Mercury contamination from mine and natural sources in Harley Gulch, downstream from the Abbott and Turkey Run Mercury Mines, Lake County, California

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INTRODUCTION

The Abbott and Turkey Run Mercury (Hg) mines in central California have released Hg tailings into the Harley Gulch watershed since 1862. Harley Gulch flows into Cache Creek, which is a significant source of Hg into the San Francisco Bay Delta. Despite remediation efforts, Hg tailings and enriched sediment remain in the Harley Gulch wetlands and in the stream downstream from the mine area. Water, sediment, and biota were sampled from below the mine area to the confluence with Cache Creek to assess the impact of Hg on water quality and biota.

STUDY SITES

METHODS

Sediments

- Wet-sediment samples were collected and analyzed for total mercury (Hg_T) and monomethyl Hg (MMeHg) by cold vapor atomic absorption spectroscopy (CVAAS), major elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and minor elements by inductively coupled plasma mass spectroscopy (ICP–MS).

Water

- Filtered and unfiltered stream-water samples collected with a peristaltic pump.
- Anions were analyzed by ion chromatography, alkalinity by titration, and major and minor elements using ICP-AES and ICP-MS.
- pH, conductivity, temperature, dissolved oxygen, and oxidation-reduction potential were measured using a Hydrolab sonde.

Invertebrates

- Samples were analyzed for Hg_T and MMeHg using cold vapor atomic fluorescence spectroscopy (CVAFS).
- Samples collected using dip nets:
  - Larval dragonflies (Order Odonata, families Libellulidae and Aeshnidae)
  - Adult water striders (Order Hemiptera, family Gerridae)
  - Adult giant water bugs (Order Hemiptera, family Belostomatidae)
  - Larval water scavenger beetles and adult predaceous diving beetles (Order Coleoptera, families Hydrophilidae and Dytiscidae)
  - Larval damselflies (Order Odonata, families Coenagrionidae and Lestidae)
  - Larval dobsonflies (Order Megaloptera, family Corydalidae).

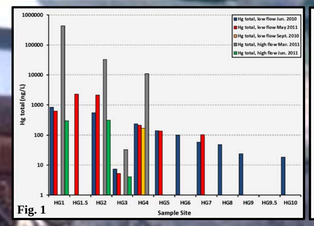
Frogs

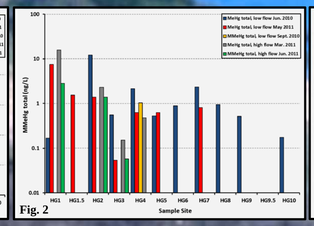
- Adult foothill yellow-legged frogs (*Rana boylii*) collected with dip net in 2007-08; compared with reference samples collected in 1997-98.
- Samples were analyzed for Hg_T and MMeHg using CVAFS.

QA/QC

- Duplicate samples, procedural blanks, spiked samples, and certified reference materials were analyzed to assess the accuracy and precision of the analyses.

RESULTS





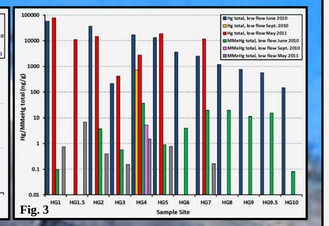


Figure 1. Extremely high Hg_T levels in water (429,000 ng/L) were observed under high-flow conditions at site HG1, located immediately downstream from the mine area. Elevated levels of Hg_T in waters downstream from site HG4 (to site HG7) correlate with input of saline connate ground water naturally enriched in Hg. Hg_T concentrations in waters are lower under low-flow conditions, but still significantly elevated compared to local background concentrations. Hg_T levels decrease systematically downstream, but remain slightly elevated.

Figure 2. MMeHg in water is elevated under all flow conditions compared with the reference site (HG3). During low flows, the highest MMeHg occurred between sites HG4 and HG8 where biogenic sediments occur.

Figure 3. Hg_T in sediment is highest near the mine area (HG1) and decreases downstream to site HG10. MMeHg is lowest near HG1, but increases in and just downstream from the Harley Gulch wetlands. The highest MMeHg occurs in biogenic sediments where saline connate ground water predominates during low flow conditions (HG4-HG9.5).

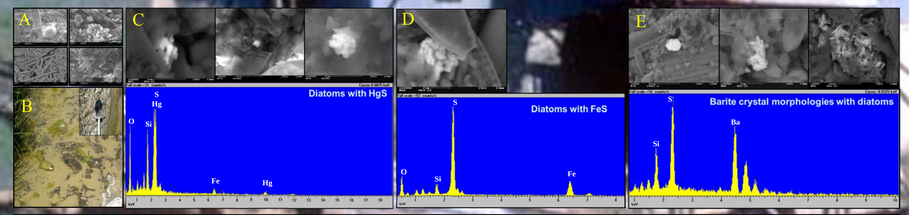


Figure 4. Biogenic sediment is a natural source of Hg contamination to Harley Gulch. During the dry season, diatoms (A) accumulate in the stream. Biogenic sediment consists of a 1-2-cm layer of living diatoms that form a light tan layer on the surface and a black 10-cm-layer of dead diatoms below the surface (B). The black reduced biogenic sediment contains HgS (C), FeS (D), Barite (E), W, and Ti phases. Because diatoms bioaccumulate mercury, this layer has high concentrations of Hg_T (1–16 µg/g) and MMeHg (up to 36 ng/g). Evaporation leads to high concentrations of Ba, Mg, and sulfate that results in precipitation of barite, magnesite, and $CaCO_3$.

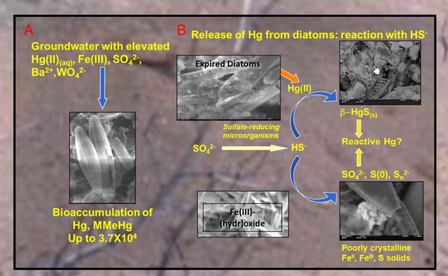


Figure 5. The conceptual model for Hg enrichment in biogenic sediment: In the initial stage (A), diatoms bioaccumulate Hg and MMeHg from saline waters with elevated Hg concentrations. (B) Dead diatoms in the reduced layer release Hg into pore waters, which reacts with sulfide, produced by sulfate-reducing bacteria, to form HgS. Fe in the pore fluids reacts with the sulfide to precipitate FeS.

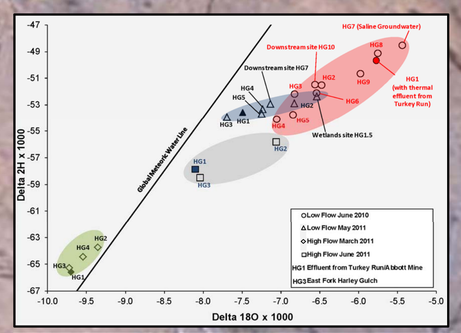


Figure 6. Isotopic data for oxygen-18 and deuterium indicate the presence of three distinct waters in Harley Gulch, with the composition varying seasonally. During winter high flows, water is predominantly meteoric. During low flows, stream waters are a mixture of meteoric and isotopically heavy saline ground water. Thermal water from Turkey Run mine (red dot) is a major contributor only at HG1, immediately downstream from the mine.

Preliminary Data – Not for citation

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

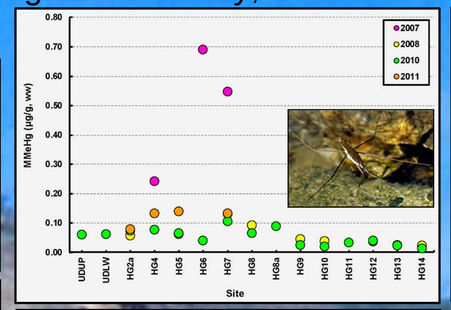


Figure 7. Concentrations of MMeHg in water striders (Gerridae) from Harley Gulch, 2007-08 and 2010-11.

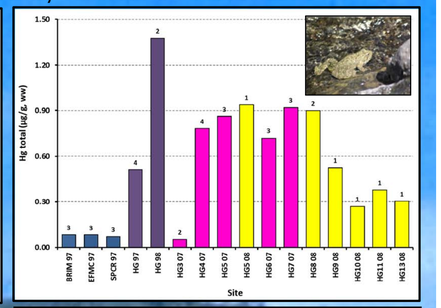


Figure 8. Concentrations of Hg_T in foothill yellow-legged frogs from Harley Gulch before (1997-98 in purple) and after (2007 [pink]-2008 [yellow]) remediation of Hg mines. Blue bars are reference sites in 1997. HG3 is reference in 2007.

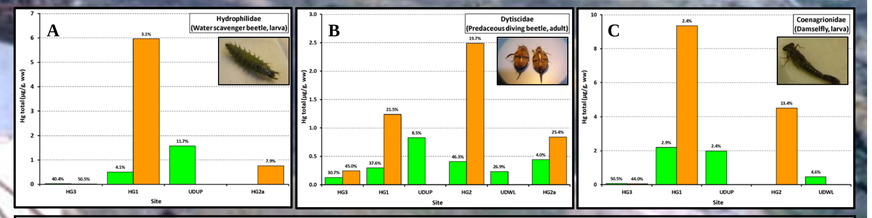


Figure 9. Hg_T and percent MMeHg in composite samples of larval Hydrophilidae (A), adult Dytiscidae (B), and larval Coenagrionidae (C) from Harley Gulch wetland sites and a reference (HG3) in 2010 (green) and 2011 (orange).

CONCLUSIONS

1. Connate groundwater is a previously unrecognized natural source of elevated levels of Hg in the Harley Gulch Watershed (Fig. 1). It first enters Harley Gulch in the central part of the wetland and continues to contribute water downstream for about 1.5 km.
2. Biogenic sediment, composed of living and dead diatoms, is a second natural source of elevated Hg_T and MMeHg (Fig. 4-5). This sediment is transported downstream during high flows. Bioaccumulation factors for diatoms are high for both Hg_T and MMeHg, resulting in high concentrations of Hg_T (1.8-29.8 µg/g) and MMeHg (1.4-7.3 ng/g).
3. In composites of aquatic invertebrates from the Harley Gulch wetland, the percentage MMeHg was low in most samples, concentrations of MMeHg (113 –604 ng/g, wet mass) were moderate, and Hg_T concentrations were extremely high (1,240 – 9,940 ng/g) (Fig. 9).
4. Concentrations of both MMeHg and Hg_T were lower in invertebrates from downstream sites compared with the wetlands and the area where connate groundwater enters the stream. Concentrations of both Hg_T and MMeHg in water and sediment were also lower at the downstream sites (Fig. 1-3). Concentrations of Hg_T and MMeHg in biota from the reference site (HG3) were lower than all other sites in Harley Gulch.
5. Compared with data collected before the remediation of the Hg mines, concentrations of Hg_T and MMeHg in invertebrates were generally lower following remediation (Fig. 7). However, Hg_T concentrations remained substantially elevated in 2011 compared to the reference site (HG3) and other sites in Northern California unaffected by historical Hg mining.
6. Concentrations of Hg_T in foothill yellow-legged frogs were lower in samples collected after the 2006 mine remediation than in those collected prior to the remediation (1997-98) (Fig. 8). Hg_T concentrations in frogs declined with distance from the mines, but concentrations of Hg_T and MMeHg remained elevated in frogs collected in 2007 and 2008, especially from upper Harley Gulch.
7. Data from 2010 and 2011 documented that during high flows, waters with elevated concentrations of particulate Hg continue to be released from the remediated mine area. These high flows deposit sediment with elevated concentrations of Hg_T in the wetland area and in broad areas of the stream channel, as compared to background samples (Fig. 1-3).

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