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Mercury dispersion through streams draining the Mt. Amiata district, southern Tuscany, Italy

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Abstract

The Mt. Amiata area hosts the 3rd largest Hg district in the world, overlapping with a present-day geothermal system that is exploited for energy production. Mining activity ceased in 1980; remediation of mining areas was only partial, and is still under way. A significant transport of mercury is documented in the streams draining the district. By far the largest output occurs to the southeast in the Paglia River catchment; this river is tributary of Tiber River, the largest river of central Italy. A much smaller transport occurs to the north, in the Orcia-Ombrone catchment. Most transport is in particulate form; mercury is temporarily stored in stream and overbank sediments, and can be significantly mobilized and redistributed by extreme events such as flash floods. Transfer to the biosphere and food chain is not negligible, as some fish in Paglia and Tiber Rivers show Hg contents that may be harmful for human consumption. The overall output from the Monte Amiata district represents a significant contribution to the Mediterranean Sea budget of this metal.

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Keywords: mercury; stream transport; Monte Amiata

1. Introduction

Mt. Amiata (Monte Amiata; 1738 m a.s.l.) is the remnant of a Quaternary (ca. 0.3 Ma) volcano that stands out against the hills of southeastern Tuscany, Italy. The region hosts the third largest mercury district of the world, with a cumulate production exceeding 100,000 tonnes[1], as well as an active geothermal field, which is exploited in

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several power plants[2]. The mining district extends for several kilometers to the south of the volcanic centre (Fig. 1a,b); the largest mine was Abbadia San Salvatore (ASSM; n. 2 in Fig. 1b).

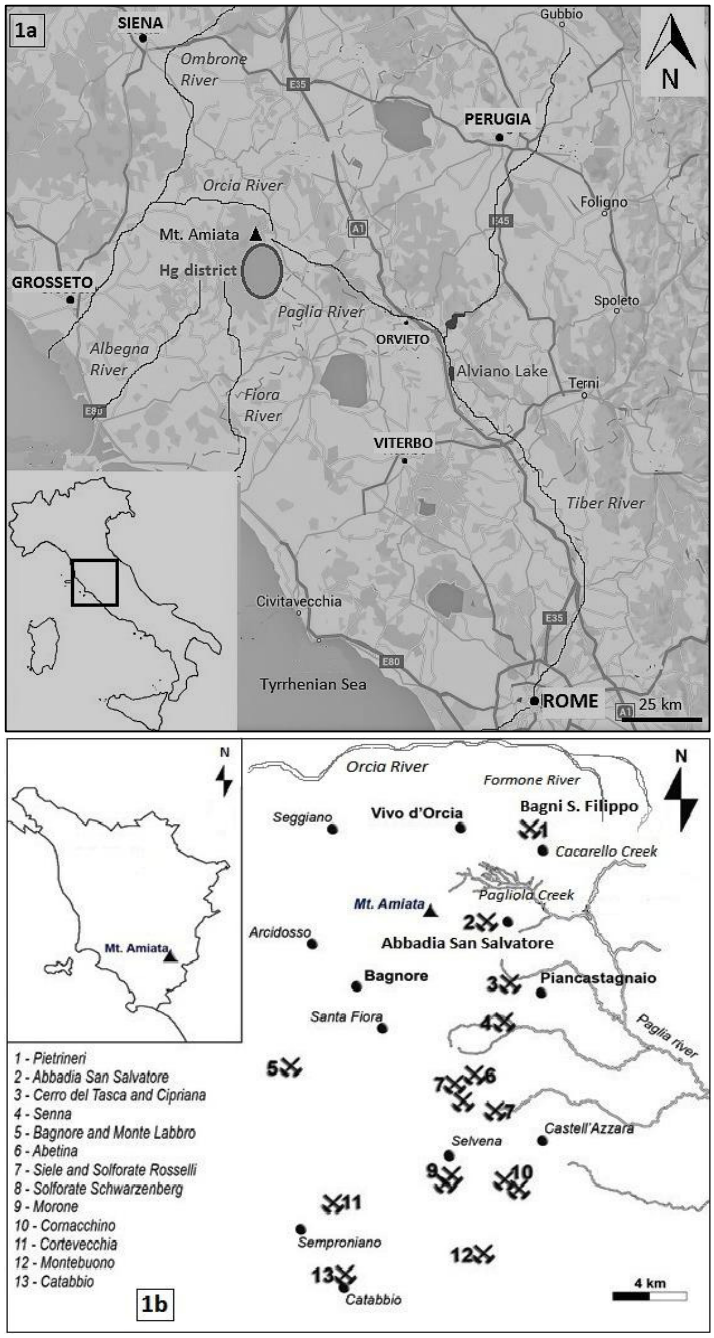

Fig. 1. Maps of the Mt. Amiata mercury district. a) General map showing the principal river basins of the region; b) the Paglia and Orcia river basins, with the mercury mines of the district.

Most mines occur in the drainage basin of the Paglia River, which flows southeastward to join the Tiber River (the largest river of Central Italy) near Orvieto (Fig. 1a). Other rivers that drain the district include Albegna to the southwest, Fiora to the south, and the Orcia-Ombrone system to the north (Fig. 1a). Mining activity peaked between 1880s and 1970s, and ceased in 1980; remediation of mining areas was only partial, and is still under way. Beginning in the 1980s, the environmental impact of the district has been documented by several studies[1]. On the other hand, mercury and other toxic substances such as H_2S can occur in present-day geothermal fluids[3]. It is important to accurately document the overall impact, and to discriminate the contributions of these different sources. To this end, our group started in 2010 a systematic investigation of the dispersion of mercury and associated heavy metals in the Mt. Amiata region and surrounding areas. Beginning with the first study[4], it was recognised that a significant pathway of dispersion is represented by the surface water drainage network, that eventually can transport the metals up to the Mediterranean Sea. In this contribution, we summarize the most relevant results of our studies, including preliminary data of ongoing research; for the reasons reported above, most data refer to the Paglia River. The data reported here refer to fluvial (stream and subordinately overbank) sediments and/or suspended particulate matter (SPM). These two materials represent by far the largest repositories of mercury released from the district. Mercury in solution represents a much smaller fraction (e.g.,[5]); its concentration in the studied streams rarely exceeds the limits (1 μg/L) established by Italian guidelines for drinking water.

2. Results

2.1 Paglia and Tiber

The Paglia River originates a few kilometers east of the Mt. Amiata summit by the confluence of the Pagliola and Cacarello Creeks. The first one flows by the town of Abbadia San Salvatore, and receives a direct drainage from ASSM (Galleria Italia). As a consequence, both SPM and stream sediments of the Pagliola Creek downstream of Galleria Italia show very high Hg contents (up to 19 mg/kg and 14 mg/kg, respectively[4,5]). Further downstream, the Paglia River receives contributions from other mines of the district, therefore Hg contents in SPM and stream sediments remain consistently high (>1 mg/kg) down to the confluence with the Tiber River. The imprint of the district is evident also in this larger river, with Hg concentrations >1 mg/kg in stream sediments down to the Alviano Lake[6] (Fig. 1a). This lake apparently acts as a sink for mercury, indeed after it concentrations decrease to hundreds of μg/kg, but remain however much higher than observed in the Tiber upstream of the Paglia confluence, and in other rivers not affected by the mines. Here Hg concentrations in stream sediments are consistently below 100 μg/kg[6]. Preliminary data[7] indicate that even within the Rome city limits Hg contents in Tiber stream sediments can exceed 100 μg/kg. There is a significant transfer to the biosphere and food chain, through conversion of inorganic mercury to methylate species (Me-Hg); as a consequence, several fish caught in the Paglia and Tiber Rivers show Hg contents exceeding the limit suggested for human consumption[5,6,11].

Based on the measured Hg contents of SPM, several authors[5] estimate that the Paglia River may transport as much as 11 kg/yr Hg; however, this is most probably a minimum estimate, because it does not account for extreme events, which are likely to mobilize large masses of Hg-bearing sediments. For instance[8] found a significant redistribution of Hg contents in the Paglia sediments following the flood event of November 2012.

An ongoing study[9,10] is aimed to quantify the distribution of mercury (and arsenic) in the different morphological units in overbank sediments accumulated along the Paglia watercourse. The study attempts a reconstructing a historical sequence where the pre-industrial background can be discriminated from anthropogenic (essentially from mining and metallurgy) contributions. Values as high as 97 mg/kg Hg were recorded; a preliminary estimate[10] suggests that as much as sixty tonnes of mercury could be stored in these sediments, making them an extremely significant potential source of this metal. On the other hand, fluvial terraces that could positively be ascribed to a pre-industrial age consistently show values below 1 mg/kg.

2.2 Orcia and Ombrone

The Orcia River also originates a few km east of the Mt. Amiata summit, but it flows almost due north until it receives the confluence of Formone Creek (Fig. 1b). The river then turns west until its confluence with the Ombrone,

which flows southwestward to the Tyrrhenian Sea. Only one Hg mine (Pietrineri; n. 1 in Fig. 1b) occurs in this watershed. Accordingly, an ongoing study[11] found high (>30 mg/kg) Hg in stream sediments only in two creeks very close to this mine. All other sediments in the Orcia River and its tributaries show Hg contents <1 mg/kg.

2.3 Albegna and Fiora

Our studies so far did not include the watersheds of these two rivers. Evidence of significant mercury transport in these basins arises from studies of coastal sediments of the Tyrrhenian Sea[11]. For instance, Hg contents as high as 1.7 mg/kg were measured in offshore sediments facing the mouth of the Fiora River[12].

3. Conclusions

The Mt. Amiata mercury district represents a major source of mercury that is transported by the drainage network as far as the Tyrrhenian Sea. It is likely that this contribution has a remarkable influence on the overall Hg budget of the Mediterranean Sea, with important consequences on the marine ecosystem and food chain. Ongoing remediation at ASSM will likely decrease the current output, but contaminated sediments dispersed along the course of the Paglia River (and, possibly, of other less studied streams such as Fiora) will remain a long term potential source.

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