Geosciences

AIMS Geosciences, 8(4): 525–551.
DOI: 10.3934/geosci.2022029
Received: 20 June 2022
Revised: 08 August 2022
Accepted: 15 August 2022
Published: 31 August 2022

http://www.aimspress.com/journal/geosciences

Review

Environmental impact of past Hg mining activities in the Monte Amiata district, Italy: A summary of recent studies

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Abstract: The environmental impact of mining and smelting in the world-class Monte Amiata mercury (Hg) ore field has long been studied, before and after the final closure in 1982. A first summary was presented in 2015. With this contribution, we review the studies conducted in the last eight years. The most significant results include i) Hg-isotope characterization of primary ore (cinnabar), smelting waste (calcines), soil, fish and stream sediments; ii) analysis of the interplay between geomorphological evolution, fluvial dynamics and Hg distribution in the Paglia River catchment, which drains the main mining areas; iii) an improved quantification of the Hg loads discharged to the Mediterranean Sea; iv) the use of biomonitors to reveal the dispersion of Hg; v) new detailed surveys, including innovative techniques, of Hg distribution in air; vi) specific investigations to support the ongoing reclamation at Abbadia San Salvatore, the main mining and smelting center of the district, and vii) the assessment of the variability of Hg distribution in air, water and soil from the reclaimed Siele mine. Despite these progresses, there are further steps to be conducted to achieve optimal management of the wide contamination evidenced in this district. It is now fully clear that the diffuse character of contamination results in unfeasible hypotheses for total remediation. Therefore, the goal is that of a sustainable coexistence between contamination and human activities. This goal may involve the following activities: a) implementation of GIS-based contamination maps as a direct operational instrument for local authorities to tune up specific limitations and regulations of human activities (e.g., fishing, instream quarrying and wildfire management); b) mitigation measures such as increasing the vegetal cover of river banks to limit erosion and runoff, and c) continuous monitoring of air, water and soil contamination, including transfer to the food chain.

Keywords: mercury; contamination; remediation; Monte Amiata; Mediterranean Sea

1. Introduction

Mercury (Hg) is a top-priority contaminant at a global scale because of its highly toxic effects on living organisms (especially human beings) and the environment (e.g., [1–3]). Mercury occurs in many environmental matrices, such as air, water, soils, plants and living organisms. Its release to aquatic systems is critical because the toxic methyl-Hg (MeHg) is formed in such environments and then it bioaccumulates in the food chain [4]. Mercury transfer to water bodies occurs in many ways: seepage from industrial, agricultural and waste sites and uptake from air through rain and snow [5]. The atmosphere is the foremost transport pathway of Hg emissions, contributing to the redistribution of Hg in terrestrial, freshwater and marine ecosystems [6]. On a global scale, the net atmospheric deposition is controlled by the overall emissions. Detecting and quantifying the different Hg airborne forms is essential because of their different bioavailability [7]. Mercury transfer from soil to plants is complex and controlled by soil properties and plant species. Mercury accumulation in plants reflects the environmental exposure of Hg and ecological niches. A widespread increase in the atmospheric deposition of Hg may favor the increments of Hg in plant tissues, enhancing its bioaccumulation. Regarding transfer to the food chain, it is well known that many fish species tend to accumulate Hg. Fish bioaccumulate MeHg in muscle tissues; biomagnification of MeHg proceeds in the food chain due to fish consumption by predators [5,8].

Mercury occurs in three forms: elemental (Hg^0), inorganic (Hg_2^{2+}, Hg^{2+}) and organic (MeHg CH_3Hg^+, $(CH_3)_2Hg$, $CH_3CH_2Hg^+$, $C_6H_5Hg^+$). These compounds have different absorption, distribution, accumulation and toxicity characteristics for the human body [9]. The adverse health effects of Hg depend on the speciation of Hg accumulated in the body, the extent of exposure and the subject's age [5]. Mercury can cause various disorders such as neurological, nephrological, immunological, cardiac, motor, reproductive and genetic disorders [8,10]. Methyl-Hg is the most toxic form of Hg: it is a neurotoxin that can cause severe health effects, such as deafness, blindness and death [11]. The acute toxicity of elemental or divalent Hg points to the kidneys and the central nervous system as target organs. Divalent Hg compounds have been reported to produce skin sensitization in humans. Adverse effects on the male and female reproductive functions have also been recognized. Mercury exposure can potentially cause birth defects, impotency and infertility. During pregnancy, Hg from the tissues of the mother passes through the placenta and into the developing fetus; this transfer may cause severe neurological effects and disorders in newborns. Inorganic mercury is also released through breast milk to the nursing infant [5].

Anthropic activities are the main source of Hg release in the environment, although it also has natural sources (e.g., weathering of rocks, especially mineral deposits, volcanic emissions and volatilization from the ocean). Its use is progressively banned, as required by the Minamata Convention [12]. Even if current Hg mining is limited to China and Kyrgyzstan, legacy Hg mines are still releasing this metal (and other potentially toxic elements (PTEs)) to the environment (cf. [13]). Therefore, studies of processes occurring at and around these legacy mines are important to understand the associated risks and plan appropriate remediation/mitigation measures.

Most of the historical Hg production occurred from five districts: Almadén (Spain), which is by far the largest; Idrija, Slovenia; Monte Amiata, Central Italy; California Coast Ranges, USA and Huancavelica, Peru [14,15]. Specifically, the Monte Amiata mining district (MAMD; Figure 1) in southern Tuscany was the third largest producer of Hg worldwide, with more than 100,000 tons of liquid mercury bottled, mostly between the end of the 19th century and the 1970s [16]. All activities ceased in 1982. Therefore, practically all mining and associated smelting activities were carried out in historical contexts where minimization of the environmental impact was hardly a priority. Consequently, enormous amounts of Hg were dispersed into the environment. A release of about 8,000 tons was estimated for the period of 1943–1973 [17]; in earlier decades, considering the less efficient processing methods, dispersion was even greater. Benvenuti and Costagliola [18] estimated that up to 20,000 tons for the total release of Hg from the MAMD between 1880 and 1970. Moreover, other PTEs, such as As, Sb, and Tl, are present in the district, although at much lower levels than those of Hg. Reclamation after closure was only partial (see § 3.8); it is therefore not surprising that the impact on the environment was quite serious and is still perceived 40 years after the mine closure. Studies on Hg dispersion from MAMD date back at least to the 1960s [19,20]; in the following decades, there was a large number of environmental studies. Rimondi et al. [21] summarized the most significant results achieved up to 2014. Since then, there have been several remarkable progresses in further understanding the environmental impact of the MAMD, and these have been reviewed in the present work. The importance of such understanding arises from a) Hg dispersion through waterway draining from the MAMD, extending for almost 200 km up to Rome and the Mediterranean Sea, and b) the impacts of mining and smelting activities in the MAMD, which overlap with those arising from present-day exploitation of geothermal energy; a distinction between the two sources is obviously critical for the development of geothermal resources. This review highlights that, despite these progresses, there are a number of points requiring further investigation. Because of the extent of Hg dispersion, a total reclamation does not seem feasible; rather, mitigation measures should be considered to achieve a sustainable coexistence of human communities with anomalous levels of Hg (and other PTEs).

2. Background information

2.1. Geological setting

The geology of the Monte Amiata area is linked to the formation of the Apennines Mountain chain during the Tertiary Period, and the subsequent post-collisional events [22]. From bottom to top, the following units occurred (Figure 2): i) Tuscan Units (Late Triassic—Lower Miocene); ii) Ligurian and Subligurian Units (Jurassic—Oligocene); iii) continental sedimentary successions (Miocene); iv) Pliocene marine sediments; v) volcanic and volcano-sedimentary successions (Upper Pliocene—Upper Pleistocene) and vi) continental deposits, debris and alluvial deposits (Quaternary). Specifically, the magmatic activity at Monte Amiata mostly occurred at about 300 ka, although minor final products could be as young as 230 ka [23].

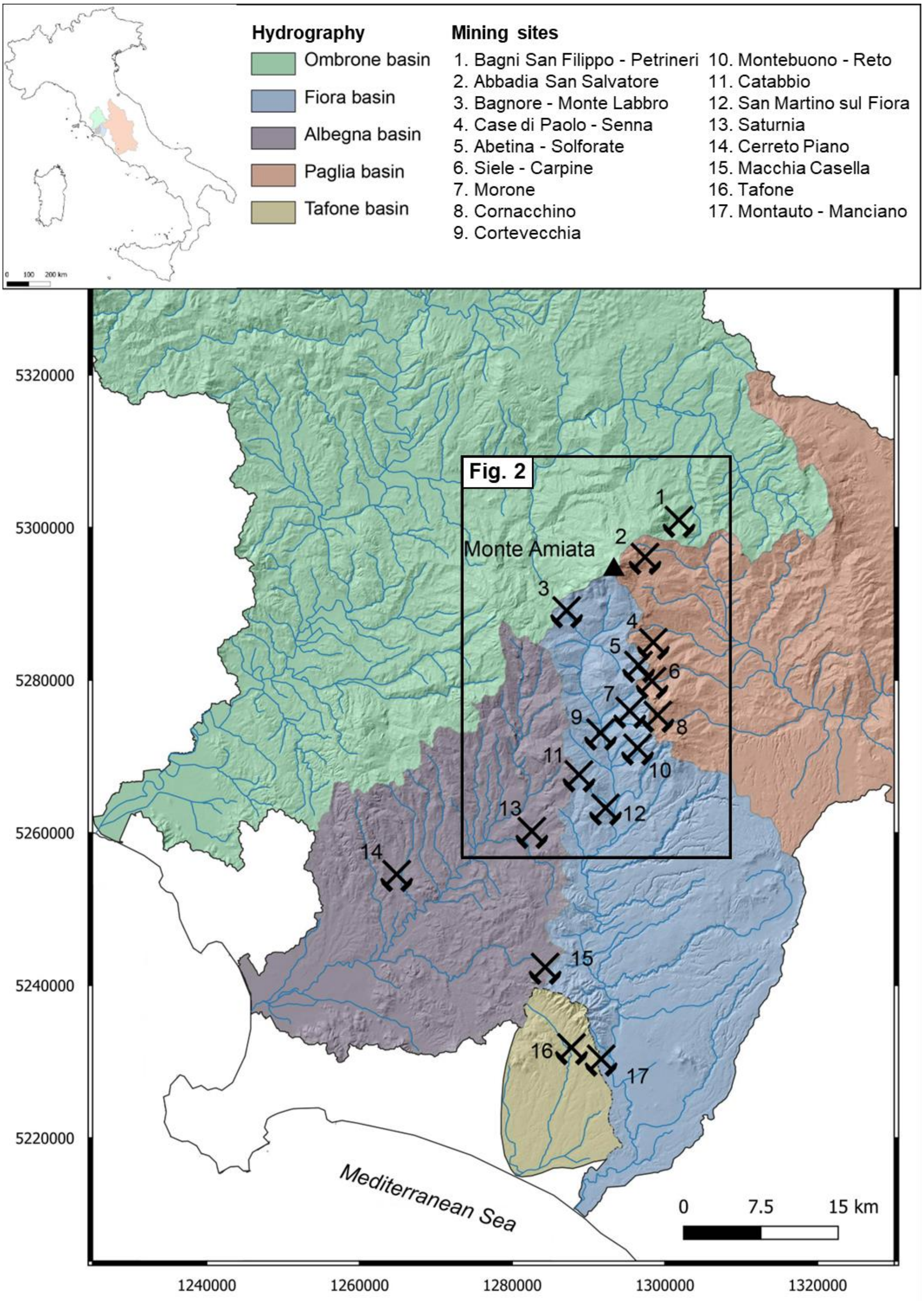

Figure 1. Main hydrographic catchments of southern Tuscany in Central Italy. The mining sites are reported. The box highlights the MAMD location (see Figure 2 for details).

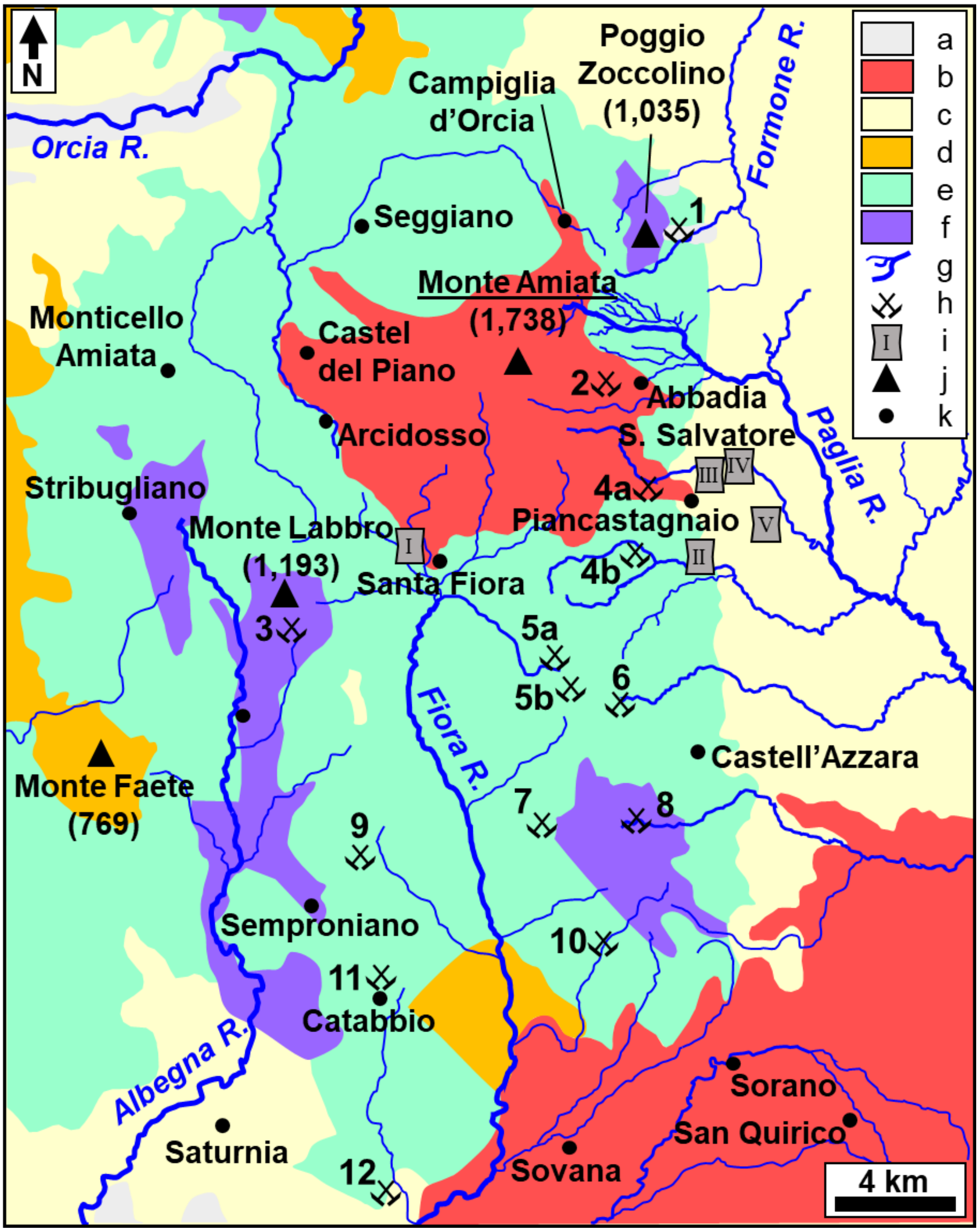

Figure 2. Simplified geological map of the MAMD. The main rivers draining the mining district are reported. The numeration of the mining sites matches that of Figure 1 (in addition: 4a = Cerro del Tasca, 4b = Senna, 5a = Abetina, 5b = Solforate). Legend: a) continental deposits, debris and alluvial deposits (Quaternary); b) volcanic and volcano-sedimentary successions (Upper Pliocene—Upper Pleistocene); c) Pliocene marine sediments; d) continental sedimentary successions (Miocene); e) Ligurian and Subligurian Units (Jurassic—Oligocene); f) Tuscan Units (Late Triassic—Lower Miocene); g) rivers and creeks; h) mining sites; i) geothermal power plants (I = Bagnore 4–5, II = Piancastagnaio 5, III = Piancastagnaio 4, IV = Bellavista, V = Piancastagnaio 3); j) mountain peaks (the numbers in brackets refer to elevation in m asl); k) town and villages. Modified from [21].

2.2. Ore deposits

The MAMD belongs to the Tuscan metalliferous province [24,25], and it is a world-class resource. Considering the importance of the resource, ore deposit studies are surprisingly scarce and old. The most complete descriptions remain those of the 1970s literature (reviewed by Rimondi et al. [21]). Mercury mineralization occurs as veinlets, impregnations or sizable, massive replacements of host rock (mainly sandstones, limestones and marls, but also volcanic rocks; see Figure 2B in [21]). Cinnabar (a-HgS) was the main ore mineral; minor metacinnabar (b-HgS), native Hg and montroydite (HgO) are reported. Pyrite and/or marcasite (FeS_2) are ubiquitous and locally abundant; other minor sulfides include realgar (As_4S_4), orpiment (As_2S_3) and stibnite (Sb_2S_3). The deposits are classically described as "epithermal", in agreement with limited fluid inclusions evidence (summary in [21]); they indeed bear some similarities with hot spring-type deposits of North America, but they also show noticeable differences (see [21]). Pribil et al. [26] provided the first Hg-isotope characterization of the deposits. Primary cinnabar shows a range of δ^{202}Hg between −0.96 and −2.25‰, and a slightly positive (0.00 to 0.24‰) δ^{199}Hg, typical of deposits associated with active continental margins [27]. The markedly negative δ^{202}Hg values are likely due to isotopic fractionation of Hg in hydrothermal circuits as a result of the Hg boiling and separating into a Hg-bearing gas phase (cf. [21]). A present-day geothermal spring and its precipitate show similar values (δ^{202}Hg: −1.32‰ water, −1.96‰ precipitate; δ^{199}Hg: 0.15‰ water, 0.24‰ precipitate), which is in agreement with the concept that present-day geothermal circuits are related to ore-forming hydrothermal systems (cf. [21]).

In the district, there were up to 42 mining sites [17,28], including Cerreto Piano (n. 14 in Figure 1), that actually lie outside of the Monte Amiata physiographic region. The main sites are shown in Figure 2; the Abbadia San Salvatore mine (ASSM) was the most important, with about 50% of the total production. Smelting was conducted on site at the main mines; ASSM and Siele were the most important smelting centers.

2.3. Geomorphology and climate

Monte Amiata (1,738 m above sea level,) stands as an isolated, high-prominence peak above the hills of southern Tuscany. The drainage network has developed radially around the mountain (Figure 1), mostly controlled by Late Apennine tectonic features (e.g., the Paglia River basin developed along the Siena-Radicofani graben). The area is characterized by a Mediterranean temperate climate, with hot and dry summers and cold and rainy winters. The average annual temperature is 10.5 °C (period 1953–2000), and the average annual precipitation is 1480 mm (reference period: 1925–2000; [29]). About two-thirds of the total annual precipitation is concentrated in the autumn-winter season [30]. Rivers draining Monte Amiata have a typical torrential character, at least in the initial stretches; flow regimes are strongly dependent on seasonal variability, and hydrological periods are highly irregular [31].

3. Environmental impact

In this section, we summarize the most significant environmental implications of recent (post-2014) studies in the MAMD. Following the previous review by Rimondi et al. [21], descriptions have been divided with respect to the main matrix/process addressed; this division is obviously purely operational. A summary of the main data collected in the papers described in this review can be found in Table 1.

3.1. *Natural background*

In any environmental study, it is essential to distinguish anthropogenic inputs from those related to the natural local background. This task is often complex, and the MAMD is no exception. First, the area is naturally anomalous, and a distinction between the two sources may be problematic, especially considering that mining-related activities span a history of more than two millennia [16]. Second, Hg is easily redistributed among different compartments via airborne transport (either in gaseous or in particulate forms); it is therefore difficult to find totally pristine areas where natural, pre-anthropic levels can safely be established. Despite this, three contributions attempted to establish a (quasi)natural Hg background in the area. Protano and Nannoni [32] analyzed four soil samples near Vivo d'Orcia, 6 km north of Abbadia San Salvatore and outside of any known mine area; they obtained Hg values between 0.9 and 1.2 mg/kg. This range of values agrees with a recent study by Montefinese et al. [33], who attempted to establish a local background for the first section of the Paglia River basin by sampling alluvial terraces presumably predating any mining activity (see §3.3). They reported Hg concentrations between 0.08 and 2.98 mg/kg and suggested a local background value of 1.3 mg/kg. Fornasaro et al. [34] attempted to establish a specific background for the Siele mining area, collecting three stream sediment samples upstream of—and at a higher elevation than—any known mining work. These three samples returned Hg values between 2 and 9 mg/kg, suggesting that, either the area is highly anomalous, or unrecognized mining works occur outside of the known limits of the mining area. In summary, a reliable estimate of the district-scale natural background seems on the order of 1 mg/kg, i.e., coincident with the Italian law limit for residential, public green and agricultural soils [35]; however, specific areas may show higher values. Finally, even if outside of the MAMD area, the study by Pasquetti et al. [36] is to be mentioned, as major and trace element chemistry from Late Pleistocene sediment profiles that are cropping out along the coast of southern Tuscany (Ansedonia Gulf, Orbetello Lagoon) were investigated. In particular, Hg (0.2–2.7 mg/kg) and As (15.8–44.9 mg/kg) contents were found to be distinctly higher than reference values for southern Tuscany (0.2–0.3 mg/kg and 7 mg/kg, respectively), indicating a marked anomaly of supposedly natural origin. Specifically, the main pathway for Hg could be the Fiora River, whereas, for As, this area would be part of a much wider anomaly characterizing southwestern Tuscany (cf. [37]). Leaching tests indicate that both elements are scarcely mobile; however, Hg (0.6–9.7 μg/L) and As (2.1–42.2 μg/L) concentrations in leachates are mostly higher than the Italian limits for groundwater (1 μg/L for Hg and 10 μg/L for As). Quaternary sediments from southern Tuscany could then be a potential source of Hg and As to groundwater systems.

3.2. *Characterization of sources*

There was little progress in the knowledge and characterization of primary (ores) and secondary (mine and smelting waste) Hg sources. We previously mentioned the Hg-isotope study by Pribil et al. [26]; in addition to primary cinnabar and precipitates from geothermal springs, they analyzed calcines, soils and stream sediments. Calcines (smelting waste) show distinctly more positive δ^{202}Hg (−1.05 to +0.96‰) values than those of primary cinnabar, a typical isotopic effect of loss of the light isotope during the roasting process [38]. This difference is useful for distinguishing contributions from primary ore and calcines in environmental samples (see next sections). Protano and Nannoni [32] and Meloni et al. [39] analyzed samples from the large "Le Lame" mine waste dump at Abbadia San Salvatore, which is among the objects of the reclamation plant. Therefore, the results of these studies are reported under § 3.8.

3.3. Soil and sediment

Both earlier ([40–42], as reviewed by Rimondi et al. [21]) and more recent studies were essentially devoted to stream sediments and riparian soils. Also, most studies focused on the Paglia-Tiber system because i) the Tiber River is the most important river in Central Italy, flowing through the city of Rome and ii) the Paglia River receives runoff from the ASSM (as said, the principal mining and smelting center of the district, Figure 2) and from other important mines/smelters (Siele and Cornacchino). Colica et al. [43] first emphasized the relationship between the evolution of fluvial geomorphology and Hg transport. In their study of the first reach of the Paglia River (from the source to Allerona), they showed how Hg was unevenly distributed in the various morphological units (MUs) of the river. Specifically, they defined five orders (from T1, oldest, to T5, youngest) of alluvial terraces, two of which (T1 and T2) predate the main mining activity. In fact, they show relatively low (2–6 mg/kg) Hg contents, slightly higher than background values, as defined above. By contrast, younger terraces (T3 to T5), the baseflow channel and the floodplain show typically higher values (up to 98 mg/kg). The authors estimated that no less than 63 tons of Hg are contained in these terraces and in the stream sediments and thus continuously remobilized by fluvial dynamics, especially during floods. Specifically, the high Hg content (average 19 mg/kg) of the modern floodplain is ascribed to erosion of contaminated MUs upstream. The same study also analyzed As in stream sediments, but its values were always within the local baseline values (11 mg/kg). Rimondi et al. [44] and Fornasaro et al. [45] further developed an analysis of the interplay between the geomorphological changes of the river, mine exploitation and other anthropic activities. Rimondi et al. [44] carried out an extensive sampling of surface waters, overbank soil and stream sediments for about 200 km along the Paglia-Tiber system from the Paglia source to Castel Giubileo, about 10 km north of Rome. Mercury content in sediments ranged from <0.20 mg/kg to 1,900 mg/kg, whereas, in soils, it varied from <0.20 mg/kg to 100 mg/kg. The highest value was found in the Stridolone creek, which drains the Cornacchino mine; by contrast, sediments in creeks draining present-day geothermal plants returned much lower values (1–4 mg/kg). Overall, about 70% of soil and sediment show Hg contents above 1 mg/kg, i.e., the Italian law limit for residential, agricultural and public green soil [35]. Improper disposal of Hg mine waste is the principal source of metal dispersal in these fluvial catchments. Fornasaro et al. [45] analyzed in more detail the Tuscan section of the Paglia River. Consistent with the results by Brigante et al. [46], they found out that evolution of the Paglia riverbed in the last 200 years first experienced a progressive narrowing, which was moderate until 1954 and became more marked in the following decades; subsequently, due to some major flood events, the trend reversed and the riverbed regained part of its original area. The distribution of Hg in the Paglia floodplain results from the combination of the exceedance of sediment yield to the river during mining activities, which fed the floodplain with large amounts of Hg-contaminated sediments during its braided stage about 100 years ago, and the morphological changes of the river, which led to the evolution from a braided to the present-day single channel river with low sinuosity. The magnitude of the extension of Hg contamination, the river geomorphologic changes and the processes of transport, deposition and re-suspension did not allow a natural "clean up" of the river system, which shows low resilience. Due to the gradual deepening and narrowing of this single fluvial channel, Hg-contaminated sediments were deposited at higher topographical levels than the channel itself. One of the main consequences of this process led to a change in the transport/deposition cycle and a tendential loss of mobility of the material deposited on the overbanks. Under high flow conditions, and especially in coincidence with intense rain events (such as the 2010, 2012 and 2019 events [34,41,43, 45,46]), large amounts of Hg stored in the overbank sediments are physically mobilized and redistributed, contributing to making the floodplain a secondary Hg source. Extreme weather events, which are expected to intensify due to climate change, will contribute to the recurrent distribution of Hg-contaminated legacy sediments in the floodplain and along the Paglia River course.

The only study that addressed a watershed outside of the Paglia-Tiber system is that by Chiarantini et al. [47], who investigated the contamination by Hg and As in water and stream sediments of the Orcia River and its tributaries, which lie north and west of the MAMD, to the confluence with the Ombrone River (Figures 1 and 2). The watershed hosts only one important Hg mine (Bagni San Filippo—Pietrineri; Figures 1 and 2), whereas several thermal manifestations occur, some of which (Bagni San Filippo and Bagno Vignoni) are important tourist attractions. Water samples and travertine/unconsolidated sediments were collected in the thermal springs. The analysis of stream sediments revealed moderate concentrations of Hg and As (median values of 0.118 mg/kg and 5.25 mg/kg, respectively). These concentrations do not exceed Italian law limits for residential soil (Hg: 1 mg/kg, As: 20 mg/kg), with the exception of a sample collected close to the Pietrineri mine (Hg: 195 mg/kg, As: 35 mg/kg). Travertine and unconsolidated deposits associated with thermal springs generally exhibit low Hg concentrations (0.004–0.32 mg/kg), with a significant exception of 23 mg/kg at Bagni San Filippo. Arsenic is extremely variable (from 1 up to 358 mg/kg); the most anomalous values were found in the deposits associated with the Bagni San Filippo and Acquapassante springs (358 and 102 mg/kg, respectively). Overall, the input of PTEs from the mining areas to the Orcia and Ombrone watersheds is lower than those observed in the Paglia and Tiber catchments [48]. However, remobilization of Hg-contaminated sediments during flood events may cause occasional PTE peaks in the Orcia-Ombrone basin.

Studies on soil are comparatively scarce (see, however, § 3.8). The authors of [45] reported values from <0.20 to 100 mg/kg. Importantly, there is a progressive Hg dilution in both sediment and soil from north (source) to south. Notably, an appreciable decrease of Hg concentrations occurs downstream of the Alviano lake at a hydropower reservoir along the Tiber River that lies a few kilometers south of the Paglia River confluence. Therefore, artificial reservoirs may act as efficient hydraulic trap barriers for Hg-contaminated particulates; on the other hand, they may represent a transient pollution source during routine dam flushing operations. The magnitude and the longitudinal extension of Hg contamination make remediation not viable. People and human activities must coexist with such an anomaly; there is some concern that gravel and sand quarries along rivers may spread material with Hg contents beyond the legal limits (cf. [49]).

We finally mention a few studies on Hg speciation in soil and sediment. By means of X-ray absorption spectroscopy (XAS), Chiarantini et al. [50] and Bardelli et al. [51] confirmed an earlier study by Rimondi et al. [52] showing that Hg speciation in MAMD soil is dominated by scarcely soluble sulfides, i.e., cinnabar and metacinnabar; the latter is presumably released by calcines, as suggested also by a Hg-isotopic composition of stream sediments intermediate between primary ore cinnabar and metacinnabar-rich calcines [26]. After the paper by Rimondi et al. [40], there were few instances of new data on the occurrence of the highly toxic MeHg species ([45], summarized in § 3.8).

3.4. Water

Consistent with earlier data [40], more recent research confirmed that both stream water and geothermal-influenced water in the MAMD have in general low dissolved[1] Hg contents. For instance, Rimondi et al. [44] reported for the entire Paglia-Tiber system a range of 0.01–0.08 µg/L. These values are well below the Italian mandatory limit of 1 µg/L for Hg in drinking water [53]; therefore, these

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[1] Following an established convention, “dissolved” is hereby defined as everything passing through a 0.45-µm filter.

waters should not represent a threat for humans and the environment. Similar results were obtained by Chiarantini et al. [47] for surface waters sampled at the same sites as stream sediments in the Orcia-Ombrone basin. All waters showed Hg and As concentrations below the Italian limits for drinking waters (1 µg/L for Hg and 10 µg/L for As) [53]. By contrast, thermal waters, while showing low values of Hg (Hg_{tot}: 0.32–5.76 ng/L), returned relatively high contents of As (up to 23.4 µg/L), as already found in previous studies (e.g., [54]; see also [55]). However, close to the ASSM area, a study on well and spring waters from the main aquifer ([56]) yielded values up to 11 µg/L, although average values were 0.2–0.3 µg/L. In some hypothermal springs, Hg contents up to 2.5 µg/L were recorded, whereas higher concentrations were measured in waters discharging from the regional carbonate aquifer near the volcanic edifice. Vaselli et al. [57] reported the results of discontinuous (2009–2020) monitoring of waters discharging from the Galleria Italia that collect waters draining most galleries of the former Hg-mining area of Abbadia San Salvatore. Galleria Italia feeds the 2.5-km-long Fosso della Chiusa creek, whose waters were analyzed from the source to the confluence with the Pagliola creek in June 2020. In most cases, dissolved Hg was below the instrumental detection limit (<0.1 µg/L), although concentrations slightly higher than 1 µg/L were measured. Also, Hg concentrations in the Fosso della Chiusa creek waters never exceeded 2.2 µg/L. By contrast, all studies show that suspended particulate matter (SPM) is the main carrier of Hg in waters draining the MAMD (cf. [48]). For instance, SPM in waters flowing out Galleria Italia contains 0.27 mg/kg of Hg (i.e., more than 100 times the concentration in the liquid phase); the Hg content in SPM in the Fosso della Chiusa reaches 17.5 mg/kg before the confluence with the Pagliola creek [58].

3.5. Air

Following the study by Vaselli et al. [59], several investigations were carried out to determine gaseous elemental mercury (GEM) by using a portable Zeeman atomic absorption spectrometer with high-frequency modulation of light polarization (Lumex RA-915)—see e.g., [44] and [34] (the main results of this paper are reported under § 3.8). In this section, we specifically mention some contributions that resulted in new approaches. Cabassi et al. [60] coupled the Lumex instrument with a pulsed fluorescence gas analyzer for the simultaneous measurement of GEM and H_2S; this coupled measurement was of specific interest to recognize the dispersion of these contaminants from geothermal power plants, i.e., the study was not specifically directed to assess the impact from mines; we notice here that the highest GEM concentration determined at Piancastagnaio (194 ng/m^3) is order of magnitudes lower than that measured close to mining/smelting plants [59,34]. Of more direct interest for this review is the study by McLagan et al. [61], who installed a network of specifically designed passive air samplers (PASs) around the ASSM that are able to measure air concentrations of GEM. Concentrations ranged over more than three orders of magnitude in the Abbadia San Salvatore town (4.47 to 6,700 ng/m^3 in an area of 0.56 km^2), whereas, at more distance, i.e., along the eastern Mt. Amiata flank, concentrations were markedly lower, ranging from 1.26 to 166 ng/m^3. Furnaces and condensing units in the former smelting plants were identified as the major emission sources. Total emission fluxes estimated from the study area were 16 ± 8 and 31 ± 15 µg/hr^1·m^2 for October 2015 and July 2016, respectively. Within the town of Abbadia San Salvatore, concentrations were largely below the local recommended limits of 300 ng/m^3; however, under specific wind conditions, an increase was noticed; therefore, occasional overruns cannot be excluded. Additional data on GEM distribution in the ASSM area subject to reclamation are reported under § 3.8.

3.6. Transfer to the biosphere

Several studies on Hg transfer to the biosphere (mostly to plants) were carried out in the last decades of the past century (e.g., [62–67]). These studies found high total Hg and MeHg concentrations in edible mushrooms and vegetables of the Monte Amiata area (0.06–9.8 µg/g) [65]. Mercury contents in food products from Monte Amiata were also investigated. Mercury concentrations were similar to those found in commercial products, except for beets, lettuce, rosemary and sage. These vegetables showed the highest concentrations in samples collected near the former ASSM (from <2 to 319 ng/g fresh weight). Low Hg levels were found in foods of animal origin (from <2 to 19.4 ng/g fresh weight) [67].

New studies in the last few years were mostly focused on the use of plant tissues as monitors of the airborne dispersion of Hg and other PTEs. Chiarantini et al. [47] demonstrated that black pine (*Pinus nigra* J.F. Arnold) bark is an excellent trap for airborne Hg, both as gaseous species and as wind-blown particulate. Values up to 8.6 mg/kg were measured in trees close to the former mining and smelting plants at Abbadia San Salvatore, compared to a range of 5–98 ng/kg determined at a "blank" site near the city of Florence. Even higher (up to 28.8 mg/kg) Hg contents in *P. nigra* outer bark near the ASSM were reported by Rimondi et al. [68], who attempted to optimize sampling parameters with respect to height from the ground and direction. Samples taken from the same tree at 70 cm and 150 cm above ground had Hg contents of the same order of magnitude, even if values for 150 cm were slightly less dispersed; this is possibly because, at 70 cm, the bark is more influenced by random soil particles resuspended in air by wind. There is no statistically significant dependence of Hg content on direction and tree age. Leaching tests simulating rain events, caused a negligible loss of Hg from the bark. Rimondi et al. [69] compared Hg concentrations in *P. nigra* bark and in lichens grown in the proximity of them. Mercury concentrations in both the bark and lichens decreased exponentially with distance from the mine; however, the Hg concentration in lichens was lower than that in the bark at the same site. There was a fairly good correlation between Hg in lichen and bark, suggesting similar mechanisms of Hg uptake and residence times. By contrast, a comparison with GEM concentrations measured by PASs ([61], see §3.5) was moderate at best. The difference is ascribed to a) PAS-collected gaseous Hg, whereas lichen and bark also picked up particulate Hg; and b) the face that the lichen and bark had a dynamic exchange with the atmosphere. The lichen, bark and PAS outline different and complementary aspects of airborne Hg content; efficient monitoring programs in contaminated areas would benefit from the integration of data from different techniques. We also mention the exploratory results by Fornasaro et al. [70] on the use of chestnut growth rings to reconstruct the history of airborne Hg at Monte Amiata. Chiarantini et al. [50] and Bardelli et al. [51] investigated, by means of XAS, the speciation of Hg in *P. nigra* bark. The results suggest that, in the outermost bark layer (~ 0–2 mm), roughly 50% of Hg is in the form of metacinnabar (β-HgS). A progressive increase in Hg-organic species (Hg bound to thiol groups) is found below the surface (down to 30 mm from the surface), while β-HgS may totally disappear in the deepest layers. The absence of cinnabar (α-HgS) in the bark, which, on the contrary, was found in the nearby soils along with β-HgS, suggests that, at least in part, β-HgS does not represent mechanically trapped wind-blown particulate from surrounding soil, but it likely represents the product of biochemical reactions within the bark. In fact, the absence of Hg^0, which is the dominant airborne Hg form in the surrounding atmosphere, suggests that gaseous elemental Hg is quickly transformed at the bark surface by reaction with thiol- and amine-containing proteins, and with the COOH and OH groups of tannins. This mechanism is important in regulating the biogeochemical Hg cycle when bark returns to soil as litterfall. Monaci et al. [71] used leaves of the evergreen holm oak *Quercus ilex* L. to assess the airborne contamination of several PTEs (including Hg) in five towns (Abbadia San Salvatore, Arcidosso, Bagnore, Piancastagnaio and Santa Fiora) located on the slopes of

Monte Amiata. The sampled leaves were generally characterized by relatively low levels of PTEs, as compared to other similar studies carried out in much larger and populated Italian urban agglomerations. However, three times higher average Hg concentrations were found at Abbadia San Salvatore than those from other towns of the study, clearly reflecting the contribution by former mining and smelting facilities.

Concerning the potential transfer of Hg to the food chain, an unpublished report by Mattioli [72] (summarized by Rimondi et al. [44]) suggests that there is limited risk for human health by consumption of vegetables, whereas it confirms earlier reports by Rimondi et al. [40] and Gray et al. [42], indicating Hg content in fish in the Paglia River (from 0.052 to 1.2 µg/g) frequently exceeds the USEPA fish muscle guideline (0.30 µg/g wet weight, methyl-Hg [73]). Moreover, the analysis of fish muscle revealed that MeHg represented more than 90% of the Hg content [40]. Such high Hg concentrations in fish pointed to active methylation, significant bioavailability and the uptake of Hg by fish in the Paglia River ecosystem. Mattioli [72] proposed 130 g/day and 80 g/day as thresholds of local fish consumption for adults and children, respectively. Fishing is indeed currently banned by several local authorities along the Paglia River. Finally, an implication of Hg transfer to the biosphere, and specifically plants, is the potential release of Hg during wildfires [74].

3.7. Long-distance transport

It is well known that Hg in the gaseous form can travel very long distances (thousands of kilometers). In the case of the MAMD, as noted above, Hg and other PTEs are transported for long distances (up to hundreds of kilometers) from the MAMD, mostly in particulate form, and also by waterways, eventually reaching the Mediterranean Sea and contributing to its Hg budget. Such a Hg input to the Mediterranean Sea can be considered a primary environmental hotspot, because this sea is a semi-closed water body surrounded by heavily populated countries; therefore, it is vulnerable to anthropogenic inputs. Its Hg content is indeed low compared to other seas (1.32 ± 0.48 pmol/L against 2.4 ± 1.6 and 2.9 ± 1.2 pmol/L for the North Atlantic and South/Equatorial Atlantic oceans, respectively) [75], but the highly toxic MeHg species is particularly abundant (43% of the total Hg against 10–30% in oceanic waters) [76]. Earlier studies outlined the role of the MAMD as a source of Hg in the Mediterranean Sea (e.g., [77–82]). More recent studies [83,84] have documented distinct Hg anomalies at the mouths of rivers draining the MAMD. Specifically, Scanu et al. [83] determined up to 2.2 mg/kg Hg in marine sediments off the northern Latium coast. Mercury distribution maps show a distinct anomaly at the mouth of Fiora River, which drains the southern sector of the MAMD (Figures 1 and 2). Although there are other anthropogenic contributions (e.g., from a coal-fired power plant), the impact of past mining and smelting in the MAMD is evident. Montuori et al. [84] analyzed Hg and other seven PTEs (As, Cd, Cr, Cu, Ni, Pb and Zn) in waters and sediments in the final tract of the Tiber River and in the Mediterranean Sea off the river estuary (up to a 1.5-km distance). They calculated a load of about 23 kg/yr of Hg delivered by the river to the Mediterranean Sea, i.e., the same order of magnitude of the load released by the MAMD to the Paglia-Tiber system [42,85] (see also below). More recently, Fornasaro et al. [86] reported the results of a survey conducted in the Tuscan section of the Paglia River from June to November 2020. They emphasized the seasonal variability of the Hg loads, which are strongly dependent on hydrological conditions. A maximum load of 42 g/day before the confluence with the Tiber River was estimated. The combination of data obtained for different seasons and hydrological conditions suggest that up to 40 kg/yr of Hg is drained to the Tiber River and, finally, to the Mediterranean Sea.

3.8. Remediation

There are only two mines in the district where remediation was accomplished or is ongoing, even if there were preliminary plans for other sites (e.g., [87]). After closure in 1981, the Siele mining and smelting area underwent the first reclamation of the MAMD, which ended in 2001 [88,89]. Reclamation was limited only to the main mine and smelting area. Other nearby mining centers and small operations were not included in the plan. Reclamation actions included i) excavation of contaminated soils around the buildings; ii) removal of wooden parts and plaster from buildings; iii) removal of metallurgical wastes; iv) creation of two dedicated dump sites to store all contaminated materials and v) hydraulic regulation of the hydrographic drainage system of the area [34]. Fornasaro et al. [34] analyzed soils and stream sediments, GEM concentration in air, leachable Hg and MeHg 20 years after reclamation to evaluate the present risk for the environment and human health. Stream sediments in the Siele creek downstream of the mine still showed highly anomalous Hg values (from 0.9 up to 5400 mg/kg; Figure 3); soils showed concentrations that ranged between 1.3 and 1,200 mg/kg. GEM concentrations in the air near the former metallurgical buildings and immediately downstream of the mining area were also high (up to 16,233 ng/m^3), although they were than before reclamation (values up to 237,000 ng/m^3; [90]).

The leaching tests demonstrated that Hg mobility is lower than 1 μg/L, and the MeHg concentrations were mostly below 1 ng/kg (with a single value of 6 ng/kg). Therefore, the actual risk to the environment and human health is deemed low. On the other hand, the results obtained in this study showed that the fluvial sediments of the Siele creek are among those with the highest concentrations of Hg in the MAMD. The highest Hg concentrations occurred within 500 m from the mine, suggesting that the mining area remains the largest source of Hg. Although the mining and smelting areas were subjected to reclamation, the concentrations of Hg found in sediments and soils in the Siele creek are comparable to those of the Pagliola creek, which drains the ASSM site, where reclamation is still under way. Reclamation of this latter mine and smelting center is being conducted by the municipality of Abbadia San Salvatore. The main targets [91,92] include the i) clean-up of buildings and mining and smelting plants; ii) removal of the most contaminated material and its delivery to a specially designed landfill; iii) impermeabilization of the contaminated soils to preclude any percolation to the water table; iv) installation of a hydraulic barrier and a water treatment plant and v) conversion of buildings to a museum, and of open grounds to public green. The mine area was operationally divided into seven sectors, among which the most contaminated is Sector 6, which hosts the former roasting furnaces, condensers, driers and storage areas (Figure 4). Reclamation plans include an area of about 65 ha (blue contour in Figure 4) that was defined by regional guidelines for the environmental rehabilitation of the mining areas and buildings for museum purposes and public greens.

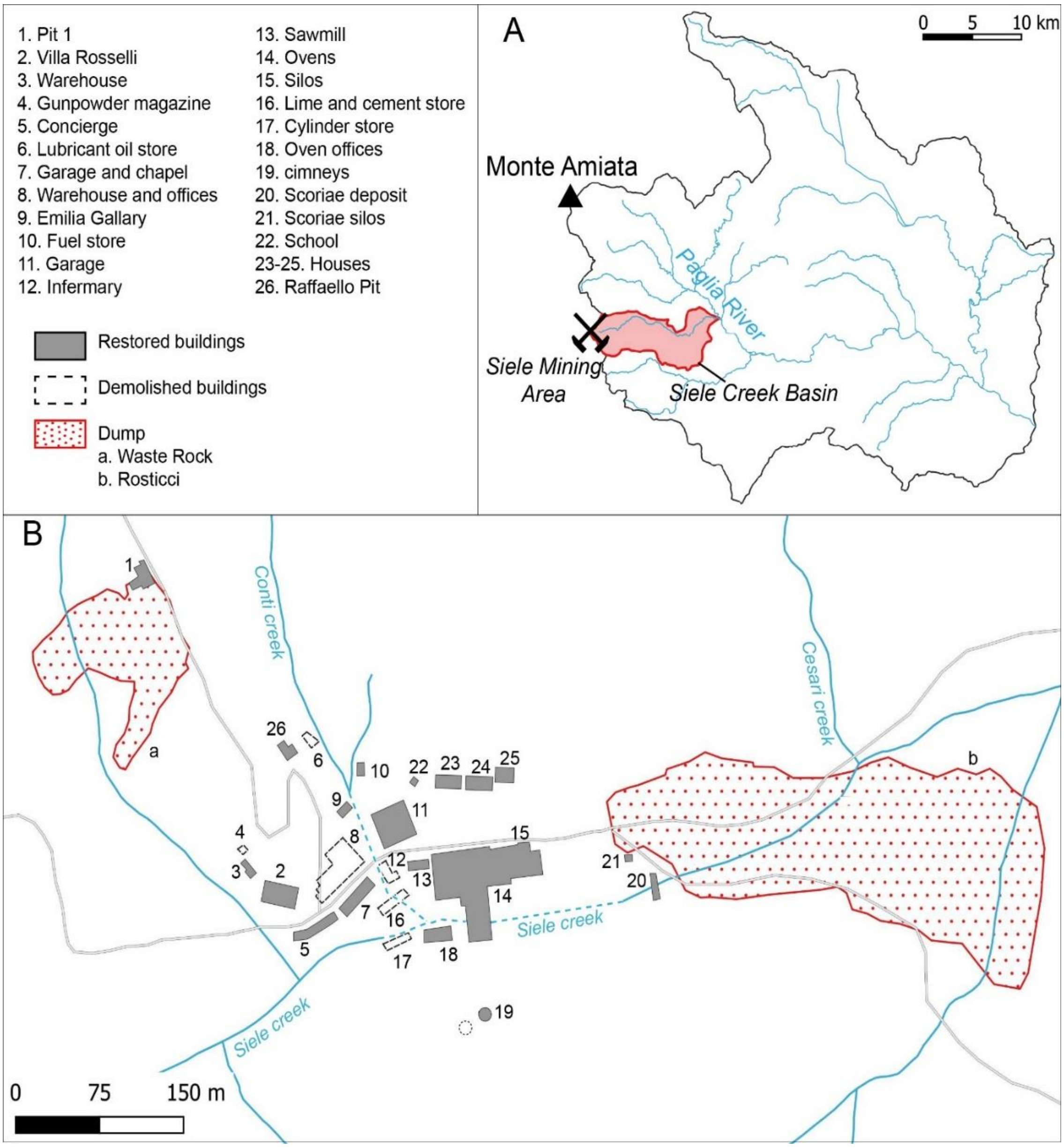

Figure 3. A) Location of Siele mine within the Paglia River basin; B) Map of the Siele mine, with the location of the mining buildings before and after remediation. The location of the two mining dumps is also shown (modified from [34]).

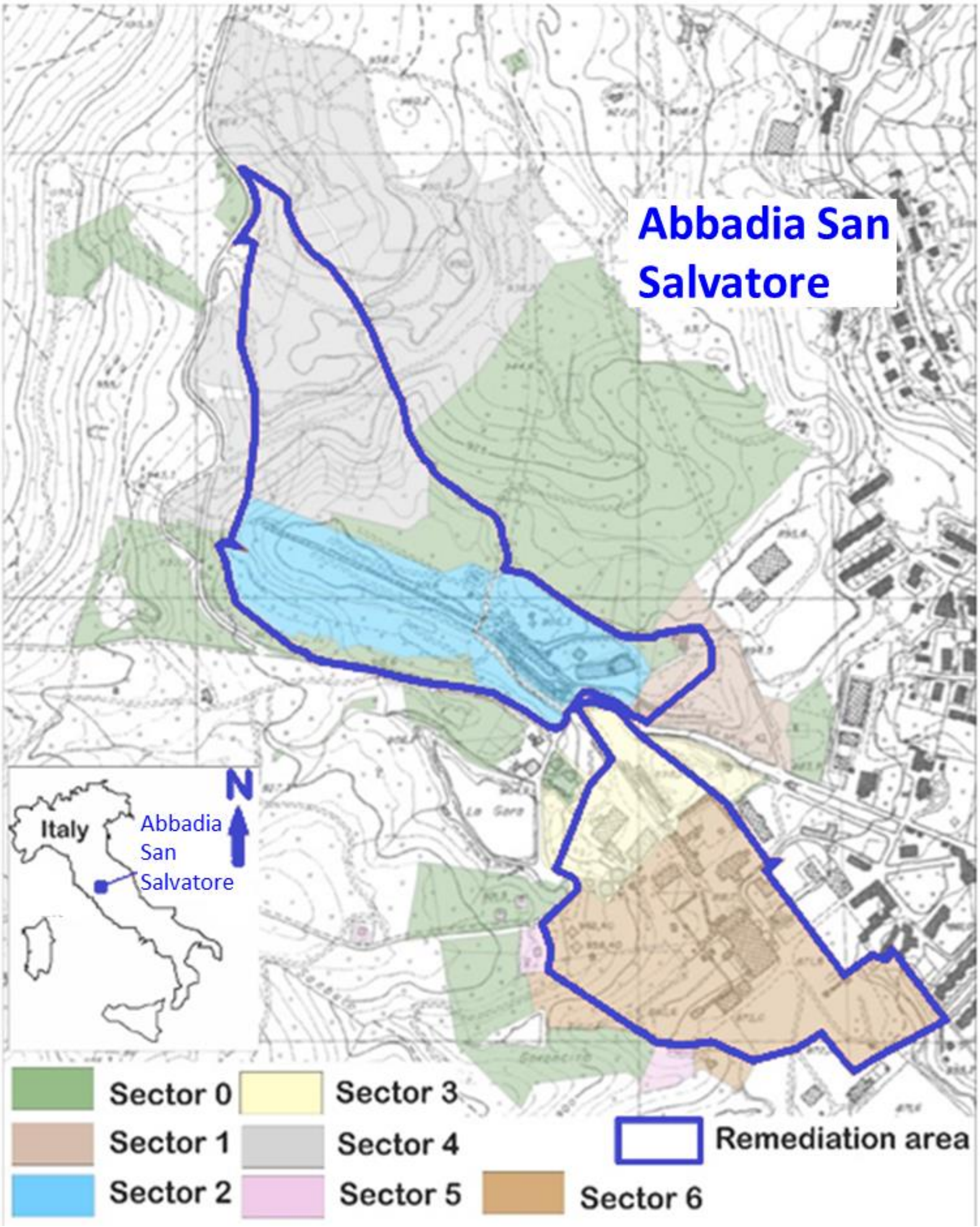

Figure 4. Location of the Hg-mining and smelting area of Abbadia San Salvatore and the seven sectors into which the area was divided according to the different reclamation activities (modified from [93]). Scale: 1:15,000.

The soil in front of furnaces may contain up to 2 wt.% Hg [91]. Several GEM surveys were carried out between July 2011 and August 2015 inside and outside of the buildings in Units 2, 3 and 6 [93]. These measurements showed that the GEM concentrations in the buildings hosting the furnaces (Sector 6) may exceed the upper instrumental limit (>50,000 ng/m^3). Moreover, a general increase of GEM values was recorded from June to September, when the ambient temperature could be >30 °C. A significant decrease was observed in winter (temperature down to 0° C), or on windy days. High concentrations of Hg^0 and leachable Hg were also detected in edifices used for machinery maintenance and in offices, suggesting that their plasters and paints act as Hg adsorbents when exposed to high GEM concentrations. In fact, after removal of the surficial portion of the internal walls of these buildings, the GEM values abruptly decreased. Lazzaroni et al. [94] developed a simple, low-cost method to estimate the potential release of GEM by building materials such as bricks, tiles and concrete. Fragments of the material to be tested were placed under PVC cylinders, which were then sealed. At the top of the cylinders, a 3-way valve system connected to a Lumex detector allowed real-time monitoring of the released GEM. Finally, Cabassi et al. [95] tested a new method of real-time GEM measurements by transporting a Lumex instrument using an unmanned aerial vehicle (Figure 5A). In this way, it was possible to represent the 3D distribution of GEM in the atmosphere up to 60 m above the ground (Figure 5B). Gaseous elemental Hg concentrations in the urban area located a few hundred meters from the mining plants were relatively low (between 18 and 30 ng/m^3). By contrast, significant variations and higher GEM concentrations (up to 5,000 ng/m^3) at increasing heights or downwind were observed above the structures hosting the old furnaces.

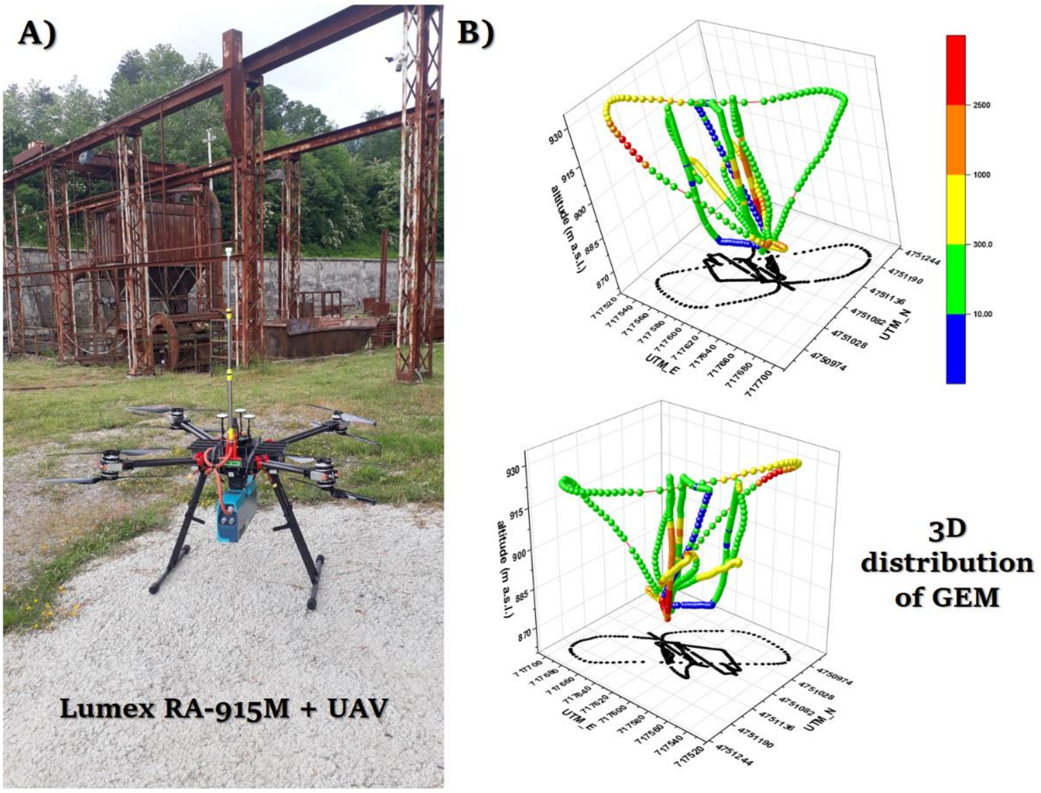

Figure 5. A: Photo of a Lumex RA-915M instrument coupled with an unmanned aerial vehicle. B: 3D distribution of GEM over the explored area (modified from [95]).

Water sampling surveys of the shallow aquifer underlying the reclamation area have been carried out three times a year since 2013. In March 2013, the construction of a bypass canal cutting across the entire mining area was completed. The canal drains runoff waters, thus minimizing the water-rock interaction processes between rainwater and Hg-contaminated soils. The efficiency of the canal was evidenced by a significant decrease of Hg concentration in the groundwater system. In particular, 41 waters were analyzed for physicochemical data and main, minor and trace species in January 2017 [96]. Waters can be divided into two distinct geochemical families: Ca-HCO$_3$ and Ca-

SO_4. The Hg concentrations were generally above the maximum permissible concentration (MPC) for potable (>1 µg/L) and industrial (5 µg/L) waters. However, groundwaters downstream of the mining area showed Hg contents lower than MPC.

Thirty-four topsoil samples from the “Le Lame” mining dump (Sector 4 of the reclamation area, Figure 4) were analyzed for bulk Hg, As and Sb contents. Leaching tests were conducted based on interaction with CO_2-saturated water (liquid to solid ratio 5:1) [39]. The highest values of total and eluate Hg (1,910 mg/kg and 7 µg/L, respectively) were found in the northern portion of the mining dump, where older calcines, which formed from older, less efficient Spirek-Cermak furnaces, are accumulated (Figure 6). According to PHREEQC simulations [97], the main species in solution is Hg^0. The lower concentrations of Hg in the soil leachates from the southernmost part of the dump may be related to a higher efficiency of the roasting process (Gould furnaces), or to the fact that Hg is not retained by Fe-(oxy)hydroxides.

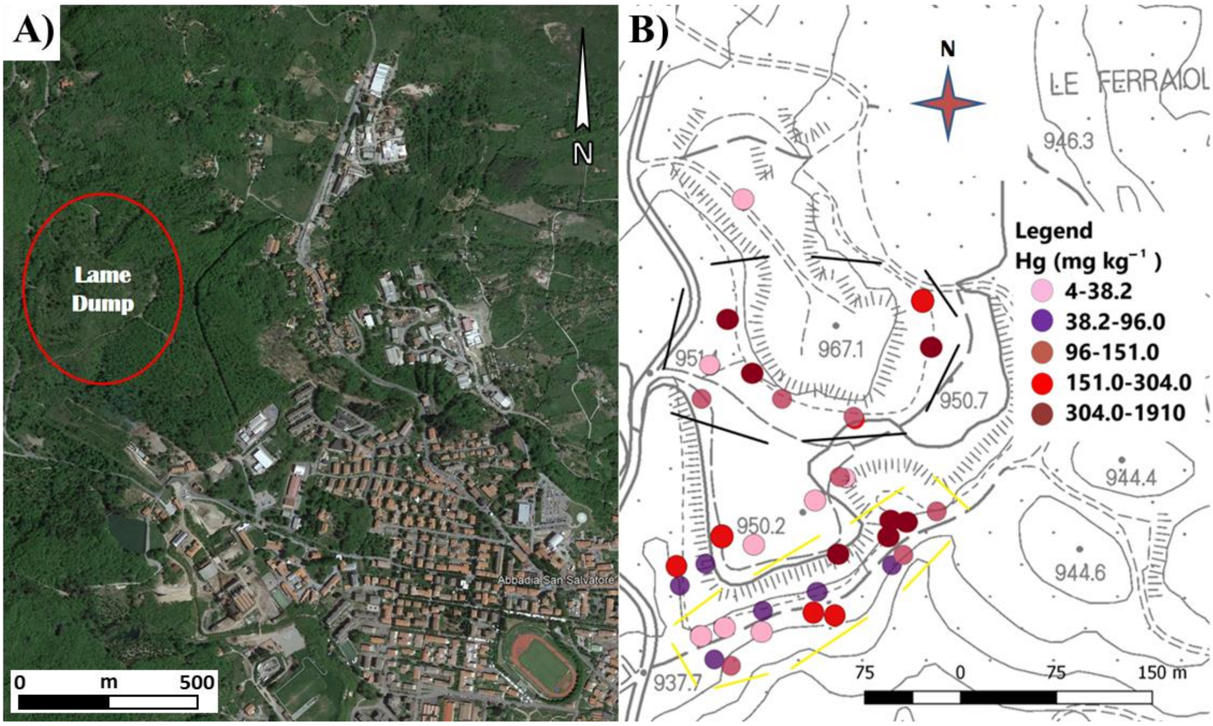

Figure 6. A. Satellite image of the town of Abbadia San Salvatore and its surroundings; the location of B is marked by the red circle. B. Dot map of Hg of the studied topsoils in the Le Lame dumping area. The yellow and pale-black dashed lines are defining the probable areas where the post-roasting wastes produced respectively by the Gould and Cermak-Spirek furnaces were located (modified from [39]).

Additional data on soil and waste materials in the target area of the reclamation were provided by Protano and Nannoni [32]. They reported quite high Hg, Sb and As contents (up to 526, 138 and 97 mg/kg, respectively). Through speciation studies, they concluded that the Hg in these samples was quite mobile, whereas As and Sb mostly occurred in the residual phase (i.e., they are scarcely mobile).

3.9. Health effects

During mine exploitation, silicosis affected underground miners [98], and professional exposure to Hg was quite high, especially at smelters [20], producing remarkable health diseases [28,99,100]; however, according to this last paper, during exploitation, the problem was perceived as of minor concern, even by workers' unions.

The study by Bellander et al. [28] considered blood and urine data obtained between 1968 and 1982 for a cohort of workers at the Abbadia San Salvatore smelter, and for exposure to Hg in air (1982 data for a smaller cohort). All different tasks in the smelter involved substantial exposure to Hg, well beyond the recommended standards. The highest exposure was during the production of cinnabar pigment (mean air exposure: 160 $\mu g/m^3$, i.e., more than 500 times the recommended limit of 300 ng/m^3 [101]; urine concentration: 1,100 µg/L, i.e., almost 800 times the reference mean value of 1.5 µg/L [102].

Other studies explored the exposure of, and effects on, the general population [103, 104, 105]. More recent papers about the health status of residents in the Monte Amiata communities were mostly focused on the assessment of the supposed effects of the exploitation of geothermal power plants [106–109]. These studies were focused on the general population; therefore, individuals with a known history of professional exposure were commonly excluded. However, exposure from geothermal plants and from past mining/smelting activities, as well as from other sources (e.g., dietary or smoking habits) obviously overlap, and are not easily distinguished.

The most recent study [109] was based on consideration of four parameters: 1) evaluation of human exposure to H_2S, As and Hg emissions from geothermal power plants; 2) metal (As, Hg, Tl, Cd, Co, Mn, Ni, V) concentration in urine and blood samples; 3) As concentration in tap water and 4) respiratory tests and clinical questionnaires. The study did not reveal any direct relationship between exposure to H_2S emissions and the insurgence of respiratory diseases. Also, no correlation was found between Hg and As concentrations in air and the risk of respiratory diseases insurgence. These results confirmed those found by Bates et al. [110] in Rotorua, New Zealand, and they are at variance with other studies that were based on hospitalization and mortality rates (which are biased due to the non-hospital treatment of many respiratory diseases). No correlation was found between H_2S, Hg and As concentrations in air and the insurgence of cardiovascular diseases, but a clear correlation was found between those concentrations and hypertension symptoms. Overall, the biological samples collected for this study in the Monte Amiata area showed mean values of metal concentrations that were higher than the average for the Italian population, with the exceptions of V and Cr. The inhabitants of the main municipalities (Abbadia San Salvatore, Piancastagnaio, Arcidosso, Castel del Piano, Santa Fiora, Castell'Azzara) showed As, Hg, Tl, Co and Cr concentrations higher than those of the control groups. The contents of some metals were clearly related to smoking and/or dietary habit. Specifically, for As, it showed high concentrations in urine samples of citizens that drink local tap water rather than bottled water. The chronic exposure to As from drinking tap water was correlated with an increasing risk of respiratory and cardiovascular diseases and cancer in the Monte Amiata municipalities. By contrast, the concentration of metals in urine and blood samples from the Monte Amiata area collected for this study does not appear critical for the insurgence of renal, respiratory, liver or thyroid diseases. On the other hand, a possible correlation between some chronic diseases and the high concentrations of the aforementioned metals cannot be ruled out.

Table 1. Ranges of Hg values obtained in the reviewed papers. (b) = background value for the selected environmental matrix; * = values measured outside the MAMD.

Site	Sample/matrix	Hg	Reference
Italian law limit for residential, public green and agricultural soil	soil	1 (mg/kg)	D.Lgs 152/06 [35]
Siele mining area	soil (b)	ca. 1 (mg/kg)	Fornasaro et al. [34]
	soil	1.3–1,200 (mg/kg)	
	sediment	0.9–5,400 (mg/kg)	
Paglia River	sediment	< 0.2–100 (mg/kg)	Fornasaro et al. [45]
Paglia River basin	soil (b)	0.08–2.98 (mg/kg)	Montefinese et al. [33]
Fosso della Chiusa creek	SPM	0.27–17.5 (mg/kg)	Lazzaroni et al. [58]
Abbadia San Salvatore mining dump	soil	4–1,910 (mg/kg)	Meloni et al. [39]
Fosso della Chiusa creek	precipitating sediment	1.2 (mean) (mg/kg)	Vaselli et al. [57]
Paglia River	soil	2–98 (mg/kg)	Colica et al. [43]
Paglia—Tiber River catchment	soil	0.02–100 (mg/kg)	Rimondi et al. [44]
	sediment	0.02–1,900 (mg/kg)	
Vivo d’Orcia	soil (b)	0.9–1.2 (mg/kg)	Protano and Nannoni [32]
Abbadia San Salvatore	soil/mining waste	1–526 (mg/kg)	
Orcia River	sediment	0.2–195 (mg/kg)	Chiarantini et al. [47]
Orcia-Ombrone confluence	sediment	0.06–0.09 (mg/kg)	
Italian law relating to the quality of water for human consumption	water	1 (μg/L)	D.Lgs 31/01 [53]
Fosso della Chiusa creek	water	< 0.1–2.8 (μg/L)	Lazzaroni et al. [58]
Fosso della Chiusa creek	water	0.1– 2.2 (μg/L)	Vaselli et al. [57]
Abbadia San Salvatore	water	0.2–0.3 (mean) (μg/L)	Magi et al. [56]
Paglia-Tiber River catchment	water	0.01– 0.08 (μg/L)	Rimondi et al. [44]
Orcia River	water	< 0.002–0.46 (μg/L)	Chiarantini et al. [47]
Monte Amiata	air	3–5 (ng/m^3)	Local background
Abbadia San Salvatore	air	18–5,900 (ng/m^3)	Cabassi et al. [95]
Abbadia San Salvatore	air	3.8–6,700 (ng/m^3)	McLagan et al. [61]
Monte Amiata flank	air	1.3–166 (ng/m^3)	
Piancastagnaio	air	21–194 (ng/m^3)	Cabassi et al. [60]
Northern Latium coast*	marine sediment	0.03–2.2 (mg/kg)	Scanu et al. [83]
Tiber River*	water/sediment	23 (load kg/yr)	Montuori et al. [84]
Monte Morello	black pine barks (b)	5–98 (μg/kg)	Chiarantini et al. [47]
Monte Amiata	black pine barks	19–8,651 (μg/kg)	
Monte Amiata	black pine barks	0.1–28.8 (mg/kg)	Rimondi et al. [68]
Monte Amiata, Abbadia San Salvatore	lichens	180–3,600 (ng/kg)	Rimondi et al. [69]

4. Concluding remarks

In the last eight years, new investigations, mainly carried out at the University of Florence, made significant advances toward understanding the dispersion of Hg (and other PTEs) from the MAMD. The main achievements can be summarized as follows: i) Hg isotopic characterization of primary ores, calcines, soil and sediments and Hg concentration ranges in each environmental matrix (Table 1); ii) definition of the relationship between the geomorphological evolution of the Paglia River valley and Hg transport in particulate form; iii) quantification of the extent of contamination in the Paglia-Tiber system to the city of Rome, including improved estimates of the mass loads discharged to the Mediterranean Sea; iv) detailed measurements of gaseous Hg in the Abbadia San Salvatore and Siele areas; v) use of biomonitors to reveal the dispersion of Hg (and other PTEs) and vi) a detailed follow-up of the ongoing remediation at the ASSM and evaluation of the remediation effects at the Siele mine. In spite of these progresses, there are still points requiring further investigations, specifically, the i) Hg distribution in the basins of the Fiora and Albegna Rivers and quantification of their contributions to the Mediterranean Sea; ii) soil drilling to estimate the vertical extent of contamination; iii) specific studies on the contamination around other mine sites (e.g., Cornacchino, Bagnore and Morone); iv) quantification, as precise as possible, to quantify the loads discharged into the Mediterranean Sea and assessment of the impact by intense rain events, and v) a follow-up of mitigation and remediation projects. In this respect, it is now fully clear that the diffuse and continually changing character of contamination eliminates the feasibility of hypotheses of total remediation. Therefore, the goal to be addressed is a sustainable coexistence between contamination and human activities. This goal may involve the following activities: i) implementation of GIS-based contamination maps as a direct operational instrument for local authorities (such as that developed by Fornasaro et al. [111]) to tune specific limitations and regulations of human activities (e.g., fishing, instream quarrying and wildfire management); ii) mitigation measures, such as increasing the vegetal cover of banks to limit erosion and runoff and iii) continuous monitoring of air, water and soil contamination, including transfer to the food chain.

Acknowledgments

This review paper did not receive any specific funding. However, the studies on the MAMD carried out at the Dipartimento di Scienze della Terra, Università di Firenze, were substantially supported by the following institutions: MIUR, Università di Firenze, Regione Toscana (through ARPAT), Unione Comuni Val d’Orcia. We thank the two anonymous reviewers for their useful comments.

Conflict of interest

The authors declare no conflict of interest.

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