TRANSPORT AND DEPOSITION OF MERCURY FROM MINE DRAINAGE AND TAILINGS IN WATERSHEDS WITH SERPENTINITE BEDROCK, NEW IDRIA, CALIFORNIA

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ABSTRACT

The New Idria mercury district, California, is the second largest producer of mercury in North America, and release of mercury and associated metals from mine drainage and tailings impact water quality in the district. Mercury phases in mine tailings consist of soluble mercury phases; mercuric oxide and corderoite; and less soluble phases: metacinnabar and cinnabar. The mercury deposits are within and adjacent to a large serpentinite body. Natural drainage waters from the serpentinite body are highly alkaline, with high concentrations of Mg and HCO_3^-. During low flow, mercury content is highest, up to 36 ng/L, in unfiltered stream waters; particulate mercury accounts for 70-90 % of total mercury transported in streams impacted by mine tailings. Methylmercury in unfiltered samples is less than 0.2 ng/L and constitutes less than 1% of total mercury concentration. Mercury levels return to background concentrations within one km of the tailings because precipitation of Mg carbonate sequesters mercury-enriched particles in the bed load of the stream. Where mine effluent is released into streams, total mercury concentration can be up to 13 μg/L; particulate mercury accounts for 65-99% of total mercury transported in streams impacted by mine drainage. Methylmercury concentration is high, up to 4.5 ng/L. Both mercury and methyl mercury are adsorbed onto iron oxy-hydroxide and clay particles, but the concentration of both mercury species in stream waters remains above background concentrations for more than 10 km from the mine site. In watersheds dominated by serpentinite bedrock, mercury transport from mine areas is mitigated by precipitation of carbonate minerals. Where streams are also impacted by acid mine drainage, alkalinity is depleted and carbonate precipitation is insufficient to sequester mercury resulting in an increase in the mobility of mercury.

INTRODUCTION

The New Idria mercury district is located in the central part of the California Coast Range mercury mineral belt and is the second largest producer of mercury in the United States, having produced over 500,000 flasks. Mining began in the district in the early 1800's and continued until the closing of the New Idria mine, the largest mine in the district, in the 1970's. The mercury deposits are located adjacent to and within a large oval body of serpentinite, emplaced into the Cretaceous sedimentary rocks of the Panoche Formation and rocks of the Franciscan complex (Eckel and Myers, 1946). The mercury deposits are localized in serpentinite that has been altered to a silica-carbonate alteration assemblage, and in adjacent argillically altered sedimentary rocks. Release of mercury from mine drainage and tailings from many of the mines in the district poses a water quality concern. The U. S. Bureau of Land Management is presently evaluating several mines for possible remediation. This paper presents the results of geochemical studies to characterize mine tailings and establish pre-remediation baseline concentrations of mercury and associated elements in watersheds impacted by mercury mine sites.

METHODS

Samples were collected to characterize mine wastes and establish baseline stream water quality adjacent to mercury mine areas and from each of the rock compositions in the area. Water samples were collected during

July and October 1997, and May 1999, after runoff had occurred but prior to the streams reaching base flow. Temperature, pH, and conductivity were measured at the site. An unacidified sample was filtered for anion analyses and an unfiltered, unacidified sample was collected for alkalinity measurement. The samples were stored in an ice chest and refrigerated until analyzed. Cations were analyzed by inductively coupled plasma - atomic emission spectromentry or inductively coupled plasma - mass spectromentry. Duplicate water samples, blank samples, and standard reference waters were analyzed with each data set. Sampling for mercury analysis followed ultra-clean sampling and handling protocols (Bloom, 1995) during the field collection and analysis. Borosilicate I-CHEM^{TM} glass with teflon-lined caps were used for water sampling. Mercury analytical procedures were carried out by Frontier Geosciences, and USGS laboratories. USGS analyses followed methods by Crock (1996). Primary standards were NIST certified. EPA Method 1631 was used. Total mercury was determined by BrCl oxidation, SnCl2 reduction, and dual gold amalgamation. Mercury analysis was performed using cold vapor atomic fluorescence CVAF (Bloom et al., 1989). Monomethyl mercury was liberated from water through distillation using an all teflon distillation system (Horvat et al., 1993). Distilled samples were analyzed using aqueous phase ethylation purging onto Carbotrap, isothermal gas chromatography separation, and CVAF (Bloom, 1989).

RESULTS AND DISCUSSION

Mine wastes are the major source of dissolved and particulate mercury that is released from mine sites in the New Idria district. The release of mercury is enhanced by interaction of mine drainage with mine wastes at the New Idria mine (Rytuba, 2000), and by the interaction of mercury enriched spring water (784 ng/L) with mine wastes at the Aurora mine. Mine wastes listed in increasing content of mercury consist of waste rock (1-200 ppm), mine furnace tailings (20-300 ppm) low grade ore (500-1000 ppm) and condenser soot (1100-11000 ppm). Mine wastes were typically placed in a drainage adjacent to the mine so that stream erosion would remove the material and continue to provide space for the mine tailings. Soils in the mine areas have become enriched in particulate and elemental mercury released during roasting of the ores and are an additional source of mercury from mine sites. Mercury content in surface soils is as high as 50 ppm and decreases to background levels at a depth of about 0.5 meters. The speciation of mercury phases present in mine wastes is important in determining the amount of mercury that is released and transported from the mine area. Synchrotron radiation-based X-ray absorption fine structure (XAFS) spectroscopy was used to determine the individual mercury species present (Kim et al., 1999). Mine tailings at the Aurora mine were found to consist of 33% mercuric oxide, 29% metacinnabar, and 18% corderoite, all of which are more soluble (under weathering conditions) than cinnabar which comprises the remaining 20%. Sorbed mercury was determined not to be a significant contributor to the XAFS spectrum of the Aurora mine tailings.

Natural waters evolving within the serpentinite body are highly alkaline with high concentrations of Mg and HCO_3^-. The serpentinite host rocks and carbonate alteration assemblage provide both high alkalinity and pH to stream waters impacted by mine wastes and drainage. Because of the high pH values, which causes metal hydroxides to form, the concentrations of Cu, Zn, Sb, As, Cd, Fe, Mn, and Al are low. An exception where Fe and Al are high, is a segment of San Carlos creek which is impacted by acid mine drainage released from the New Idria mine. During low flow, mercury content is up to 36 ng/L in unfiltered stream waters from the Aurora, Alpine, Archer and Larious Canyon mine sites, indicating that particulate mercury accounts for 70-90 % of total mercury transported in streams impacted by mine tailings (Fig. 1). In contrast, baseline concentrations of mercury in streams from watersheds underlain by serpentinite or sandstone and not impacted by mine wastes have total mercury concentration of less than 3.5 ng/L. In these waters (Fig. 1), mercury is transported primarily as dissolved species. Mercury concentration in groundwater from serpentinite bedrock is very low, 0.8 ng/L except in mineralized areas such as the Aurora mine, where total and dissolved mercury concentrations are up to 876 ng/L and 784 ng/L respectively. Based on modeling of stream waters using PHREEQC (Parkhurst, 1995), dissolved mercury is undersaturated with respect to all mercury phases present in mine tailings including elemental mercury which has the highest solubility under these conditions. Groundwaters from serpentinite bedrock are similarly undersaturated with respect to elemental mercury.

Total methylmercury in unfiltered samples is less than 0.2 ng/L from streams impacted by mine tailings and in baseline samples from watersheds underlain by serpentinite and sandstone (Fig. 2). Methylmercury constitutes less than 1% of total mercury present and there is no measurable difference between baseline streams and streams impacted by mine tailings. Significant methylation does not occur in streams below mine areas where mercury loading comes only from mine tailings. However, in streams impacted by mine drainage that has interacted with mine wastes, such as in San Carlos Creek below the New Idria mine, methylation of mercury occurs in the stream and methylmercury is adsorbed onto iron oxyhydroxide resulting in concentrations of total methylmercury up to 4.5 ng/L (Rytuba, 2000).

Modeling of the stream waters using PHREEQC indicates that the waters are supersaturated (SS) or saturated (S) with respect to magnesite (SS), dolomite (SS), and sepiolite (S), at the Aurora mine area as well as calcite (S) and chalcedony (S) at the Alpine and Archer mine areas. These phases precipitate in the streams and locally cement the bed load. In streams impacted by only mercury mine tailings, precipitation of Mg-Ca phases sequesters mercury-enriched particles in the bed load of the streams causing mercury levels to return to background concentrations within one km of the mine areas. However, where mine drainage is released into streams, total mercury concentration can be high, up to 13 µg/L and particulate mercury accounts for 65-99% of total mercury transported in impacted streams. Methylmercury concentration is high, up to 4.5 ng/L. Both mercury and methylmercury are adsorbed onto iron oxy-hydroxide and aluminum clays, and the concentration of both mercury species remains above baseline concentrations for more than 10 km from the mine site. In streams impacted by acid mine drainage, alkalinity is depleted and carbonate precipitation is insufficient to sequester mercury resulting in more highly impacted streams.

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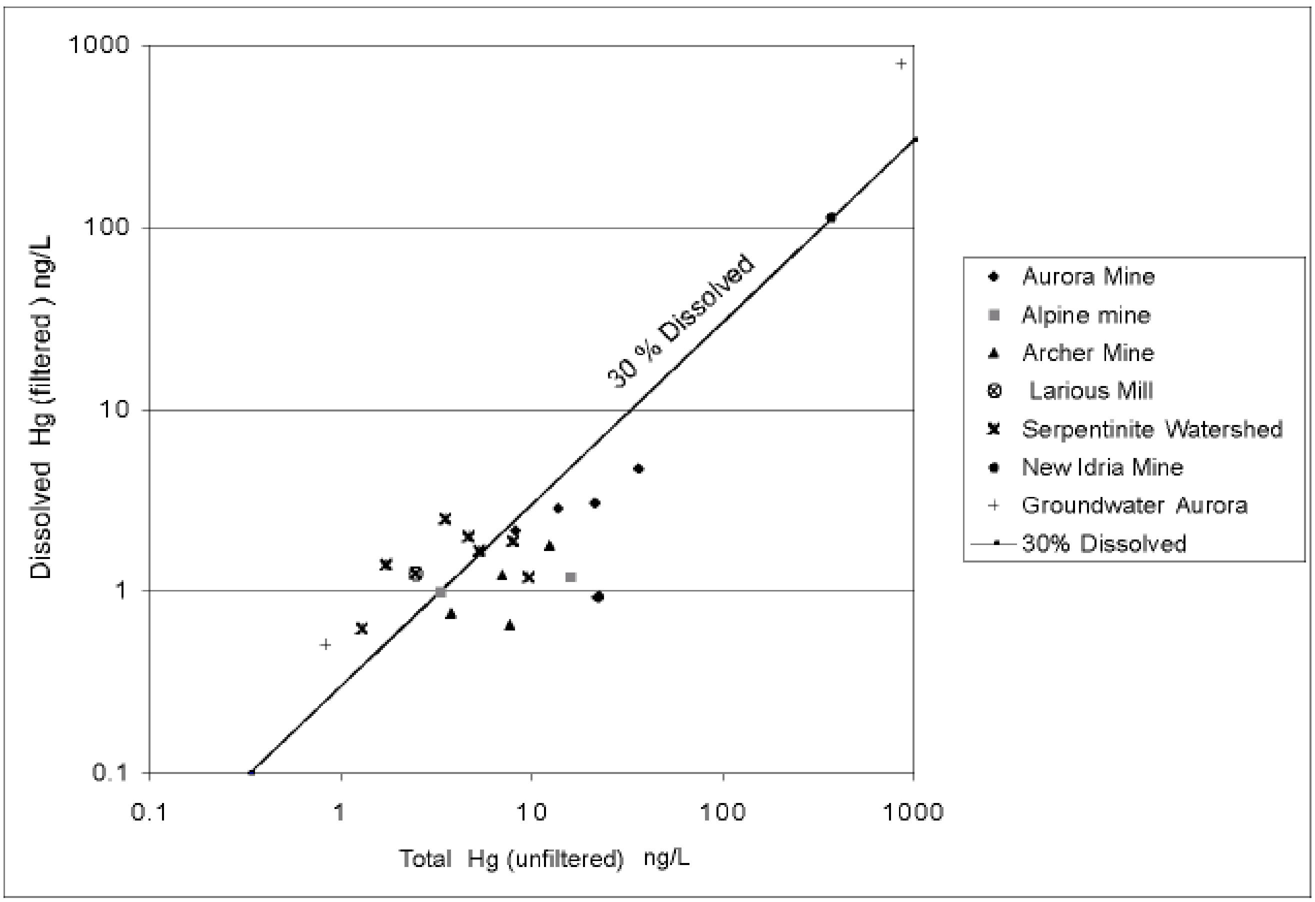

Figure 1 Dissolved mercury concentration (.45 µm filtered) and total mercury concentration in stream and ground waters impacted by mercury mine tailings and baseline samples from watersheds underlain by serpentinite from the New Idria mercury mining district.

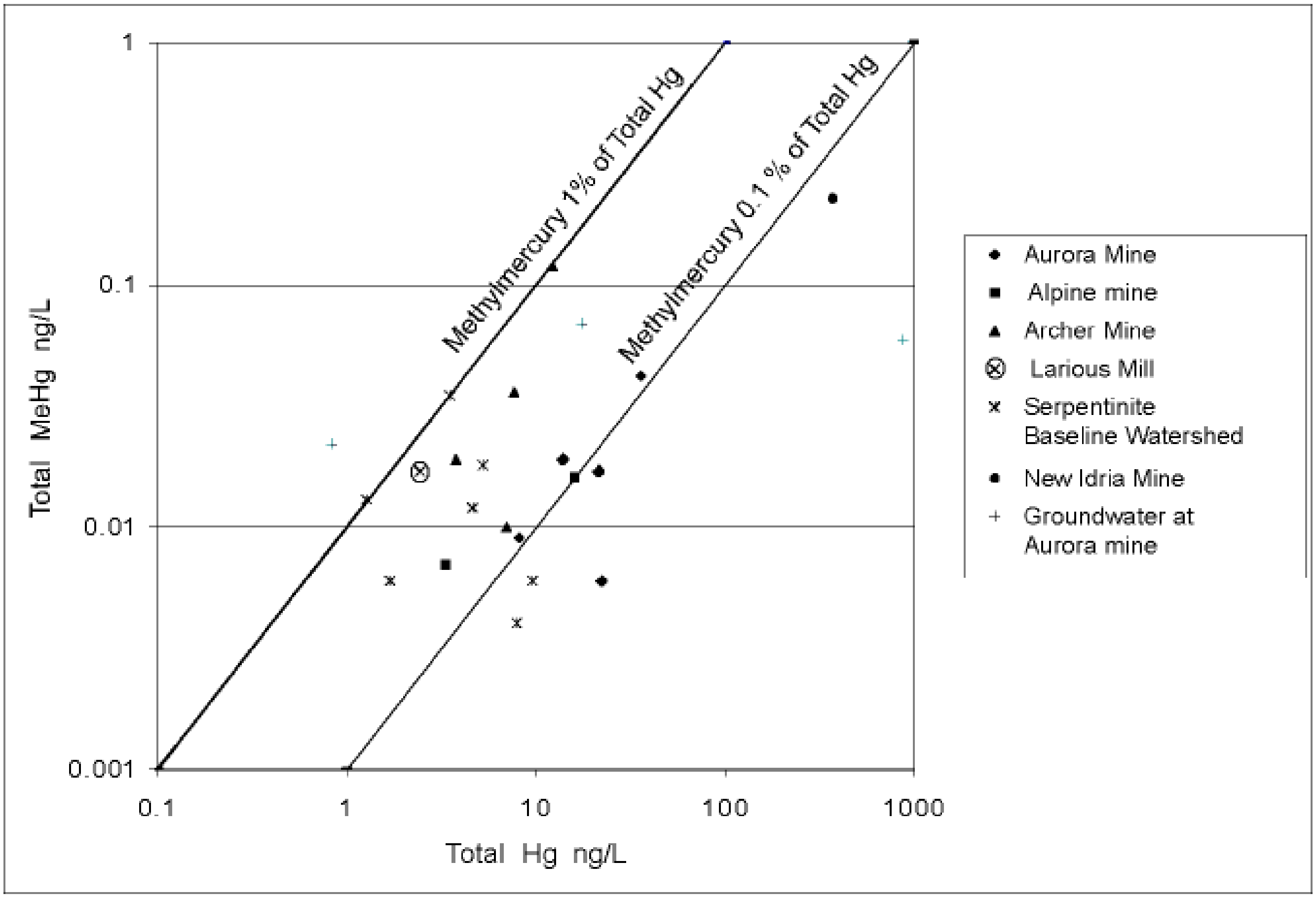

Figure 2 Total methyl mercury concentration and total mercury concentration in stream and ground waters impacted by mercury mine tailings and from baseline watersheds underlain by serpentinite bedrock in the New Idria mercury mining district.