Mass loading of Hg in the Monte Amiata mining district, Southern Tuscany (Italy)

V. Rimondi[1], P. Costagliola[1], J. E. Gray[2], P. Lattanzi[3], M. Nannucci[4], A. Salvadori[4] and O. Vaselli[1,5]

[1] Dipartimento di Scienze della Terra, Università di Firenze, Via G. La Pira 4, 50121 Firenze, ITALY, valentina.rimondi@unifi.it; pilario.costagliola@unifi.it; orlando.vaselli@unifi.it
[2] U.S. Geological Survey, MS 973, Federal Center, Denver, CO 80225, USA, jgray@usgs.gov
[3] Dipartimento di Scienze della Terra, Università di Cagliari, Via Trentino 51, 09127 Cagliari, ITALY, lattanzp@unica.it
[4] Regione Toscana, Piazza della Resistenza 54, 5110 Pistoia, ITALY, andrea.salvadori@regione.toscana.it; marco.nannucci@regione.toscana.it
[5] CNR-IGG Istituto di Geoscienze e Georisorse, Via G. La Pira 4, 50121 Firenze, ITALY

Abstract. Mercury (Hg) transport in natural environments is of concern because Hg bioaccumulates in the food web. Particularly methyl-Hg is the form of Hg of major concern as it is highly toxic to humans and is ingested through food consumption, dominantly fish. Quantification of Hg mass loads in watersheds draining Hg mine districts allows (1) the identification of sources of contamination, (2) the evaluation of the effect of Hg on the environment, and (3) the identification of processes affecting Hg transport. This study focuses on the determination of Hg loads in the Paglia River, which drains the Hg district of Monte Amiata (Italy), world's 4th largest Hg producing district. Mass loads were determined for total Hg, particulate Hg, and dissolved Hg. Data obtained from two sampling campaigns carried out in 2011 indicated that up to 34 g/d of Hg were transported during the rainy season, of which up to 99% was as particulate Hg. Maximum Hg loads were related to runoff from the Abbadia San Salvatore mine (ASSM), and thus, this mine is the main source of Hg to the Paglia River basin. Data indicate that particulate Hg has been deposited along with river sediment, forming a natural sink where resultant chemical reactions promote conversion of Hg from particulate matter to dissolved Hg. These results suggest that mining of Hg has affected this area. Even today, 30 years after the cessation of mining, considerable amounts of Hg are continuously transported downstream from mined areas by local rivers.

Key words: mercury, mass loading, particulate matter, Monte Amiata

Introduction

In mining districts, quantification of metal loadings to streams is particularly important, because it offers the opportunity to identify contaminant sources, and to assist in decisions about remediation of contaminated areas. Among metals, Hg is of particular concern in natural environments because methyl-Hg, an organic form of Hg, is a neurotoxin (USEPA, 1997). In Hg mining districts worldwide, large quantities of Hg are transported by streams, mostly as particulate Hg; for example, particulate Hg loads are estimated as high as 1500 kg/y for the Isonzo River (Idrjia Hg mine, Slovenia; Širka et al., 1999), 4-30 kg/y for the Guadalupe River (New Idrija Hg mine, USA; Thomas et al., 2002), and up to 98 kg/y for the Sacramento River (California Coast Ranges mines, USA; Choe et al., 2003). The volcanic edifice of Monte Amiata (Central Italy) hosts the 4th largest Hg producing district (about 102,000 t of Hg) worldwide, which is part in the circum-Mediterranean Hg belt. As a consequence of this widespread natural ("geogenic") Hg anomaly, Mediterranean fish have been reported to contain higher Hg concentrations than fish in the Atlantic Ocean (Horvat et al., 2003). The Mediterranean basin is then an important site to study Hg geochemistry and mass loadings. Mining of Hg has affected the Monte Amiata area, as there has been considerable transport of Hg downstream to the Paglia River (Rimondi et al., 2012), which flows into the Tiber River (Fig. 1), the main river of Central Italy. Furthermore, mine wastes containing significant Hg concentrations were discarded near mined areas and are widespread in the region, representing an additional source of Hg to the environment. Presently, Hg loads discharged by the Tiber River have not been determined. Therefore, the aim of this study was to (1) quantify the mass load of Hg in the Paglia River, and (2)

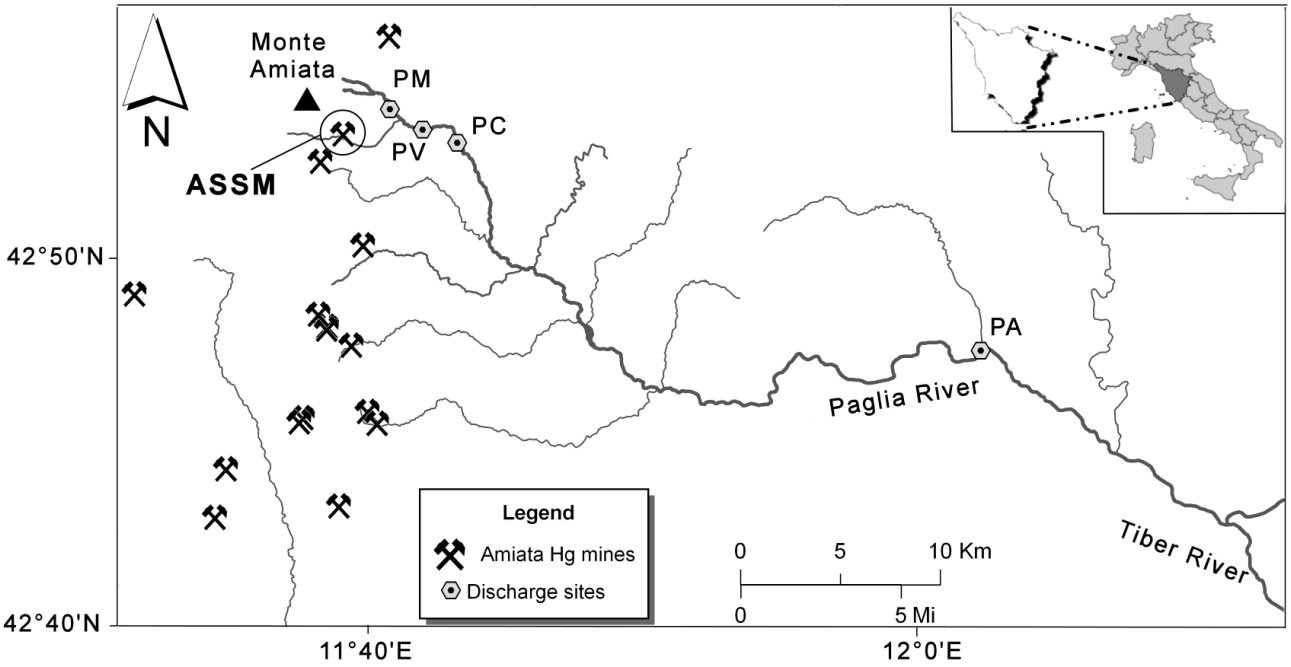

Fig. 1. Location of the Monte Amiata Hg district, Abbadia San Salvatore mine (ASSM) and sites of river discharge measurements; PV, PC, PA (see text for explanation of labels) are located 5, 6 and 35 km downstream from ASSM, respectively.

evaluate downstream transport of Hg and potential contamination of river sediment. Abundant Hg in the Paglia River possibly affects the Tiber River as well as the Hg delivered to the Mediterranean Sea. Mass loadings were determined for both dissolved and particulate Hg in the Paglia River system.

Materials and Methods

The amount of Hg entering a stream is defined as mass loading, and is calculated as the product of Hg concentration and stream discharge measured simultaneously. Combination of stream flow longitudinal profile and spatially related samples of stream chemistry (Hg concentrations) allows the calculation of mass loading profiles. Hg mass loadings were determined in four sites along the Paglia River (Fig. 1): (1) one site upstream ASSM, which is a "background" site for the Amiata region (Pagliola Monte, PM); (2) two sites located just downstream ASSM, in order to quantify the mass loads of runoff from the ASSM (Pagliola Valle, PV, Paglia Casetta, PC); and (3) one at the end of the Hg district (Paglia Allerona, PA), which was collected to account for all Hg runoff from the southeastern part of the Monte Amiata district (Fig. 1). In this study, two sampling campaigns were conducted, one during the rainy season (March 2011), and one in the dry season (September 2011) in order to measure Hg fluxes in these two seasons. Unfiltered and filtered (0.45 μm) water samples were collected in order to determine, respectively, total Hg (THg) and dissolved Hg (DHg) forms. Ultraclean protocols were employed during sampling and sample preservation. Particulate Hg fraction (PHg) was obtained by the difference between total Hg (particulate + dissolved) and total dissolved Hg.

In order to determine metal mass loads, accurate measurements of water discharge are required. Traditional flow measurements are made using flow meters, which can be applied for smooth river beds. Tracer dilution methods (Kimball, 1997) are commonly used for mountain creeks because much of the water flows through the stream cobbles, preventing measurement by a flow meter. In this study, both methods (meter and tracer) were used for PM, PV and PC sites, characterized by stream-like channel bottoms, while at PA the discharge was measured by the Istituto Idrografico Regionale of Umbria using a magnetic flow meter. At this site, the great width of the river prevented the use of the tracer dilution method.

Dilution measurements were made by the injection of a specific tracer (NaCl). Conductivity curves were reconstructed in the field with two electrical conductivity meters for each sample site. Specific calibration constants for each sample site and conductivity measurements were obtained in the laboratory through the analysis of chloride by ion chromatography. Equations based on the mass balance principle were then applied to compute the stream discharge, expressed as the average of the values obtained by the two salt curves.

As no water was found during the September field campaign at site PM, there are no data for this site for the dry season.

Results

Water discharges calculated from tracer dilution are commonly higher than those obtained by flow meter (Kimball, 1997). In this study, differences between these techniques ranged from 12 to 39% with a mean of 25 ± 11%. As discharges calculated by tracer-dilution were considered more reliable in this study, mass loads were calculated using tracer-dilution measurements, and thus, represent the maximum estimated Hg loads in the basin.

Mercury mass loads were calculated for total Hg, dissolved Hg and particulate Hg during the rainy and dry seasons (Fig. 2). In the rainy season, total Hg load reached as much as 34 g/day for site PV, while similar, but lower loads, were found at PC and PA. Hg load at PM was two orders of magnitude lower than at the other sites (Fig. 2). For all sites, Hg fluxes were higher during the rainy season. Considerable differences were observed for sites PM, PC and PA, showing September Hg loads as one to two orders of magnitude lower than during March. In the dry season, the Hg load at PV was comparable (24 g/day), albeit lower, to that of the rainy season (34 g/day). Data indicate that particulate matter Hg load represents the largest part of total Hg flux (Fig. 2), ranging from 67 up to 99% of the total. These data likely indicate that Hg transport was dominantly as Hg attached to suspended particles. Downstream from the ASSM (PV site), transported load of total and particulate Hg decreased with increasing distance from the mine (Fig. 2). Specifically, a considerable decrease in Hg load was found between sites PV and PC, while a more gradual decrease was measured between PC and PA (Fig. 2). Dissolved Hg only accounted for small percentages of the total Hg load (1-33%). The maximum dissolved Hg load was reported for site PA during the rainy season (4 g/day), while dissolved Hg was less than 200 mg/day during the dry season (Fig. 2). Nevertheless, different from the other Hg species, the highest quantities of dissolved Hg were found at PA (4 g/day), the furthest site from ASSM, during the rainy season.

Discussion

Quantification of Hg loadings along Paglia River has shown that a significant amount of Hg is transported by surface water as a result of runoff from ASSM. This finding is supported by elevated Hg loads at site PV, located 5 km downstream from the ASSM, and this mine supplies 100% of the total Hg budget to the basin. Furthermore, a progressive decrease of Hg load was observed with increasing distance from ASSM, suggesting deposition of Hg (total and particulate forms) along the river course. Thus, Hg supply to the Paglia River is mainly a result of past mining activity developed in this area until the end of 1970s, and particularly from the ASSM. Data collected from site PM, located upstream from ASSM, indicates minor Hg runoff and transport from background areas. The load of 0.6 g/day Hg was measured at site PM and is the regional background flux of Hg. The presence of Hg bearing rocks and potentially undiscovered cinnabar deposits leads to high background Hg in the Monte Amiata area.

Significant variations of Hg loads observed between dry and rainy seasons suggest the importance of surface runoff associated with heavy winter rain as the major factor promoting the mobilization of Hg from the ASSM to the Paglia River basin.

Data suggest that (1) Hg-rich sediment is supplied to the Paglia River in the rainy season as a result of runoff from the ASSM, (2) during low water flow in the dry season, this sediment is deposited in the basin and acts as a Hg sink, and (3) Hg is again resupplied and resuspended in the Paglia Basin in the following rainy season. Furthermore, data show that Hg is dominantly transported on suspended particles in the Paglia River, a finding previously reported in other mining districts worldwide (Faganeli et al., 2003). The decrease of total particulate loads between sites PV and PC is likely due to deposition of particulate Hg along this section of the river, which is influenced largely by reduced water flow resulting from the decreased hydrological gradient between these two sites.

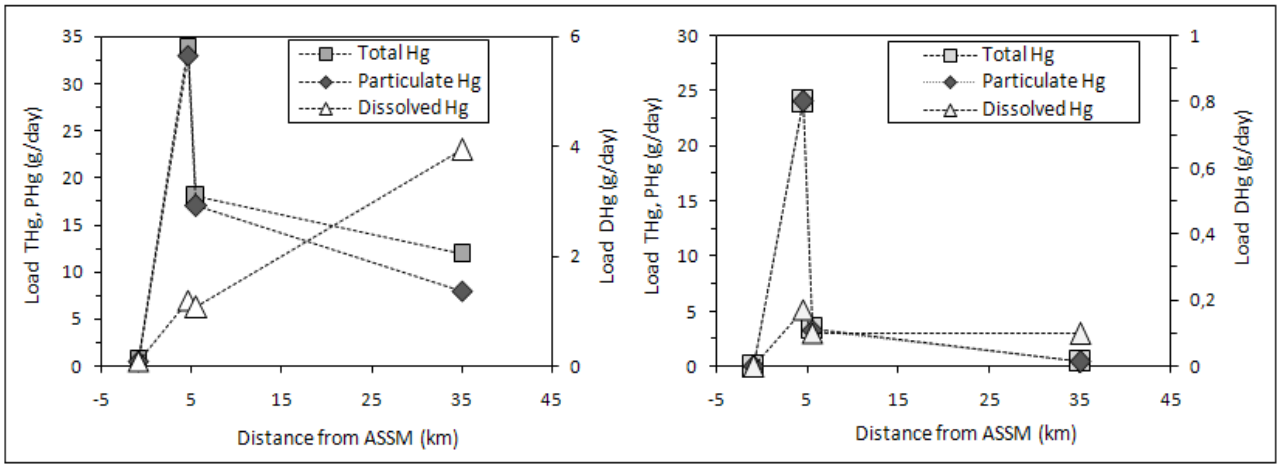

Fig. 2. Hg loads for total, particulate and dissolved Hg during the rainy (left) and dry (right) seasons plotted versus distance from the ASSM.

Deposition of suspended sediment with attached Hg significantly reduces the load of Hg transported downstream from the PV site. River sediment rich in Hg is chemically reactive, and data suggest conversion from particulate Hg to the more mobile dissolved Hg. This conclusion is supported by the higher dissolved Hg load found at site PA. Dissolved Hg species are readily available for methylation reactions, which potentially increases the bioavailability of methyl-Hg in the Paglia River. Accordingly, methyl-Hg has been recently reported in sediment and water of Paglia River (Rimondi et al., 2012), suggesting that this Hg organic compound is actively formed in this ecosystem.

Conclusions

Using tracer injection and water sampling, loads of Hg along the Paglia River were quantified. High loads of Hg are found to be a result of runoff from the ASSM, the most important Hg producing mine in the Monte Amiata district, as Hg load profiles substantially decreased downstream from the mine area. In the Monte Amiata Hg district, elevated Hg loads were found to be associated with particulate Hg even three decades after the end of mining, a finding common to other mining districts worldwide (Faganeli et al., 2003; Gray et al., 2000). Results from this study may be useful for watershed remediation planning in this area. Moreover, the presence of dissolved Hg species in the Paglia River should be monitored by local agencies for environmental protection as they could promote active formation of methyl-Hg.

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References

Choe K-Y, Gill GA, Lehman R. Distribution of particulate, colloidal, and dissolved mercury in San Francisco Bay estuary. 1. Total mercury. Limn Ocean 2003; 48: 1535–1546.

Eaton AD, Clesceri LS, Greenber AE. Standard methods for the Examination of Water and Wastewater, 2540D, 19th Ed. American Public Health Association 1995. Washington, DC.

Faganeli J, Horvat M, Covelli, S, Fajon V, Logar M, Lipej L, Cermelj B. Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). Sci Total Environ 2003; 304 315-326.

Gray JE, Theodorakos PM, Bailey EA, Turner RR. Distribution, speciation, and transport of mercury in stream-sediment, stream-water, and fish collected near abandoned mercury mines in southwestern Alaska, USA. Sci Total Environ 2000; 260:21-33.

Horvat M, Kotnika J, Logara M, Fajona V, Zvonari T, Pirrone N. Speciation of mercuryin surface and deep-sea waters in the Mediterranean Sea. Atm Enviro 2003; 37 Suppl No. 1: S93–S108.

Kimball BA. Tracer Injection & Synoptic Sampling. U.S. Geological Survey Fact Sheet 1997; FS-245-96.

Rimondi V, Gray JE, Costagliola P, Vaselli O, Lattanzi P. Concentration, distribution, and translocation of mercury and methylmercury in mine-waste, sediment, soil, water, and fish collected near the Abbadia San Salvatore mercury mine, Monte Amiata district, Italy. Sci Total Environ 2012; 414:318-327.

Širca A, Horvat M, Rajar R, Covelli S, Žagar D, Faganeli J. Estimation of mercury mass balance in the Gulf of Trieste. Acta Adriatica 1999;40:75-85.

Thomas MA, Conaway CH, Steding DJ, Marvin-Di Pasquale M, Abu-Saba KE, Flegal AR. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. Geochemistry: Expl Env Analysis 2002; 2: 211-217.

USEPA. Mercury study report to Congress. U.S. Environmental Protection Agency 1997. I-VIII, EPA-452/R-97-003.

USEPA. Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. U.S. Environmental Protection Agency 2002. 821-R-02-01.