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Article

Effects of the November 2012 Flood Event on the Mobilization of Hg from the Mount Amiata Mining District to the Sediments of the Paglia River Basin

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Abstract: The Mount Amiata mining district (southern Tuscany, Italy) was, for decades, one of the world's largest mercury (Hg) producing regions, where mining activity lasted until the 1980s. The Paglia River drains the eastern part of the district and is also the main western tributary of the Tiber River. Recent studies show that, still today, high total Hg contents severely affect the downstream ecosystems of these rivers. In November 2012, a major flood event occurred in the Paglia River basin, which drastically changed the river morphology and, possibly, the Hg concentrations. In the present work, stream sediment was sampled before and after the flood to evaluate possible changes in sediment total Hg concentrations as a consequence of this event. The comparison between pre- and post-flood Hg concentrations shows that Hg content increased up to an order of magnitude after the flood, suggesting that this event triggered Hg mobilization in the basin rather than its dilution.

Keywords: mercury; mining; Mount Amiata; sediment; flood; dam

1. Introduction

In recent decades, human civilization and a concomitant increase in industrial activity have gradually redistributed many toxic metals from the Earth's crust to the environment, increasing the possibility of human exposure. Mercury has accumulated in soils, where it is present in a large variety of chemical forms, bound to the finest soil fractions [1].

Mercury does not serve any known biological benefits or functions, and most of its compounds are toxic, even at low doses [2].

Globally, approximately one million metric tons mercury (Hg) have been extracted from various ore bodies in the world [3], most notably in the Mediterranean region [4–7], which hosts about 65% of the world's cinnabar (HgS) deposits [8]. Recent studies documented high mercury concentrations in Mediterranean fish, likely due to this geogenic (and anthropogenic) anomaly [4].

The Mount Amiata mining district (MAMD), located in southern Tuscany (Italy), belongs to the circum-Mediterranean Hg belt (Figure 1) and covers 400 km^2 [9].

About 102,000 metric tons of Hg were produced from the 1860s to 1980 in this region [9], ranking it as the fourth largest Hg producing district worldwide. The Paglia River draining this area is one of the main tributaries of the Tiber River (the third longest river in Italy), which discharges into the Mediterranean Sea. The Tiber River may then be considered as one of the main contributors to the total Hg budget of the Mediterranean Sea.

Because the process of Hg recovery involves roasting (calcination), the mine waste generated is referred to mine waste calcine, or simply calcine. As the retorting of Hg ore mineral (generally cinnabar) is an inefficient process, waste calcines found at most Hg mines contain unconverted cinnabar, Hg(0) and ionic Hg compounds formed during processing [10,11]. Leaching and erosion of mine-waste result in anomalously high Hg concentrations in stream sediment and water [12–15], even decades after the end of mining [13,16–19]. The presence of Hg in rivers results in a contamination reaching coastal areas and marine ecosystems hundreds of kilometers away from the primary source [13,20].

The Paglia River has a key role in the transport of Hg, because it drains the south-eastern part of the MAMD, collecting water from different mines located at the head of its tributaries (Figure 2). This river has a torrential regime, especially in the upper mountain part [21], and in association with intense rainy events, flash floods are often documented [22]. Storm events are known to have a major role in the remobilization of river bank sediment, providing large amounts of Hg into ecosystems in the surroundings of Hg mines [23,24]. Under these conditions, enormous quantities of contaminated particulate are mobilized as a result of the high runoff, increasing the capacity of the stream to erode contaminated banks and sediment transport.

In a recent study carried out on fish, soils, stream water and sediment, Rimondi *et al.* [16] showed that, although more than 30 years have passed since the mining activity came to a complete halt, Hg-rich processing residues and abandoned mine structures still constitute an environmental pollution problem.

A further study [25] documented the long-distance transport of Hg on the Tiber River, testifying long-range transport downstream from the MAMD (Figure 2).

In November 2012, a major flood event occurred in the Paglia and Tiber river catchments, causing mobilization of huge masses of sediment and changes in river morphology (Figure 3). Data from a

pluviometric station in this area (Piancastagnaio) indicate an intense precipitation of 328 mm in 48 h, and 350 million m^3 water were estimated to have precipitated in the Paglia River basin following this event [26].

In the present work, we compare analyses of stream sediment of the Paglia and Tiber rivers before (September 2012; Figure 2) and after (March–May 2013; Figure 4) the flood event, which occurred in November 2012, to assess its effects on total Hg contents.

Figure 1. Distribution of mercury (Hg) global belts. The circum-Mediterranean Hg belt (red area) and the most important mining districts for Hg production are reported.

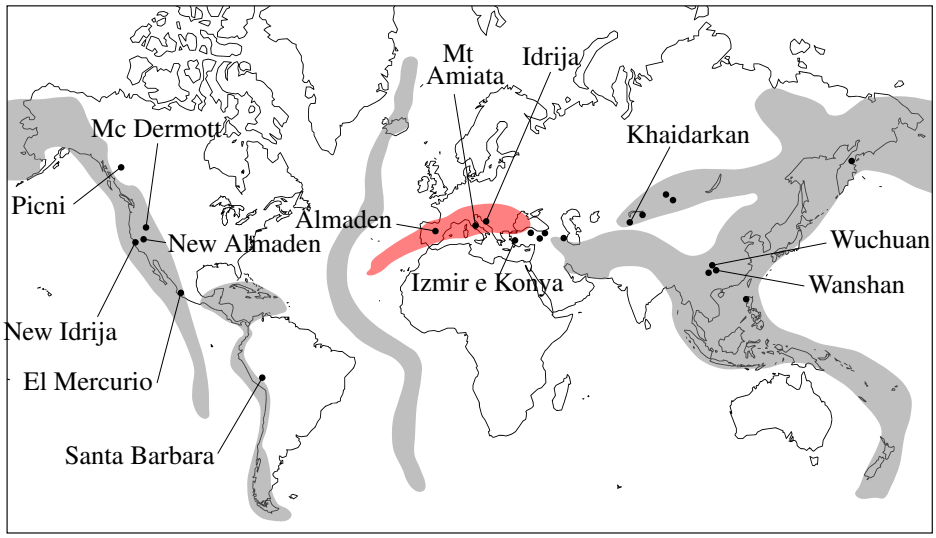


Figure 2. Localization of the study area and sampling sites of the September 2012, campaign (pre-flood). MAMD stands for the Mount Amiata mining district.

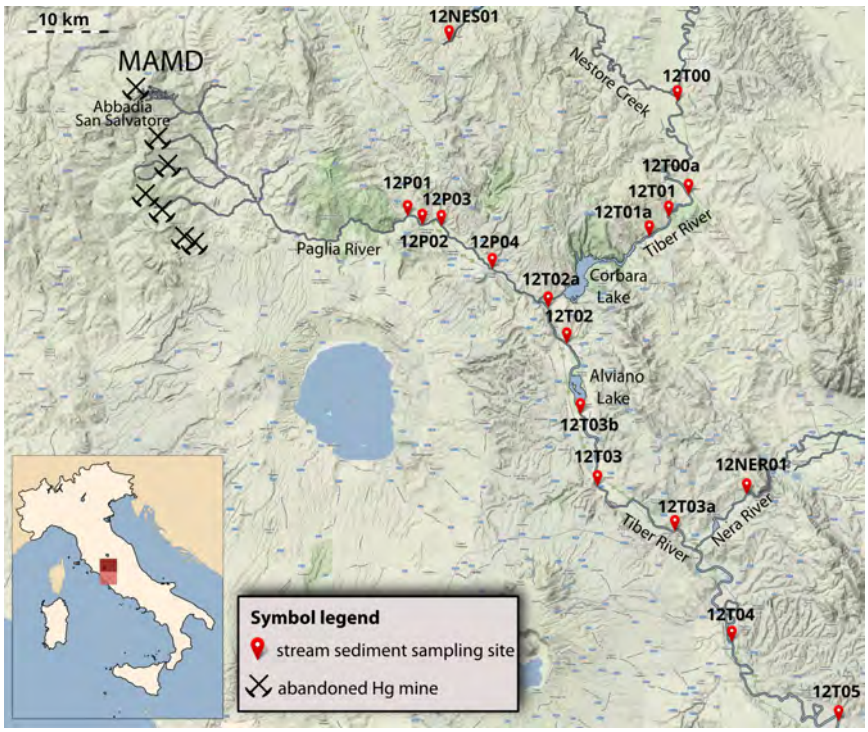


Figure 3. Comparison of the channel morphology of the Paglia River before and after the flood event of November 2012. (**a**) represents the pre-flood state (September 2012), while (**b**) shows the post-flood set-up (March–May 2013). Pictures refer to the PC01 sampling point (collocation in Figure 4). The trees indicated by the red arrows may be employed as reference spatial points.

(a) (b)

Study Area

In southern Tuscany, a wide Hg metallogenic province has clustered around the volcano-geothermal area of Mount Amiata, as a result of the post-collisional events of the Northern Apennines orogenesis [34]. Although mining exploitation in this district started with the Etruscans (about 800 BC) [27–29], large-scale mining activity in this region began only in the late 19th century.

The main mining center was in Abbadia San Salvatore, which was the last mine to close in this district in 1982, after a total production of more than 50,000 metric tons Hg [30]. The Hg content in Mount Amiata ore ranges between 0.6 and 2 wt %. The primary ore assemblage is essentially cinnabar [31]. Non-economic minerals found in association with cinnabar are marcasite (FeS_2), pyrite (FeS_2), stibnite (Sb_2S_3) and rare arsenical sulfides (realgar, As_4S_4, and orpiment, As_2S_3) [32,33]. The typical gangue mineral is calcite ($CaCO_3$) and, rarely, celestite ($SrSO_4$), gypsum ($CaSO_4 \cdot 2\,H_2O$), native sulfur and hydrocarbons [34,35].

A remediation project is presently being carried on at the mine site of Abbadia San Salvatore by the local municipality. Although the runoff from contaminated waste has been reduced, tailings deposits are still present along the river banks.

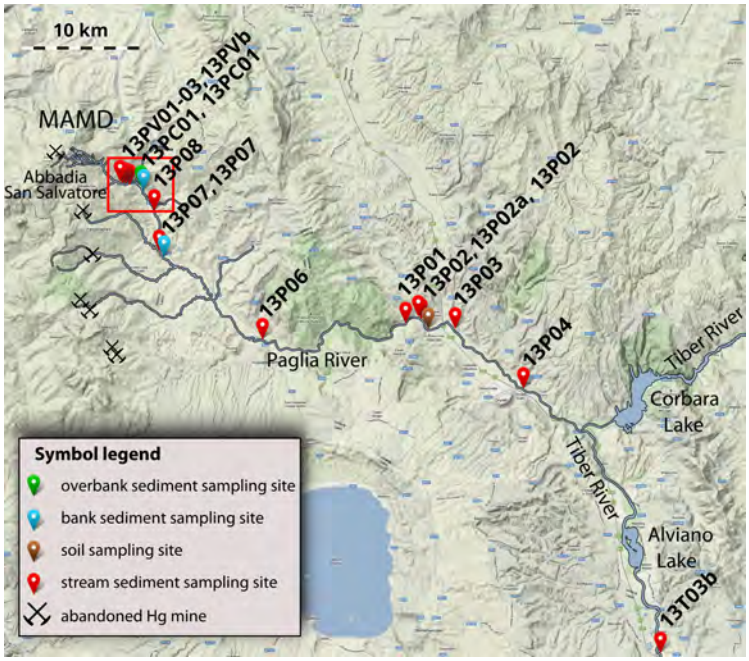
In the present work, the study area includes the western part of the Paglia River (which has a drainage basin of about 1330 km^2) and a portion of the Tiber River catchment together with some of its tributaries (Figure 2). The Paglia River drains the eastern part of the MAMD, and after about 40 km, it flows into the Tiber River (Figure 2).

From a geological point of view, the Tiber River Valley is an extensional basin developed since the late Early Pliocene, characterized by a wide outcropping of sedimentary and volcanic successions [36].

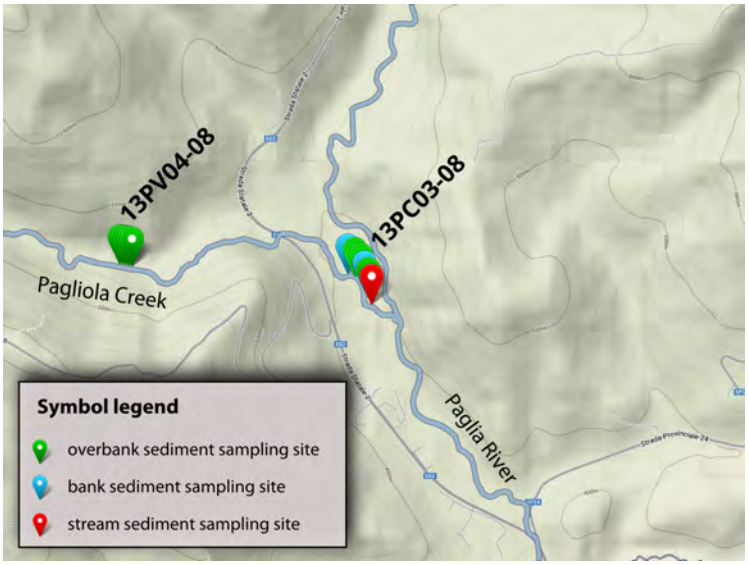
The Tiber River basin is highly urbanized with a population exceeding 4,000,000 residents (70% of which live in the urban area of Rome); moreover, the basin area is relevant for agriculture, ranching and industrial activities. Two dams have been built along the Tiber River in the 1960s, when Hg mining and production in the MAMD were still active, forming the reservoirs of Lake Corbara and Lake Alviano (Figure 2).

In spite of its importance, until recently, no investigations have been carried out in the Tiber River basin to determine the impact of Hg transported by the Paglia River and to quantify the amount of Hg that is consequently delivered to the Mediterranean Sea.

Figure 4. Representation of the sampling sites of the March–May 2013, campaigns (post-flood). (**b**) is an enlargement of the red square in (**a**).



(a)



(b)

2. Experimental Section

2.1. Sample Collection

In this study, two time-distinct sampling campaigns were performed, *i.e.*, before and after the major flood occurred in the Paglia River in November 2012, which has greatly affected the river morphology (*cf.* Figure 3).

The pre-flood campaign (Figure 2) was carried out in September 2012, and consisted of 17 stream sediment samples. Sampling sites coincide with some of Gray's *et al.* study [25], collected at the same time.

The post-flood campaign was conducted in March–May 2013. Twenty-nine samples of stream sediment, topsoil, bank and overbank sediment were collected in the Paglia and Tiber rivers downstream of the mining site (Figure 4). Overbank sediment refers to the one deposited on the floodplain overtopping the river banks. Sampling focused on the Paglia River basin, extending from a site (PV) located 5 km downstream of the MAMD, down to Orvieto (P04). A single sample (13T03) was taken along the Tiber River, 23 km downstream of the confluence with the Paglia River and downstream of the Alviano dam (Figure 4a).

Nera River and Nestore Creek have been chosen as the regional baseline for Hg concentrations, since they are tributaries of the Tiber River located far away from MAMD (Figure 2).

All sediment samples were collected using a plastic scoop; to avoid contamination, sampling was started from sites distal from the Hg district, where the lowest Hg concentration samples were expected. Samples were taken in the top 2 cm and transferred in new plastic bags. Stream sediment was collected on the shoreline next to the river, where accumulation of fine material was observed. A sample was made of three subsamples recovered in different locations of the same sampling site.

In the following, the suffix of the sample ID, 12 or 13, refers to the year of sampling, 2012 and 2013, and it is then distinctive of pre-flood and post-flood campaigns.

2.2. Sample Analysis

Stream, bank and overbank sediment and soils were air-dried, sieved at 200 μm and ground before analysis. The concentration of Hg was determined using aqua-regia microwave digestion (20 min, 175 °C). The supernatant solution was separated from the remaining solid by centrifugation for 30 min at 4000 rpm. Dissolved Hg concentrations were determined by flow injection cold vapor atomic absorption spectroscopy (FI-CVAAS) with a Perkin Elmer FIAS 100 (Waltham, MA, USA) at Department of Earth Sciences, University of Firenze.

The precision and accuracy for Hg analysis were established using a blank method and standard reference materials (SRMs): 2710 (certified value: 32.6 μg/g) and 2711 (certified value: 6.25 μg/g). The relative percent differences for the SRMs were $\leq 4\%$. Method blanks and SRMs were run as 1 per every 10 samples. Method blanks contained Hg close or below the lower limit of determination (1 ng/g). As an additional control of analytical accuracy, 20 samples were analyzed by ACME International laboratories (Vancouver, BC, Canada): with the exception of 4 samples (12NES01(stream sediment (ss)), 12T01(ss), 13T03(ss), 12T05(ss)), differences with our values were, on average, about 25%. These four samples all

have low Hg concentrations (Tables 1 and 2) and did not influence the overall data interpretation. For internal consistency, in Tables 1 and 2 we report the analytical values determined by our laboratory.

3. Results and Discussion

The concentration of Hg in stream samples collected from the Paglia and Tiber rivers in 2012 pre-flood and in the 2013 post-flood campaigns is reported in Tables 1 and 2, respectively. In 2012, Hg in stream sediment varies from 0.1 to 7.5 μg/g, average 1.2 μg/g, a range comparable to that reported by Gray *et al.* [25] for the same sampling sites. Stream sediment with the lowest Hg concentrations (0.1 to 0.5 μg/g) are those collected from the eastern section of the Tiber River (upstream of the confluence with the Paglia River), which does not receive runoff from the Hg mines of the MAMD (Figure 2). Along the Paglia River, stream sediment Hg concentration ranges from 0.9 to 7.5 μg/g, with an average of 3 μg/g.

Table 1. Total mercury concentrations for stream sediment (ss) collected along Paglia and Tiber rivers during the September 2012, campaign. Samples are ordered from the nearest to the farthest from the Mount Amiata mining district (MAMD).

Sample	km from the MAMD	River	Total Hg (μg/g)
Downstream of the mine			
12P01(ss)	33	Paglia	1.7
12P02(ss)	35	Paglia	7.5
12P03(ss)	38	Paglia	1.8
12P04(ss)	46	Paglia	0.9
Downstream of the confluence			
12T02a(ss)	1	Tiber	2.5
12T02(ss)	6	Tiber	1.3
12T03b(ss)	13	Tiber	0.7
12T03(ss)	23	Tiber	0.7
12T03a(ss)	35	Tiber	0.5
12T04(ss)	60	Tiber	0.4
12T05(ss)	90	Tiber	1.0
Upstream of the confluence			
12T00(ss)	–15	Tiber	0.1
12T00a(ss)	–20	Tiber	0.4
12T01(ss)	–25	Tiber	0.5
12T01a(ss)	–45	Tiber	0.1
Baseline			
12NES01(ss)	-	Nestore	0.3
12NER01(ss)	-	Nera	0.2

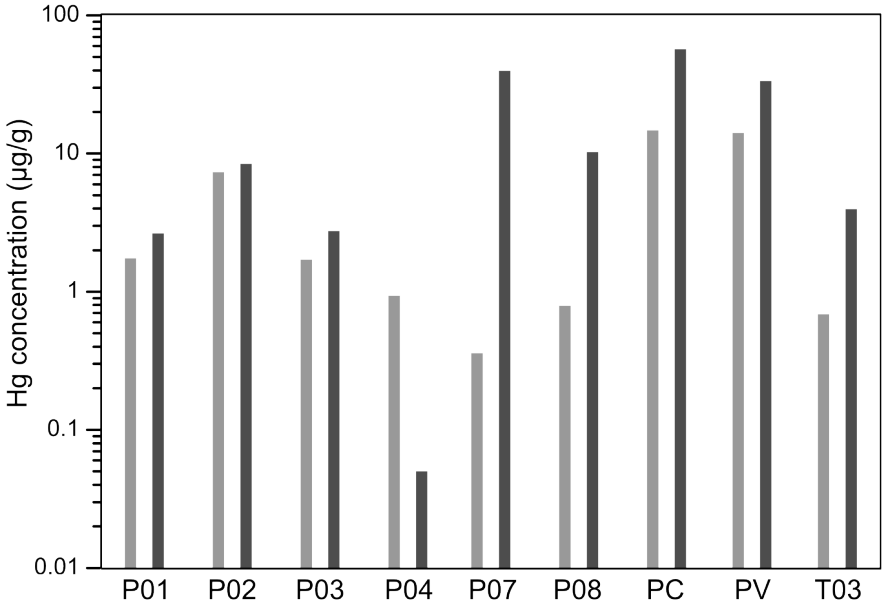
Table 2. Total mercury concentrations for stream sediment (ss), soil (so), bank (b) and overbank (ob) collected along Paglia River after the November 2012, flood event.

Sample	River	Total Hg (µg/g)
13PV01(ss)	Pagliola	53
13PV02(ss)	Pagliola	20
13PV03(ss)	Pagliola	5
13PV04(ob)	Pagliola	225
13PV05(ob)	Pagliola	67
13PV06(ob)	Pagliola	297
13PV07(ob)	Pagliola	20
13PV08(ob)	Pagliola	27
13PVb(ss)	Pagliola	19
13PC01(b)	Paglia	905
13PC01(ob)	Paglia	2
13PC02(ss)	Paglia	3
13PC03(b)	Paglia	300
13PC04(ob)	Paglia	2
13PC05(ob)	Paglia	63
13PC06(b)	Paglia	125
13PC07(ob)	Paglia	115
13PC08(ss)	Paglia	105
13P01(ss)	Paglia	2
13P02(so)	Paglia	2
13P02(ss)	Paglia	13
13P02a(ss)	Paglia	4
13P03(ss)	Paglia	3
13P04(ss)	Paglia	0.05
13P06(ss)	Paglia	16
13P07(ss)	Paglia	40
13P07(b)	Paglia	17
13P08(ss)	Paglia	10
13T03(ss)	Tiber	3

Data collected during the 2013 survey exhibit a Hg range between 0.05 and 105 µg/g, with an average of 18.6 µg/g (Table 2). Almost all Hg concentrations in the post-flood stream sediment samples are apparently increased, if compared to the pre-flood data (Figure 5) (to increase the comparison, data from the study of Rimondi *et al.* [16] conducted in 2010 were also evaluated). Accordingly, statistical analysis performed applying the F test indicates that differences between the two datasets shown in Figure 5 are statistically significant, although the low number of samples may impair these results.

In particular, samples P07 and P08 are increased by an order of magnitude. Accordingly, even in the stream sediment collected along the Tiber River at the site T03 in 2013, the Hg content was four times bigger than the value obtained in 2012.

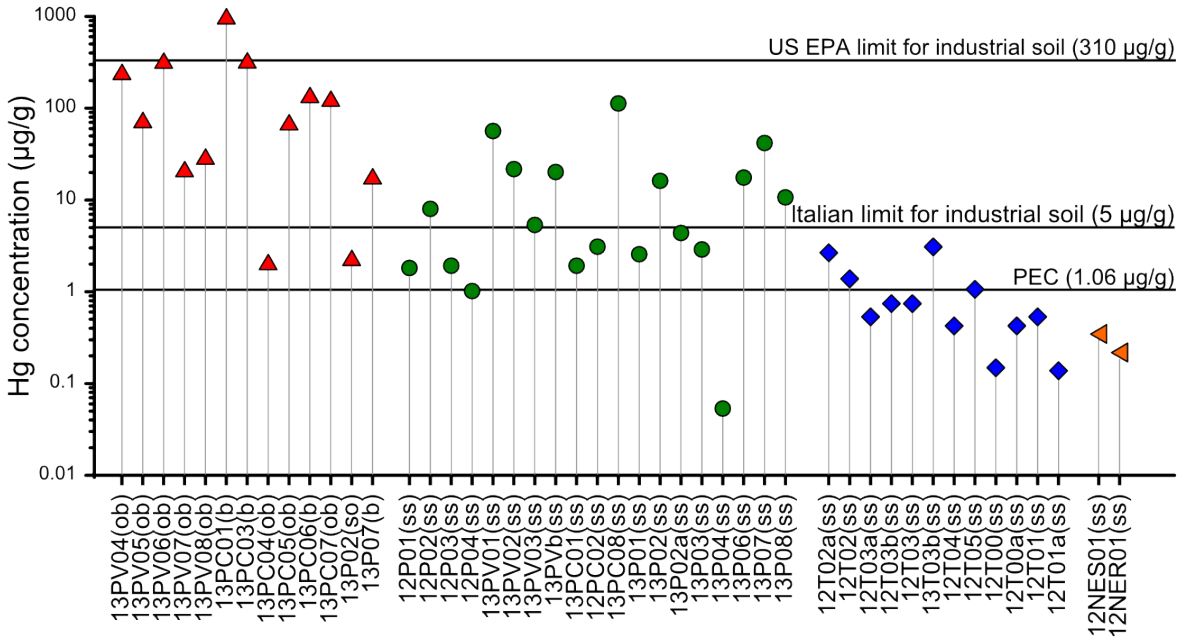
Figure 5. Semi-logarithmic plot showing the comparison between total Hg concentrations before and after the November 2012, flood event. Light grey columns represent the concentration before the flood (from the 2010 and 2012 campaigns), while the dark grey ones indicate the post flood data (2013). 2010 data are available in the literature [16] and refer to P07, P08, PC and PV sampling sites.



Mercury in bank sediment collected during 2013 has an average of 337 µg/g and showed a peak of 905 µg/g at the PC sampling site (Figure 4a), located 5 km downstream of the mine of Abbadia San Salvatore. Such concentrations are two orders of magnitude higher than those observed in stream sediment samples collected in the same period (March–May 2013).

MAMD clearly influences sediment Hg concentration in both the Paglia and Tiber Rivers. Considering the complete stream sediment dataset, more than 45% of the samples exceeded both the Italian industrial soil sediment limit for Hg of 5 µg/g [37] and the probable effect concentration of 1.06 µg/g (PEC, concentration above which harmful effects are likely to be observed in sediment dwelling organisms [38]) (Figure 6), particularly during 2013. This percentage increases up to 66% if samples collected along the Paglia River are exclusively considered, suggesting that Hg could be easily delivered to the river, especially during flood events, thus potentially influencing the whole river ecosystem. In particular, river banks show extremely elevated Hg contents (approaching 1000 µg/g), greatly exceeding both the Italian and the U.S. Environmental Protection Agency (EPA) limits for industrial soils (five and 310 µg/g, respectively) (Figure 6), and thus, they represent a potential source for Hg mobilization through erosion. The case of MAMD and the associated Paglia River is not an exception. For example, more that 2.000 Hg metric tons are estimated to be presently stored in the alluvial sediment of Idrijca River (Idrija mine, Slovenia), suggesting that the erosion of these deposits may greatly increase the remobilization and transport of Hg to the Adriatic Sea long after mining has ceased [39].

Figure 6. The semi-logarithmic scale graph shows the 2012 and 2013 total Hg concentrations in all samples compared with the probable effect concentration (PEC), Italian and U.S. Environmental Protection Agency (EPA) limits for industrial soils. Red triangles represent soils, bank and overbank sediment collected along the Paglia River; green circles and blue squares represent stream sediment total Hg concentrations of the Paglia and Tiber rivers, respectively, while orange triangles symbolize stream sediment collected along Nestore Creek and Nera River. The latter two sites are considered regional baseline sites, located upstream of the known mining impact. The analytical error is below 5%.



The comparison of Hg concentrations in stream sediment before and after the flood of November 2012, indicates that during this event, the Paglia River ecosystem did not experience a dilution, due to the admission of sediment with relatively low Hg concentrations, but, on the contrary, the Hg concentration underwent an appreciable increase. Because river banks of the Paglia River turned out to be highly enriched in Hg, such a Hg increase is likely related to the erosion and transport of the Hg stored in these areas of the Paglia River. In this way, flood deposits in the Mount Amiata area are, depending on the environmental conditions, both a source and a sink of the mass exchange between river and floodplain areas. Hence, river banks and overbank deposits reflect the present quality of the fluvial system and, to some extent, they could determine its future quality.

These results demonstrate that stream sediment compositions are highly time-dependent in streams, especially where pollutants are mainly partitioned in the particulate matter (*cf.* [40]). Accordingly, the measurement of contaminant mass loadings, although being one of the most reliable tool in monitoring watercourse quality, provides only a snapshot of their actual distribution (*cf.* [41]).

Due to the torrential regime and, particularly, in association with intense rainy events, flash floods and associated sliding-like mud and debris flows are very common along the Paglia River catchment [22]. According to some global climate change scenarios [42], the frequency of the so-called extreme events might increase in the future. Such events, coupled with the severe denudation processes that characterize this area (Mio-Pliocene deposits, which extensively crop out along the Paglia River, represent erodible

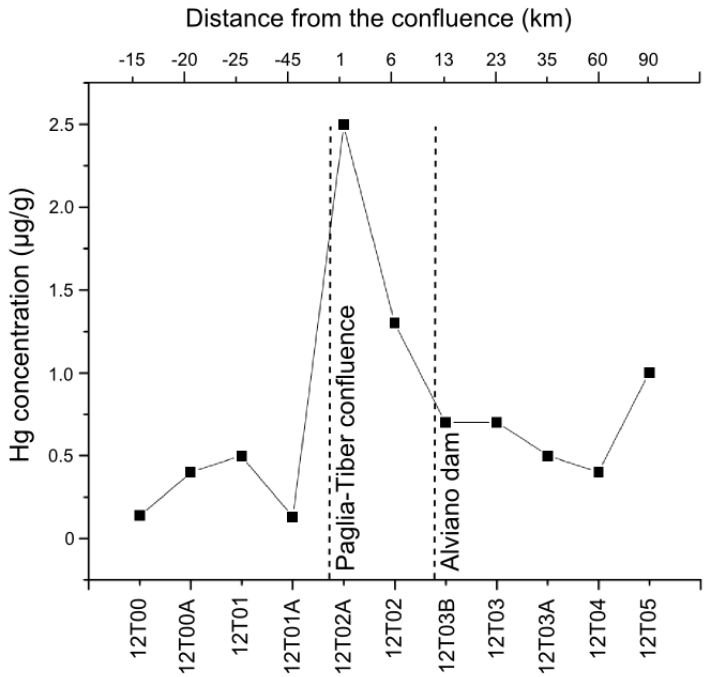
lithologies [43]), will lead to the remobilization of river bank sediment. The importance of the episodic transport of Hg following storm events is stressed in various mining districts [44,45]. Under water floods, enormous quantities of Hg-contaminated suspended particulate matter are mobilized as a result of higher runoff, the increased capacity for the stream to erode contaminated soils and transport sediment [46], resulting in up to an 80-fold increase of Hg transport [46]. Particularly, eight days of the flood event in the Isonzo River (Idrija mine) were sufficient to mobilize up to three times the amount of Hg transported in a whole year [47].

As documented by Gray *et al.* [25] and confirmed by this study, the concentration of Hg drops almost to background levels immediately downstream of the Alviano dam (Figure 7), indicating that this dam acts as a physical barrier for Hg transport, promoting the deposition of Hg-contaminated particulate. Accordingly, Hg contents of fish tissues show a remarkable decrease along with distance from MAMD, suggesting that bioavailable Hg (mainly methyl-Hg) follows a similar trend.

This effect on Hg transport is well documented in the literature [48,49]. Three dams located along the Idrijca-Isonzo River system cause a drastic decrease of sediment, together with a considerable decrement of Hg concentrations [48].

It has been estimated that the annual sediment load in Alviano Lake is about 850,000 m^3/year. During intense hydrological events, as those affecting the Paglia River catchment, the Alviano dam can be opened in order to release sediment downstream. This operation could potentially represent a hazard for the Tiber River ecosystem, since Hg-rich sediment could be transported to the river mouth, resulting in Hg contamination up to coastal areas. Hence, even if this dam seems to work as an environmental filter, it halts Hg transport only temporarily and does not solve the pollution problem.

Figure 7. Total mercury concentrations in the Tiber River stream sediment samples collected in the 2012 campaign. Dashed lines represent the confluence point with the Paglia River and Alviano dam.



4. Conclusions

As recently documented by previous studies in this area, the data here presented confirm that, after three decades from the end of mining activity in the Mount Amiata district, a pervasive Hg diffusion is still present in the Paglia River and extends to the Tiber ecosystem, becoming a contamination of regional importance.

The most elevated Hg concentrations refer to bank and overbank sediment along the Paglia River, where Hg reached 905 μg/g.

Bank erosion and remobilization function as a source of Hg during floods, which are very common and well-documented in the Paglia River. During these events, water is able to remobilize high volumes of sediment, and a significant amount of Hg enters the river water course, representing a hazard for the ecosystems of both the Paglia and Tiber rivers. The recent trends of climate change might increase the frequency of extreme events, including extraordinary rainfalls and consequent floods. Dams along the Tiber River, like that of Alviano, represent a physical barrier for Hg-rich sediment, which limits, at least temporarily, the Hg input in the lower part of the basin. However, such a barrier is limited in time, as extraordinary opening of the dam would result in the release of Hg-rich sediment in the downstream environment.

Future studies are therefore needed in order to plan adequate monitoring and remediation strategies, given the potential influence of the Paglia-Tiber river system on the Hg geochemistry of the Mediterranean Sea. Specifically, the ongoing reclamation at the Abbadia San Salvatore mine should reduce runoff from the mine area to the Paglia River. The actual effect of this reclamation should be quantitatively assessed by new studies of Hg transport in the Paglia and Tiber basins. This represents an unavoidable prerequisite for any program of sediment quality management in this area (*cf.* [50]).

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Author Contributions

Pattelli, Rimondi, Paolieri, Costagliola, Rinaldi, Benvenuti, Chiarantini, Colica, Di Benedetto, Lattanzi: sampling and results interpretation. Paolieri: sample preparation and laboratory analyses.

Conflicts of Interest

The authors declare no conflicts of interest.

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