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Mercury Release from the Rathburn Mine, Petray Mine, and Bear Valley Saline Springs, Colusa County, California 2004–2006

By Aaron J. Slowey and James J. Rytuba

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Abbreviations, definitions, and datum used

Vertical and horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27 CONUS).

aq, dissolved aqueous species (operationally defined as the filtered water fraction).

DOC, dissolved organic carbon

DOM, dissolved organic matter

EE/CA, Engineering evaluation/cost analysis for “non-time-critical removal actions,” as defined by the U.S. Environmental Protection Agency’s Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

EEM, Excitation-emission matrix of ultraviolet fluorescence of dissolved organic carbon.

FI, fluorescence index of dissolved organic carbon, computed by dividing the emission intensity at 470 nm (I_{470}) by that at 520 nm (I_{520}) at an excitation wavelength of 370 nm.

Hg, generic shorthand for mercury; does *not* denote speciation.

$Hg_{T,}$ total mercury (inorganic plus organic).

$Hg_{F,}$ total mercury (inorganic plus organic) in a filtered sample (either 0.1 µm or 0.45 µm, as specified in the text).

Hg(II), compounds containing divalent inorganic mercury (Hg^{2+}) and anionic ligands (for example, Cl^-, S^{2-}).

meq/L, milliequivalents (10^{-3} charge equivalents) per liter.

MMHg, monomethyl mercury, methylmercury, and monomethylmercury (CH_3Hg^+)

ng/g, nanogram per gram, equivalent to one (1) part per trillion.

ng/L, nanogram per liter, approximately equivalent to one (1) part per trillion.

ppm, parts per million, equivalent to mg/kg or µg/g.

s, sample standard deviation

SC, specific (electrical) conductivity, reported in units of millisiemens per centimeter (mS/cm).

$SUVA_{254}$, Specific ultraviolet absorbance, calculated by dividing the UV absorbance at a wavelength of 254 nm by the DOC concentration and reported in the units of $L \cdot mg\ C^{-1}\ m^{-1}$.

v/v, volume per volume

Mercury Release from the Rathburn Mine, Petray Mine, and Bear Valley Saline Springs, Colusa County, California 2004-2006

Aaron J. Slowey[*] and James J. Rytuba[†]

1. Introduction

1.1 Background and objectives

The Rathburn and Petray mercury (Hg) deposits are the northernmost and youngest Hg deposits in the Coast Range Hg mineral belt and are located in the Bear Creek portion of the Cache Creek watershed, Colusa County (fig. 1). The Rathburn Hg mine is relatively small, having produced 100 flasks of Hg, primarily in the period from 1892-1893. More recent mining in the late 1960s and early 1970s recovered about 400 flasks of Hg from the Petray open pit mines located immediately to the north of the Rathburn Mine. The Petray open pits caused considerable surface disturbance and contributed mine waste material to the headwaters of several small tributaries to Bear Creek located to the east. The mines are located on federal land managed by the U.S. Bureau of Land Management (BLM). The BLM requested that the U.S. Geological Survey (USGS) measure and characterize Hg and geochemical constituents in tailings, sediment, and water at the Rathburn and Petray Mines, tributaries draining the mine area, and within Bear Valley west of Bear Creek (fig. 2). This request was made in response to a California State Water Board mandate that the BLM conduct an Engineering Evaluation/Cost Analysis (EE/CA) of "non-time-critical removal actions." The EE/CA applies to removal of Hg-contaminated mine waste from the Rathburn and Petray Mines as a means of reducing Hg transport to Bear Creek. The mandate presupposes that the Rathburn and/or Petray Mines are the primary sources of Hg to Bear Creek, although we consider this assumption to be a question. We also consider the question of how to directly evaluate the efficacy of eliminating the mines as Hg sources, should they be remediated.

Accordingly, the following are the objectives of this study:

i. Determine all potential natural and anthropogenic sources of Hg to Bear Creek.
ii. Evaluate the extent to which Hg is transported to Bear Creek from all sources.
iii. Identify physicochemical and biogeochemical processes affecting the transport of Hg based on existing (preremediation) field conditions.

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[*] U.S. Geological Survey, 345 Middlefield Rd, MS 901, Menlo Park, California 94025; aslowey@usgs.gov; 650 329-5474.
[†]jrytuba@usgs.gov; 650 329-5418.

Figure 1. Location of Bear Valley, Colusa County, California.

This report summarizes data obtained from field sampling of mine tailings and waste rock at the Rathburn and Petray Mines that was initiated in July 17, 2001 and water and sediment in regional springs and tributaries that drain from the mine area into Bear Creek on December 14, 2004 and February 16 and May 27, 2005. Although it was initially assumed that the mines were the cause of elevated levels of monomethyl Hg measured by the Central Regional Water Quality Control Board in tributaries near their confluence with Bear Creek (Foe and others, unpublished results), it became apparent during this study that ground water springs were also potential sources of Hg. In addition to sampling of springs in May 2005, saline ground water seepage along an unnamed fault on the west side of Bear Valley was sampled on December 13-14, 2006. We did not sample water or sediment in Bear Creek itself during this study. Our results permit a preliminary assessment of mining and natural sources of Hg and associated chemical constituents that could elevate levels of monomethyl Hg in Bear Creek.

The Bear Creek drainage basin comprises the northeastern part of the much larger Cache Creek basin, which has been the subject of several studies of mercury transport to the San Francisco Bay Delta (Bloom, 2001; Domagalski and others, 2004a; Domagalski and others, 2004b; Slotton and others, 2004; Cooke and Morris, 2005). We compare our results to some of the findings recapitulated by Domagalski and others (2004b) but do not attempt to reconcile our findings with these previous studies. Here, we attempt to develop a basis for incorporating biogeochemical and hydrological processes into a future monitoring program. A more fully developed conceptual model is the objective of a new California Bay Delta Authority-funded project that intends to ensure that future monitoring improves our understanding of the ecology of Hg contamination in the Cache Creek basin, on the basis of the evaluation of past work.

1.2 Geology

Mercury mines in the Bear Creek watershed are located near the major tectonic boundary that separates the sedimentary rocks of the forearc Great Valley Sequence from varied lithologies of the Franciscan accreted terrain. The Rathburn and Petray Hg deposits are localized along fault zones in serpentinite that has been hydrothermally altered and cut by numerous quartz and chalcedony veins. Cinnabar occurs as fine-grained masses on fractures and disseminated in low-angle fault and shear zones. The Hg ores formed in a hot spring system in the steam-heated environment present above the boiling paleo ground water table.

Cold saline springs and travertine terraces (sample locations M and MB, fig. 2) and drainages with sediment cemented by carbonate minerals (sample locations C, K, and L; see fig. 2 and figs. 11, 17, and 18 in the appendix) are present to the east of the Petray Mine and represent the waning stage of the hydrothermal system that formed the Hg deposits. Numerous saline springs, such as Cain springs (sample location CS, fig. 2) are present in the Bear Creek watershed. A previously unrecognized north-northwest-trending fault in Bear Valley, here termed the Bear Fault, is located 2 kilometers east of the Petray Mine and about 1 kilometer west of Bear Creek (fig. 2). Saline springs are localized along the length of the fault zone, exposed by areas of vegetation and whitish-gray carbonate-rich material (figs. 19-21). The largest volume of spring water is released from the central part of the fault and flows into tributaries 1 and 2 (fig. 2). These spring waters are derived from connate fluids within the Great Valley sedimentary rocks and consist of evolved Cretaceous seawater having high concentrations of CO_2, methane, and as-yet unknown hydrocarbons (referred to later as organic carbon). The fluids reach the surface along fault zones located within the Bear Creek watershed and account for the unusually high chloride, carbonate and sulfate concentrations of Bear Creek and several of its tributaries.

1.3 Hydrology

It is hypothesized that there are two sources of Hg to Bear Creek: surface water drainage from the Petray and Rathburn Mines and saline ground water from Bear Valley. Each source may differ in the speciation of mercury at the point of release. The aqueous geochemistry of each source also differs. However, at Bear Creek, aqueous geochemistry will reflect mixing of meteoric water and saline ground water to varying degrees, depending on rainfall intensity (assuming saline springs dominate ground water flow). It is expected that the aqueous geochemistry in Bear Creek will be dominated by that of saline ground water during the dry season and by surface runoff during the wet season but transiently and to a limited extent. As a result, it is expected that assessing the hydrological (and therefore geochemical) importance of surface water drainage from the mined areas relative to saline ground water to the aqueous geochemistry of Bear Creek and downstream water bodies (for example, Cache Creek) will be difficult without extensive geochemical, geophysical, and hydrological investigation over a multi-year period that captures appreciable hydrological variability (see also section 4).

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Figure 2a

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Figure 2. Petray and Rathburn Mine and Bear Valley sample locations

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Figure 2b

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Figure 2c

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Water inputs to Bear Creek consist of a combination of ground and surface water. Surface water at the Petray Mine location is believed to arise from meteoric precipitation and is, therefore, ephemeral. Surface water from the north pit of the Petray Mine drains primarily through one incised channel, referred to here as the north fork of tributary 1 and shown in figure 2. On the basis of topography, surface flow from the middle pit of the Petray Mine flows eastward to the south fork of tributary 3 and northeastward into the south fork of tributary 1. A saline spring east of the north pit actively releases carbonate-rich water, forming a carbonate terrace (travertine), depositing carbonate minerals, and cementing the sediment throughout the downstream channel of the south fork of tributary 1. It is unclear where surface drainage from the Rathburn Mine location goes, but it may join drainage from the south pit of the Petray Mine and/or drain to tributary 2 (fig. 2). Another drainage channel called Dead Shot Creek originates north of the Petray Mine. As can be viewed in current aerial photographs of the area, Dead Shot Creek has flowed parallel to tributary 1 before merging with it just upstream of the Bear Creek confluence. In 2005, however, we observed Dead Shot Creek to merge with tributary 1 much further upstream, just downstream of the confluence of the north and south forks of tributary 1. Recent debris flow deposits have caused the active channel of Dead Shot Creek to move southward on the alluvial fan such that it no longer is accurately represented on the topographic map.

As stated above, some surface flow in Bear Valley is due to upward percolation of ground water originating from connate fluids, some of which are heated and thus geothermal, primarily in the Sulphur Creek tributary to Bear Creek. Several 1- to 2-m depressions at the surface of Bear Valley were observed in December 2006. Some of these depressions were dry or moist from rainfall, but nearly all had narrow and shallow channel depressions leading towards Bear Creek and indicative of past discharge (fig. 24). When meteoric input is minimal, surface water is likely dominated by seepage of cold saline connate water.

Seepage of saline ground water appears to change in its spatial occurrence and extent over time. Ground water was clearly observable in shallow pits dug for sampling location BF1. In several pits dug in the vicinity of location BF2, a hard layer was encountered approximately one foot below ground surface. This layer is presumed to be a travertine deposit formed from past spring flow. Evidence of past ground water seepage was also observed north of Bear Creek Ranch Road in December 2006, but soil in the vicinity of location BF3 (fig. 2) was not saturated at the time. Vegetation varies appreciably, presumably depending on the stability of soil as affected by ground water inundation. One location (BF4) supported growth of tall plants, most had short grasses, and a few lacked vegetation. Several surface depressions were noted along the Bear Fault, most of which were not actively seeping water.

In addition to surface water and runoff of seepage, it is hypothesized that Bear Creek receives a substantial input of ground water via direct subsurface transport. Several brief investigations in late-2004 (Aug. 5, Sept. 22, and Oct. 26th) by Foe and others revealed that the specific electrical conductivity (SC) of Bear Creek water increased by about 10% (roughly 800 to 900 µS/cm) downstream of the Bear Valley segment that includes drainage from the Petray and Rathburn Mines (Foe, pers. comm.; unpublished data).

These hydrological features influence the transport and biogeochemical transformations of Hg in Bear Valley primarily through the physicochemistry[1] of carbonate-rich materials. For example, carbonate minerals could be cementing mineral particles to which Hg is likely sorbed. Dissolution of carbonate minerals would release particles. In addition, carbonate and other constituents of saline ground water, such as dissolved organic carbon (DOC), likely influence both geochemical and biological processes that affect the reactivity of inorganic Hg in the vicinity of Bear Creek, thus affecting its potential to be methylated and taken up by resident biota (Slotton and others, 2004).

1.4 Physicochemical and biogeochemical[2] considerations for mercury in Bear Valley

Both the drainages from the Petray Mine area and Bear Valley tributaries (1 through 5, fig. 2) to Bear Creek are supplied with carbonate from saline springs located throughout the drainage basin. Sulfate is also present in both mine drainage and ground water. In addition, ground water contains high levels (up to 20 mg/L, as discussed later) of dissolved organic carbon. These constituents can strongly influence the environmental geochemistry of Hg (discussed in section 3.2). Figures 3 and 4 summarize physicochemical and biogeochemical processes that could affect the transport and reactivity of mercury in the Bear Valley/Bear Creek system. The following paragraphs briefly explain these processes.

Precipitation of carbonate minerals will cement sediment (including mine waste), such as in the south fork of tributary 1, and therefore should retard physical transport of Hg from the Rathburn and Petray Mines. However, periods of intense rainfall may sufficiently lower the pH of surface water in Bear Creek tributaries to partially dissolve carbonate cements, and dissolve and release Hg-bearing particles (fig. 3). As the wet season ends and meteoric input wanes, water seeping from the western hills may mix with upwardly flowing saline ground water and provide a base flow through the Bear Creek tributaries. This temporary hydrological state may reduce the physical and chemical transport of Hg. However, lower flow and warmer temperatures likely enhance a number of biologically mediated processes that affect the speciation of Hg and formation of monomethyl Hg. Such processes will be related to geochemical conditions dominated by carbonate, sulfate, dissolved organic carbon (DOC), and, on the basis of visual observations (figs. 12 and 22), iron.

Figure 4 summarizes a number of biogeochemical processes that may influence the speciation and transport of mercury in Bear Valley. Photosynthetic organisms such as algae consume carbonate, which can change pH: the change is dependent on the assimilation of other ions (Stumm and Morgan, 1996). For example, ammonia (NH_4^+) assimilation as part of photosynthesis generates acid, which could sufficiently lower the pH enough to dissolve carbonate minerals. Dissolution of carbonate minerals may release Hg-bearing particles. Ammonia is highly enriched in active mercury geothermal systems such as at the Sulphur Bank mercury deposit where elevated concentrations of NH_4^+ are present in springs (King and Rytuba, pers. communication). Sources of ammonia to the Bear Creek watershed are likely saline ground water and urine excreted by cattle grazing in the area. The latter source implicates land-use as an

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[1] In this report, physicochemistry refers to coupled chemical and physical processes (for example, precipitation, dissolution, and colloid transport).

[2] In this report, the term biogeochemical refers to processes mediated by microorganisms as well as abiotic geochemical constituents.

influence on the speciation and mobility of Hg in Bear Valley. The relatively high concentrations of nitrate, up to 90 ppm in the most saline spring waters along the Bear Fault, are likely a result of the oxidation of NH_4^+ in ground water when it mixes with more-oxygenated meteoric water.

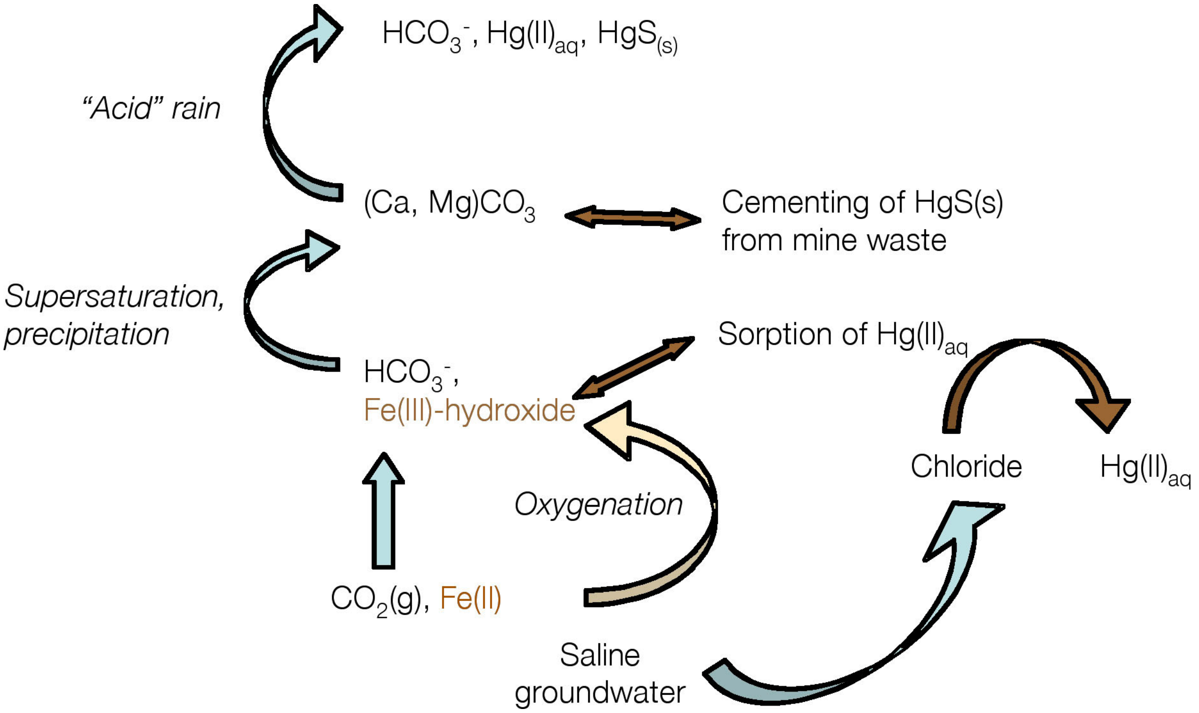

Figure 3. Physicochemical model of mercury transport from Rathburn and Petray Mines and within Bear Valley.

Sulfur cycling is important to Hg speciation and transport due to the ubiquity of sulfate-reducing microbial activity in subsurface and near-surface environments (Gibson, 1990; Rabus and others, 2006) and the strong chemical affinity between reduced sulfur species and Hg(II) (Hepler and Olofsson, 1975; Paquette and Helz, 1997; Jay and others, 2000; Brandon and others, 2001). As shown in figure 4, reduction of sulfate to form bisulfide is only one of several potentially important reactions. In particular, oxidation of sulfide [S(-II)] by microorganisms such as *Beggiatoa* and *Thioploca* spp. (Teske and Nelson, 2006) and abiotic oxidation of S(-II) by Fe(III) and Mn(IV) (hydr)oxides to elemental sulfur [S(0)] (Thamdrup and others, 1994; Poulton and others, 2004) introduces reaction mechanisms that can release mercury from species such as cinnabar (α-$HgS_{(s)}$) or authigenic metacinnabar (β-$HgS_{(s)}$) (Slowey and Brown Jr., 2007). The roles of organic carbon—an abundant constituent in saline ground water within Bear Valley—may include dissolution of α– and β–$HgS_{(s)}$ (Ravichandran and others, 1998; Waples and others, 2005), which may be photochemically influenced. Organic carbon can also limit the nucleation and crystal growth of β–$HgS_{(s)}$ in the presence of sulfide (Ravichandran and others, 1999).

The mining sources of mercury are small in spatial extent compared to the transport pathways in Bear Valley. As a result, Hg from the mines is expected to be widely dispersed. Saline ground water may also contribute Hg to Bear Creek via seepage/surface runoff and subsurface flow.

Understanding the net transport of Hg from the mines to Bear Creek is addressed to a limited extent by this brief field investigation. To understand whether there is a net flux of Hg to Bear Creek, seasonal, multi-year monitoring of Hg in water and sediment in the Bear Creek tributaries and in Bear Creek downstream of the confluences of these tributaries is required. These considerations for Hg transport to Bear Creek are developed in light of the results of this study and are recapitulated in section 4.

Subsurface flow, seepage, and runoff of ground water throughout Bear Valley are expected to strongly influence the aqueous chemistry of Bear Creek. Since Bear Creek is a small part of the Cache Creek watershed, the spatial extent to which ground water influences the geochemistry of downstream waterways is unclear. However, the larger Cache Creek basin includes several other sources of saline ground water that, to our knowledge, have yet to be characterized or enumerated.

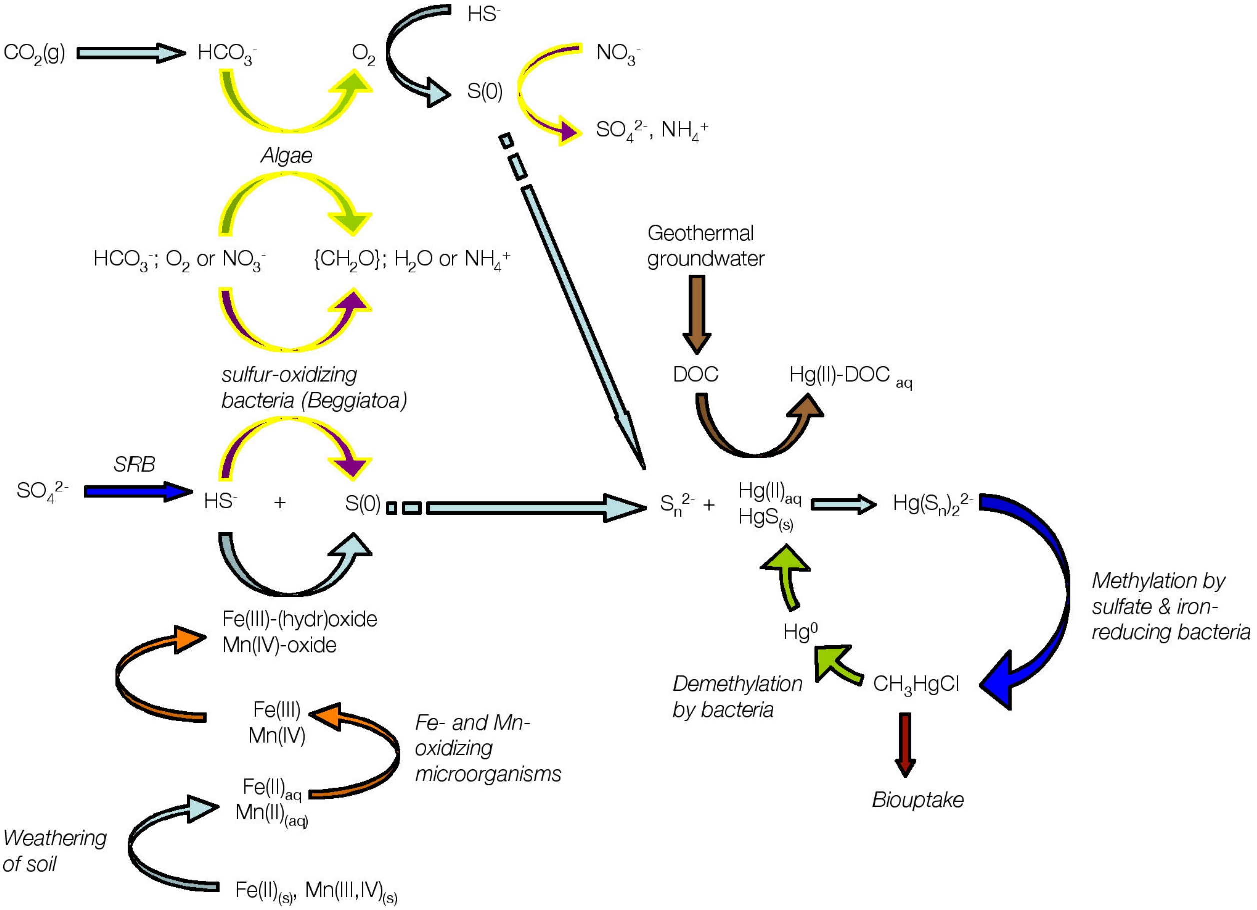

Figure 4. Biogeochemical model for processes putatively affecting the transport of mercury in the Bear Creek basin. Sources of bicarbonate include dissolution of CO_2 gas evolved from connate ground water seeps and travertine dissolution during acidic rainfall.

2. Sample locations and methods

2.1 Sample locations and conditions

Samples were collected to assess the concentration of Hg and biogeochemically relevant constituents in rocks within the open pits at the mine (altered serpentinite) and in tailings in waste rock piles at the Rathburn and Petray mines (figs. 10, 15, 16). Water, soil, and sediment were sampled along Dead Shot Creek (fig. 13), stream channels (referred to as tributaries 1 through 5) originating near the Petray open-pit mine and coursing through Bear Valley toward Bear Creek (fig. 23), and along an inferred fault zone in Bear Valley marked by numerous saline springs. Tables 1 and 2 detail the various types of samples collected, locations, and collection dates during the Winter 2004, February 2005, May 2005, and December 2006 periods. Field locations are shown on figure 2. During the December 2004 period, stream flow was low with no precipitation; in February 2005, sampling occurred during a storm that resulted in higher stream flow; the weather was stable and no precipitation occurred in May 2005; and while rainfall did occur over days prior to the December 2006 sampling period, precipitation while sampling was negligible and surface runoff was minimal

2.2 Sample handling

2.2.1 Rock, tailings, and stream sediment

Samples consisting of from 100 to 500 g of altered serpentinite and mine tailings were collected from exposures and waste rock piles in the Rathburn and Petray Mine pits. 125 mL jars were nearly filled with wet stream sediment. Rock and tailings samples were stored and shipped in zip-lock bags at ambient temperature. Wet sediment for total Hg (Hg_T) and methyl Hg (MMHg) analysis were stored on dry ice within approximately one hour after collection and kept frozen in the laboratory until shipped on dry or wet ice overnight to analytical laboratories, where upon receipt they were kept frozen until analysis. The temperature of samples arriving at the analytical facilities ranged from 1 to 4°C, which is within the limits specified in EPA Method 1631E.

Table 1. Altered serpentinite, calcine and sediment sample locations at open pits at the Rathburn and Petray Mines.

[See fig. 2 for a map of these locations. Geographic coordinates are referenced to the NAD 27 CONUS]

Location	Latitude	Longitude	Description
Rathburn calcine, sediment, and altered rock			
1	39.07507	-122.44825	Brick retort and soil
2	39.07607	-122.43822	Sand and silt in open cut
9	39.07677	-122.44838	Waste rock of altered serpentinite
10	39.07677	-122.44838	Altered serpentinite
Petray Open Pit sediment			
3	39.07677	-122.44492	Silt and clay sediment in middle pit
4	39.07677	-122.44825	Silt and clay sediment in middle pit
5	39.08605	-122.45140	Silt and fine sand from north-middle pit drainage
6	39.08578	-122.45098	Clay in north-middle pit
Petray ore and altered rock			
7	39.08178	-122.44933	Argillic alteration in shear zone
8	39.07680	-122.44490	Opal veins in silicified serpentinite
11	39.08608	-122.45155	Cinnabar on fractures in south trench
12	39.08876	-122.45208	North pit quartz-chalcedony vein in shear zone
13	39.08879	-122.45210	North pit opal veins in altered serpentinite
14	39.08606	-122.45140	Quartz-chalcedony vein in silica-carbonate rock alteration
15	39.08880	-122.45015	Waste rock east end, north open pit
R	39.0889	-122.4493	Medium-to-coarse sand below Petray north pit, north fork of tributary 1
S	39.0885	-122.4486	Pyroxenite sand in north fork of tributary 1 above confluence with north pit
15	39.1200	-122.4800	Waste rock channel, Petray north pit outlet
D	39.0949	-122.4424	Coarse sand sediment, north fork of tributary 1
V	38.0869	-122.4500	Sand below middle petray pit, north fork of tributary 1

Table 2. Stream water and sediment sample locations, quantities, and dates.

[See fig. 2 for a map of these locations]

Location	Latitude	Longitude	Water	Sediment	Dates	Description
Cain Spring	39.06765	-122.39883	1	1	12-20-04	Saline spring, Cain Valley
A	39.09579	-122.43401	1	1 1 1	12-21-04 12-23-04 02-21-05	Fine sand in bank deposit of tributary 1
B	39.09566	-122.44049	1	1 1	12-21-04 12-23-04	Fine sand and silt in bed sediment of tributary 1
C	39.09408	-122.44180		2	2-21-05	Carbonate-cemented fine-to-coarse sand sediment, south fork of tributary 1
D	39.09498	-122.44233	1 1 1	1	12-23-04 02/16/05 05-27-05	Fine-to-medium sand bed sediment, north fork of tributary 1
E	39.09568	-122.44143		1	05-31-05	Fine sand bed sediment, north fork of tributary 1
F	39.09572	-122.44038		2	05-31-05	Carbonate-silt sediment, south fork of tributary 1
G	39.09136	-122.43813		1	05-31-05	Fine-to-silt sand & clasts of Great Valley siltstone sediment, tributary 2
H	39.08657	-122.43434		1	05-31-05	Fine, black silt in dry creek bed with dunite clasts, north fork of tributary 3
I	39.08593	-122.43310	1	1	02-16-05 05-31-05	Fine-to-medium sand sediment, south fork of tributary 3
J	39.08239	-122.43082	1	1	12/21/04 2/16/05	Medium sand sediment, tributary 4
K	39.09232	-122.44411		1	12/21/04	Carbonate-cemented clay and silt, south fork of tributary 1
M	39.08856	-122.44614	1 1	1 1	12-21-04 12-23-04 05-27-05	Carbonate-coated clay and ferric (hydr)oxide precipitated from a saline spring
MB	39.08797	-122.44550	1		05-27-05	Upper part of terrace formed by deposition of carbonate minerals from spring
N	39.09510	-122.42956	1 1	2	12-21-04 05-27-05	Medium-to-coarse sand sediment, tributary 1
N	39.09502	-122.42932	1	0	12/14/06	Lower reach of tributary 1, 5 m downstream from location N

Table 2 – continued

O	39.09546	-122.44466	1 1		02-16-05 05-27-05	Dead Shot Creek
P	39.09502	-122.42932	1	1	05-28-05	Upper reach of tributary 1 below Petray north pit
Q	38.92457	-122.32381	1		02-23-05	Spring along road cut above Bear Creek

2.2.2 Water

Spring and stream water samples were collected with new 60-mL sterile polypropylene syringes. Bulk water samples were subsampled for analysis of metal(loid)s and anions. Subsamples for metal(loid)s determinations were acidified to pH<2 with trace metal (*Ultrex*, J.T. Baker)-grade HNO_3 and stored in acid-washed, high-density polyethylene (HDPE) bottles. Subsamples for anion and alkalinity measurements were filtered, stored in HDPE bottles, and chilled to approximately 4°C until analysis, in accordance with U.S. Geological Survey protocols for trace metals (http://pubs.water.usgs.gov/twri9A). Water samples were filtered in the field for analysis of anions, alkalinity, and ICP-MS and ICP-AES analysis. Pore fluids were filtered in the lab with 0.45 µm syringe filters within a few days of collection.

Water parameters including pH, conductivity, dissolved oxygen, and temperature were measured in the field with a Hydrolab multimeter, either by placing the probe directly into the flowing stream water (fig. 14) or by filling a container and placing it over the probe.

Samples for Hg_T and MMHg analyses were collected in trace-metal-free-certified 1-L borosilicate bottles (Nalgene ICHEM) with minimal headspace and Teflon[3]-lined caps. Samples were kept on ice until shipped. Samples were shipped on dry ice or blue ice packs, arriving the next morning at the analytical facilities at temperatures ranging from 1 to 9º C.
Some samples arrived at temperatures exceeding 4ºC, which is specified by EPA Method 1631E to minimize biologically induced phase changes and MMHg degradation.

Samples collected for dissolved organic carbon (DOC) analysis were filtered in the field with 0.45 µm filters into amber borosilicate vials with Teflon-lined caps and put on ice. Samples were refrigerated at 4º C for approximately five days, shipped overnight to the analytical lab, and analyzed within a few days.

2.3 Analytical methods

In addition to documenting methods, the following sections mention sample preparation issues that appreciably affect the interpretation of the results reported in Section 3.

2.3.1 Sediment and tailings

Multi-element analyses for all tailings (material processed in a retort, also referred to as calcines), waste rock (material moved from open pits and adits but not processed), and dry sediments were performed in the laboratories of ALS Chemex (Reno, NV) or SGS Minerals Services (Elko, Nevada; formerly X-ray Assay Laboratories (XRAL)). Bulk samples were

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[3] Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. government.

ground in a zirconia ring mill and subjected to a near-total four-acid digestion. Major elements in digests were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Trace elements other than Hg were determined by inductively coupled plasma–mass spectrometry (ICP–MS). Hg was determined by cold vapor atomic absorption spectroscopy (CVAAS) following methods similar to those described by Crock (1996) and O'Leary and others (1996).

Hg analyses of altered serpentinite, tailings, and waste rock, and wet sediment were performed by Frontier Geosciences Inc. and Brooks Rand LLC (Seattle, WA). Solids were not homogenized prior to subsampling the approximately one gram of sediment from the bulk (on the order of 100g) sample taken in the field. Nor did either laboratory grind subsamples prior to digestion. This approach unnecessarily introduced an additional source of inhomogeneity, or a possible "nugget" effect because some samples contained abundant fine grained HgS. We recommend that future investigators discuss sample preparation measures in detail and, if homogenization cannot be provided, homogenize subsamples themselves if particulate HgS is present in the sample.

At Frontier Geosciences, subsamples for total Hg (Hg_T) analysis were digested at room temperature with aqua regia (10 parts HCl and 3 parts nitric acid) (Bloom and others, 2003; Fernandez-Martinez and Rucandio, 2005). At Brooks Rand, for Hg_T, approximately one gram of sediment was digested with 7:3 conc. nitric:sulfuric acids and heated to 100°C for one hour, followed by refluxing at 150°C for two hours in a glass vial with Teflon-lined lids. Bromine monochloride BrCl was added to the digest after it had cooled to room temperature, diluted with deionized water such that the concentration was within instrumental range), and followed by stannous chloride reduction, single-stage gold amalgamation, and cold vapor atomic fluorescence spectroscopy (CVAFS) (U.S. EPA Method 1631E). The acid digest procedure should recover elemental, adsorbed, and amalgamated Hg, and Hg sulfide ($HgS_{(s)}$; cinnabar and metacinnabar), but does not appreciably dissolve silicate minerals. While previous studies suggest that Hg is sorbed to silicate minerals that comprise some if not most of the solids sampled here (excepting carbonate-rich concentrates), only minor fractions of Hg have been found to be within the aluminosilicate mineral structure (Sladek and Gustin, 2003; Lowry and others, 2004; Slowey and others, 2005). Detection limits for Hg_T in solids by this method ranged from 0.03 to 0.3 ng/g based on three standard deviations of method blank recoveries.

MMHg in sediment was determined by acid bromide-methyl chloride extraction, followed by aqueous phase ethylation, trapping (Carbotrap and Tenex; Scientific Instrument Services, Inc.), isothermal gas chromatographic separation, and CVAFS detection modification of EPA Draft Method 1630 (Horvat and others, 1993b). Results are reported on a wet-weight basis along with gravimetrically measured water contents. Detection limits for MMHg in solids ranged from 0.008 to 0.010 ng/g based on three standard deviations of method blank recoveries. Recoveries from certified reference materials at both analytical facilities did not indicate that they had problems analyzing certified reference materials. Two matrix spike recoveries from the Rathburn soil/retort brick sample 1 were 87% and 104% of 62,000 ng Hg_T/g and 95% and 103% of 5.0 ng MMH/g. Analytical precision based on these matrix spike duplicate analyses was $1\sigma = 0.06$ ng MMHg/g, or 11% of the mean concentration, and 640 ng Hg_T/g, or 14% of the mean concentration. Sediment subsamples were not tested for analytically induced formation of MMHg due to potentially high organic matter content (Bloom and others, 1997).

2.3.2 Water

The acid-neutralizing capacity (ANC) of samples collected in 2005 was measured at room temperature on November 14, 2006 after thawing samples frozen in polypropylene bottles. Samples for ANC were collected in December 2006 in polypropylene bottles, transported on wet ice to the laboratory, refrigerated for one week, and then titrated. A titration system equipped with a 1 µL-resolution burette delivered 1.6 N sulfuric acid at 10 to 100 µL/min to stirred, open 30 to 50 mL samples. Titration data points were numerically interpolated. Potential equivalence points (pH at which a buffering constituent(s) is titrated) were identified from peaks in the first derivatives of interpolated titration curves, known as the inflection point titration (IPT) method (USEPA 310.1) (Rounds, 2006). Waters containing saline spring water likely contain buffering agents other than carbonate (for example, organic acids and humic substances).

Sulfate, chloride, nitrate, and fluoride were determined by ion chromatography (Fishman and Friedman, 1989). Cations were analyzed by inductively coupled plasma atomic absorption spectrometry (ICP–AES) and mass spectrometry (ICP–MS). Duplicate water samples, blank samples, and USGS Water Resource Division standard reference waters were analyzed with the data set and yielded acceptable results.

Total Hg (Hg_T) was measured in samples collected in 2004 and 2005 by USEPA Method 1631 at Brooks Rand and Frontier Geosciences (Seattle, WA). Water samples collected in December 2006 were sent to Studio Geochimica (Seattle, WA) for Hg_T analysis by USEPA Method 1631. MMHg was analyzed at all facilities using aqueous phase ethylation, GC separation, isothermal decomposition, and CVAFS detection (Horvat and others, 1993a). Analytical detection limits for Hg_T and MMHg in water ranged from 0.1 to 0.2 ng/L and 0.01 to 0.02 ng/L, respectively, based on three standard deviations of blank recoveries. The field reagent blank recovery analogous to Hg_T sample preparation (0.5 percent v/v BrCl in deionized water) was 3.59 ng/L, indicating that the BrCl reagent used to preserve Hg_T samples in the field contained measurable Hg. As reported in section 3, this level of Hg ranged from 1 to 60 percent of concentrations recovered from water samples (23 percent on average from 16 recoveries of Hg_T and Hg_D combined). Although this contamination did not affect conclusions provided in this report, it should be considered in future interpretations.

Concentrations of dissolved iron and dissolved organic matter (DOM) in some spring water samples collected in December 2006 resulted in precipitation of ferric hydroxide and coagulation of humic substances (Myneni, 1999) upon addition of acidic BrCl reagent in the field. Both ferric hydroxide and coagulated humic substances can sorb Hg(II) and therefore may have partially impeded full recovery of Hg from the bulk samples provided for analysis. Two tests were performed to assess the potential for this problem. Two samples were analyzed at several dilutions. If a Hg-exchangable interferent (for example, a sorbent) is present, the dilution-corrected measured concentration of Hg would be observed to increase as the sample is diluted. This was not observed, suggesting that interference due to sorption did not occur. The second test involved adding incrementally higher levels of BrCl (up to 5% v/v) to one water sample to determine if some compound (for example, organic or reduced sulfur) was preventing Hg(II) from being reduced to Hg(0) to be purged and quantified. In no case did the sample tested release additional Hg(0) after incrementally stronger BrCl digestion and $SnCl_2$ reduction. This further suggests that interference due to sorption did not occur.

Because of the high concentration of dissolved organic matter (DOM) in some of the samples collected in December 2006, Studio Geochimica investigated the potential for potential positive artifact formation of MMHg during the aqueous distillation step (Bloom and others, 1997). This check was not performed on the 2004 or 2005 samples but all of these samples were surface waters and only two were spring waters with high DOM.

Total dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) was measured by USEPA Method 415.3 with modifications according to Aiken (1992). UV_{254} is normalized by DOC concentration to yield an operational parameter called the specific ultraviolet absorbance (SUVA). SUVA is an indirect characterization of the degree of aromaticity of dissolved organic carbon compounds (Weishaar and others, 2003). A complementary characterization of DOC was performed by measuring UV-spectral fluorescence over a range of UV wavelength excitation energies. The fluorescence intensities were compiled into three-dimensional excitation-emission matrices (EEMs), from which a two-dimensional emission spectrum and a one-dimensional fluorescence index (FI) were obtained at an excitation wavelength of 370 nm (McKnight and others, 2001). The FI was computed by dividing the emission intensity at 470 nm (I_{470}) by that at 520 nm (I_{520}) (both measured at 370 nm excitation).

3. Results and discussion

Given the scale and complexity of the Rathburn and Petray Mines-Bear Valley system and the limitations of the current database, this section summarizes findings while providing preliminary interpretation. After summarizing the Hg results for tailings and altered rock, the results for stream water, sediment, and saline ground water seepage along the Bear Fault are presented. These discussions develop preliminary source-receptor relationships throughout the region and begin to identify Hg transport processes. Since the brevity of this study leaves appreciable data gaps and uncertainty, recommendations for a future hypothesis-driven study are provided in section 4 on the basis of considerations presented in section 1.4.

Table 3. Elemental composition of tailings, waste rock, and sediment at the Rathburn and Petray Mine sites.

Sample Identification	Location	Hg	Ag	Al	As	Au	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Ge	Hf	In	K	La	Li	Mg	Mn	Mo	Na	Nb	Ni	P
		ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	%	ppm	ppm	ppm
Rathburn brick retort contaminated soil																															
21 - RB - C1	1	1020	0.2	2.01	2.6		165.5	0.3	0.05	0.65	0.4	7.3	101.7	1825	13.2	35	6.26	4.3	0.4	0.5	0.03	0.33	4	72	7	775	1.05	0.32	1.9	2140	240
Rathburn waste rock																															
21 - RB WR - 1	9	38.6	0.12	0.55	<0.2		34	0.05	<0.01	0.1	0.02	0.77	150.9	1660	2.3	11	7.58	1.15	0.45	<0.1	0.005	0.01	0.5	84.4	12.15	1035	0.2	<0.01	0.8	3950	30
Rathburn sediment in open cut																															
21 - RB - S1	2	35.8	0.06	0.54	0.4		48	0.05	<0.01	0.15	0.02	0.96	153.8	1105	3.65	11.4	6.8	1.1	0.45	<0.1	0.005	0.04	0.5	223	12.15	935	0.25	0.01	0.1	3450	80
Rathburn altered rock																															
21 - RB AR 1C	10	11.5	0.16	0.22	0.6		54.5	<0.05	<0.01	1.15	0.02	0.09	101.4	909	1.1	4.2	4.6	0.65	0.4	<0.1	0.005	<0.01	<0.5	72	>15.00	815	0.15	<0.01	1.2	2390	<10
Rathburn brick retort contaminated soil																															
21 - RB - C1	1	1020	0.2	2.01	2.6		165.5	0.3	0.05	0.65	0.4	7.3	101.7	1825	13.2	35	6.26	4.3	0.4	0.5	0.03	0.33	4	72	7	775	1.05	0.32	1.9	2140	240
Petray sediment accumulated in open pit																															
21 - PT S1	3	250	0.06	0.66	1.4		23.5	0.05	<0.01	0.12	0.02	1.71	252.7	999	16.8	15.8	8.34	1.65	0.6	<0.1	0.005	0.04	1.5	65	8.84	1570	0.2	0.03	0.3	4440	80
21 - PT S2	4	120	0.1	0.61	1.4		11.5	<0.05	<0.01	0.06	0.02	0.94	204.8	998	5.85	12.4	8.51	1.55	0.45	<0.1	0.005	0.03	1	29.4	9.31	1275	0.2	<0.01	0.3	4400	40
21 - PT S4	5	160	0.08	0.63	<0.2		23.5	<0.05	<0.01	0.3	0.02	0.7	153.9	1550	6.15	13.4	6.94	1.4	0.5	<0.1	0.01	0.01	0.5	54.8	11.65	925	0.2	<0.01	0.1	3340	10
21 - PT S5	6	42	0.06	1.04	0.8		35	<0.05	0.01	0.19	0.04	2.4	241.7	1525	9.6	19	10.25	2.4	0.6	0.1	0.015	0.03	1.5	36.4	7.16	1385	0.25	0.02	0.5	4900	90
Petray ore and altered rock																															
21 - PTOR - 2	7	2.5	0.08	0.62	0.2		4	<0.05	<0.01	0.64	<0.02	0.32	104.1	2060	17.2	12.6	5.13	1.1	0.45	<0.1	0.005	0.03	<0.5	33.6	6.08	575	0.15	<0.01	0.1	2450	<10
21 - PTOR - 1C	8	12	0.06	0.07	<0.2		2.5	<0.05	<0.01	0.01	<0.02	0.16	101.9	370	0.15	5.6	4.73	0.65	0.35	<0.1	<0.005	<0.01	<0.5	1.2	5.33	620	0.15	<0.01	<0.1	2780	10
21 - PTOR - 3	11	2490	0.4	1.07	<0.2		63	<0.05	<0.01	2.2	0.06	0.14	101.7	1875	40.8	16.2	5.49	1.4	0.4	<0.1	0.01	0.04	<0.5	294	12.5	795	0.15	<0.01	0.7	2150	<10
21 - PTOR - 4	12	180	0.02	0.28	0.6		61	5.25	<0.01	0.28	<0.02	0.12	30.5	593	33.2	6.2	1.84	0.5	0.25	<0.1	<0.005	0.06	<0.5	24.8	3.18	330	0.2	0.05	0.3	720	<10
21 - PTOR - 5	13	4.6	0.04	1.54	1.8		151	1.95	<0.01	0.08	<0.02	0.1	24.4	2990	170	12.6	10.65	1.6	0.45	<0.1	<0.005	0.22	<0.5	12.4	0.6	120	0.2	0.08	<0.1	586	<10
21 - PT AR 3	14	53	0.06	0.03	0.4		26	<0.05	<0.01	0.36	0.02	0.06	62.5	502	4.2	3	3.77	0.25	0.35	<0.1	<0.005	0.01	<0.5	62.2	10.05	495	0.3	0.03	<0.1	1790	<10
Rathburn waste rock																															
05PN2WR		178	<1	1.79	<1	0.019	304	0.6	<0.04	0.78	<0.1	1.84	209	1550	57.6	20.9	9.2	3.15			<0.02	0.08	1.1	71	9.82	2220	<0.05	0.05	0.4	3370	50
Sediments in unnamed drainages adjacent to the Rathburn and Petray mines																															
04RP1S	A	52.1	0.12	3.14	2.7		530	0.54	0.05	5.18	0.09	13.7	80	2530	82.6	25.4	5.62	6.93	0.22	0.7	0.027	0.6	6.8	54.6	10.7	945	0.37	0.55	2.7	1480	280
04RP2S	B	69.2	0.07	1.58	6		730	0.35	0.01	14.7	0.05	7.15	58.3	1095	33.4	14.4	3.92	3.41	0.17	0.3	0.013	0.32	3.7	33.9	8.18	949	0.24	0.38	1.2	1095	270
04RP4S	C	1.41	0.12	2.83	2.1		320	0.35	0.02	1.44	0.1	11.75	81.4	4310	61.7	27.5	5.51	6.2	0.2	0.6	0.021	0.48	5.5	62.6	11.95	929	0.33	0.39	2.2	1460	400
04RP5S	D	357	0.06	1.04	0.6		70	0.1	<0.01	1	0.03	1.83	126	5970	14.4	15.9	6.26	2.28	0.23	0.1	0.007	0.07	0.8	50.1	15.2	1085	0.58	0.06	0.4	2370	90
04RP6S	E	355	0.07	0.94	0.4		70	0.11	<0.01	0.77	0.04	1.68	138	3700	15.15	15.4	7.01	1.93	0.28	0.1	0.008	0.06	0.8	64.2	14.45	1210	0.32	0.06	0.3	2770	90
04RP7S	F	18.1	0.05	0.62	2		310	0.2	0.02	1.34	0.09	9.37	67.1	910	56.4	21.2	4.49	4.52	6.38	0.5	0.017	0.42	4.4	69.7	12.25	807	0.26	0.42	1.9	1350	400
04RP8S	G	0.23	0.16	5.83	3.7		380	0.8	0.11	0.74	0.31	29.4	55.8	7450	4.1	42	5.27	13.05	0.19	2.2	0.044	1	13.9	26.4	4.27	684	0.42	0.76	5.3	720	580
04RP9S	H	0.19	0.21	5.75	8.3		470	0.95	0.12	0.35	0.22	29	25.5	1415	2.88	41.2	3.62	12.25	0.15	2.1	0.041	1.02	13.6	28.4	1.82	519	0.77	1.22	5.9	319	500
04RP10S	I	38.3	0.13	4.95	3.9		330	0.67	0.06	0.56	0.16	22.8	76.3	3920	7.03	39.4	5.71	10.15	0.18	1.3	0.037	0.88	10.8	29.2	7.71	925	0.53	0.67	4.1	1335	590
04RP11S	J	0.16	0.22	6.89	7.4		520	1.04	0.13	1.16	0.21	34.9	37.2	1470	4.89	56.4	5.05	15.6	0.24	2.8	0.055	1.24	17.4	36.9	3.52	607	0.62	0.91	6.5	655	510
04RP16S	N	60	0.08	2.69	2.4		440	0.41	0.03	2.01	0.07	11.95	83.7	1840	110	23.3	5.6	5.75	0.2	0.6	0.021	0.52	5.9	75.8	12.85	929	0.33	0.47	2.2	1800	280
04RP17S	M	0.01	0.03	0.1	0.3		5120	0.06	<0.01	0.4	<0.02	2.77	7.7	79	24.3	1.2	23.8	0.32	1.04	<0.1	<0.005	0.26	1.5	33.2	2.73	105	0.09	0.75	0.3	161	810
04RP20S	A	0.86	0.07	4.15	3.9		380	0.58	0.07	0.99	0.09	22.1	93.1	1925	94.8	36.4	6.81	9.86	1.02	1.3	0.035	0.85	11.2	76.7	10.75	1100	0.45	0.89	3.9	1720	310
04RP21S	K	1.22	0.06	1.69	1.5		360	0.15	0.01	1.04	0.08	6.38	81.1	2100	58	19.9	4.78	3.72	0.17	0.4	0.012	0.3	3.1	76	12.7	937	0.24	0.35	1.3	1515	360
05PN4S	R	408	<1	0.96	<1	<0.005	40	<0.1	<0.04	1.38	<0.1	0.85	94.6	3510	11.1	17.5	7.64	1.27			0.03	0.02	0.5	76	18.2	959	<0.05	0.01	0.3	2060	<50
05PN3S	S	319	<1	0.8	<1	<0.005	41	<0.1	<0.04	0.53	<0.1	1.44	179	1850	9.09	17.1	8.42	1.43			<0.02	0.03	0.8	85	13.6	1390	<0.05	0.03	0.3	3300	60
05RP1S	D	250	3	0.74	<1	<0.005	51	0.1	<0.04	0.59	<0.1	0.66	98.5	1240	17.7	17	5.88	1.23			<0.02	0.04	<0.5	105	16.6	742	2.04	0.05	0.3	2270	<50
04RP7S	V	139	<1	0.57	<1	<0.005	29	<0.1	<0.04	0.34	<0.1	1.17	170	1090	6.74	14.1	7.43	1.09			<0.02	0.02	0.7	44	12.9	1220	<0.05	0.02	0.2	3280	<50

Table 3 - continued

Sample Identification	Pb	Rb	Re	S	Sb	Sc	Se	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Rathburn brick retort cont																				
21 - RB - C1	78.5	18.7	<0.002	0.11	7.55		<1	2.8	30.4	0.1	0.7	1.4	0.11	4.26	0.3	59	3.7	4.6	140	24
Rathburn waste rock																				
21 - RB WR - 1	1.5	1.6	<0.002	<0.01	3.1		<1	0.2	4.2	<0.05	0.65	<0.2	0.02	1.62	<0.1	24	10.3	0.8	44	4.5
Rathburn sediment in ope																				
21 - RB - S1	3.5	2.3	<0.002	0.01	3.55		<1	0.2	11.6	<0.05	1.05	<0.2	0.01	2.06	<0.1	21	5.1	1	38	4.5
Rathburn altered rock																				
21 - RB AR 1C	0.5	0.3	<0.002	0.1	1.7		<1	0.2	34	0.05	2.95	<0.2	0.01	0.58	<0.1	12	19.9	0.1	32	3
Rathburn brick retort cont																				
21 - RB - C1	78.5	18.7	<0.002	0.11	7.55		<1	2.8	30.4	0.1	0.7	1.4	0.11	4.26	0.3	59	3.7	4.6	140	24
Petray sediment accumul																				
21 - PT S1	4	11	<0.002	0.01	0.15		<1	0.6	5.6	<0.05	1.15	0.2	0.01	0.06	0.1	21	<0.1	1.8	42	7
21 - PT S2	3	5.2	<0.002	<0.01	0.15		<1	0.2	2.6	<0.05	1.25	<0.2	0.01	<0.02	<0.1	16	<0.1	1.5	46	7
21 - PT S4	1	2.2	<0.002	<0.01	0.3		<1	0.2	4	<0.05	1.35	<0.2	0.01	0.06	<0.1	27	1.1	1.1	42	3.5
21 - PT S5	2.5	4.1	<0.002	0.01	0.15		<1	0.2	6.4	<0.05	0.7	0.4	0.03	0.04	0.1	31	0.7	1.6	48	10
Petray ore and altered roc																				
21 - PTOR - 2	0.5	11.3	<0.002	<0.01	<0.05		<1	<0.2	1.2	<0.05	0.25	<0.2	0.01	<0.02	<0.1	38	<0.1	0.7	44	3
21 - PTOR - 1C	0.5	0.4	<0.002	<0.01	<0.05		<1	<0.2	2.2	<0.05	1	<0.2	<0.01	<0.02	<0.1	6	<0.1	0.7	32	2
21 - PTOR - 3	<0.5	13.3	<0.002	0.04	<0.05		1	0.2	3	<0.05	2.8	<0.2	0.03	0.04	<0.1	59	4.6	1.4	26	2
21 - PTOR - 4	0.5	8.9	<0.002	0.21	<0.05		<1	<0.2	58.5	<0.05	0.05	<0.2	0.01	6.06	<0.1	16	12.2	0.4	16	2
21 - PTOR - 5	<0.5	39.2	<0.002	0.56	<0.05		1	0.2	37.4	<0.05	0.1	<0.2	0.03	8.18	<0.1	70	5.1	0.7	34	2
21 - PT AR 3	0.5	1.1	<0.002	0.1	<0.05		<1	0.2	63.9	<0.05	1.35	<0.2	0.01	0.2	<0.1	3	18	<0.1	20	1.5
Rathburn waste rock																				
05PN2WR	1.3	16.9		0.04	0.51	12.2		0.5	87.8		<0.1	0.4	0.05	5.5	<0.1	57	51.5	2.7	48	
Sediments in unnamed dr																				
04RP1S	4.8	59.4	<0.002	0.02	0.46		1	0.5	252	0.21	0.06	1.9	0.156	0.28	0.5	80	15.2	7.5	70	27.6
04RP2S	2.7	23.5	<0.002	0.03	0.22		1	0.3	555	0.09	<0.05	0.9	0.069	0.25	0.3	40	12.4	4.5	37	15.4
04RP4S	4.5	44.2	<0.002	0.05	0.26		1	0.6	121.5	0.17	0.05	1.5	0.167	0.06	0.4	88	4.7	7.4	87	24.6
04RP5S	2	7.1	<0.002	0.02	0.12		<1	5.2	42.8	<0.05	<0.05	0.2	0.036	0.34	0.1	65	6.3	1.8	79	3.5
04RP6S	1.1	6.8	<0.002	0.02	0.13		<1	0.7	33.4	0.06	<0.05	<0.2	0.032	0.46	0.1	49	7.5	1.7	61	3.2
04RP7S	4.3	39	<0.002	0.07	0.25		1	0.5	147	0.24	<0.05	0.8	0.135	0.09	0.3	59	4.9	5.3	54	17.3
04RP8S	8.7	49.2	<0.002	0.08	0.59		1	1	75.5	0.4	0.05	4.1	0.31	0.29	1.2	156	0.8	14.6	170	61.2
04RP9S	9.4	46.1	<0.002	0.02	0.88		1	1	77.1	0.43	0.07	4.1	0.334	0.3	1.4	120	0.9	15	102	63.7
04RP10S	6.6	41.2	<0.002	0.04	0.53		1	1	51.2	0.3	<0.05	3.1	0.248	0.27	0.9	122	1.2	11.6	114	47.2
04RP11S	9	61.5	<0.002	0.02	0.89		1	1.2	202	0.48	0.05	5.1	0.349	0.38	1.5	146	1	16.3	124	72
04RP16S	4.3	57.9	<0.002	0.03	0.24		1	0.5	174.5	0.17	0.05	1.6	0.129	0.23	0.4	68	14.2	6.3	60	23.8
04RP17S	1	17.4	0.003	0.05	0.05		<1	<0.2	568	<0.05	0.05	<0.2	<0.005	<0.02	<0.1	4	268	2.3	7	0.7
04RP20S	5.7	74.9	<0.002	0.01	0.36		1	0.7	79.2	0.3	0.07	2.9	0.223	0.2	0.8	103	21.6	10.4	82	40.8
04RP21S	3.5	35.2	<0.002	0.08	0.14		<1	0.4	147	0.1	<0.05	0.7	0.102	<0.02	0.2	51	6.9	4.5	54	13
05PN4S	0.5	3.4		0.03	<0.05	11.6		<0.1	9.7		<0.1	<0.2	0.03	0.2	<0.1	69	2.5	1.8	76	
05PN3S	2.8	4.3		0.03	0.08	8.6		<0.1	10		<0.1	0.2	0.02	<0.1	<0.1	40	2.8	1.3	55	
05RP1S	0.5	6.6		0.03	0.18	7.8		0.1	16.1		<0.1	<0.2	0.02	0.7	<0.1	39	5.5	1.3	39	
04RP7S	1.2	3.4		0.02	0.08	7.2		0.7	5.1		<0.1	<0.2	0.01	<0.1	<0.1	28	2	1.1	42	

3.1 Tailings and dry sediment at the Rathburn and Petray Mines

The concentration of Hg in waste materials at the Rathburn Mine varies depending on material type. Ores were processed at the Rathburn Mine in a brick retort, and a small amount of calcines are present near the remains of the retort. The calcines sampled in 2001 contain 1020 ppm Hg, compared to 470 ppm measured in similar material collected by Churchill (Churchill and Clinkenbeard, 2002) (table 3). Waste rock derived from open cuts developed to mine Hg ore from altered serpentinite contains considerably less Hg (39 ppm), as does the exposed altered serpentinite (12 ppm). Waste material and sediment has accumulated in several of these open cuts. Sediment in one of these disturbed areas contains 36 ppm of Hg (table 3). While calcines contain much higher Hg concentrations than waste rock and serpentinite, they comprise a minor fraction of the mass of material exposed at the Rathburn Mine.

Unlike the Rathburn Mine, Petray Mine Hg ores were processed offsite in a rotary furnace at the Abbott Mine during 1971 with only 10-100 flasks of Hg produced, according to limited production records (Churchill and Clinkenbeard, 2002). Visible cinnabar is present on fractures in the south and central pits, with the largest area of visible cinnabar mineralization occurring in the northeast part of the central pit where 2490 ppm of Hg was measured (location 11). Other areas of altered rock in the south and central pit contained considerably less Hg (2.5 to 53 ppm). The north Petray pit was developed to expose several quartz-chalcedony veins that trend northwest. No cinnabar was observed, and 180 ppm Hg was measured in a visually representative sample. The Hg concentration in adjacent altered serpentinite was low (4.6 ppm) and similar to concentrations measured in serpentinite in the south and central pits. Due to its abundance, waste rock consisting of altered serpentinite is the primary Hg-enriched material of environmental interest at the Petray Mine. The amount of surface disturbance is relatively large given the small Hg production when compared to other Hg mines in the Coast Ranges of California.

Some, but not all, of the large waste rock piles that exist at the Petray Mine’s south pit have apparent hydrological transport pathways to adjacent drainage. A large waste rock pile northeast of the south pit (previously called the “central pit” by Churchill and others 2002) contains 80 to 170 ppm Hg. Erosion of this waste rock contributes Hg-enriched sediment to Tributary 3 (fig. 2), on the basis of 90 ppm of Hg measured in sediment immediately downstream of the pile (Churchill and Clinkenbeard, 2002). In contrast, altered rock eroded from pit walls and waste rock from adjacent piles in the south pit are apparently trapped in the pit with no apparent hydrological outlet. Sediment in this vicinity contains elevated Hg (120 to 250 ppm), on the basis of measurements of material collected from locations 3 and 4 (fig. 2). Again, this material will not likely move off-site as long as the area remains undisturbed.

High concentrations of Hg in sediments in the north fork of tributary 1 result from the release of Hg-enriched sediment from two of three open pits at the Petray Mine. The Petray central pit (called the “south pit” by Churchill and others 2002) contains several small waste rock piles with Hg concentrations ranging from 170 to 1070 ppm. Hg-enriched sediment (42 ppm, location 6) accumulates in the western part of the pit, most likely after eroding from altered rock on the walls of the pit. The northeast end of the central pit does have an outlet leading to the south fork of tributary 1, and Hg-enriched sediment has been measured there (160 ppm, location 5). A large waste rock pile located at the east end of the Petray north pit occurs on a very steep slope, has been partially eroded, and is likely a source of Hg-enriched sediment to the north fork of tributary 1 (fig. 2). A sample collected from this pile contained 178 ppm Hg, and sediment downstream of the point where drainage from the north pit enters tributary 1 contained a Hg concentration higher than that above the confluence (410 ppm at location R, versus 320 ppm at location S; table 4). Thus, high concentrations of Hg in sediments in the north fork of tributary 1 likely result from the release of Hg-enriched sediment from both the central and north pits.

Very high concentrations of Hg (46-355 ppm) in sediment persist in the active channel of the north fork of tributary 1 downstream from the central and north Petray Mine pits. However, Hg concentrations vary considerably and do not consistently decay from the source. Where the North fork of tributary 1 enters Bear Valley, the Hg concentration in sediment is variable but comparable to upstream locations closer to the North pit, on the basis of limited measurements: 357, 250, and 136 ppm (location D on Dec. 2004, Feb. 2005, and May 2005, respectively; table 4) and 355 (location E, Dec. 2004). Cinnabar was panned at both of these locations. Pan concentrate from this site was analyzed by Hg L_{III} edge extended X-ray absorption fine structure (EXAFS) spectroscopy and found to contain equal proportions of cinnabar and metacinnabar (data not shown), suggesting that these are the main Hg phases in sediments.

If relatively coarse mineral particles account for the Hg present in sediment, measurements of total Hg should be expected to be variable (because of the nugget effect) and provide only a limited basis on which to derive reliable Hg loading estimates for the north fork of tributary 1 to Bear Creek. Further downstream on tributary 1, after inflow from the south fork, the sediment Hg concentration decreases (52 and 75 ppm at location A, 60 ppm, location N), suggesting that sediment transported from the south fork of tributary 1 and Dead Shot Creek dilutes Hg transported from the north fork of tributary 1. At location A, conglomerate exposed in the walls of the creek contains 0.86 ppm Hg, indicating that premining sediment has a much lower concentration than that present in the active channel. Concentration of Hg in sediment from tributaries that do not drain the mine area (that is, tributaries 2, north fork of 3, and 4), have a lower Hg concentration (0.16-0.23 ppm Hg) than the premining sediment (0.86 ppm Hg) exposed in tributary 1, indicating that natural erosion of the Petray deposit contributed Hg enriched sediment to this tributary.

Sediment in the Bear Creek tributaries in Bear Valley is partially cemented with carbonate minerals. Spring water nearly or fully saturated with calcium carbonate enters the south fork of tributary 1 downstream of the Petray south pit. This water is at times supersaturated with respect to calcium or magnesium carbonate, based on observed deposition of carbonate minerals on the creek bed and cementation of sediment in the active stream channel (fig. 23). Cementation of particles should limit the amount of Hg-enriched sediment that is transported from the upper part of this tributary to Bear Creek, as discussed further in the following section. The sediment in this tributary contains relatively low concentrations of Hg, ranging from 0.9 to 5 ppm.

3.2 Surface and saline ground water seepage

In addition to the Hg content of sampled waters, additional parameters are discussed below to evaluate which components can reliably indicate the provenance of water observed in the Bear Creek tributaries adjacent to the Rathburn and Petray Mines. This combined approach estimates the proportions of two presumptive end-member sources—meteoric water and saline ground water derived from connate fluids in sedimentary rocks in the Great Valley Sequence—and their Hg content, indicating the importance of each to the Hg contamination of Bear Creek. The following paragraphs focus on the distinct properties of each end-member on the basis of analyses of water collected at times when we assume the samples were dominated by one end-member. For example, surface water collected in February 2005 during a rain storm is less dominated by saline ground water seepage than in May 2005 under dry-season conditions.

Bulk water quality parameters, such as pH and specific conductivity (SC), reflect the influence of saline spring and ground water in stream channels draining the Petray Mine and within Bear Valley. Specific conductivities vary widely (standard deviation (s) = 1.8 mS cm^{-1} for 2004-2005 stream waters and s = 6 mS cm^{-1} for saline ground water seepage collected in December 2006) and are not clearly diagnostic of whether the water in the Bear Creek tributaries is predominantly meteoric versus ground water (t test P = 0.09, comparing the means of each dataset). For example, SC is similar in waters sampled during periods of high and low meteoric input, as determined on tributary 1 water collected in February and May 2005. This is likely due to rapid dissolution of carbonate minerals in tributary stream beds by acidic meteoric water during the wet season. The exceptionally high conductivities measured along the central part of the Bear Fault (for example, 9.4 and 19 mS cm^{-1}; table 6) reflect the significant component of saline ground water in these springs.

Alkalinity is relatively high in both spring and surface waters because of contributions from saline ground water and interaction of meteoric water with serpentinite and ultramafic country rock. Alkaline pH from 8.0 and higher (table 6) suggests aqueous equilibrium with calcium carbonate in the stream channels (Stumm and Morgan, 1996). The alkalinities of all sampled waters varied greatly, from 2.8 meq L^{-1} at location S (presumably less dominated by ground water) to 29 meq L^{-1} in water collected at a saline cold spring that is actively depositing travertine and is estimated to consist of about 20% saline connate ground water (location M, fig. 2). Most waters in the Bear Valley tributaries are highly alkaline (table 6 and fig. 5). However, the eight saline ground-water seepage samples collected along the Bear Fault had alkalinities (9.7 to 26.3 meq L^{-1}; average 15.4 meq L^{-1}, s = 5.7 meq L^{-1}) that were significantly higher, by 80 percent on average, than nine stream surface waters sampled in 2004-2005 (averaging 8.6 meq L^{-1}, s = 3.3 meq L^{-1}; t test P = 0.013)[4]. This reflects the relatively larger component of saline ground water in these springs. On the basis of the topology of the acid-titration curves (fig. 5), bicarbonate was most likely the dominant buffering agent, although organic matter may also buffer these waters.

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[4] The saline spring (location M) alkalinity datum was excluded from this statistical analysis.

Table 4. Hg and methyl Hg in surface water, sediment, and porewater and sulfide in pore water.

[Italicized sediment Hg data are results from larger, homogenized samples]

Location	Date	Hg in water (ng/L)[1]		Methyl Hg in water[2]	Hg in sediment[3,6]			Methyl Hg in sediment[4]	
		Unfiltered	Filtered (<0.45 µm)	Unfiltered	wt-% solids	µg/g-wet	µg/g-dry[1]	ng/g-wet	ng/g-dry[5]
Cain Spring	12/20/04	16	5.4	0.12	0.45		0.07		2.5
	5/23/05	-	-	-	0.54		0.07		0.82
A	12/21/04	460	-	-	0.58	44	*76*		0.82
					-		*52*		
					-		0.9		
B	12/21/04	14	5.8	<0.02	0.52	23.5	45		0.6
	5/23/05	-	-	-	0.65		46		0.08
C	12/21/04	-	-	-	-		5.0		-
					-		*1.4*		-
D	12/21/04	860	-	-	-		*360*		
	2/21/05	50	11	-					
	5/31/05	75	9.0	-	0.73		188		5.8
E	12/21/04	-	-	-	-		*360*		
F	12/21/04	-	-	-	0.21	*7.5*	36		68
	5/23/05				0.28		10		57
G	12/21/04	-	-	-	-		*0.23*		-
H	12/21/04	-	-	-	-		*0.19*		-
I	12/21/04	-	-	-	-		*38*		-
	2/21/05	122	9.9	-	-		-		-
J	12/21/04				-		*0.16*		-
	2/21/05	12	9.5	-	-		-		-
K	12/21/04	-	-	-	-		*0.86*		-
L	12/21/04	20	-	-	0.26	0.6	2.3		0.21
	12/21/04	-	-	-	0.68	52	76		0.06
M	12/21/04	2.0	1.1	<0.03	0.16		0.02	0.3	2.0
	5/23,27/05	-	-	-	0.21		0.04		-
MB	5/27/05	20	1.1	-	0.23		1.7		6.0

Table 4 – continued

N	12/21/04	690	440	0.05	-		*60*		-
	5/27/05	588	24	-	-		-		-
O	2/21/05	7.8	4.4	-	-		-		-
	5/31/05	3.9	0.9	-	0.8		0.09		<0.01
P	5/*26*/05	110	15	-	0.75	250	337		0.27
Q	2/23/05	1.1	0.5	-	-		-		-
R	5/26/05	-	-	-			408		
S	5/26/05	-	-	-			319		
V	5/23/05	-	-	-			139		
06RP1	12/13-14 /06	102	110	0.06					
BF1		37	32	0.60					
BF7		40	29	0.29					
BF8		38	32	0.33					
BF2		6.9	6.6	<0.04					
06RP8		7.6	5.9	<0.04					
06RP9		252	-	0.09					
Pore water					**Sulfide, µmol/L**				
BF1	12/13-14/06	-	9.03	0.24	2.4 ± 0.1[7]				
BF2		-	14.3	0.54	3.5 ± 1.1				
BF7		-	18.9	3.4	4.4 ± 1.7				

[1-4] Analytical detection limits based on 3s of reagent blank recoveries were [1] 0.2 ng/L, [2] 0.04 ng/L, [3] 0.12 ng/g, and [4] 0.02 ng/g.

[5] Concentrations on a dry weight basis were computed by dividing the ng/g-wet sediment by the weight-% solids of the sediment.

[6] Matrix spike recovery was *less* than unspiked recovery, indicating substantial heterogeneity in the distribution of Hg within the sediment sample. The true bulk concentration of this and the other sediment samples may be substantially different than these reported values.

[7] Error intervals for sulfide are 1σ of replicate sample analyses.

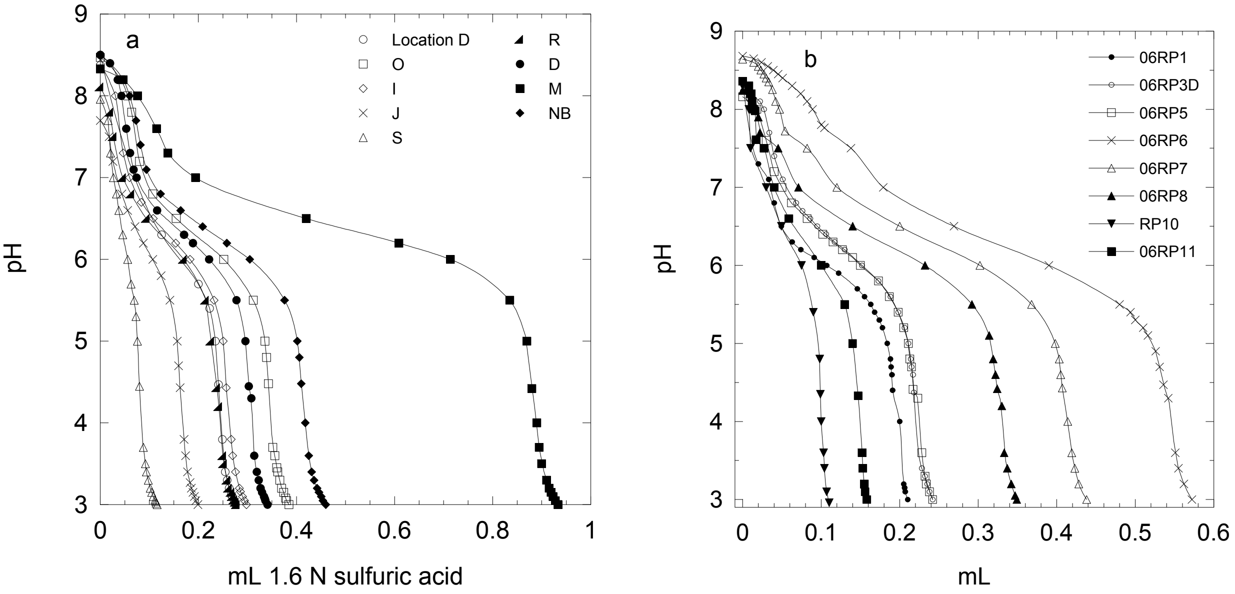

Figure 5. Acid titration curves for filtered (<0.45 μm) Rathburn and Petray Mine drainage sampled in May 2005 (a) and Bear Valley saline spring-influenced surface water sampled in December 2006 (b).

If the waters are simply binary mixtures of meteoric water and saline ground water, all conservatively transported ions should show a linear mixing line when plotted against Cl. A plot of Na verses Cl (fig. 6) demonstrates that surface and spring waters plot along a two-end-member linear mixing line with springs having higher concentrations of Na and Cl than surface waters. The most saline spring water with the highest Na concentration is from a CO_2 spring (fig. 20, sample 06RP06 in table 6) located in the central part of the Bear Fault. This water likely represents the saline ground water source end member. The concentrations of Cl and Na in this water are comparable to saline geothermal spring waters in the Sulphur Creek to the south of the study area.

In comparison to all other waters in the study area, this water also has the highest concentration of K, Rb, Li, Se, Sr, W, and nitrate, sulfate, and DOC. Plots of these cations against Cl define a linear mixing line similar to that for Na and Cl and indicate that these elements behave conservatively. In contrast, because of carbonate mineral precipitation in the tributaries and at springs, Ca and Mg do not plot on a linear mixing line.

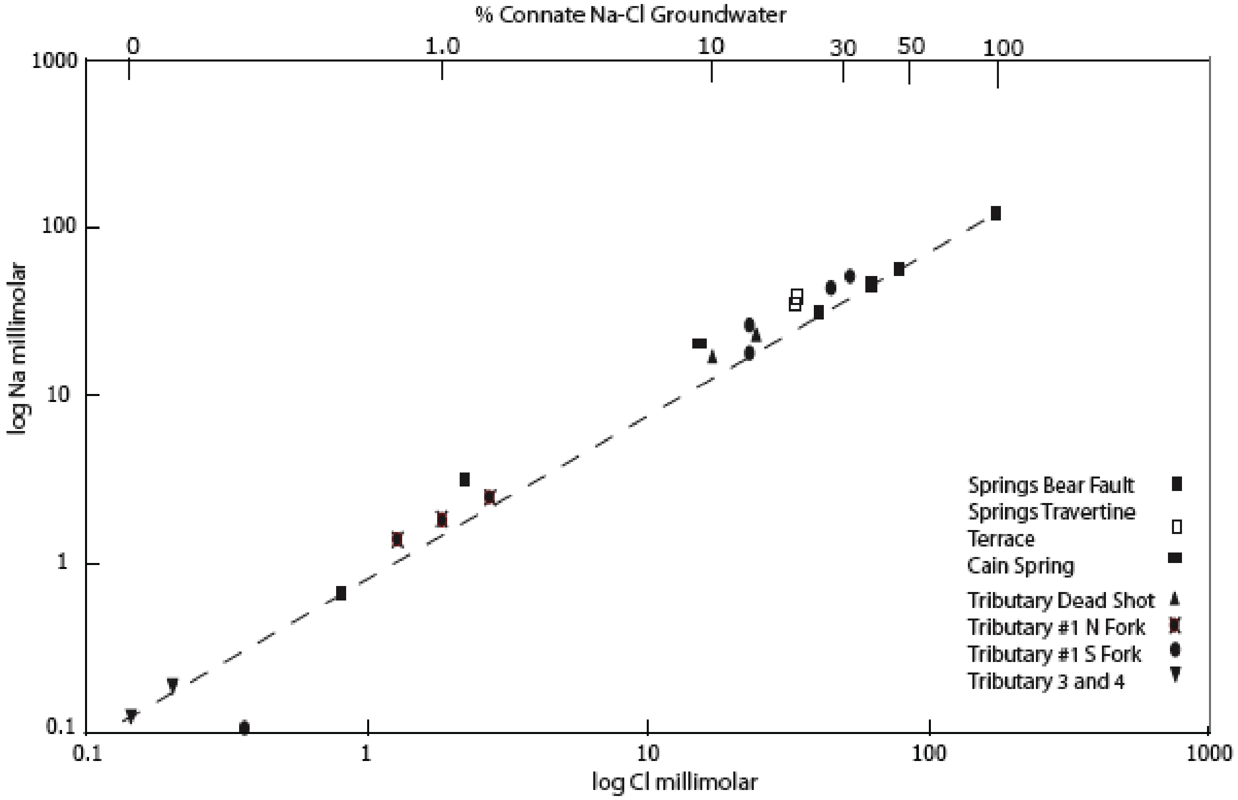

Figure 6. Correlation between $\log_{10}$ transforms of Na and Cl in filtered (<0.45 μm) spring, pore, and surface water in streams draining the Petray Mine and Bear Valley.

[The ANOVA statistics shown in the figure suggest that a correlation this large (R^2 = 0.97) could happen by chance alone only 0.07 percent of the time. The dashed line represents the mixing line between the most saline spring water and background meteoric surface water in tributary 4. The percent (%) connate Na-Cl ground water in each sample is based on the Cl concentration present in the water sample and that in the two end members of the mixing line]

The relative percentage of meteoric and saline ground water can be determined for various spring and surface waters on the basis of the computed binary mixing line (fig. 6) where the most saline spring water is defined as the pure ground water end member and the pure meteoric water is defined by surface water from a background site in tributary 4 sampled during a storm event (sample J, table 6). The percentage of ground water in each water sample is:

$$\%\ \text{ground water} = \left[\frac{\mathrm{Cl}_{\mathrm{MW}} - \mathrm{Cl}_{\mathrm{meas}}}{\mathrm{Cl}_{\mathrm{MW}} - \mathrm{Cl}_{\mathrm{GW}}}\right] \bullet 100 \qquad \text{(equation 1)}$$

where the subscripts MW and GW denote the chloride concentration in the end member meteoric water and saline ground water, and meas is the concentration in a water sample. Both spring and surface waters contain less than 50% saline ground water (fig. 6, table 5). The highest component of saline ground water is present in spring waters along the central part of the Bear Fault. Pore waters and springs sampled at either end of the fault zone are predominantly meteoric water.

Effluent from springs associated with the travertine terrace in the head waters of the south fork of tributary 1 causes the relatively high component of saline ground water in this tributary at site B.

A simple mixing of saline ground water and meteoric water does not explain the observed Hg concentrations in spring or surface waters. The concentrations of Hg in both filtered and unfiltered waters are not correlated with chloride concentration or any other major or minor element. Processes that control mercury concentration in surface and spring waters are not conservative and may include precipitation and dissolution of carbonate, dissolution of HgS by DOC, and seasonal changes in surface water flow. These processes are discussed in detail below. The highest total Hg concentration (855 ng/L) measured under dry season low flow conditions occurs in surface water in the north fork of tributary 1 (location D). The waters in this tributary are predominantly meteoric, less than 1.5% saline ground water, in both the dry and wet season. This site has the highest concentration of Hg in sediment (350 ppm) and HgS can be panned from the sediment.

Spring waters that emanate from the central part of the Bear Fault also have elevated concentrations of Hg with the highest total Hg (102 to 690 ng/L) and Hg in filtered water (24-435 ng/L) occurring where tributary 1 crosses the fault (locations A and N, and samples 06RP 1 and 9, table 5). Spring waters located along the fault contain a significant but highly variable proportion of saline ground water, from 13 to 100 % (table 5), and the Hg concentration in the spring waters is not correlated to the proportion of saline ground water present. Pore fluids sampled from the north and south end of the Bear Fault also have elevated concentrations of Hg even though these waters are predominantly meteoric.

Seasonal changes in flow in some cases increase Hg concentration in surface waters (tributary 3) and in other cases decrease it (north fork tributary 1).Sampling of one storm event was carried out in the middle of the 2005 wet season (February). Elevated concentrations of total Hg (122 ng/L) were measured in tributary 3 that receives runoff from the Petray Mine. The high concentrations of Hg present in the north fork of tributary 1 were considerably lower during the storm event, 49 ng/L as compared to 855 ng/L during low flow conditions. At the background site in tributary 4 (site J) low concentrations of total Hg, 12.4 ng/L,and Hg in filtered water, 9.5 ng/L, were present during the storm sampling. Somewhat lower concentrations of total Hg (7.8 ng/L total Hg and 4.4 ng/L in filtered fraction) occur in Dead Shot Creek that is not impacted by mining.

Table 5. Predicted proportions of saline ground water in water samples based on Cl concentration in spring, pore, and surface waters.

[Weather conditions and mercury concentration are listed]

Location	Site Description	Weather Condition	Cl^- (mg/L)	% Saline Ground water	Hg in water (ng/L)	
Springs along Bear Fault					**Unfiltered**	**Filtered (<0.45 µm)**
06RP1	At tributary #1	Dry season	1445	23.8	102.1	109.9
A	At tributary #1	Dry season	1882	31.0	458	
N	At tributary #1	Dry season	1600	26.3	690	435
	At tributary #1	Dry season	811	13.3	588	24
06RP6	CO_2 Spring	Dry season	6065	100.0	38.08	32.43
06RP7	Carbonate deposition	Dry season	2757	45.4	6.89	6.57
06RP8	No carbonate deposition	Dry season	2210	36.4	7.60	5.93
Springs with travertine terraces						
M	Spring terrace	Dry season	1184	19.5		
M	Spring terrace	Dry season	1202	19.7	1.97	1.05
Cain	Cain Spring					
Spring	Cain Spring	Dry season	543	8.9	15.9	5.44
Tributaries						
D	North fork, tributary 1	Rain storm	46	0.7	49.3	11.4
D	North fork, tributary 1	Dry season	98	1.5	855	
D	North fork, tributary 1	Dry season	66	1.0	75.3	9.04
MB	South fork, tributary 1	Dry season	13	0.1	19	1.06
B	South fork, tributary 1	Dry season	820	13.4	14.1	5.81
L	South fork, tributary 1	Dry season	8	0.0	19.9	
I	Tributary 3	Rain storm	7.3	0.0	122	9.93
J	Tributary 4	Rain storm	5.2	0.0	12.4	9.46
O	Dead Shot Creek	Dry season	864	14.2	3.94	0.85
O	Dead Shot Creek	Rain storm	604	9.9	7.78	4.40
Pore fluid along Bear Fault						
06RP3	North end, pore fluid	Dry season	113	1.8	37.06	31.83
06RP5	South end, pore fluid	Dry season	29	0.4	40.00	29.21

Dissolved organic carbon (DOC) may qualitatively indicate the proportion of meteoric surface water versus ground water. The pure saline ground water end member has the highest DOC. Three other springs along the Bear Fault with lower proportions of saline ground water have lower DOC, with log DOC correlated to the log percent saline ground water present ($R^2 = 0.92$). In contrast, pore fluids sampled near the north and south end of the fault consist of meteoric waters with relatively high DOC indicating a terrestrial source. In addition, DOC is biogeochemically relevant to Hg and its methylation. DOC is abundant in saline ground water seepage and consists of a complex mixture of aliphatic acids and humic substances. The yellow color of most of the seepage collected along the Bear Fault is characteristic of aquatic fulvic acid, but we presume, with reservation (see below), that the origin of the organic matter is from connate fluids that have leached both marine and terrestrial organic matter from sedimentary rocks of the Great Valley Sequence. DOC analyses of filtered (0.45 µm) spring and pore waters collected along the Bear Fault in December 2006 found DOC concentrations ranging from 2.4 to 30 mg L^{-1} carbon that, on average (21 mg L^{-1}, $n = 6$) were elevated relative to most fresh waters (table 7). Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) values range from 2.1 to 5 L·g C^{-1} m^{-1} (averaging 3.8 L·mg C^{-1} m^{-1}, $n = 6$), which are moderate to high compared to a variety of marine and freshwater determinations. According to a model developed by Weishaar and others (2003), these $SUVA_{254}$ values suggest that 17 to 36 percent of the organic carbon in these ground water seepage samples belong to aromatic molecules or moieties or, more specifically, sp^2-hybridized carbon.

Aromatic carbon is important to Hg transport because it can dissolve $HgS_{(s)}$ (cinnabar and metacinnabar) and chemically stabilize dissolved aqueous Hg(II) complexes (Benoit and others, 2001; Qian and others, 2002; Waples and others, 2005; Drott and others, 2007) (fig. 4). The percentage of aromatic carbon derived from $SUVA_{254}$ should be considered as estimates and subject to correction based on pH and metal ion concentrations (especially transition metals), which can affect UV_{254} absorbance regardless of aromatic carbon content. Comparisons would only be valid when matrix similarity with respect to such constituents can be demonstrated. Nevertheless, the DOC analysis elucidates that ground water seeping along the Bear Fault contains appreciable amounts of organic carbon that could be capable of dissolving Hg(II), including cinnabar transported from the Rathburn and Petray Mines. In December 2006, Hg_T in water sampled from tributary 1 at a seep was less than half that measured tens of meters downstream in a larger pool (fig. 23) (102 ng L^{-1} and 252 ng L^{-1}, respectively; table 5). The Hg concentrations measured in filtered and unfiltered seepage sampled at the upstream location were similar, suggesting that the ground water seepage contained predominantly dissolved Hg. The increased Hg_T (Hg_F is not available) at the downstream location further suggests that DOC in the seepage enhanced dissolution of Hg in the tributary 1 channel, possibly from cinnabar transported from the Petray Mine.

Another useful parameter and DOC characteristic is ultraviolet (UV) fluorescence upon excitation with UV radiation. Figure 7a shows a representative matrix of fluorescence (sometimes referred to as emission) intensity as a function of excitation wavelength, called the emission-excitation matrix (EEM). Figure 7b shows a two-dimensional view of this and the other measured EEMs at an excitation wavelength of 370 nm. Further dimensional reduction yields fluorescence indices (FI), obtained by dividing the emitted intensity at two wavelengths (typically near the maximum and half-maximum intensity) for a given excitation energy (see guide lines in fig. 7b; FIs are reported in table 7). The FI takes into account the relative intensity and width of the fluorescence spectra, and so can be compared among samples. Interpreting FIs in our study relies on previous studies that quantified carbon speciation using ^{13}C nuclear magnetic resonance. However, we were unable to find a report of FI for connate fluid, and so this characterization is currently preliminary.

While we have tentatively maintained that DOC in the saline ground-water-dominated water sampled in December 2006 came from connate fluid (that is, thermally degraded organic matter from Cretaceous Great Valley sedimentary rocks), the $SUVA_{254}$ and FI results together question whether an appreciable fraction of DOC does not derive instead from terrestrial plant matter excreted from livestock that graze in parts of Bear Valley. The FIs of the December 2006 sampled Bear Fault waters, ranging from 1.24 to 1.45 (table 7), are similar to waters containing DOC primarily sourced from degraded terrestrial organic matter, as opposed to microbially generated DOC, which typically has a higher FI (McKnight and others, 2001). A lower FI, coupled with a higher $SUVA_{254}$ value, further suggests that DOC is proportionally more aromatic. This coupling is noteworthy given that FI is significantly correlated to $SUVA_{254}$ ($R^2 = 0.92$, $P = 0.008$) for the Bear Fault ground water seepage sampled (fig. 8).

In December 2006, we did not find evidence of grazing in the more southern Bear Fault sampling locations (06RP5 and 6), but grazing had recently occurred near the north locations (06RP1, 3, 7, and 8). As shown in figure 2, a fence restricts grazing in the Rathburn/Petray portion of Bear Valley. Pore fluids sampled in an area of apparently recent grazing, location 06RP3, had the highest $SUVA_{254}$ and lowest FI, suggesting a larger fraction of aromatic carbon consistent with terrestrial organic input. Because the pore fluid is meteoric water, appreciable fractions of aromatic carbon from connate water could not explain this result. However, it would be useful to have further data to characterize the typical FI and $SUVA_{254}$ values of deep ground water and various surface and pore waters in Bear Valley. It is also important to know the sensitivity of $SUVA_{254}$ and FI to short-term land-use change (if samples were collected frequently enough), and to determine if end-member waters have distinct $SUVA_{254}$ and FI signatures and if mixing of ground and surface waters significantly changes these parameters. The DOC results from December 2006 sampling are too few to be definitive with respect to these questions. The relatively high DOC and aromatic carbon in pore fluids can be attributed to terrestrial organic matter inputs linked to grazing on the basis of $SUVA_{254}$ and FI. This realization emphasizes the importance of (1) coordination with land owners to better understand short-term land-use practices and (2) closer monitoring of meteoric water inputs to the system. With constraints applied by knowledge of land use and hydrology, continued measurement of DOC, $SUVA_{254}$, and FI are recommended to help understand water dynamics in the Bear Valley system.

Table 6. Temperature, pH, alkalinity, and concentrations of selected anions.

[mS/cm = millisiemens per centimeter, meq/L = milliequivalents of charge per liter, mmol/L = millimoles per liter, μmol/L = micromoles per liter]

Sample	Date	T (°C)	pH	Specific conductivity (mS/cm)	Acid-neutralizing capacity (meq/L)	Cl- (mmol/L)	SO_4^{2-} (μmol/L)
Cain Spring	12/20/2004	10	7.9	2.4	-	15	700
A	12/21/04	10	8.7	1.2	-	53	40
B		10	8.9	3.1	-	23	40
C		28	8.7	3.6	-	-	-
D		10	7.1	1.0	-	2.8	70
	2/16/2005	10	8.5	0.9	9.0	-	-
	5/27/2005	24	8.8	1.0	9.5	-	-
I	2/16/2005	10	8.5	0.7	7.9	0.20	77
J		10	8.2	0.5	4.8	0.13	81
L	12/21/04	10	8.7	3.6	-	<0.002	26
M		10	7.6	5.9	29	34	<17
	5/27/2005	28	8.3	6.1	-	-	-
MB		22	8.3	1.2	-	-	-
N	12/21/04	12	8.4	1.3	-	45	52
	5/27/2005	-	-	-	12	-	-
O	2/16/2005	10	8.6	2.9	11	-	-
	5/27/2005	25	8.7	3.8	13	-	-
P	5/28/2005	16	7.2	0.7	-	-	-
Q	2/23/05	10	7.7	1.2	-	-	-
R	5/26/05	-	-	-	7.6	-	-
S		-	-	-	2.8	-	-
06RP1	12/14/06	15.3	8.0	5.10	9.70	41	280
06RP3		15.0	8.0	1.53	10.9	3.2	170
06RP5	12/15/06	15.3	8.0	1.20	11.0	0.82	420
06RP6		16.4	8.4	19.1	26.3	170	1,800
06RP7		15.1	8.4	9.37	18.2	78	690
06RP8		12.3	8.1	8.11	17.9	62	760

Table 7. Concentrations and properties of dissolved organic matter in saline ground water seepage sampled in Bear Valley, December 2006.

Sample Location	UV Absorbance[1]	DOC (mg/L C)	$SUVA_{254}$[2]	FI[3]
06RP01	0.049	2.4	2.1	1.45
06RP3	1.484	29.9	5.0	1.24
06RP5	0.939	22.2	4.2	1.29
06RP6	1.986	50	4.0	1.37
06RP7	0.225	7.6	3.0	1.39
06RP8	0.594	14.2	4.2	1.35

[1] Ultraviolet Absorbance measured at a wavelength of 254 nm.
[2] $SUVA_{254}$ = UV(254nm) / DOC (mg/l) * 100.
[3] FI = Fluorescence Index (ratio of the emission at 470nm / emission at 520nm, when excited at 370nm.)

The presence of higher Hg_T concentrations in unfiltered drainage from the mined area compared to unfiltered saline spring water may discriminate mine versus natural sources of Hg. For example, in May 2005 at locations R (close to the Petray north pit) and D approximately 1,050 in-stream meters downstream along the north fork of tributary 1, Hg_T in water was 110 ng/L and 75 ng/L, respectively (table 4). These concentrations are higher than Hg_T measured in six of seven spring waters collected in December 2006. Surface water collected 1,250 meters further downstream from location D (2,300 stream meters from the Petray north pit) along tributary 1 had an even higher Hg_T concentration (590 ng/L, location N) in May 2005. At these same locations and times, however, the proportion of 0.45 µm-filtered Hg (Hg_F) in drainage from the mined area was approximately a third that in saline ground water. These results suggest that identification of mine-related drainage dominance over saline ground water can be discriminated on the basis of higher Hg_T concentrations (100s ng/L) with smaller fractions of Hg_F.

The Hg species in drainages from the mined area include cinnabar, metacinnabar, and Hg(II) that is loosely bound to particles and subject to carbonate-mediated release and sequestration. Filtered Hg (Hg_D) appears to be correlated to Hg_T (fig. 9), which suggests that physicochemical regulation of carbonate mineral cements by stream flow strongly affects both the release of colloids and dissolution of Hg(II) sorbents in Bear Creek tributaries (see section 1.4 and fig. 3).

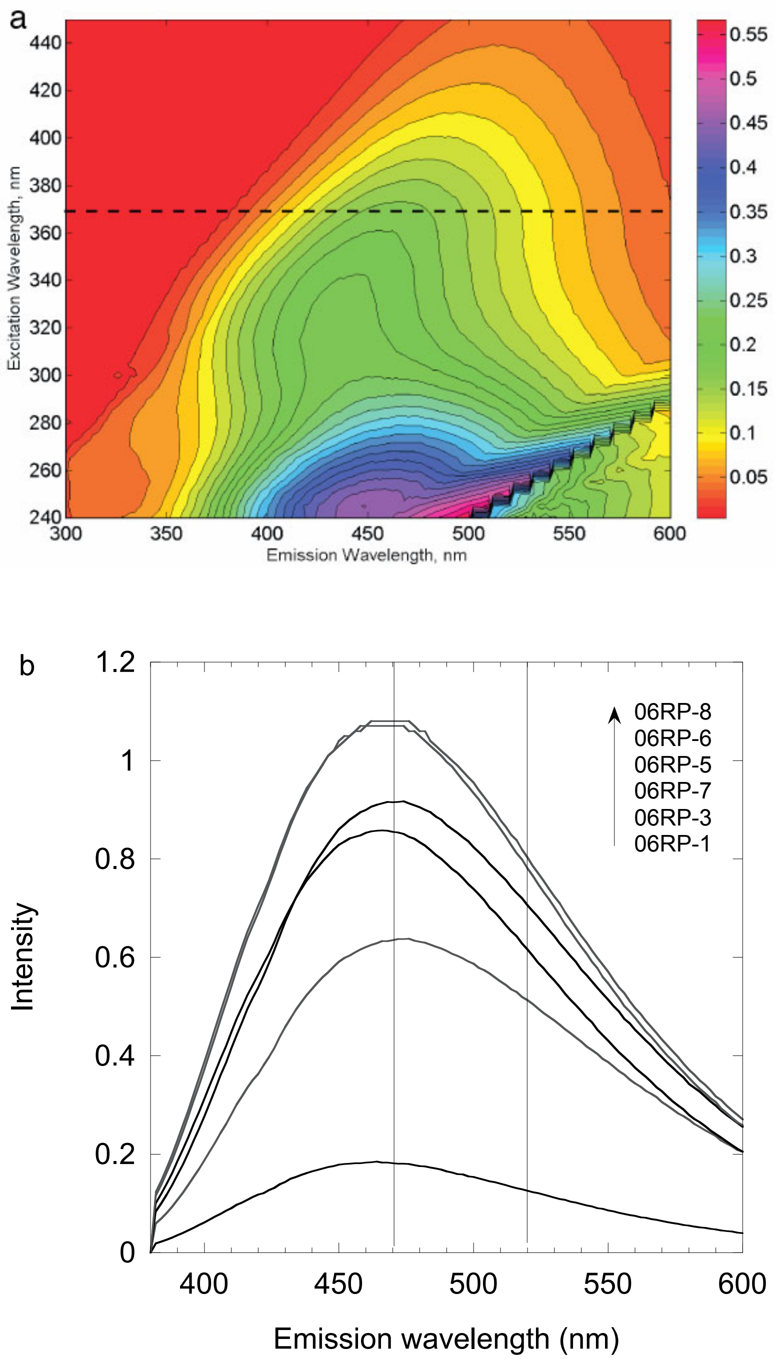

Figure 7. (a) Excitation-emission matrix for Bear Valley ground water seepage location 06RP1. (b) Fluorescence emission spectra at 370 nm excitation wavelength, as indicated by the dashed line in (a).

[The vertical guide lines indicate the emission wavelengths used to compute the fluorescence index (FI = I_{470} / I_{520})]

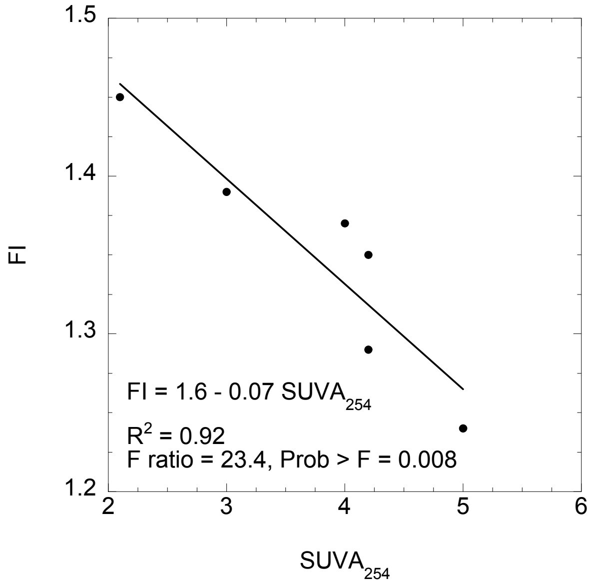

Figure 8. Apparent correlation between DOC the fluorescence index and $SUVA_{254}$.

[The ANOVA statistics shown in the figure suggest that it is highly unlikely (only 0.8 percent of the time) that a correlation this large (R^2 = 0.92) could happen by chance alone]

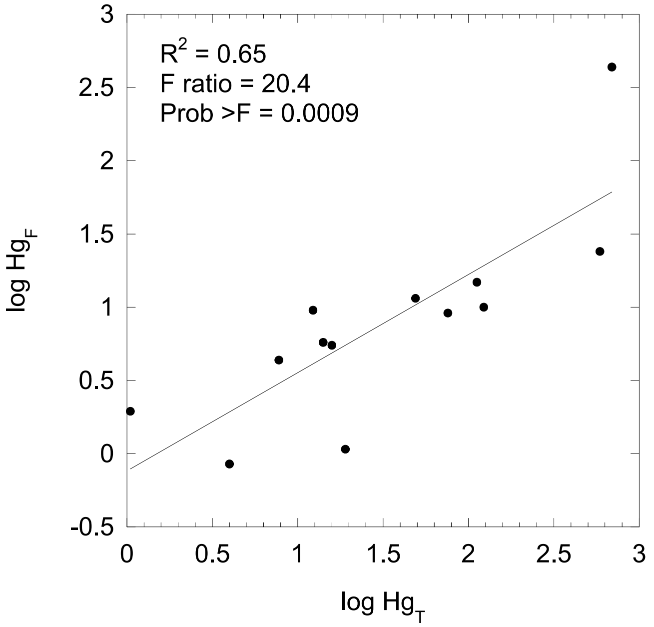

Figure 9. Correlation between $\log_{10}$ transforms of filtered (<0.45 μm) and total Hg in surface water in streams draining the Petray Mine and Bear Valley.

[The ANOVA statistics shown in the figure suggest that it is highly unlikely (only 0.09 percent of the time) that a correlation this large (R^2 = 0.65) could happen by chance alone]

Although the Petray Mine has the potential to export Hg to Bear Creek, on a time-integrated basis, saline ground water is an appreciable and possibly dominant source of Hg. The concentrations of Hg_T in filtered spring water in Bear Valley were often similar to unfiltered water and suggest that the majority of Hg is dissolved or colloidal. Dissolved organic matter (DOM) may help solvate Hg (for example, by inhibiting precipitation of Hg or carbonate-cementation of Hg-bearing particles). Both dissolved and colloidal Hg are mobile in subsurface flow and seepage runoff. The springs in Bear Valley are closer to Bear Creek than are the Rathburn and Petray Mines. A similar hypothesis was proposed by Domagalski and others (2004b) for waters in Sulphur Creek (another tributary to Cache Creek). They also hypothesized that saline geothermal springs elevated Hg concentrations in Sulphur Creek. Additional monitoring, and particularly hydrogeological investigations (see section 4), is required to determine whether saline ground water is an appreciable or dominant source of Hg to Bear Creek.

Pore water sampling provided the most reliable method to-date to characterize connate water with respect to Hg content and methylation potential. In December 2006, pore water sampling devices were deployed at locations where conditions appeared conducive to Hg accumulation and methylation. Sampling of pore water reduces dispersion and oxidation, which can change the speciation of major constituents such as sulfur and iron that, in turn, can affect the speciation of Hg. In addition, since pore water is not exposed to sunlight, sampling of pore water minimizes photochemical degradation of MMHg. Rainfall consisted of intermittent drizzling at the time of sampling in December, 2006. Although the wet season had just begun and surface runoff in the tributaries from the mine area was not evident (a relatively drier water year), most of the near-surface pore water and surface water sampled on December 13-14, 2006 consisted of less than 50 percent connate waters and the pore waters were predominantly meteoric (table 4).

Despite having less dissolved Hg in pore fluids compared to surface water, the shallow subsurface may more efficiently produce MMHg. In most cases, the concentration of dissolved Hg in pore waters near active Bear Valley seeps (9 to 19 ng/L, mean 14 ng/L; $n = 3$) was about half that measured in surface water (0.04 to 110 ng/L, mean 31 ng/L; $n = 7$; table 4 and fig. 2). However, fractions of dissolved MMHg relative to Hg_F were one to two orders of magnitude larger in pore water compared to surface water. The simplest explanation for the difference in Hg_D between surface and pore water is that sulfide [S(-II)] generated in the subsurface by sulfate-reducing microorganisms (2 to 4 μM S(-II), table 4) reacted with Hg(II) to form metacinnabar (β-$HgS_{(s)}$). Another possible, but less likely reason for the observed elevated Hg_D concentrations in surface versus pore water is that 0.45 μm filtrates of surface water contained more Hg-bearing colloids than the 0.1 μm pore water filtrates. Biogeochemical conditions in the near-subsurface were more conducive to Hg(II) methylation than in surface water environments. Sulfate-reducing microorganisms were not likely living in oxygenated surface water but were evidently present in the subsurface, on the basis of sulfide pore water measurements. Therefore, at least one known pathway for MMHg formation likely differs appreciably between the surface and subsurface environment. Although sulfide formed in the subsurface may sequester a fraction of Hg(II) as β-$HgS_{(s)}$, dissolution of β-$HgS_{(s)}$ (Ravichandran and others, 1998; Waples and others, 2005) or partial inhibition of Hg(II) precipitation (Ravichandran and others, 1999) by DOM may provide a persistent source of dissolved Hg(II) to methylating microorganisms. The high concentrations of MMHg in pore waters at the north and south end of the Bear Fault indicate that pore fluids in the near surface ground water east of the fault are a potentially significant source of MMHg to

Bear Creek. Effluent from the springs maintains a large wetland area east of the fault (in the area around locations BF8 in fig. 2c) and subsurface flow likely contributes MMHg to Bear Creek.

4. Conclusions

4.1 General conclusions

The Rathburn and Petray Mines and saline spring waters are sources of Hg to Bear Creek. An understanding of the relative importance of these two sources of Hg and Hg transport requires an understanding of the hydrology in the Bear Valley drainage basin. Although the Petray Mine and, to a lesser extent the Rathburn Mine, has the potential to yield mobile forms of Hg to Bear Creek tributaries, saline ground water is an appreciable and possibly dominant source of Hg. While we infer from interpretation of geochemical characteristics of water and sediment that carbonate plays a major role in the physicochemical transport of Hg, the data are not adequately sensitive to discern the relative contributions of meteorically derived drainage from the mined area versus saline ground water sources of Hg to Bear Creek. The results of this study provide a basis for developing a conceptual model to effectively reinvestigate the Bear Valley region in order to predict the effects of cleanup of the Rathburn and Petray Mines on Bear Creek. Further study of the Bear Valley drainage basin in light of the conclusions provided below is required to achieve such predictive capability.

The concentration of Hg in waste materials at the Rathburn Mine varies and depends on material type. While calcines contain much higher Hg concentrations than waste rock and serpentinite, they comprise a minor fraction of the exposed material at the Rathburn Mine and are absent at the Petray Mine. The majority of easily eroded Hg-contaminated materials at both mines consist of waste rock and Hg-enriched altered serpentinite and quartz-chalcedony veins.

Although all three pits at the Petray Mine have potential to release Hg-enriched sediment into the adjacent drainages, not all waste piles in the vicinity of each pit appear to have transport pathways emanating from them (section 3.1). Two of three open pits at the Petray Mine release Hg-enriched sediment and account for the high Hg concentrations in sediments in the north fork of tributary 1. Erosion of waste rock from a large dump northeast of the south pit contributes Hg-enriched sediment to tributary 3.

Although high concentrations of Hg in sediment persist in the north fork of tributary 1 downstream from the central and north Petray Mine pits, Hg concentrations vary considerably and do not consistently decay from the source. Cinnabar and metacinnabar are likely the primary Hg phases in sediments of the north fork of tributary 1. Evidence suggests that sediment in tributary 1 is diluted by sediment (primarily calcium carbonate) transported from the south fork of tributary 1. Spring water entering the south fork of tributary 1 downstream of the Petray South pit is cementing particles in the stream channel: precipitated carbonate retards the transport of Hg-enriched sediment.

While pH, specific conductivity (SC), and alkalinity certainly reflect the influence of saline spring water in stream channels draining the Petray Mine and within Bear Valley, they do not clearly indicate the proportion of meteoric versus high-salinity ground water. Ambiguity arises from the dissolution and precipitation of carbonate-bearing solids, which affects all of these parameters. However, elements such as Cl and Na are not affected by carbonate precipitation and redox reactions and, therefore, are useful in establishing, under contrasting hydrological conditions, water origin and dominance. The most saline spring water is present in the central part of the Bear Fault and is likely representative of a nearly pure connate ground water end-member. This water also has the highest concentration of other transition elements such as B, Ca, K, Mg, Rb, Sr, and W. Other springs along the Bear Fault and at the travertine terrace consist of variable proportions of saline ground water and meteoric water. Surface waters are predominantly meteoric except where the effluent from saline springs mixes with surface water such as in the south fork of tributary 1 and where this tributary intersects the Bear Fault. This investigation would be greatly assisted by contemporaneous hydrological and geophysical study of the system to understand the saline ground water reservoir and its response to seasonal changes in meteoric water flow.

Spring waters that consist of variable proportions of near-surface meteoric water and saline ground water have unique DOC characteristics. The pure saline ground water end member has the highest DOC. Limited data indicate that DOC is correlated with the proportion of saline ground water present in spring waters along the Bear Fault. This investigation characterized DOC using indirect measures of aromaticity, $SUVA_{254}$, excitation emission matrices, and fluorescence indices (EEM/FI), but was limited by the possibility that springs and pore fluids also contained a component of terrestrially derived organic carbon present in near-surface meteoric ground water (that is, from bovine manure and degradation of plants). At the time of spring water sampling, no surface flow in the tributaries and low subsurface flow was likely because only minor rainfall had occurred in the drainage basin after the prolonged dry season. Pore waters sampled along the north and south end of the Bear Fault are meteoric and have relatively high DOC and a larger fraction of aromatic carbon likely derived from a terrestrial source. $SUVA_{254}$ and EEM/FI are likely sensitive to end-member water mixing as well as contributions from terrestrial derived sources but additional data is necessary to characterize the ground water end member and other DOC sources in meteoric water.

The presence of higher Hg_T concentrations in unfiltered drainage from the mined area compared to unfiltered saline spring water may discriminate mine versus natural sources of Hg. The Hg in drainage from the mine area is primarily particulate, including cinnabar, metacinnabar, and Hg(II) that is loosely bound to particles and subject to carbonate-mediated release and sequestration. While Hg_F is always less than Hg_T because of transport of cinnabar, metacinnabar, and colloidal Hg(II)-mineral sorption complexes, the correlation of Hg_F to Hg_T (fig. 8) suggests that hydrological processes that release colloids also partially dissolve sorbents and carbonate cement in the stream channels.

The majority of Hg in Bear Valley ground water is dissolved and/or colloidal. Dissolved organic matter (DOM) may help solvate Hg (for example, by inhibiting precipitation of Hg or carbonate-cementation of Hg-bearing particles). Despite having less dissolved Hg compared to surface water, the shallow subsurface may more efficiently produce MMHg. Biogeochemical conditions in the near subsurface were more conducive to Hg(II) methylation than in surface water environments. Sulfate-reducing microorganisms present in the subsurface resulted in the net production of MMHg. Although sulfide formed in the subsurface may sequester a fraction of Hg(II) as $HgS_{(s),}$ dissolution of $HgS_{(s)}$ by DOM may provide a persistent source of dissolved Hg(II) to methylating microorganisms. Elevated MMHg concentrations in shallow subsurface pore water at the north- and south-end wetlands of the Bear Fault suggest that these areas could be a source of MMHg to Bear Creek.

Subsurface flow, seepage, and runoff of ground water throughout Bear Valley are expected to strongly influence the aqueous carbonate and organic chemistry of Bear Creek. Aside from Hg transported through Bear Creek, carbonate and DOC likely transport more conservatively than Hg and so may affect biogeochemical transformations of Hg in larger Cache Creek tributaries (for example, Sulphur Creek). The importance of the Bear Valley system to the Cache Creek basin may be based on DOC and carbonate rather than just the Hg transported from it.

4.2 Predicting the efficacy of a removal of Rathburn and Petray Mine waste

The implication of the EE/CA currently being undertaken by the BLM is that Hg-contaminated mine waste would be removed or immobilized on-site at the Rathburn and Petray Mines. If such actions would eliminate any future release of Hg from the mine sites, it is necessary to predict the transport of Hg from contaminated sediment in Bear Creek tributaries, primarily tributaries 1 and 3 (due to past mine release) and from ground water discharge along the Bear Fault. This highly complex system is not likely to be amenable to Hg transport modeling, given limited resources and the technical capabilities required. Therefore, to what qualitative or semi-quantitative extent can Hg transport be predicted?

Predictive capability depends on achieving an understanding of Hg concentrations and phase distribution and perhaps further understanding of the chemical speciation in the Bear Valley system. Two distinct, end-member sources; namely, meteoric water and saline connate ground water, contribute to the chemistry of springs and surface waters. The springs have a larger component of saline ground water: a carbonate spring in the central part of the Bear Fault has the highest component of this source. All the surface waters are predominantly meteoric with a significant component of saline ground water being present only in Tributary 1 because of the presence of effluent from saline springs. The proportions of each end member contributing to the flow in Bear Creek can be estimated under a suitable range of climatic and hydrological conditions using geochemical parameters that are conservative. However Hg is non-conservative and dependent on several chemical and physical processes.

Because of the multiple sources of mercury and the complexity of the drainage basin between the Rathburn and Petray Mine areas and Bear Creek, establishing a post-remediation sampling protocol to document the effects of the remediation of the mines will be challenging. This study provides data and considerations that establish a scientific framework to develop a conceptual model that supports a rigorous future investigation of Hg transport post remediation. Further studies are also needed to determine processes that control Hg release and methylation in the Bear Creek drainage basin.

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6. References

Aiken, G.R., 1992, Chloride interference in the analysis of dissolved organic carbon by the wet oxidation method: Environmental Science & Technology, v. 26, p. 2435-2439.

Benoit, J.M., Mason, R.P., Gilmour, C.C., and Aiken, G.R., 2001, Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades: Geochimica et Cosmochimica Acta, v. 65, no. 24, p. 4445-4451.

Bloom, N.S., 2001, Solid Phase Hg speciation and incubation studies in or related to mine-site runoff in the Cache Creek Watershed (CA): California Bay Delta Authority, 37 p.

Bloom, N.S., Coleman, J.A., and Barber, L., 1997, Artifact formation of methyl mercury during extraction of environmental samples by distillation: Fresenius Journal of Analytical Chemistry v. 358, p. 371-377.

Bloom, N.S., Preus, E., Katon, J., and Hiltner, M., 2003, Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils: Anal. Chim. Acta, v. 479, no. 2, p. 233-248.

Brandon, N.P., Francis, P.A., Jeffrey, J., Kelsall, G.H., and Yin, Q., 2001, Thermodynamics and electrochemical behaviour of Hg-S-Cl-H_2O systems: Journal of Electroanalytical Chemistry v. 497, no. 1-2, p. 18-32.

Churchill, R., and Clinkenbeard, J., 2002, Assessment of the feasibility of remediation of mercury mine sources in the Cache Creek Watershed: California Department of Conservation.

Cooke, J., and Morris, P., 2005, Amendments to the water quality control plan for the Sacramento River and San Joaquin River Basins for the control of mercury in Cache Creek, Bear Creek, Sulphur Creek, and Harley Gulch staff report: Regional Water Quality Control Board Central Valley Region, 114 p.

Crock, J.G., 1996, Mercury, *in* Sparks, D.L., ed., Methods of soil analysis; part 3, Chemical methods: Madison, WI, Soil Science Society of America, p. 769-791.

Domagalski, J.L., Alpers, C.N., Slotton, D.G., Suchanek, T.H., and Ayers, S.M., 2004a, Mercury and methylmercury concentrations and loads in the Cache Creek Watershed, California, January 2000 through May 2001: California Bay Delta Authority, 71 p.

Domagalski, J.L., Slotton, D.G., Alpers, C.N., Suchanek, T.H., Churchill, R., Bloom, N.S., Ayers, S.M., and Clinkenbeard, J., 2004b, Summary and synthesis of mercury studies in the Cache Creek Watershed, California, 2000-01: U.S. Geological Survey Water Resources Investigations Report 03-4335.

Drott, A., Lambertsson, L., Bjorn, E., and Skyllberg, 2007, Importance of dissolved neutral mercury sulfides for methyl mercury production in contaminated sediments: Environmental Science & Technology, v. 41, no. 7, p. 2270-2276.

Fernandez-Martinez, R., and Rucandio, M.I., 2005, Study of the suitability of HNO_3 and HCl as extracting agents of mercury species in soils from cinnabar mines: Analytical and Bioanalytical Chemistry, v. 381, no. 8, p. 1499-1506.

Fishman, M.J., and Friedman, L.C., 1989, Ion chromatography, methods for determination of inorganic substances in water and fluvial Sediments: U.S. Geological Survey Techniques of Water Resources Investigations 5A1, p. 38-43 (http://pubs.usgs.gov/twri/twri5-a1/pdf/twri_5-A1_b.pdf).

Gibson, G.R., 1990, Physiology and ecology of the sulphate-reducing bacteria: Journal of Applied Bacteriology v. 69, p. 769-797.

Hepler, L.G., and Olofsson, G., 1975, Mercury; thermodynamic properties, chemical-equilibria, and standard potentials: Chemical Reviews v. 75, no. 5, p. 585-602.

Horvat, M., Bloom, N.S., and Liang, L., 1993a, A comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples; Part 2, Water: Analytica Chimica Acta, v. 282, no. 1, p. 153-168.

Horvat, M., Bloom, N.S., and Liang, L., 1993b, Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples; Part 1, Sediments: Analytica Chimica Acta, v. 281, no. 1, p. 135-152.

Jay, J.A., Morel, F.M.M., and Hemond, H.F., 2000, Mercury speciation in the presence of polysulfides: Environmental Science & Technology, v. 34, no. 11, p. 2196-2200.

Lowry, G.V., Shaw, S., Kim, C.S., Rytuba, J.J., and Brown, G.E., Jr., 2004, Particle-facilitated mercury transport from New Idria and Sulphur Bank mercury mine tailings: Column experiments and macroscopic, microscopic and spectroscopic analysis: Environmental Science & Technology, v. 38, no. 19, p. 5101-5111.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., and Andersen, D.T., 2001, Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity: Limnology and Oceanography, v. 46, no. 1, p. 38-48.

Myneni, S.C.B., Brown, J. T., Martinez, G. A., and Meyer-Ilse, W., 1999, Imaging of humic substance macromolecular structures in water and soils: Science, v. 286, p. 1335.

O'Leary, R.M., Hageman, P.L., and Crock, J.G., 1996, Determination of mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic absorption spectrophotometry, *in* Arbogast, B.F., ed., Analytical methods for the Mineral Resource Surveys Program: Denver, U.S. Geological Survey Open File Report 96-525, p. 42-55.

Paquette, K.E., and Helz, G.R., 1997, Inorganic speciation of mercury in sulfidic waters; The importance of zero-valent sulfur: Environmental Science & Technology, v. 31, no. 7, p. 2148-2153.

Poulton, S.W., Krom, M., and Raiswell, R., 2004, A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide: Geochimica et Cosmochimica Acta, v. 68, no. 18, p. 3703-3715.

Qian, J., Skyllberg, U., Frech, W., Bleam, W.F., Bloom, P.R., and Petit, P.E., 2002, Bonding of methyl mercury to reduced sulfur groups in soil and stream organic matter as determined by X-ray absorption spectroscopy and binding affinity studies: Geochimica et Cosmochimica Acta, v. 66, no. 22, p. 3873-3885.

Rabus, R., Hansen, T.A., and Widdel, F., 2006, Dissimilatory sulfate- and sulfur-reducing Prokaryotes, *in* Dworkin, M., Falkow, S., Rosenberg, E., Schleifer, K., and Stackebrandt, E., eds., The Prokaryotes; (3rd ed.): New York, Springer, p. 659-768.

Ravichandran, M., Aiken, G.R., Reddy, M.M., and Ryan, J.N., 1998, Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades: Environmental Science & Technology, v. 32, no. 21, p. 3305-3311.

Ravichandran, M., Aiken, G.R., Ryan, J.N., and Reddy, M.M., 1999, Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades: Environmental Science & Technology, v. 33, no. 9, p. 1418-1423.

Rounds, S.A., 2006, Alkalinity and acid neutralizing capacity, *in* Wilde, F.D., ed., National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations: available online at, U.S. Geological Survey Techniques of Water Resources Investigations 9A, Chapter 6.6, http://pubs.water.usgs.gov/twri9A.

Sladek, C., and Gustin, M.S., 2003, Evaluation of sequential and selective extraction methods for determination of mercury speciation and mobility in mine waste: Applied Geochemistry, v. 18, no. 4, p. 567-576.

Slotton, D.G., Ayers, S.M., Suchanek, T.H., Weyand, R.D., and Liston, A.M., 2004, Mercury bioaccumulation and trophic transfer in the Cache Creek Watershed of California in relation to diverse aqueous mercury exposure conditions: California Bay Delta Authority, 74 p.

Slowey, A.J., and Brown Jr., G.E., 2007, Transformations of mercury, iron, and sulfur during the reductive dissolution of iron oxyhydroxide by sulfide: Geochimica et Cosmochimica Acta, v. 71, no. 4, p. 877-894.

Slowey, A.J., Rytuba, J.J., and Brown, G.E., Jr., 2005, Speciation of mercury and mode of transport from placer gold mine tailings: Environmental Science & Technology, v. 39, p. 1547-1554.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry; Chemical equilibria and rates in natural waters. (3rd ed.): New York, Wiley-Intersciences.

Teske, A., and Nelson, D.C., 2006, The genera *Beggiatoa* and *Thioploca*, *in* Dworkin, M., Falkow, S., Rosenberg, E., Schleifer, K., and Stackebrandt, E., eds., The Prokaryotes (3rd ed.): New York, Springer, p. 784-810.

Thamdrup, B., Fossing, H., and Jorgensen, B.B., 1994, Manganese, iron, and sulfur cycling in a coastal marine seidment, Aarhus Bay, Denmark: Geochimica et Cosmochimica Acta, v. 58, no. 23, p. 5115-5129.

Waples, J., Nagy, K.L., Aiken, G.R., and Ryan, J.N., 2005, Dissolution of cinnabar (HgS) in the presence of natural organic matter: Geochimica Et Cosmochimica Acta, v. 69, no. 6, p. 1575-1588.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K., 2003, Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon: Environmental Science & Technology, v. 37, no. 20, p. 4702-4708.

Appendix 1. Photographs

Figure 10. Petray Mine, May 2005 (denoted as photo 10 in fig. 2).

Figure 11. Near location M, looking eastward toward Bear Valley, May 2005 (denoted as photo 11 in fig. 2).

Figure 12. Location M, May 2005 (denoted as photo 12 in fig. 2).

Figure 13. South fork of tributary 1, May 2005 (denoted as photo 13 in fig. 2).

Figure 14. Algal biomass in Dead Shot Creek, May 2005 (denoted as photo 14 in fig. 2).

Figure 15. Cinnabar ore in alterred serpentine at the Petray Mine, May 2005.

Figure 16. Alterred serpentine at the Rathburn Mine (a), ppen pit at the Petray Mine (b), Petray fault zone (c), north Pit at the Petray Mine (d), waste rock at the Rathburn Mine (e), alterred serpentine at the Petay Mine (f), silica-carbonate veins at the Petray Mine (g), and terraced topography at the Petray Mine (h). (taken May 2005).

Figure 17. Travertine along tributary 1, December 2004.

Figure 18. Travertine “falls” along tributary 1, December 2004.

Figure 19. Ground-level view of vegetated land along fault zone depicted in figure 2, December 2006.

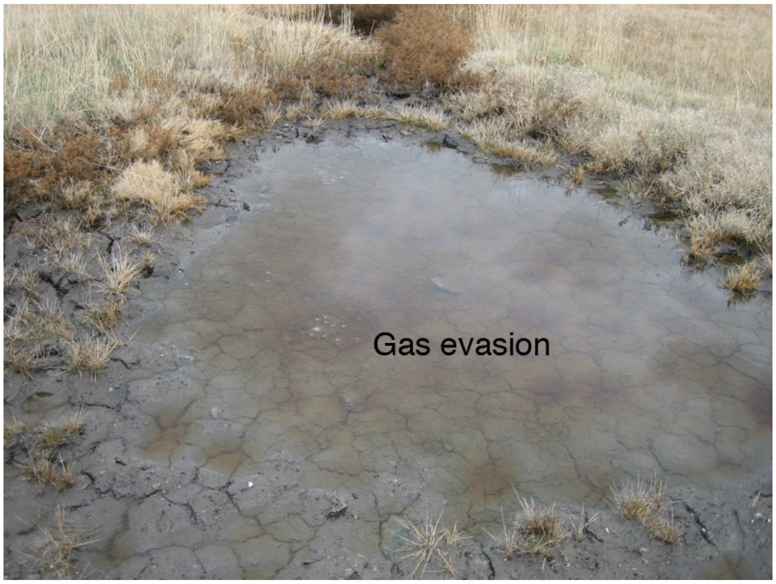

Figure 20. Large seep of connate ground water, including evolving gas (presumably CO_2, based on its lack of any detectable odor), December 2006.

Figure 21. Unsaturated carbonate-rich mud and grass coated with efflorescent salt, December 2006.

Figure 22. Carbonate and iron-rich ground water seepage. Note also faint regions of green material and the nonuniformity of iron (orange) and green coloration, December 2006.

Figure 23. Tributary 1 on December 13, 2006 at dusk (photo levels enhanced). Note white mineral coating along stream channel.

Figure 24. Ground water seepage and resulting drainage channel. Shiny object is an aluminum foil-covered pore water sampling device, December 2006.