

# Speciation of Mercury and Mode of Transport from Placer Gold Mine Tailings

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Historic placer gold mining in the Clear Creek tributary to the Sacramento River (Redding, CA) has highly impacted the hydrology and ecology of an important salmonid spawning stream. Restoration of the watershed utilized dredge tailings contaminated with mercury (Hg) introduced during gold mining, posing the possibility of persistent Hg release to the surrounding environment, including the San Francisco Bay Delta. Column experiments have been performed to evaluate the extent of Hg transport under chemical conditions potentially similar to those in river restoration projects utilizing dredge tailings such as at Clear Creek. Physicochemical perturbations, in the form of shifts in column influent ionic strength and the presence of a low molecular weight organic acid, were applied to coarse and fine sand placer tailings containing 109–194 and 69–90 ng of Hg/g, respectively. Significant concentrations of mercury, up to 16  $\mu\text{g/L}$ , leach from these sediments in dissolved and particle-associated forms. Sequential chemical extractions (SCE) of these tailings indicate that elemental Hg initially introduced during gold mining has been transformed to readily soluble species, such as mercury oxides and chlorides (3–4%), intermediately extractable phases that likely include (in)organic sorption complexes and amalgams (75–87%), and fractions of highly insoluble forms such as mercury sulfides (6–20%; e.g., cinnabar and metacinnabar). Extended X-ray absorption fine structure (EXAFS) spectroscopic analysis of colloids obtained from column effluent identified cinnabar particles as the dominant mobile mercury-bearing phase. The fraction of intermediately extractable Hg phases also likely includes mobile colloids to which Hg is adsorbed.

## Introduction

The Clear Creek tributary to the Sacramento River, located near Redding, CA (Figure 1), has been highly modified by historic placer gold mining and, since the 1950s, by aggregate mining in the flood plain. Placer gold was discovered in Clear Creek early in the history of the California gold rush and was

extensively mined by dredging and other methods since 1848. Clear Creek provides an impaired habitat for salmonid species, and numerous water-filled open pits developed from historic mining strand young salmonid species. Restoration of Clear Creek began in 2000 as part of a multiagency program headed by the Western Shasta County Resource Conservation District funded by the California Bay Delta Authority and U.S. Bureau of Land Management. The restoration program has included using placer dredge tailings to fill gravel pits, develop wetlands, and reestablish a natural stream channel that meanders through its flood plain to support salmonid species. Similar restoration programs have been implemented and are being planned for other California watersheds impacted by historic placer gold mining that used dredge and hydraulic methods.

During placer mining, mercury was used to recover gold by amalgamation and was released into sediments and placer dredge tailings. During dredging, coarse sediments are separated from fine sediments and disposed of, forming stacker cobble tailings piles. Cobbles are not processed in mercury-charged placers and so are not typically contaminated with mercury. The fine-grained sediment was passed through a mercury-charged sluice before being deposited in a dredge pond. These placer tailings are typically covered by stacker cobbles. At the contact between placer tailings and overlying stacker cobbles, fine sediment enriched in mercury may become entrained in the lowest part of the stacker cobble tailings pile.

The use of Hg-enriched sediment and tailings in the restoration of flood plains and development of wetlands raises the question of whether mercury will be mobilized from this fill as it is exposed to seasonal rains and flooding. This study characterizes species of mercury in dredge tailings from Clear Creek and determines the mobility of mercury species from tailings using column leach experiments.

In bulk, the mercury concentration recovered from Clear Creek watershed tailings and sediments is on the order of 10–100 ng/g. Due to this low level, determination of mercury speciation using molecular spectroscopy methods, such as extended X-ray absorption fine structure (EXAFS) spectroscopy, is currently not possible, even with available high-flux synchrotron X-ray beam lines. Indirect speciation methods such as sequential chemical extractions (SCE) are often used to help identify various Hg species in soils and sediments, although with some level of ambiguity (1, 2). Nevertheless, SCE and EXAFS spectroscopy can often readily identify the presence of insoluble mineral phases. Such phases exhibit a variety of environmental transport and chemical behaviors, and their identification is therefore essential to evaluating the impact of Hg-contaminated placer tailings on restored watersheds.

**Hg Transport Mechanisms from Alluvial Gold Mine Tailings.** After introduction to the Clear Creek watershed as the elemental species ( $\text{Hg}^0$ ) during gold mining activities, mercury has undergone volatilization, globule relocation, dissolution, oxidation, precipitation, and amalgamation and sorption onto sediments (3). Electrochemical and thermodynamic investigations of controlled systems suggest that chloride and various sulfur species impact the solubility of commonly observed Hg-containing minerals as well as the redox and amphoteric behavior of aqueous Hg species (4).

Amalgamation and sorption onto sediments would deplete the concentrations of dissolved Hg in water flowing through the restored Clear Creek flood plain. While the prominent role of particles in controlling dissolved heavy metal concentrations has long been recognized, a number

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of recent studies have focused on the potential role of colloid mobilization in enhancing the transport of metal contaminants (5–9). Particle-based mobilization can arise via a range of different mechanisms, including physical (hydrodynamic) perturbations and chemical mechanisms, such as surface charge enhancement/homogenization, steric stabilization, and dissolution of interparticle mineral “bridges” (10). While physical mobilization mechanisms are largely dependent on factors such as particle size and solution flow rate, chemical mechanisms are instead driven by changes in factors such as pH, ionic strength, and the nature and concentration of adsorbates such as organic acids. Organic acids are commonly found in vegetated environments (11, 12) and have been found to strongly sorb to mineral particles (13, 14), alter the charges of mineral surfaces (15, 16), and enhance mineral dissolution rates (17, 18). The effects of solution ionic strength and the presence of an organic acid on Hg mobilization are addressed in this study.

Natural sediments are complex mixtures of minerals and other solid phases and therefore exhibit a range of charging behavior (19–22). In the absence of organic acids or other strongly binding adsorbates, sediment particles of different surface charge may electrostatically attract one another, causing heterocoagulation. Conditions conducive to particle mobilization include low ionic strength and the presence of strongly sorbing ions, both of which enhance repulsive interparticle forces by increasing the thickness of their electrical double layers and homogenizing surface charge, respectively (10). Organic acids can also dissolve silicon, aluminum, and iron-bearing mineral cements (17, 18), releasing colloids (23).

Column experiments performed as part of this study involved an initial leach of mine tailings with deionized water to evaluate the extent of Hg release from these materials. After this leach, a high ionic strength solution containing malonic acid ( $C_3H_4O_4$ ), followed by a low ionic strength solution containing malonic acid, was pumped through the mine tailings to determine whether a shift in ionic strength in the presence of a sorbing organic acid might release colloids. The semi-arid climate of the Clear Creek tributary results in precipitation of efflorescent salts derived from weathering of sulfides in bedrock and from high salinity natural springs. Infiltration of meteoric water into the placer tailings initially results in high ionic strength pore water, followed by a diminishing electrolyte concentration as the wet season progresses. These column experiments simulate the initial wetting of the placer tailings after the end of the dry season, followed by low ionic strength conditions as would be characteristic of the wet season. In the long term, revegetation of the flood plain will result in the accumulation of organic acids on sediments. This accumulation may eventually dissolve interparticle cements and mobilize colloids through the tailings, including particle-associated mercury. Our experiments were designed to investigate these conditions. One limitation of our column leaching experiments was the more acidic pH of pore waters (2.5–3.0) compared to waters measured in the vicinity of the tailings pile (pH 5.6–7.3 (24)). Although the effect of acidity on colloid transport in our system was not studied, higher pH has been shown to promote colloid release in simplified, heterocoagulated porous media (25).

## Materials and Methods

**Mine Tailing Sample Collection.** Mercury-enriched dredge tailings were collected from a trench exposed in the Schmidt Gravel Pit within the Clear Creek Restoration Project area (latitude 40°29.734', longitude 122°29.15'; Figure 1). At this location, dredge placer tailings consist of well-sorted beds of sand, silt, and clay overlain by poorly sorted, coarse stacker cobble tailings. Several centimeters of surface material were

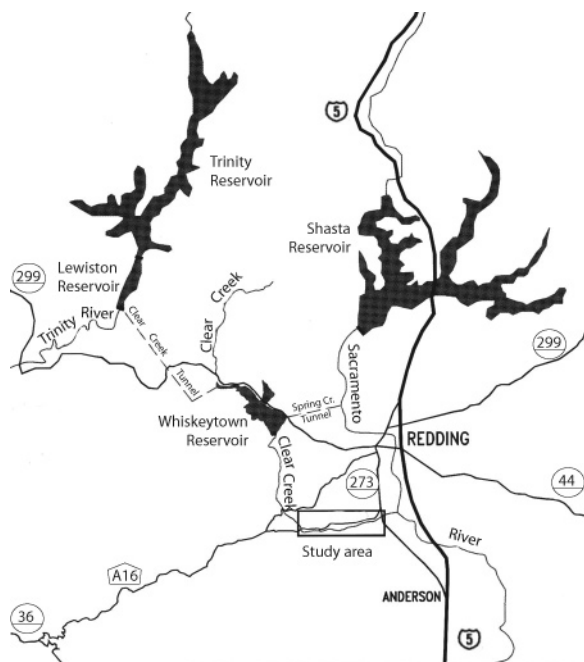


FIGURE 1. Location map of the Clear Creek Restoration Project.

removed from the exposure in the pit and about 2 kg of tailings were collected from a coarse and fine sand layer.

**Column Experiments.** Borosilicate glass columns (25 mm × 500 mm, Chrom Tech) filled with placer tailings were used to study particle release and transport. Two samples of placer tailings were used in the two column experiments: 320 g of coarse sand and 330 g of fine sand. Tailings were dried for 18 h at room temperature prior to loading into the columns, tamping every quarter volume to compact the sediment (porosities were 0.45 and 0.50 for the coarse and fine sand columns, respectively). Carbon dioxide was directed into the base of the column for approximately 10 min to aid in sediment wetting. Deionized (DI) (Barnstead Nanopure) water was pumped into the bottom of each column using positive displacement HPLC pumps with pulse dampening at 1 mL/min, resulting in average pore velocities of 5.9–6.5 m/d. The columns, having previously been weighed dry with and without sediment, were capped upon first flush of water and reweighed. Small pockets of air were still visible after the first flush of water exited the columns. Thus, the pore volumes calculated from the mass of the column, sediment, and water slightly underestimate the actual pore volumes.

The column experiments were performed in three stages, according to influent composition. Stage 1 consisted of deionized water, stage 2 of a 100 mM NaCl plus 15 mM malonic acid solution, and stage 3 of a 5 mM NaCl plus 15 mM malonic acid solution. Influent compositions are based on prior work (7) and previous studies (23, 26) designed to release colloids from packed columns via previously discussed mechanisms.

Each stage of the experiment consisted of flowing 80–100 pore volumes of fluid through the columns at 1 mL/min. The column appeared to saturate after a few pore volumes of DI water had flowed through. The columns remained saturated throughout subsequent stages, as a new influent solution displaced preexisting pore water. On the basis of the measured porosity of the columns (0.45–0.50), the average column travel time is estimated to be 110–120 min. Thus, approximately four samples initially taken during stages 2 and 3 contained solution from the previous stage prior to breakthrough of new influent solution. During stages 1 and 2, effluent samples were periodically collected in 25- or 40-

**TABLE 1. Sequential Chemical Extraction Method for Determining Hg Speciation in Preleached Tailings As Developed by Bloom et al. (1) and Results for Two Clear Creek Placer Tailings (coarse and fine sand) before Leaching<sup>a,b</sup>**

step	extractant	description	typical compds removed	concentrations (ng/g)		
				MDL <sup>c</sup>	coarse sand	fine sand
F1	DI water	water soluble	HgCl <sub>2</sub>	0.3	7	2.76
F2	pH 2 HCl/HOAc	"stomach acid"	HgO, HgSO <sub>4</sub>	0.4	7	0
F3	1 N KOH	organo-complexed	Hg humics, Hg <sub>2</sub> Cl <sub>2</sub> , CH <sub>3</sub> Hg	0.2	42	46
F4	12 N HNO <sub>3</sub>	strongly complexed	mineral lattice, Hg <sub>2</sub> Cl <sub>2</sub> , Hg <sup>0</sup>	2.0	39	13
F5	aqua regia	Hg sulfides	HgS, HgSe	4.9	22	4
F6	10:5:2 HNO <sub>3</sub> + HF + HCl	complete dissolution	residual Hg	0.3	2.4	1.9
sum of the extracted fractions					109	69

<sup>a</sup> Listed are the extraction steps, the general category of Hg phases removed in each step, and specific Hg compounds that are typically removed in that step. The concentrations for the two placer tailings are in ng of Hg/g of sediment. <sup>b</sup> SCE results for leached placer tailings are provided in the Supporting Information. <sup>c</sup> MDL = method detection limit.

mL precleaned and contaminant-free certified borosilicate glass vials with Teflon seals (I-CHEM Series 200) over a 25–30 min interval. Vials were capped with no headspace and immediately refrigerated to 5 °C. During stage 3, a fractional collector continuously sampled effluent into acid-washed borosilicate glass tubes in 26-mL aliquots. Tubes remained uncovered for a maximum of 12 h before being stored in capped 25- or 40-mL borosilicate vials at 5 °C. Samples were collected March 5–28, 2002.

All influent was stored at room temperature in an acid-washed 20-L polypropylene carboy (Nalgene). The columns were oriented vertically and connected to 1/8-in. FEP tubing with Teflon compression fittings. The bottom fitting of each column was lined with a 25 µm pore size Teflon disk filter to prevent sedimentation out of the column base.

**Aqueous Species Analysis.** Mercury concentrations in unfiltered column effluent samples were determined by Frontier Geosciences (Seattle, WA) on March 28–29 and April 16–23, 2002. For mercury analysis, water samples were oxidized at room temperature with 0.004 N BrCl plus 0.2 N HCl and then analyzed using SnCl<sub>2</sub> reduction, purge and trap dual gold amalgamation, and cold vapor atomic fluorescence spectrometry (CVAFS), in accordance with U.S. Environmental Protection Agency (USEPA) method 1631 (27). The estimated Hg method detection limit was 2 ng/L and the 95% confidence level is ±1.85 ng/L. The column influent solutions contained 2.4–13.6 ng of Hg/L. Six duplicate recoveries of a NIST standard ranged from 89.3% to 97.5%. A suite of analytes, including Al, Ca, Fe, K, Mg, Mn, Na, and Si, was measured in column effluent using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Prior to ICP-AES analysis, samples were filtered through 0.45 µm hydrophilic polytetrafluoroethylene (PTFE) syringe-mounted membranes (Millipore) into I-CHEM vials.

**Analysis of Solids.** Elemental analysis of the coarse and fine sand tailings was performed by aqua regia digestion and inductively coupled plasma-mass spectrometry (ALS Chemex, Method ME-MS41). Separate aliquots were digested with HNO<sub>3</sub>–HCl–KClO<sub>3</sub> and analyzed by cold-vapor atomic absorption spectrometry to determine total mercury concentrations (ALS Chemex, Method ME-ICP41m), in accordance with USEPA method 245.5.

Sequential chemical extraction (SCE) analyses were conducted on samples of placer tailings by Frontier Geosciences according to established protocols (1). Extractions were performed on 0.4-g aliquots of sample, which included fine and coarse sand before and after leaching. Samples were exposed to a series of six extraction steps of increasing severity (DI water, pH 2 HCl/HOAc, 1 N KOH, 12 N HNO<sub>3</sub>, aqua regia, 10:5:2 HNO<sub>3</sub>/HF/HCl (Table 1). Each extract was analyzed for mercury using CVAFS (27). The first extraction recovers water-soluble mercury. The second extraction is designed to

remove inorganic mercury salts (e.g., oxides, chlorides, and sulfates), and the third extraction (1 N KOH) removes organically bound Hg. The fourth extraction (12 M HNO<sub>3</sub>) removes elemental mercury, but the total mercury removed by this extraction cannot be interpreted to consist solely of elemental mercury unless it is present at 1,000 ppm to percent levels (1). The fifth extraction (aqua regia, 10:3 HCl:HNO<sub>3</sub>, 12 h at room temperature) dissolves most remaining Hg-bearing phases, including sparingly soluble Hg minerals such as cinnabar and metacinnabar (HgS). The sixth extraction (10:5:2 HNO<sub>3</sub>:HF:HCl in a Teflon bomb at 125 °C for 12 h) was performed to recover Hg included within aluminosilicates. A single total Hg analysis by HF digestion was also performed on separate aliquots. The reliability of SCEs and total digestion-based Hg analysis is primarily limited by the imprecision caused by heterogeneous distribution of trace amounts of Hg within a sample. Although no duplicate analyses of the placer tailings were performed as part of this study, studies by Bloom et al. (1) indicate that the precision of individual SCE steps ranges from 2 to 40%, with minor (<5%) Hg fractions subject to less precision.

The mineralogy of bulk and size-fractionated coarse and fine sand tailings was characterized using powder X-ray diffraction with an XRD-131 Rigaku Geigerflex diffractometer equipped with a Cu X-ray tube and a graphite monochromator. Sample preparation details appear in the Supporting Information. Diffraction data were collected from 2θ = 5° to 70° in 0.05° increments, counting for 2 s at each step (4 s/step for the <2 µm sample). Sample diffraction patterns were compared to those of minerals in a powder diffraction library (Inorganic Crystal Structure Database, implemented with Jade 6.5, Materials Data, Inc.) and diffraction patterns of the Source Clays of The Clay Minerals Society (28, 29). The presence of minerals was identified according to coincidence of sample and reference mineral pattern peaks.

Hg-speciation analyses using extended X-ray absorption fine structure (EXAFS) spectroscopy were performed on particles extracted from the first leaching stage of the coarse sand tailings. The effluent was centrifuged and decanted. The resulting paste was mounted in a 2-mm thick Teflon sample holder and covered with Kapton tape. The sample was stored under humidified refrigeration for 2 months prior to EXAFS data collection. Hg L<sub>III</sub>-edge spectra were collected on end-station 11–2 of the Stanford Synchrotron Radiation Laboratory in fluorescence detection mode with a 30-element germanium detector. X-radiation was monochromatized using Si(220) crystals. An average of 22 Hg L<sub>III</sub>-edge EXAFS spectra (each scanned to  $k = 9 \text{ \AA}^{-1}$ , where  $k$  is the momentum of the photoelectron) of the wet paste was structurally modeled and compared to spectra of Hg model compounds using methods previously reported (30). Details of EXAFS data analyses are provided in the Supporting Information.



**TABLE 2. Composition of Tailings Samples in  $\mu\text{g/g}$  (except for Hg, in ng/g)**

	coarse sand	fine sand		coarse sand	fine sand
Ag	0.50	0.440	Li	25.2	23.2
Al	53000	60300	Mg	7300	6100
As	5.20	5.20	Mn	265	370
Ba	413.5	441.5	Na	13700	15900
Ca	12500	13000	Ni	18.4	17.2
Cd	0.06	0.06	P	140	100
Co	11.5	6.50	Pb	5.0	6.5
Cr	109.0	146.0	S	<100	<100
Cs	1.05	1.05	Sr	136	151
Cu	27.2	28.2	Ti	1600	2100
Fe	24300	2.40	U	0.8	0.8
Hg	109–194	69–90	V	145	107
K	8300	10400	Zn	66	42

<sup>a</sup> The range of Hg concentrations is based on both total Hg analysis and the sum of sequentially extracted fractions (see Table 1).

## Results and Discussion

**Bulk Properties of Placer Tailings.** The elemental composition of the placer tailings is summarized in Table 2. Figure 2 shows XRD patterns from which quartz, albite, kaolinite, illite, and smectite are identified in most size fractions investigated (500–2000, 45–500, <45, <25, and <2  $\mu\text{m}$ ). The presence of smectite is evidenced by a peak at  $2\theta = 6.1^\circ$  (14.5 Å) in several of the diffraction patterns and, most notably, with a maximum relative intensity in the pattern of the oriented, <25  $\mu\text{m}$  sample (28). Washing of the <45  $\mu\text{m}$  tailings fraction (see Supporting Information) did not result in marked changes in the presence of peaks or the background of diffracted intensity, indicating that soluble efflorescent and amorphous materials were not present at concentrations comparable with major mineral components.

Mercury is the only trace metal present in Clear Creek sediments at concentrations above background levels in nearby sediments that have not been mined for placer gold (<10 ng of Hg/g sediment (24)). On the basis of analysis of several sediment samples, including the coarse and fine sand used in the column experiments, Hg concentrations in the placer tailings vary according to grain size, with sand beds containing 90 ng/g and clay beds containing 160 ng/g on average. Stacker cobble tailings contain an average of 70 ng of Hg/g in bulk, with finer sediments (<2 mm size fraction) averaging 140 ng of Hg/g. The relatively high mercury concentration in the stacker cobbles reflects entrainment of Hg-enriched fine sediment derived from placer tailings present below the stacker cobbles. The concentration and speciation of Hg present in Hg mine tailings (calcines) have also often been found to vary as a function of grain size (31).

**Mercury Speciation of the Placer Tailings.** Mercury speciation results for placer tailings as determined by sequential chemical extraction indicate that a significant amount of elemental Hg originally added to the tailings during placer mining has been transformed to other mercury species (Table 1 and Figure SI-1 of the Supporting Information). The coarse and fine sand tailings contain a small fraction of water-soluble Hg (F1, 3–4%), while a significant fraction is present in highly insoluble forms (F5, 20% in the coarse sand and 6% in the fine sand tailings) such as mercury sulfides (HgS; e.g., cinnabar and metacinnabar). Most of the Hg in both samples is of intermediate extractability, including organically bound (F3) and elemental Hg (F4), which comprise 75% in the coarse sand and 87% in the fine sand. In both samples, Hg bound in silicate minerals (F6) comprises about 2–3%, which is similar to the amount of Hg present in Clear Creek sediments prior to placer mining (3 ng/g).

The reliability of SCE in speciating Hg depends on the matrix and the Hg species present. More soluble mercury species such as  $\text{HgCl}_2$ ,  $\text{HgSO}_4$ ,  $\text{Hg}_3\text{S}_2\text{Cl}_2$ , and  $\text{Hg}^0$  are less consistently extracted from different samples because of matrix effects (e.g., sorption and occlusion). General validation of SCE for determining Hg speciation in Hg-bearing mine wastes by Kim et al. (2) indicates that recovery of HgS (e.g., metacinnabar) by aqua regia extractions (F5, Table 1) compares well (<10% difference) with speciation using EXAFS spectroscopy in gold mine tailings. The Hg concentrations in the tailings of the present study are 3 orders of magnitude lower than those studied by Kim et al. (2), introducing additional uncertainty. Our SCE results indicate that some portion of elemental Hg transformed to species that likely include HgS. However, the persistence of tiny globules of elemental Hg in sedimentary mining environments has been demonstrated by field observations.

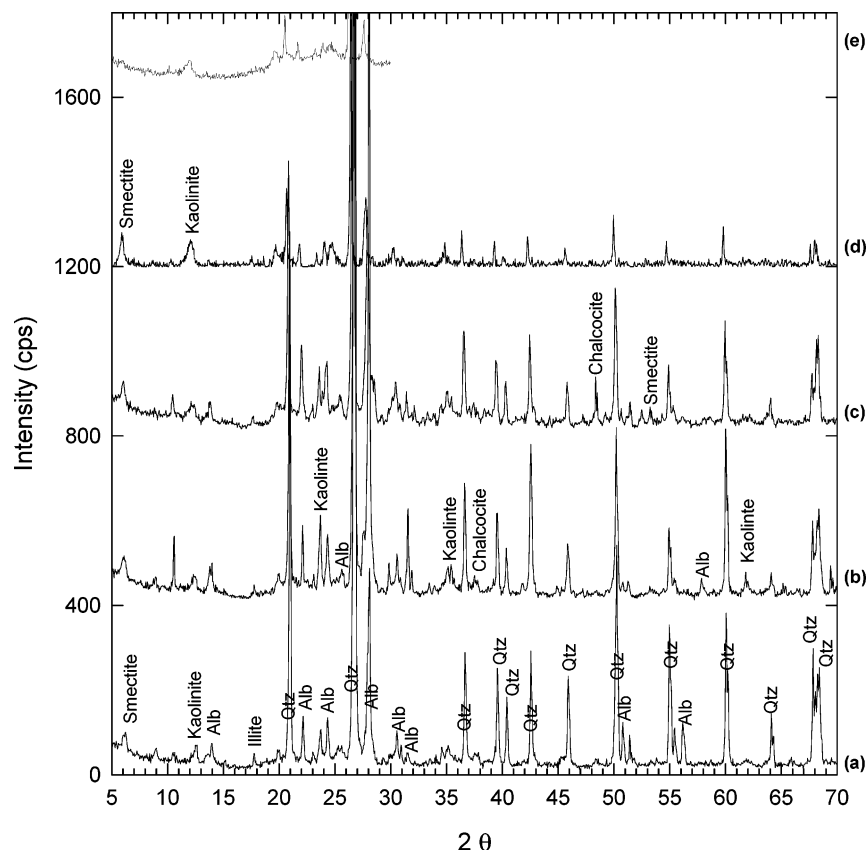
**Mercury Release from Placer Tailings.** Figure 3 illustrates the concentration of dissolved (i.e., <0.45  $\mu\text{m}$ ) Hg during the coarse sand column experiment. The column experiment with coarse sand tailings leached by deionized water released the highest concentration of water-soluble mercury. The majority of Hg was released during flushing of the first 12 pore volumes, with a maximum concentration of 16  $\mu\text{g/L}$ . The Hg concentration gradually decreased to between 10 and 30 ng/L after about 50 pore volumes had passed through the column.

Another relatively large pulse of Hg exited the column upon introduction of high ionic strength (~100 mM) malonic acid solution, with a maximum concentration of 700 ng/L. A steady concentration (about 20 ng/L) was reached within 30 pore volumes of second-stage leaching. A third spike of 30 ng/L was discernible after introduction of low ionic strength (~5 mM) malonic acid solution, more rapidly reaching a steady concentration of 1–7 ng/L after 10 pore volumes.

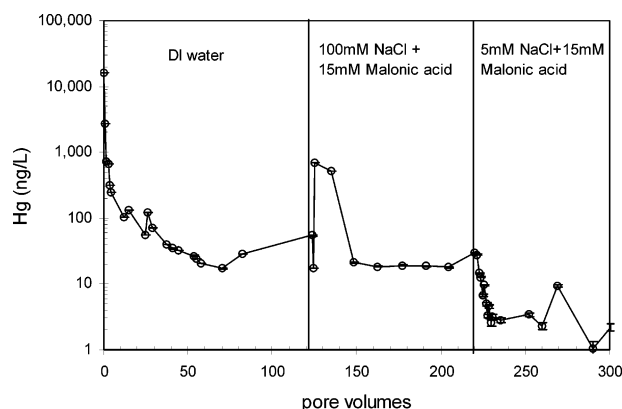
The fine sand column experiment exhibited similarly episodic Hg release in response to the introduction of new leaching solutions, decaying to successively lower baseline concentrations (Figure 4). The maximum Hg concentration during the DI water leach was 1200 ng/L, and introduction of each successive leaching solution resulted in a lower maximum Hg concentration.

Sequential chemical extractions of coarse sand taken from the column after leaching reflect a loss of 5.2 ng of Hg from the sediments (Figure SI-1). This loss of Hg cannot be solely accounted for by the reduction of water-soluble Hg (the difference in F1 fractions was 0.8 ng). This 84% difference exceeds the estimated reproducibility of the analyses (1), suggesting that insoluble fractions of Hg were also transported during leaching. Intermediately soluble fractions (F3 and F4) did not change more than the estimated reproducibility of the extractions. The aqua regia fraction (F5) was reduced significantly (4.4 ng) by column experiment leaching, suggesting that the majority of mercury lost from the coarse sand column was in an insoluble form, such as HgS. More direct evidence of colloidal HgS transport was provided by EXAFS spectroscopy.

Among several Hg minerals (30), the EXAFS spectrum of the colloids eluted from the coarse sand tailings (Figure 5a) most closely resembles that of cinnabar. A radial structure function (RSF, Figure 5b) was calculated by Fourier transforming the background-subtracted,  $k^3$ -weighted Hg  $L_{III}$ -EXAFS spectrum and structurally analyzed as a more direct means of identifying Hg species present in the colloids (analytical details are provided in the Supporting Information). This analysis indicates that the colloids contain cinnabar, directly indicating a colloidal mode of Hg transport from the placer gold mine tailings. Due to the detection limits of the EXAFS measurements performed during this study



**FIGURE 2.** XRD identification of major mineral components in size fractions of the Clear Creek sediments: (a) 500–2000  $\mu\text{m}$ , (b) 45–500  $\mu\text{m}$ , (c) <45  $\mu\text{m}$ , (d) <25  $\mu\text{m}$  (oriented), and (e) <2  $\mu\text{m}$ . Except for d, all size fractions were analyzed as randomly oriented powders. XRD patterns are offset for visual clarity. Qtz = quartz and Alb = albite.

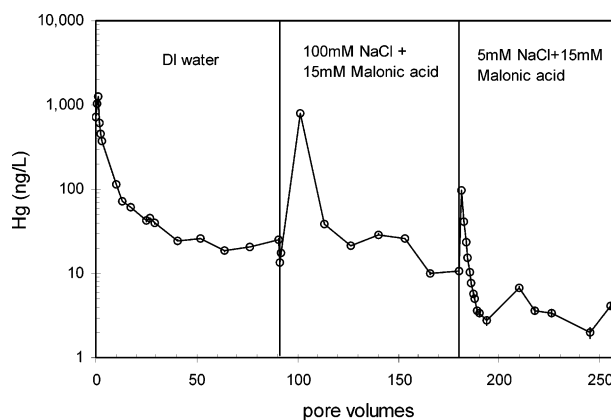


**FIGURE 3.** Hg leached from coarse sand tailings. In some cases, error bars at the 95% confidence level ( $\pm 2\sigma$ ) are smaller than the symbols.

(10–100  $\mu\text{g/g}$ ), cinnabar likely comprises most of the colloidal Hg in this placer tailing system. However, adsorbed Hg also likely comprises a fraction of the colloidal Hg phase.

**Colloid Transport from the Placer Tailings.** Release of colloids from the placer tailings poses the possibility of Hg transport as an adsorbed phase. Hg has been found to adsorb to several environmentally ubiquitous materials, including iron and aluminum (oxyhydr)oxides (32, 33) and clay minerals (34). While the trace Hg concentrations present in the placer tailings preclude direct identification (e.g., using EXAFS spectroscopy) of adsorbed Hg, SCE provides indirect evidence for adsorbed Hg (Table 1, F2–F4 fractions).

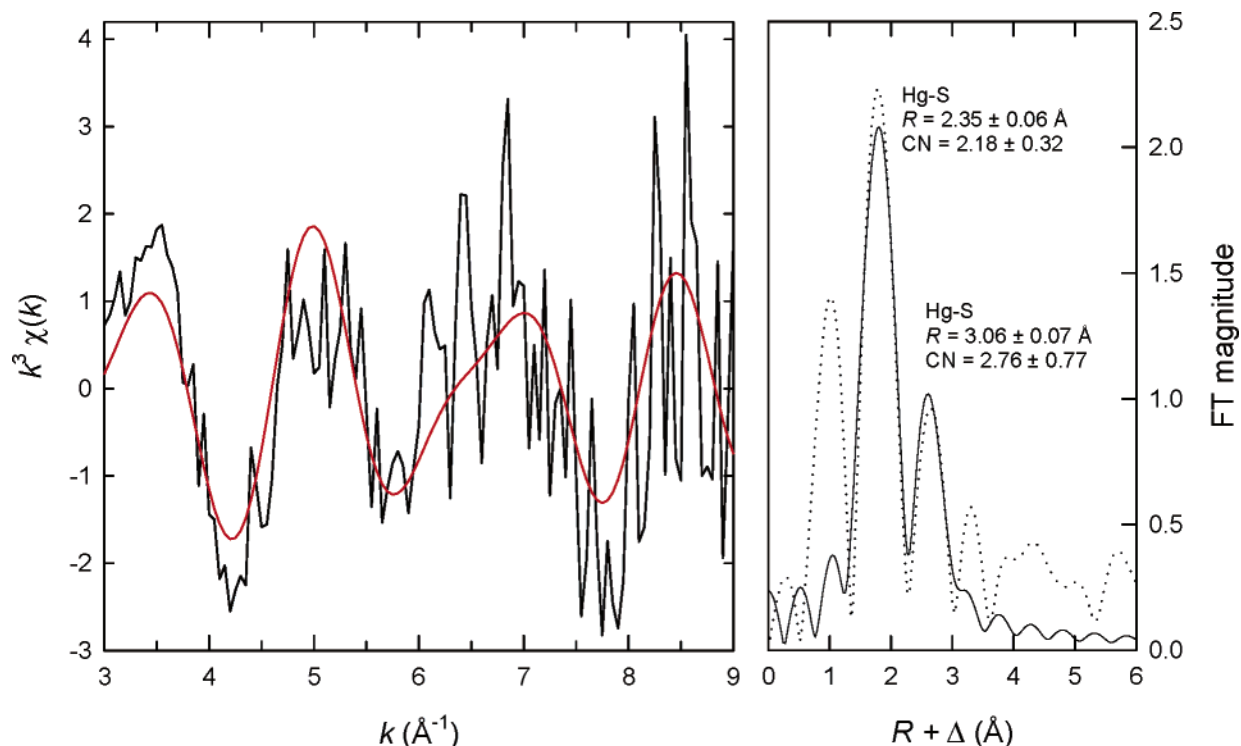
The deionized water flush produced the most visible particles in the effluents, indicating that an osmotic perturbation (10), which expanded the electrical double layer



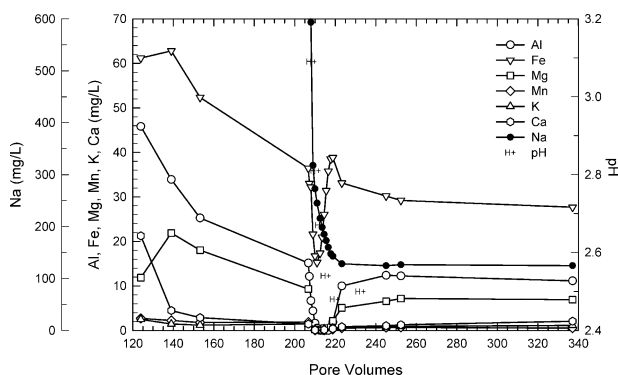
**FIGURE 4.** Hg leached from fine sand tailings. In some cases, error bars at the 95% confidence level ( $\pm 2\sigma$ ) are smaller than the symbols.

at particle surfaces, was sufficient to disperse particles. Although no particles were visible in the effluent during the high ionic strength, malonic acid leach, introduction of malonic acid under low ionic strength conditions (third stage) resulted in appreciable particle release (evident from difficulty in effluent filtrations), suggesting that aggregate cements dissolved. Measured concentrations of aqueous constituents further point to disaggregation as a mechanism of colloid transport.

Metal cations measured in effluent solutions obtained during the second leaching stage (Figures 6 and 7) indicate release of Al-, Ca-, Fe-, Mg-, and Mn-bearing constituents primarily as a result of acid and malonate ligand-promoted dissolution and cation exchange of  $\text{Na}^+$  for  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in the tailings. When the influent ionic strength decreased while the same concentration of malonic acid was



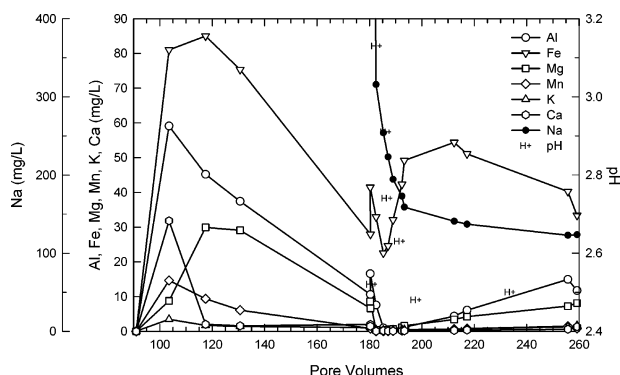
**FIGURE 5.** (a) EXAFS of a composite of colloids released during leaching of the coarse sand column. (b) Radial structure function (dotted line) with two fitted Hg–S shells (solid line); the reduced  $\chi^2$  between these curves is 1.77. The structural parameters, including bond lengths ( $R$ , corrected for phase shift ( $\Delta$ )) and Hg coordination numbers (CN) match the structure of cinnabar. The gray line in part a illustrates the EXAFS function back-transformed from the fit of the RSF.



**FIGURE 6.** Metal cations leached from coarse sand tailings during the second (100 mM NaCl + 15 mM malonic acid) and third (5 mM NaCl + 15 mM malonic acid, starting at 207 pore volumes) stages of leaching.

maintained, the concentrations of some elements, notably Al, Fe, and Mg, increased significantly before slightly decreasing (Figures 6 and 7). This is attributable to the release of preexisting colloids, a portion of which more readily dissolved as a result of enhanced mixing with pore water. In addition, increased Al, Fe, and Mg concentrations observed during stage 3 may have been due to a portion of these colloids passing through the  $0.45 \mu\text{m}$  membranes, which were used to filter all effluents prior to ICP-AES analysis. On the basis of their relative enrichment in column effluent (Figures 6 and 7), Al-, Fe-, and Mg-bearing colloids may serve as the primary colloidal adsorbents for aqueous Hg species in this placer tailing system.

From both columns, effluent silicon concentrations were consistent over 1–25 pore volumes, decreasing slightly thereafter (data not shown). A shift of Si concentration from 15 to 38 mg/L upon introduction of low ionic strength solution in the fine sand column was larger than a change of 3 mg/L



**FIGURE 7.** Metal cations leached from fine sand tailings during the second (100 mM NaCl + 15 mM malonic acid) and third (5 mM NaCl + 15 mM malonic acid, starting at 181 pore volumes) stages of leaching.

(20–23 mg/L) in the coarse sand column. While these changes in Si concentration did not correlate with particle release behavior, these significant concentrations suggest that siliceous materials were dissolving, promoting particle release.

**Environmental Implications.** The concentration of Hg in placer tailings derived from historic dredging in Clear Creek ranges from 70 to 140 ng/g, which is about an order of magnitude greater than that present in unmined sediments. Finer grain-sized tailings typically have higher Hg concentrations. Over half the elemental Hg added to the sediments during gold mining has been transformed to soluble and particulate (including organically bound, adsorbed, and HgS) species.

Column experiments indicate that significant amounts of mercury can be released from placer tailings as a result of advective flow in the presence of 5–100 mM electrolyte and/or an organic acid. The maximum mercury concentration in the effluent, which occurred during the initial

deionized water leach, was remarkably high (16  $\mu\text{g/L}$ ) in comparison to the concentration of mercury in the tailings (90  $\text{ng/g}$ ). Successive leaching, in which the ionic strength was raised and then lowered, caused spikes of mercury release that decreased to successively lower concentrations. EXAFS analysis indicates that cinnabar ( $\text{HgS}$ ) is a significant mobile species of Hg in the placer gold mine tailings. Insofar as the column experiments approximated natural conditions, these results indicate the potential for the release of significant quantities of both dissolved and particulate phases of Hg.

Placer tailings used to fill open pits and to grade flood plains are likely to release significant amounts of mercury to the surrounding watershed. Seasonal rains and flooding will release Hg according to the extent of wetting and the quantity of placer tailings used. Mobilized Hg-bearing phases will include soluble and particulate Hg species such as  $\text{HgS}$  and Hg sorbed on colloidal particle surfaces. In the long term, revegetation of flood plains restored with dredge tailings may enhance Hg release via complexation (35, 36) and colloid release promoted by plant-root-exuded organic acids. Mobilized Hg species may become methylated in the flood plain environment, especially where wetlands are present (37). Field studies into the potential impact of placer tailings on the release of Hg in restored rivers are required before the true impact of such processes can be accurately assessed. However, long-term Hg contamination and the ecological impact of both dissolved and particulate Hg species should be considered when deciding whether to use or where to place contaminated placer tailings as part of river restoration.

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## Supporting Information Available

Additional details of sample preparation for XRD and EXAFS data analysis and additional SCE results that illustrate method limitations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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