

Tracing the impact of geothermal plants in the Monte Amiata area, Tuscany, Italy: evidence from Hg contents in stream sediments and tree barks

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ABSTRACT

The Monte Amiata area hosts the 3rd largest mercury (Hg) district worldwide, and an important geothermal field actively exploited for energy production. Mining activities ceased in the 1980s, but left an impressive legacy of environmental impact; on the other hand, the geothermal fluids contain several potentially toxic substances (gaseous Hg, hydrogen sulphide, ammonia...), that may be released into the environment during exploitation. For this reason, since 2002 abatement measures have been implemented at geothermal plants; emissions are constantly monitored by the regional environmental agency (ARPAT). It is obviously important to discriminate the contributions from different sources for impact minimization and optimal resource and land management.

Ongoing studies of Hg dispersion from the Monte Amiata mining district in the environment, mostly in the catchment of the Paglia River, give also indications on the contribution from geothermal power plants. A recent survey conducted in the catchment of small creeks draining the eastern flank of Monte Amiata showed that most stream sediments are highly anomalous (>1 mg/kg) for Hg contents, but the highest values (up to 1,900 mg/kg) occur in creeks directly draining abandoned mines and/or smelting plants; creeks closest to present day geothermal plants show definitely lower (<10 mg/kg) Hg contents in stream sediments.

The use of tree (*Pinus nigra*) barks as biomonitors of airborne Hg clearly indicates that the highest (up to 28.8 mg/kg) Hg contents in barks are all within 2 km from the largest former mining and smelting site; tree barks closest to geothermal plants show lower (<1 mg/kg) contents. An *ad hoc* monitoring program involving more trees at increasing distances from

geothermal plants could reinforce this conclusion, and give more quantitative constraints on the long-term Hg contribution from geothermal plants.

1. INTRODUCTION

Monte Amiata (shortly, Amiata) is an extinct Quaternary (~ 300 Ka) volcano in southeastern Tuscany, Italy. The area hosts the 3rd largest Hg district worldwide (closed in 1980s; Rimondi et al., 2015), and an important geothermal field actively exploited for energy production (Fulignati et al., 2014).

As detailed below, both activities involved significant environmental impacts; it is obviously important to discriminate the contributions from different sources for impact minimization and optimal resource and land management.

In this contribution, we review recent data acquired on Hg distribution in tree (*Pinus nigra* J.F. Arnold) barks and in stream sediments of creeks draining the eastern flank of Amiata. Even if these data were obtained with the main purpose of documenting dispersion from the former mining district, they have implications for estimating the impact of geothermal plants.

2. BACKGROUND INFORMATION

Mercury mines in the Amiata district were active from 1848 to 1982. Several mines and smelting centres, including the largest (Abbadia San Salvatore, ASS) were located in the eastern flank of Amiata, in the drainage basin of the Paglia River (Fig. 1), which eventually merges with Tiber River south of the city of Orvieto. Exploitation of geothermal energy started in 1959; currently, there are five active plants. The Bellavista and Piancastagnaio 2 power plants are out of service since year 2000 and 2011, respectively.

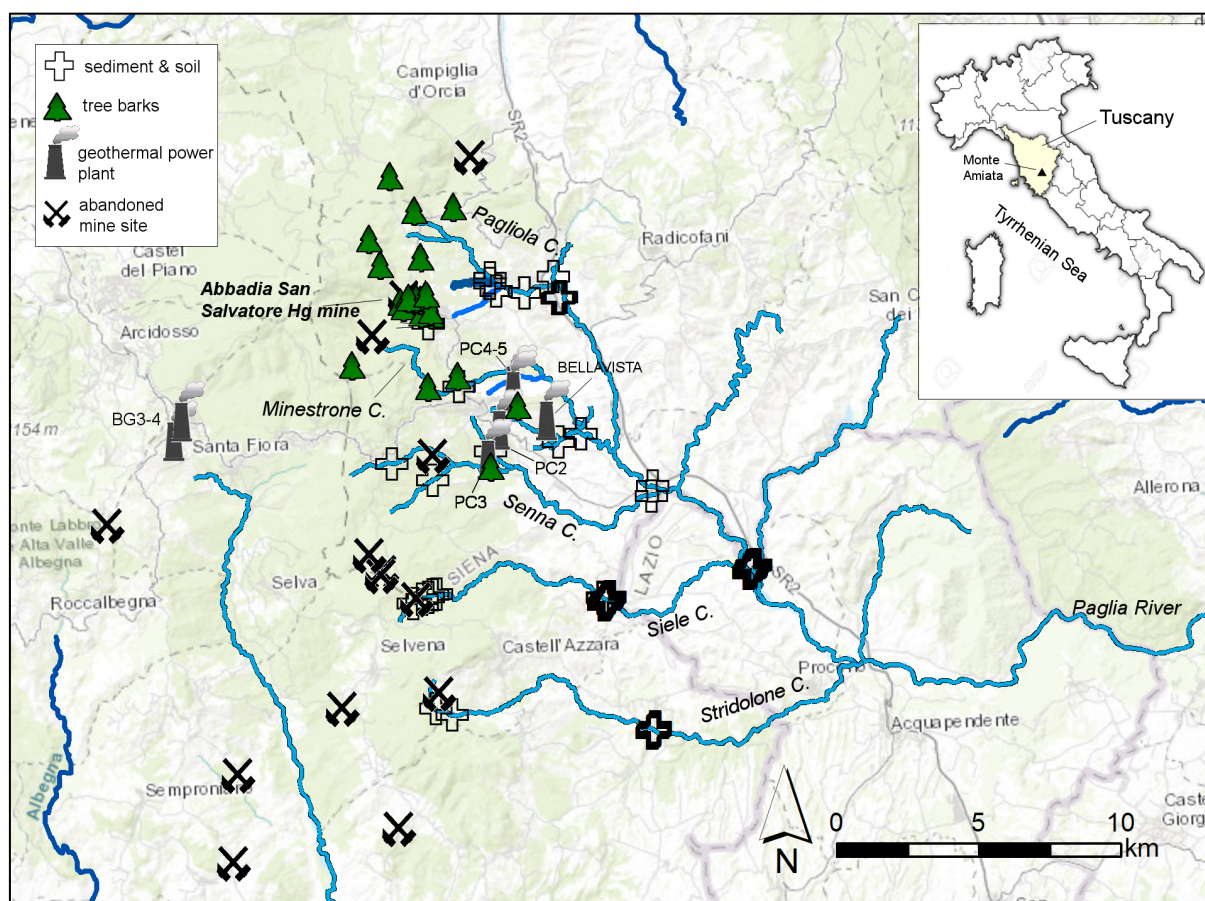


Figure 1: Sketch of the Monte Amiata area showing location of main mines, geothermal plants, and sampling sites for this study. Geothermal power plants are: Piancastagnaio 2 (PC2), Piancastagnaio 3 (PC3), Bellavista, Piancastagnaio 4 and Piancastagnaio 5 (PC4-5), Bagnore 3 and Bagnore 4 (BG3-4).

Mining and smelting activities caused dispersion in the environment of very large amounts of Hg (not less than 30,000 tonnes; Benvenuti and Costagliola, 2016).

Dispersion occurred as direct emission in air from smelting furnaces, and through the drainage network collecting both fallout of airborne material and runoff from waste piles. Dispersion was enhanced by the common practice of periodically dumping excess waste materials directly into streams. In spite of partial remediation, many waste piles still remain in the area (Rimondi et al., 2012), and large amounts of Hg are contained in stream sediments of the Paglia-Tiber river system (Gray et al., 2014; Colica et al., 2019). Preliminary speciation studies (Rimondi et al., 2014) suggest that a significant proportion of Hg is still present in sediments as sulphide (either cinnabar or metacinnabar).

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On the other hand, emissions from geothermal plants contain several potentially harmful substances, including Hg, hydrogen sulfide, ammonia, and boron compounds. All geothermal plants currently operating in the Amiata area are equipped with emission-

controlling systems (AMIS; Baldacci et al., 2005); however, the efficiency of these systems is not 100%: some Hg is still emitted from geothermal plants, and is monitored by the regional environmental agency (ARPAT). Data for 2016 (ARPAT, 2018) indicate emissions of 1 to 4 g/h. From 2010, there have been several studies of Hg dispersion into the Paglia-Tiber river system (Colica et al., 2019, and references therein). Although the Hg mass released from mining works is at least two orders of magnitude larger than that resulting from geothermal emissions (Benvenuti and Costagliola, 2016), local opinion groups opposing geothermal plants expressed the concern that Hg of geothermal origin may represent a significant contribution to the Paglia river budget.

In cooperation with the University of Firenze, ARPAT recently carried out a detailed sampling campaign of stream sediments in the drainage network of the eastern flank of Amiata (Costagliola et al., 2018). Moreover, our research group tested the use of tree (*Pinus nigra* J.F. Arnold) barks as biomonitors of airborne Hg in the area (Chiarantini et al., 2016; Rimondi et al., 2018). These studies follow an earlier literature of biomonitoring through lichens and mosses (Loppi et al., 2006, and references therein). Instrumental determinations of gaseous elemental Hg (GEM) in the area include the works by Ferrara et al. (1998, and references therein), Vaselli et al. (2013),

Cabassi et al. (2017), and McLagan et al. (2019). Finally, of relevance for this study are the preliminary data by Pribil et al. (2018) on Hg isotope composition of Amiata ores, geothermal fluids, and stream sediments.

Details of sampling and of analytical methods were presented in the above cited literature, and will be not repeated here.

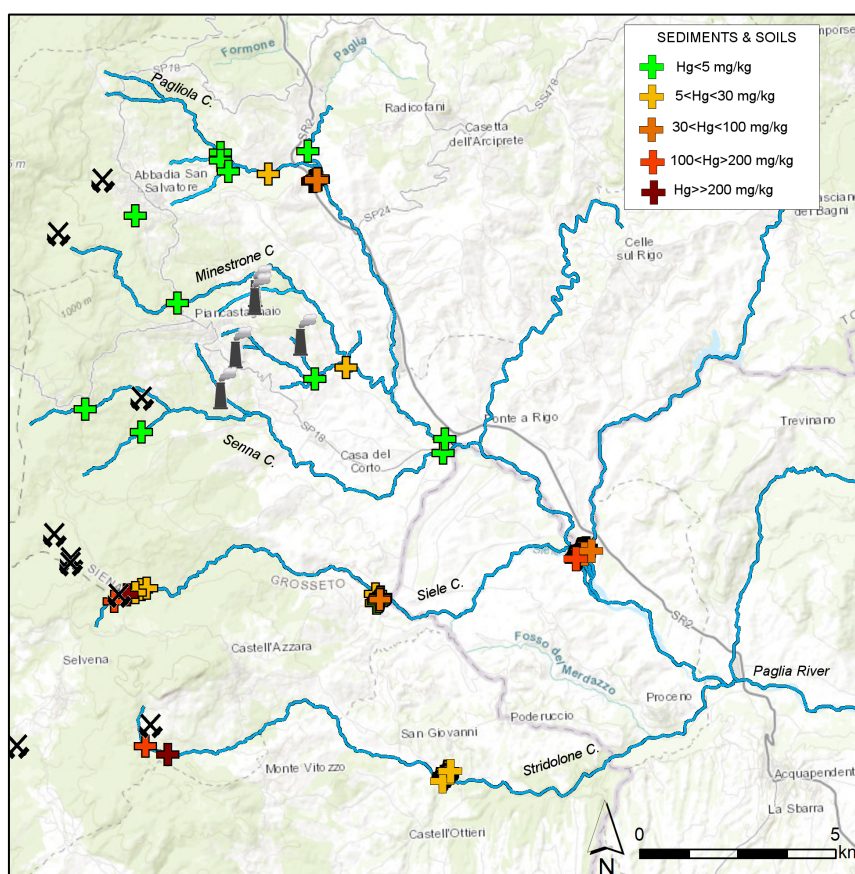


Figure 2: Distribution of Hg concentrations in sediments and soils in the study area.

3. RESULTS AND DISCUSSION

3.1 Stream sediments

Mercury concentration in stream sediments shows a quite wide range from 0.2 to 1,900 mg/kg; many values exceed the Italian limit for green and residential soil (1 mg/kg), and most exceed the environmental quality limit (SQA) for sediments (0.3 mg/kg). The highest values (> 30 mg/kg) are restricted to drainages of mining areas (Figure 2), specifically to the north (Pagliola Creek, downstream of the ASS mine), and to the south (Siele and Stridolone Creeks, downstream of the Siele and Cornacchino mines). In the central area, where drainage from the geothermal plants and the small Senna mine occurs, Hg contents in stream sediments are definitely lower (mostly < 5 mg/kg).

Preliminary Hg isotope data (Pribil et al., 2018) indicate a similar range of $\delta^{202}\text{Hg}$ for primary Hg ores and geothermal waters, whereas smelting wastes (calcine) have a heavier isotopic signature; stream

sediments are more similar to calcines, suggesting an important contribution from this waste.

Therefore, we support the previous conclusion by Benvenuti and Costagliola (2016) that the largest Hg contribution to the Paglia River catchment derives from previous mining and smelting activities, whereas contribution from geothermal plants is comparatively negligible.

3.2. Tree barks

Mercury concentration in barks also covers a quite wide range from 0.1 to 28.8 mg/kg dry weight. However, all highest values (>1.8 mg/kg) are restricted to the immediate surroundings of the ASS mine and smelting plant. Next to the geothermal power plants, Hg concentrations in barks are of the same order of magnitude as the regional background (Figure 3).

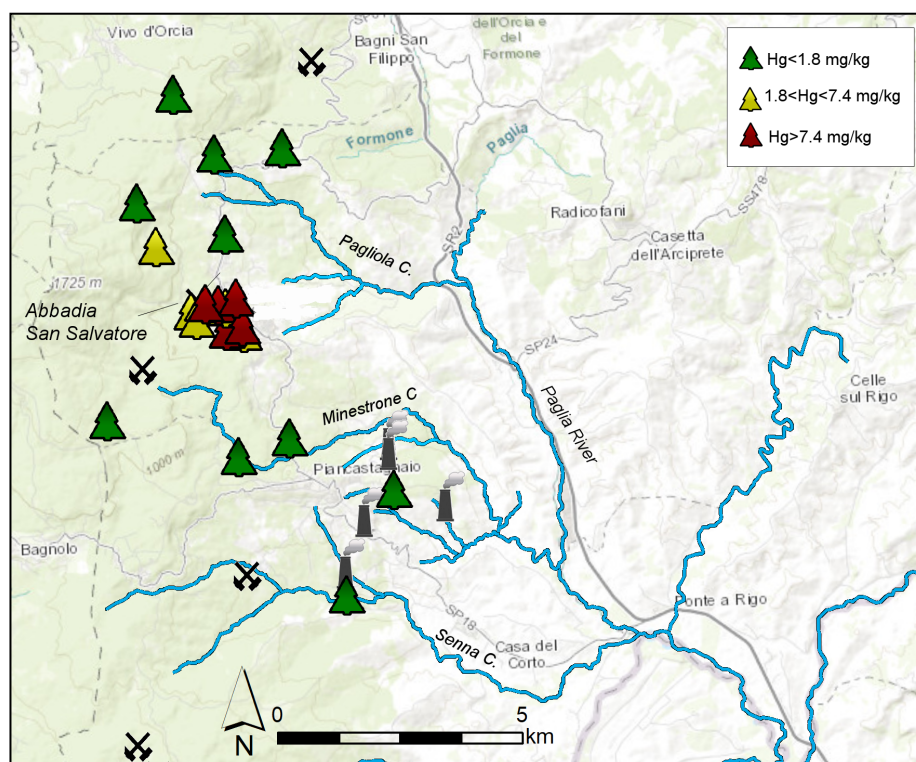


Figure 3: Distribution of Hg concentrations in tree barks of the study area.

These results are consistent with previous studies of GEM distribution in the area. In the 1990s, when the AMIS systems did not exist, GEM emissions from geothermal plants were of the same order of magnitude as from former mine buildings and spoil banks (Ferrara et al., 1998). By contrast, post-2005 studies (Vaselli et al., 2013; Cabassi et al., 2017) document much higher emissions from the ASS mine area than from geothermal areas. The recent study by McLagan et al. (2019) clearly documents that the maximum GEM emission is centered around the ASS mine, and rapidly decreases of at least two orders of magnitude a few hundred meters away from it. The study does not extend to the close proximity of geothermal plants; the nearest sampling stations, lying about 1 km north of Piancastagnaio geothermal plants, are not affected by emissions from them. Earlier biomonitoring studies (mostly using lichens; e.g., Loppi, 2001; Loppi et al., 2006, and references therein) also suggest similar or higher Hg airborne concentrations in former mining areas than in proximity of geothermal plants. Notice that most of these studied were conducted before installation of AMIS in the geothermal power plants; at the time of the study by Loppi et al. (2006), only the BG3 plant was equipped with AMIS.

4. CONCLUSIONS

In the Monte Amiata area contributions of Hg to the environment from present day geothermal plants are comparatively minor in respect to contributions from

abandoned mining areas. Specifically, contributions from geothermal plants to stream sediments in the drainage catchment of the Paglia River are negligible. After implementation of AMIS, Hg emissions to air from geothermal plants are also definitely lower than emissions from former mining buildings and plants. Tree barks represent an easy to use suitable instrument for monitoring airborne Hg, and could be used in an *ad hoc* monitoring program involving more trees at increasing distances from active plants. The results could be a useful complement to the current monitoring programs by ARPAT.

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