Geochemistry, toxicity, and sorption properties of contaminated sediments and pore waters from two reservoirs receiving acid mine drainage

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ABSTRACT

Acid mine waters from the Iron Mountain Superfund Site, Shasta County, California, flow through Spring Creek Reservoir and into Keswick Reservoir on the Sacramento River. In Keswick Reservoir, the acid mine waters have neutralized on mixing with neutral-pH lake water, producing fine-grained, metal-rich sediments. Sediment cores were collected during 1997 from both reservoirs for characterization and pore waters were extracted under anoxic conditions. Chemical composition, mineralogical identification, redox chemistry, sorption properties, and toxicity were determined on several samples. Metal concentrations in sediment ranged from 4 to 47 % for Fe, 200 to 4,800 mg/kg (milligrams per kilogram) for Cu, and 85 to 6,600 mg/kg for Zn. Pore waters ranged in pH from 4.7 to 6.7 and their Fe(II) concentration range was 10 to 2,000 mg/L (milligrams per liter). Although pore-water Zn concentrations ranged from 0.1 to 9 mg/L, Cu concentrations were less than 0.01 mg/L. Considerable reductive iron dissolution has occurred in the Keswick Reservoir sediments, but there is little or no indication of sulfate reduction. Adsorption and desorption experiments for Cu, Zn, and Cd on composite sediment samples demonstrated typical sorption behavior for metal ions on iron oxides, except that the adsorption edge is moved about one pH unit lower than expected compared to a hydrous ferric oxide substrate, but similar to that for a schwertmannite (ferric oxyhydroxysulfate) substrate. Schwertmannite was identified in the sediments by x-ray diffraction and Mössbauer spectroscopy. Toxicity tests, using dilutions of Keswick sediment pore waters and *Ceriodaphnia dubia* as a test animal, demonstrated that iron is the causative agent for both acute and chronic toxicity with a minor contribution to toxicity from zinc.

INTRODUCTION

The Iron Mountain Superfund Site is located in Shasta County, northern California, 9 mi. (miles) northwest from the town of Redding (fig. 1). Mineral deposits of the West Shasta district are Kuroko-type massive-sulfide deposits of Devonian Age. The ore bodies are pyrite-rich and hosted in quartz-porphyry rhyolite which has minimal acid-buffering capacity. Iron Mountain is a group of mines that include Old Mine, No. 8, Confidence-Complex, Brick Flat Open Pit, Mattie, Richmond, and Hornet. Recovery for silver (Ag) and gold (Au) from surficial gossan began in the 1860s and by 1896, underground mining for copper (Cu) and Ag had begun. Some zinc (Zn) was produced during World War II and open-pit mining for pyrite to produce sulfuric acid was active during 1955–62. Iron Mountain was once the largest producer of Cu in California and now it is the largest producer of acid mine drainage in the State. Prior to Superfund remediation efforts, more than 2,500 tons of pyrite weathered every year and about 300 tons of dissolved Cu, Zn, and cadmium (Cd) drained annually into the Sacramento River via Spring Creek (fig. 2). Massive fish kills have been recorded in the Sacramento River during periods of high runoff; up to 100,000 anadromous fish have died in a major storm event (Nordstrom and
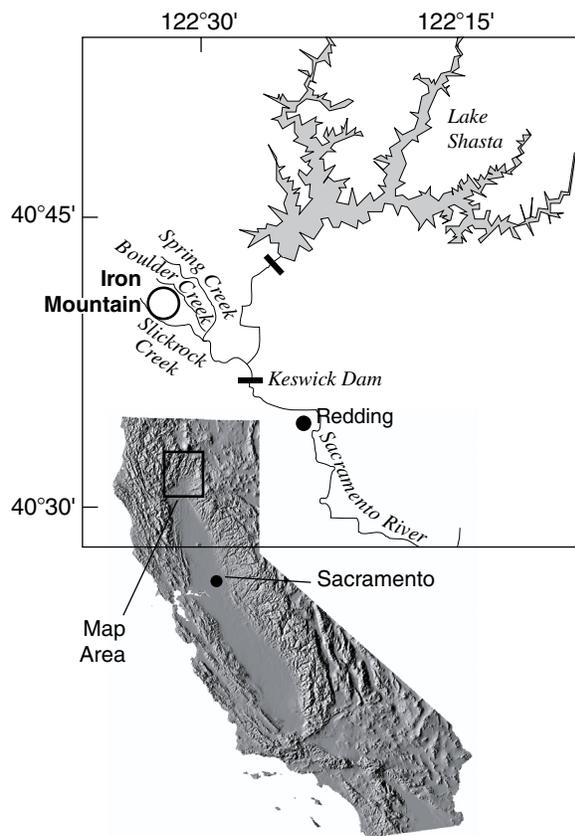
Figure 1. Map showing location of Iron Mountain, California

by the U.S. Geological Survey (USGS), including information on regulatory remedial activities, can be found in Nordstrom (1977), Nordstrom and others (1977), Alpers and others (1992), Nordstrom and Alpers (1995; unpublished data), and references therein.

Large metal-rich sediment deposits (piles) have accumulated in Keswick Reservoir, the receiving water body on the Sacramento River for acid drainage from Iron Mountain. Important questions regarding these deposits need to be addressed: How large are these piles of contaminated sediment? How much Cd, Cu, and Zn are in these piles and how mobile are these contaminants? How toxic are the sediments and are the pore waters of comparable or different toxicity? Is there an identifiable source of toxicity? Are the deposits more hazardous if left alone or removed or contained? A multi-organizational study was begun to resolve these questions. This paper describes the results from analytical, sorption, and toxicological investigations by the USGS in cooperation with the U.S. Environmental Protection Agency

(EPA), its contractors (CH2M Hill and Pacific Eco-Risk Laboratories), and the Bureau of Reclamation (BOR) on the sediments and pore waters from Keswick and Spring Creek Reservoirs. Iron Mountain was placed on the National Priority List by the EPA under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund, in 1983 and current studies continue under its auspices.

GENERAL SITE DESCRIPTION

Acid mine waters from Iron Mountain drain into Slickrock and Boulder Creeks, two tributaries of Spring Creek, which is the main drainage that flows into Spring Creek Reservoir and then into Keswick Reservoir (fig. 2). Spring Creek Debris Dam, an earth-fill structure, was built in 1963 to prevent debris and sediment from interfering with the tailrace to Spring Creek Power Plant and to provide control of acid mine waters so that they could be adequately diluted by outflows from Shasta Dam and Spring Creek Power Plant to mitigate risks to aquatic life. Prior to remediation at Iron Mountain, the pH of Spring Creek Reservoir was about 2.5 during low flow and sometimes more than 5 during high flows. The water level in Spring Creek Reservoir is generally kept as low as possible by the BOR, to provide temporary storage for flood events during the wet season. Unfortunately, the total storage capacity of only 5,850 acre-feet or 7.2 million m^3 (cubic meters) in Spring Creek Reservoir has been exceeded on several occasions since 1963, resulting in uncontrolled releases of acidic, metal-rich mine drainage into the Sacramento River. Keswick Reservoir has a total storage capacity of 23,800 acre-feet or 29.3 million m^3. The Spring Creek arm of the reservoir has been the repository for approximately 260,000 m^3 of chemically-precipitated sediment formed by the neutralization of acid mine water with the circum-neutral pH reservoir water. High-resolution seismic-reflection soundings (T. Bruns and others, USGS, written commun., 1999), combined with direct coring, have outlined three
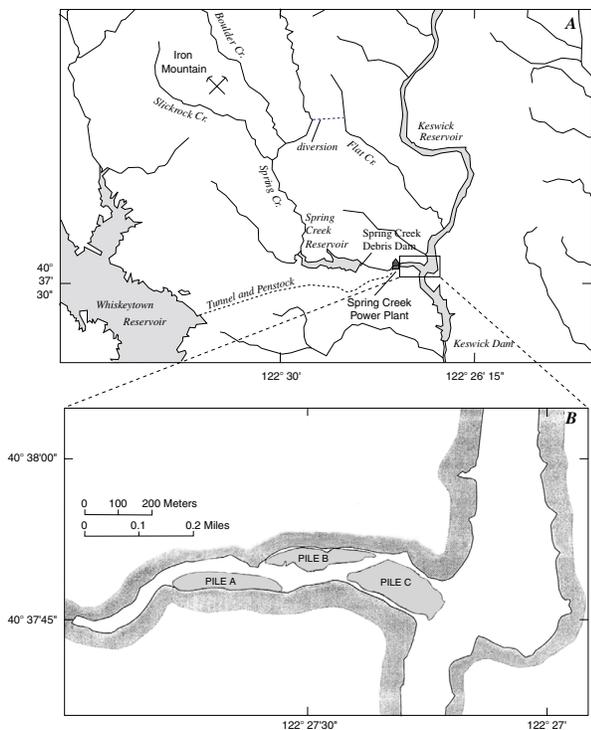
Figure 2. Maps showing location of (A) Spring Creek Reservoir and (B) sediment piles in Spring Creek arm of Keswick Reservoir, California. Pile A is up to 2 meters (m) thick, Pile B is up to 5 m thick and Pile C is up to 8 m in thickness.

contaminated sediment piles in the Spring Creek arm of Keswick Reservoir, named A, B, and C (fig. 2). The general geochemical characteristics of each pile are similar but pile C was chosen for detailed study because it is the largest, thickest, and most contaminated.

SEDIMENT CHEMISTRY

Field work was conducted at Keswick and Spring Creek Reservoirs during September, October, and November 1997. Sediment cores and extracted pore waters were obtained to determine the potential hazard that these sediments might cause if allowed to remain in place or the possible contamination that could result from resuspension or remobilization in association with proposed remediation efforts such as dredging or encapsulation. A field laboratory for sample processing and analysis was

set up at the Spring Creek Power Plant with the cooperation of the BOR.

Coring and On-Site Measurements

Sediments in Spring Creek Reservoir were collected in dry areas with a hollow-stem auger or from trenches dug with a backhoe. Some sediment cores were obtained below a shallow layer of water by advancing 2-in.-diameter PVC (polyvinyl chloride) tubes. Sediments in Keswick Reservoir piles were obtained from a barge platform by advancing 2-in.-diameter PVC tubing until refusal. Samples for chemical characterization were carefully extruded, composited, and processed into centrifuge bottles in an argon gas-filled glove bag. The samples were centrifuged at a centripetal acceleration of about 27,000 times the gravitational acceleration constant to separate pore waters from the sediment. Aliquots of pore waters were taken, under argon, to a mobile lab truck where measurements of pH, Eh, specific conductance, and alkalinity were made in an argon-filled glove box. A filtered aliquot of pore water was preserved with HCl for iron (Fe) redox determinations, that were made within 1 to 3 hours after extraction, by ultraviolet-visible spectrophotmetry using FerroZine as a complexing agent for Fe.

Sediment and Pore-Water Analyses

The top portion of every sediment core contained a layer that was predominately colloidal material and about 90% water. This layer of suspended colloids has been termed the "ghost layer" and was analyzed separately from the main sediment column by EPA's contractors. However, the ghost layer could not be distinguished chemically from the remainder of the sediment column; it differed primarily by grain size and water content.

A filtered aliquot of pore water was preserved with HNO_3 and analyzed for major cations and trace metals by inductively-coupled plasma (ICP) atomic-emission spectroscopy and ICP mass spectrometry. An unacidified, filtered aliquot was used for analysis of major anions by ion chromatography. Sediments were digested

using HNO_3-HCl-HF and analyzed for total metals by ICP.

A summary of the compositional range of selected elements in both Spring Creek Reservoir and Keswick Reservoir sediments is given in Table 1.

Table 1. Summary of iron, copper, and zinc concentrations in sediment. [Piles A, B, and C are located in the Spring Creek arm of Keswick Reservoir; SCR, Spring Creek Reservoir; mg/kg, milligrams per kilogram].

Sediment Pile	Iron %	Copper mg/kg	Zinc mg/kg
A, range	5-36	250-1,700	280-3,700
A, mean	14	780	590
B, range	6-38	410-1,900	180-2,400
B, mean	15	1,000	780
C, range	4-47	200-4,800	85-6,600
C, mean	17	1,600	1,200
SCR, range	6-21	320-960	100-340
SCR, mean	11	510	170

Plots of sediment chemistry indicate that Cu correlates closely with Fe, whereas the association of Zn and Cd with Fe are less strong. This result is expected because Cu adsorbs more strongly than Zn or Cd to iron oxides and co-precipitates with Fe more readily for a given pH and ratio of sediment to water (Davis and Kent, 1990, and references therein).
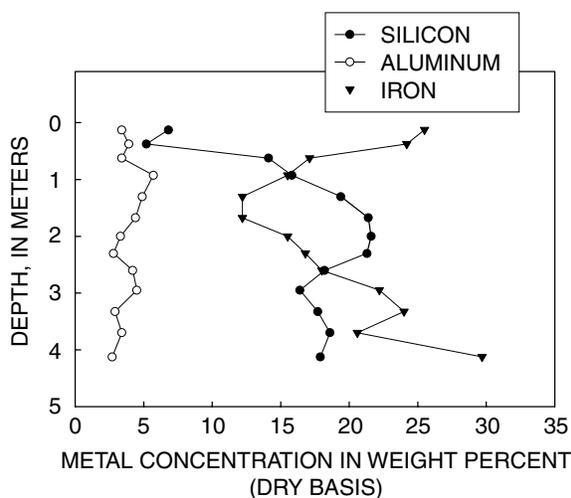
Figure 3. Concentrations of Al, Fe, and Si in sediment cores from pile C as a function of depth.
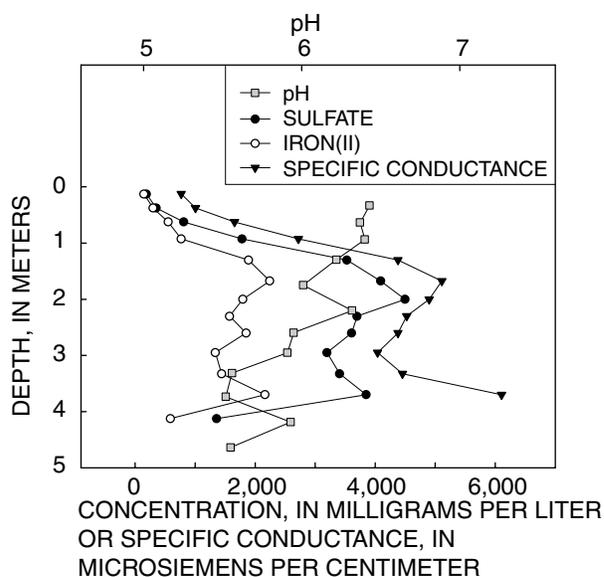
Figure 4. Concentrations of dissolved Fe(II) and SO_4 and values of specific conductance and pH in pore waters from pile C sediments as a function of depth.

One sediment core from pile C was sectioned in detail (about every 30 cm) for total metal determination and pore water extraction. Total Fe, silicon (Si), and aluminum (Al) concentrations in sediment as a function of depth are shown in Figure 3.

Combined with the data in Table 1, the enrichment in Fe is typically 3 times crustal abundance (5.4 weight percent; Krauskopf and Bird, 1995) and ranges in concentration to as high as 8 to 9 times that of the earth's crust. The tendency for Si to increase as Fe decreases suggests dilution of the mine drainage precipitates with uncontaminated silicate-rich sediment entering Keswick Reservoir.

The compositions of pore waters from the detailed core from pile C are shown as a function of depth for Fe(II), SO_4, specific conductance, and pH in Figure 4. The pore waters in the core from pile C had pH values ranging from about 5.5 to 6.5 and were dominated by Fe(II) and SO_4. Alkalinity values ranged from 1-300 mg/L (as $CaCO_3$) at the higher pH values. These Fe-SO_4 waters maintained about equimolar quantities of Fe and SO_4 and generally increased in concentration with depth.

Figure 5 shows the pore-water concentrations of Cd, Cu, Mn, and Zn with depth.
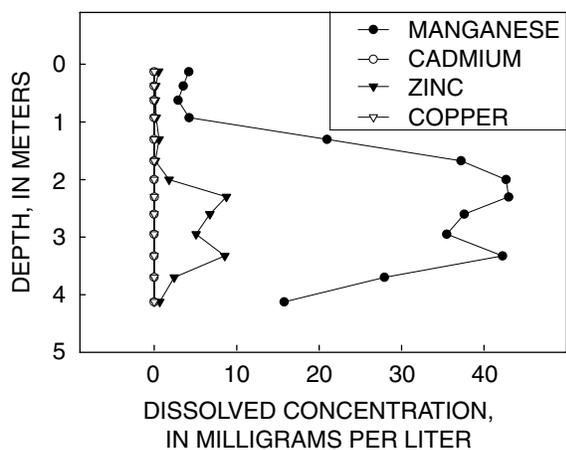
Figure 5. Concentrations of dissolved Cd, Cu, Mn, and Zn in pore waters from pile C sediments as a function of depth.

Both Cd and Cu remained very low (< 0.01 mg/L) but detectable, whereas Zn concentrations increased to a maximum of 9 mg/L and Mn concentrations increased to a maximum of 43 mg/L. The highest pore-water concentrations of Fe(II), Mn, Zn, and SO_4 occurred in the same interval, just below the midpoint of the core. The pore-water data indicate considerable reductive iron dissolution with some alkalinity production and yet little or no sulfate reduction.

Saturation Indices

Complete water analyses that gave acceptable charge balances (within 10%) were used to calculate saturation indices of phases that may have attained solubility equilibrium with pore waters in piles A, B, and C. Five minerals were frequently at or above saturation: ferrihydrite (hydrous ferric oxide), schwertmannite (hydrous ferric oxide sulfate), barite, siderite, and rhodocrosite. The reliability of the ferrihydrite and schwertmannite values is difficult to judge because of the difficulty in maintaining the samples in anoxic conditions and because of the difficulties in determining relatively low Fe(III) concentrations in the presence of very high Fe(II) concentrations. Nevertheless, saturation or supersaturation for these five minerals is reasonable given the high Fe(II), Mn, and SO_4 concentrations and relatively high pH of the pore waters. Ferrihydrite,

schwertmannite, and goethite have been identified in the sediments by x-ray diffraction and Mössbauer spectroscopy, but to date no evidence of siderite or rhodocrosite has been found.

SEDIMENT SORPTION PROPERTIES

Metal adsorption and desorption studies on reservoir sediments were conducted to quantify metal partitioning between sediments and water because it is important to estimate the amounts of metals that might be released by dredging the contaminated piles. Composite sediment and water samples were taken both from SCR and from the Keswick Reservoir sediment piles. Surface areas of the sediments were measured by the Brunnauer-Emmett-Teller (BET) method, and scanning electron microscopy (SEM) was used to characterize the grain size and morphology of the colloids and fine-grained particles (fig. 6).
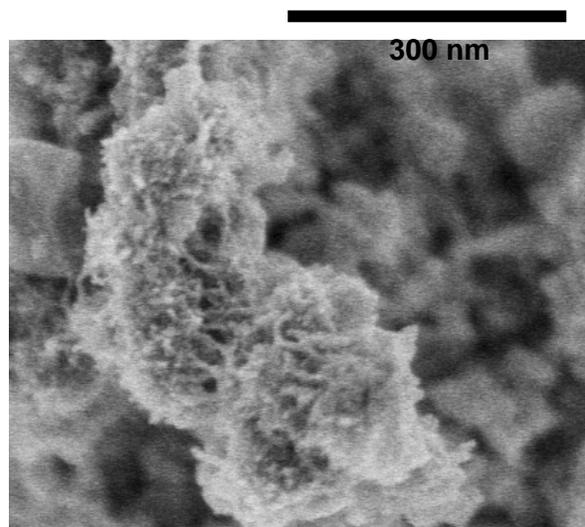
Figure 6. High resolution, cold field emission-SEM image of freeze-dried sediment from pile B. Scale bar is 300 nanometers (nm). The structure is consistent with that of synthetic schwertmannite. Major elements detected by energy dispersive spectroscopy were Fe, Al, Si, and S.

Surface areas of sediments from the three contaminated sediment piles in the Spring Creek arm of Keswick Reservoir determined by BET ranged from 19.2 to 69.6 m^2/g (square meters per gram). A weighted composite sediment sample from the Spring Creek arm had a surface area of 47.4 m^2/g. Sediment samples from Spring Creek

Reservoir were coarser grained, with BET surface areas ranging from 4.4 to 17.7 m^2/g. For reference, hypothetical spherical particles of hydrous iron oxide, 100 nanometers in diameter, would have a surface area of about 50 m^2/g.

Sorption Results

Adsorption and desorption studies were conducted with sediment composites to determine the metal partitioning with pH increases (caused by dilution with lake water on resuspension) and pH decreases (caused by iron oxidation). The adsorption and desorption curves for Cu, Zn, and Cd were found to follow normal "S"-shaped (or sigmoidal) curves typical of metal sorption isotherms (Davis and Kent, 1990). Sulfate desorption also occurred during the metal sorption experiments. Most experiments were run in 0.001 M $NaNO_3$ to maintain constant ionic strength. The sorption reaction rates approached equilibrium between 24–48 hours and sorption was found to be reversible. Comparisons between adsorption experiments (in $NaNO_3$ solutions) and whole-water mixing experiments with Spring Creek and Shasta Dam outflow or Whiskeytown Lake water gave qualitatively similar results. Sediment samples from different sites gave very similar results when normalized by surface area.
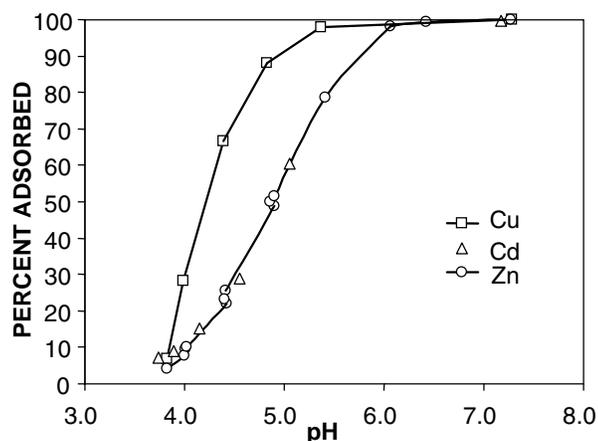
Figure 7. Cd, Cu, and Zn adsorption onto the Keswick Reservoir sediment composite in 0.001M $NaNO_3$. For a solid to liquid ratio of 11 g of sediment per liter, 50 percent of the copper is adsorbed onto the sediment at pH 4.1 and the slope of the Cu adsorption curve is steeper than the Cd or Zn slopes. Fifty percent of Cd or Zn are adsorbed between pH 4.8-4.9.

Desorption of Cu reached a minimum (with decreasing pH) at a pH of 5 and adsorption was complete (with increasing pH) at about the same pH. Although the adsorption curve shapes for Cu were typical of sorption curves for metals on hydrous ferric oxides (for example, Dzombak and Morel, 1990), the edge was displaced to a lower pH range (<4.5). This pattern is similar to adsorption of Cu onto schwertmannite (Webster and others, 1998).

Adsorption curves for Zn and Cd were similar to those for Cu but were shifted to about one pH unit higher (fig. 7). The curves were moved to a lower pH compared with adsorption onto hydrous ferric oxides, also consistent with a schwertmannite substrate. These results are entirely consistent with data from the partitioning of these metals between the sediments and their pore waters.

An interesting anomaly appeared when the Cu adsorption was measured at pH values above 7. Although maximum Cu adsorption, in terms of aqueous Cu concentration, was reached with increasing pH by values of about 5, the proportion of adsorbed Cu decreased at pH values above 7. This effect likely is caused by natural organic complexation of Cu, and has been observed in other systems (Davis, 1984). This behavior was not observed for Zn and Cd.

These results indicate that sorption is particularly effective for immobilizing the contaminant metals (especially Cu) in a resuspension scenario caused by dredging, if pH values remain above about 5. Furthermore, natural organic matter may reduce some of the effectiveness of Cu adsorption but it might also reduce aquatic toxicity if a strong Cu-organic complex is formed.

TOXICITY STUDIES

Aquatic toxicity tests were conducted on sediment pore waters and uncentrifuged sediments to determine the potential effects of sediment resuspension on aquatic life. The crustacean *Ceriodaphnia dubia* was used as a test animal. Five types of tests were completed: (1) 48-hr LC_{50} (the lethal concentration that results in 50 percent mortality of the test organisms) for the pore waters, (2) 96-hr LC_{50} for the pore waters,

(3) 48-hr LC$_{50}$ for sediment elutriates, (4) toxicity identification and evaluation (TIE) to identify the main contaminant causing the mortalities in the pore water test solutions, and (5) a toxicity test specifically for dissolved iron. Pore waters were diluted to varying concentrations with three control waters: (1) outflow from Shasta Dam, (2) water from Spring Creek Power Plant (Whiskeytown Lake outflow), and (3) "lab" water [Evian mineral water diluted to hardness and alkalinity values similar to the other control waters (The use of trade names does not imply endorsement by the USGS.)]. Pore waters were kept anoxic and refrigerated until used in the toxicity tests. Values of pH, specific conductance, and alkalinity were monitored during the tests. The pH was maintained close to neutrality (7 ± 0.5). Samples of the test solutions were collected at regular intervals for metals determinations. The Fe(II) and Fe(total) concentrations were determined at regular intervals in the iron-specific tests.

Toxicity Results

The LC$_{50}$ values were lower than expected. A summary of the dilution values for pile C pore waters is given in Table 2, along with the hypothetical concentrations of Fe, Cu, and Zn that would have been present if no oxidation of iron and no adsorption of Cu and Zn had occurred. The actual measured concentrations of these metals were significantly less than the hypothetical concentrations in Table 2. Nearly all the hypothetical and measured concentrations for Cu and Zn in tests at the LC$_{50}$ dilutions were below harmful levels based on published values of LC$_{50}$ from other studies (Fujimura and others, 1995, and references therein). The Sacramento River Basin plan for water quality limits requires Cu concentrations not to exceed 5.6 micrograms per liter (at a hardness of 40 milligrams per liter as CaCO$_3$); nearly every toxicity test indicated lower concentrations than this because of the adsorption of Cu on rapidly-precipitating iron colloids.

These results indicated that Cu and Zn concentrations were not the primary cause of toxicity. Further experiments with TIE testing indicated that dissolved iron was the primary

Table 2. Chemical Data for Toxicity Tests. [LC$_{50}$, dilution at which 50% mortality is observed; metal concentrations indicate hypothetical compositions based on dilution of starting solutions; actual metal concentrations were lower because of iron oxidation and metal coprecipitation; mg/L, milligrams per liter.]

	Pile A	Pile B	Pile C
48hr LC$_{50}$	1.8%	1.6%	0.6-7.1%
Fe (mg/L)	14	13	13-45
Cu (mg/L)	0.002	0.002	0.001-0.006
Zn (mg/L)	<0.006	<0.006	0.003-0.08

	Pile A	Pile B	Pile C
96hr LC$_{50}$	1%	0.8%	0.3-3%
Fe (mg/L)	8.2	6.7	6-15
Cu (mg/L)	0.002	0.002	0.001-0.005
Zn (mg/L)	<0.005	<0.005	0.005-0.01

cause of the toxicity, and that zinc may have been a secondary cause. The toxicity of Cu or Zn or both were nullified in the TIE by addition of reagents that selectively removed or complexed the individual metal, keeping the remaining experimental conditions the same. The final study using only dissolved Fe(II) with the three control waters gave results similar to the pore-water tests, demonstrating that concentrations of only a few mg/L of Fe were sufficient to cause acute and chronic toxicity in *Ceriodaphnia dubia*.

The identification of iron from the pore waters of the Keswick Reservoir sediments as the primary toxicant affecting aquatic life was unexpected and has some serious implications. First, no regulatory aquatic life standard for Fe has been set by the EPA or the State of California, yet Fe appears to be the most serious threat to aquatic life in this contaminated area. Second, dissolved Fe is the most abundant cation in most, if not all, acid mine waters, yet most investigators do not employ water-quality standards for measurement of Fe in waters affected by acid mine drainage. Third, other studies of the aquatic toxicity of dissolved Fe have come to the similar conclusion: that a few mg of Fe per liter is unsafe or toxic for aquatic life in freshwaters. Fish kills are the most common environmental problem from mining activities and the causative agent of acute toxicity may be Fe or Al instead of Cd, Cu, or Zn as more commonly thought. The results of this study could have important impacts on environmental regulation of mining activities, and

restoration of watersheds impacted by historical mining.

ACKNOWLEDGMENTS

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