role of other adsorbents, including organic material such as the algal mats which often occur with precipitated Fe particulates, Al hydroxide and Mn oxides, has not been fully investigated. Neither has the effect of Cu and Zn ferrite formation (14) on Cu and Zn attenuation been assessed. Future research should investigate these factors.

Appendix: Modifications of the original data

The following alterations were made to the original analytical data (1). Inconsistencies which may have been caused by sample contamination or analytical errors have been identified from anomalous metal/metal or metal/anion ratios. For the October samples, water composition for sites 5.5 and 6 have been averaged for the mass balanced calculations. A value of 0.398 mg/L (that of site 6) has been adopted for Cu as the Cu concentration for site 5 appears to be inconsistent with other trace and major ion concentrations in the sample. Also, a Cu concentration of 0.0015 mg/L has been adopted for site 28. In June, Zn concentrations of 0.0001 mg/L and 0.100 mg/L have been adopted for sites 24 and 23.5 respectively, and an Al concentration of 0.01 and a Mn concentration of 0.0052 mg/L have been adopted for site 24.

Several minor alterations have been made to the discharge data reported (1), based on the mass balance of conservative ions (as explained in the text). The following major alterations have also been made; June discharge at site 10.5 was altered from 41 L/s to 28.5 L/s, and at site 15 was altered from 40 to 53 L/s. Note that the discharge at site 29 is low owing to summer diversion of the mainstream for agricultural use. October discharge at site 23.5 was altered from 40 to 24 L/s and at site 24 from 57 to 67 L/s. An error in the discharge at site 23.5 was substantiated by K.E. Bencala (pers. comm., 1992), who calculated a discharge of 29 L/s, based on unpublished revisions of a tracer injection experiment.

Acknowledgments

The authors wish to thank Jim Ball and Reini Leinz of the USGS for their analytical assistance, and Briant Kimball, Ken Bencala and Jim Ball for reviewing this manuscript. The project has been funded by the USGS Water Resources Division and by the Institute of Environmental Health and Forensic Science (formerly DSIR Chemistry) of New Zealand.

Literature Cited

1. Ball J.W.; Nordstrom D.K. U.S.G.S. Water-Res. Invest. Rept. 89-4138 1989, 46 pp.
2. Hammermeister D.P.; Walmsley S.J. U.S.G.S. Open File Rept. 85-160 1985, 120 pp.
3. Chapman B.M.; Jones D.R.; Jung R.F. Geochim. Cosmochim. Acta. 1983, 7, 1957-1973.
4. Ball J.W.; Nordstrom D.K. U.S.G.S. Open File Rept. 91-183 1991, 188 pp.
5. Allison J.D.; Brown D.S.; Novo-Gradac K.J. U.S. Environ. Protect. Agency, 1991, EPA/600/3-91/021, 106 pp.
6. Dzombak D.A.; Morel F.M.M. Surface Complexation Modeling: Hydrous Ferric Oxide. Wiley Interscience, New York, 1990, 393 pp.
7. McKnight D.M.; Bencala K.E. Geochim. Cosmchim. Acta 1989, 53, 2225-2234.
8. Nordstrom D.K. In Proceedings of the U.S.G.S. Toxic Substances Hydrology Program; Mallard G.E. and Aronson D.A., eds. U.S.G.S. Water Res. Invest. Report 91-4034, pp 534-538.
9. Bigham J.M.; Schwertmann U.; Carlson L.; Murad E. Geochim. Cosmochim. Acta 1990, 54, 2743-2758.
10. Filipek L.H.; Nordstrom D.K.; Ficklin W.H. Environ. Sci. Tech. 1987, 21, 388-396.
11. Pierce M.L.; Moore C.B. Water Res. 1982, 16, 1247-1253.
12. Benjamin M.M.; Leckie J.O. J. Coll. Interfac. Sci. 1981, 79, 209-221.
13. Johnson C.A. Geochim. Cosmochim. Acta 1986, 50, 2433-2438.
14. Hem J.D. Geochim. Cosmchim. Acta 1977, 41, 527-538.

RECEIVED September 23, 1993