Geochemical Background and Baseline values of PTEs (Potentially Toxic Elements) in soils and stream sediments from decommissioned mining areas: the Hg-district of Mt. Amiata (central Italy)

Federica Meloni

Department of Earth Sciences, University of Firenze, Via G. La Pira 4, 50121, Firenze

DOI: 10.19276/plinius.2025.01.013

INTRODUCTION

Throughout history, mining operations have created a complicated challenge between local and global authorities over the use of natural resources in an economic circuit. Italy has a long history of mining, going back to pre-Roman times. The demand increased during the 1800s with industrialization, up to half of the 20th century, when Italy entered the Common European market (the beginning of globalization).

Tuscany, as well as Sardinia, and parts of northern and southern Italy host important ore deposits, and the former region has mineralized areas that have already been exploited since the Etruscan times. Only at the end of the 19th century, the supergiant mercury (Hg) district of Mt. Amiata (between Siena and Grosseto Province) and the large pyrite district of Colline Metallifere were discovered (Dini, 2003). Tuscany had its greatest development for metal ores, including cinnabar, around the 1930s, after which a gradual decline occurred.

The study area regards about 120 km^2 of the eastern portion of the Mt. Amiata Hg-district (Fig. 1a) and includes eight of the most important Hg mines of the area, including that of Abbadia San Salvatore (ASS) mine, which was classified as the third Hg mine in the world. The drastic decrease in HgS extraction occurred in the 1970s due to a decrease in market demand and the

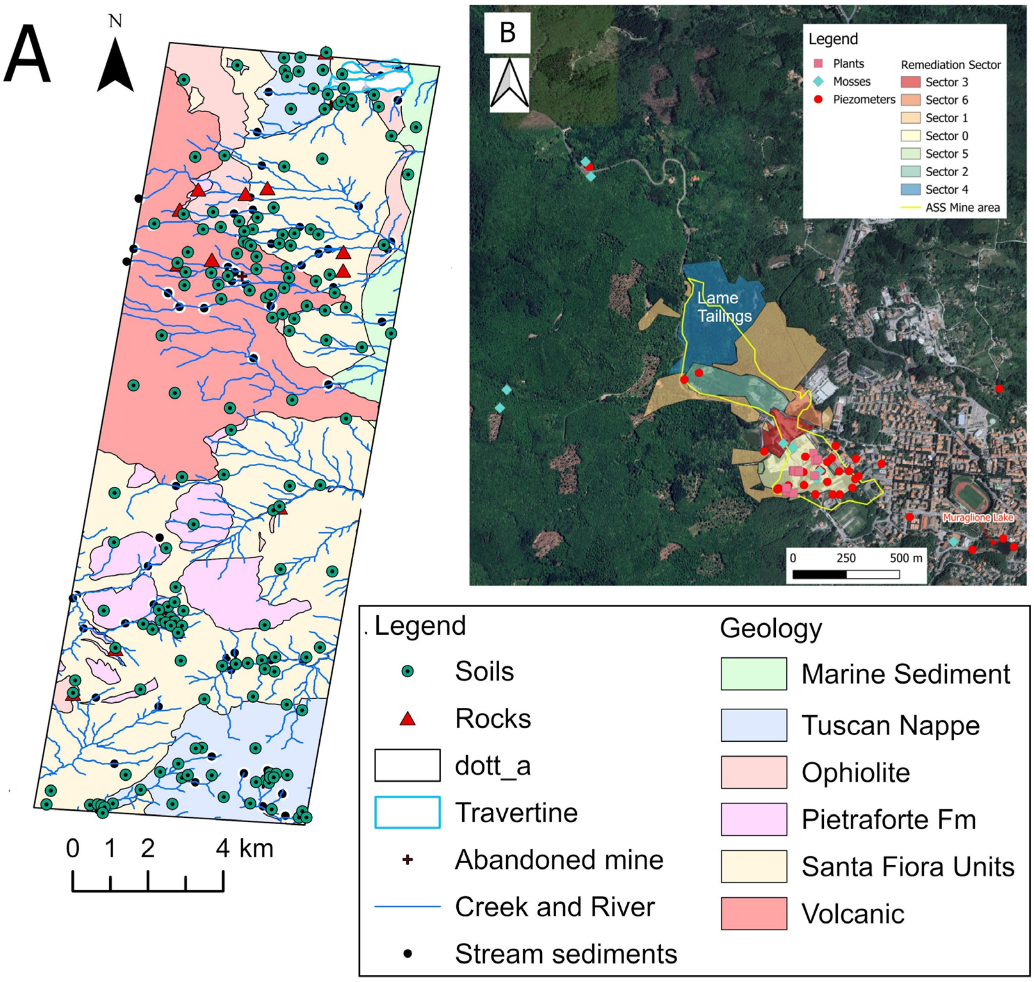

Figure 1 ***a)*** *The 120 km^2 geological map of the study area with rocks (red triangles), soils (green circles), and stream sediments (black circles) samples.* ***b)*** *The remediation area of ASS mine subdivides into different sectors according to Hg concentration, the plants samples (pink squares), mosses samples (light blue diamonds), and piezometers (red circles).*

emergence of Hg toxicity after the Minamata (1956) and the Iraq (1971) disasters. The ASS mine was the last mine that ceased its activity in the district in 1982. Mining projects have direct and indirect environmental impacts on the environmental matrices, and any decision is increasingly complex due to the large number of environmental laws that must be followed.

Thus, it becomes important to know the geochemical background value in order to establish reasonable post-mining remediation activities.

This PhD thesis investigated the mercury (Hg) contamination in the Mt. Amiata area by developing methods to assess its speciation and bioavailability in soils and sediments. Environmental matrices (sediments, streams and waters) were investigated during reclamation operations in the ASS mining area (Fig. 1b), identifying zones where further interventions are required. The study also evaluated the Le Lame tailing (Fig. 1b) as a suitable site for storing Hg-contaminated Muraglione lake sediments (Fig. 1b). Ten years of geochemical monitoring surveys were used to model Hg transport and assess mitigation strategies. Lastly, geochemical background values were established to support environmental assessment and policymaking.

MATERIALS AND METHODS

Sampling soils, stream sediments and waters

The geological map was simplified by grouping the main lithologies, *i.e.*, Volcanics, Ophiolitic Unit, Limestones, Sandstone, Mudstone and Travertine. Soil samples were collected from both top- (10-50 cm) and sub- (50-150cm) soils following a two-fold strategy: a) one sample each 2 km^2 and b) 5 to 6 samples each 1 km^2 when approaching the former Hg-mines. The sampling strategy for stream sediments (74 samples) involved the major watercourses present in the area. In addition, 11 rocks, representing the main lithologies, were also sampled. The geographical coordinates (UTM WGS84 - 32N) for all the samples were acquired with a Garmin GPS with an average error of 3 m. Every 4 months, about 29 samples, a water survey (major and minor solutes and trace elements, including Hg, As and Sb) inside and outside the ASS mine area.

Analytical method for solid matrices

The solid geological matrices were oven-dried at 30°C to minimize the release of gaseous mercury (Hg^0). All the rocks were cut to remove any layer of alteration and reduce the sample size. In all samples, XRD analysis, aqua regia digestion (3:1 ratio HCl: HNO_3) for As, Sb, Cr, Co, Cu, Ni, and V determination by ICP-AES, Hg determination by EPA 7473 Method, gravimetric method (550°C) for Organic Matter, Hg speciation by Thermal desorption (TD) technique with Lumex-Pyro 915+, leachates (rock/soil/stream-water 1:10) for As, Sb and Hg analyzed by ICP-MS were carried out.

Additionally, XRF analysis for bulk rocks and bulk streams was carried out. Moreover, Hg in eight different plants and mosses were determined by Lumex-Pyro 915+ and via atomic absorption spectrometric technique with a Hydra-C Mercury Analyzer instrument (Teledyne Instruments Leeman Labs Inc.), respectively. For more information about solid matrices analysis, see Meloni et al. (2023a, b; 2024b, c; 2025).

Analytical method for waters

At each sampling site, four aliquots were collected: *i)* 0.45 μm filtered sample in 125 mL PE bottles equipped with counter-cap for the main anions and NH_4^+; *ii)* 0.45 μm filtered and acidified (1% suprapur HCl) sample in PE 50 mL bottles for main cations; *iii)* 0.45 μm filtered and acidified (1% ultrapure HNO_3) sample in PE 50 mL bottles for trace elements (Al, Fe, Mn, Co, Cr, V, Cu, Ni, Ba, As, Se, Sb, Zn, Rb, Pb, Tl, and Sr); *iv)* 0.45 μm filtered and acidified (1% ultrapure HCl) in 50 mL dark glass bottles for the determination of Hg from piezometers. Additionally, an unfiltered and acidified with 1% ultrapure HCl or ultrapure HNO_3 (in the case that the Hg concentrations in water were > 3 μg/L) in a 50 mL dark glass for Hg for surface waters. Bicarbonates were measured by acidimetric titration, while the main anions and cations were determined by ion chromatography, respectively. Ammonium was measured by molecular spectrophotometry by the Nessler method. Total and dissolved Hg were measured by ICP-MS at the accredited Laboratory of C.S.A. of Rimini until 2021. From 2021 onward, the Hg analysis was performed in the Laboratory of the Department of Earth Science (University of Florence) by a Lumex RA-915M (Lumex Ltd., St. Petersburg, Russia) equipped with an RP-92 device. After the installation of a Lumex-Pyro 915+ in 2022, waters with Hg concentration > 3 μg/L were analyzed with this new instrument.

Statistical methods

Explorative Data Analysis (EDA), *e.g.*, graphical methods and numerical techniques, and multivariate approaches (*e.g.*, Principal Component Analysis-PCA) concerning the compositional nature of geochemical data were carried out using R and RStudio software (R Core Team, 2021). As is well known, geochemical data are compositional data (CoDa) that result in closed data, since they represent a part of a given numerical total, carrying only relative information (Aitchinson, 1986).

To solve this problem, a series of transformations (*e.g.*, centred log-ratio (clr) or isometric log-ratio (ilr)) can be applied to move the data within the real space called the simplex (Egozcue et al., 2003). Spatial distribution maps of the analyzed PTEs were constructed with Ordinary Kriging using ArcGis-Pro 3.0 software. Before the CoDa transformation, the values of the dataset below the Limit of Quantification (LOQ) were substituted with 2/3 of LOQ according to Gozzi et al. (2020, 2021).

Determination of Geochemical Background and Baseline value

The definition of geochemical background (GBc) and geochemical baseline (GB) values may have different explanations according to the context in which they are applied. According to Cicchella et al. (2022), natural GBc levels of elements vary locally, thus, a single value cannot define them. The concept of "GB" includes both natural and human-influenced contributions and is important for environmental regulations. Italian law (Lgs.D. 152/06) sets fixed thresholds for PTEs but does not account for local geology or element speciation. Therefore, local adjustments are possible through regional authorities. Therefore, in the area of Mt. Amiata, where Hg exploitation began more than 2000 years ago, it may become difficult to distinguish the anthropogenic contribution from the natural one. For this reason, in this research, it will be used the term GB. The GB of the PTEs was defined separately, *i.e.*, top-, sub-soils and stream sediments, by considering the different lithologies present in the area, and by using the ProUCL 5.2.0 software (USEPA, 2022) according to the recommendations of SNPA (2017). The GBs in soils were defined as a range of concentrations (± 10% of analytical uncertainty) and only for the PTEs that had at least one sample with concentrations higher than Lgs.D. 152/06 for residential use. For more details, see Meloni et al. (2023b, 2025).

Hg, As and Sb in aqueous solution speciation and ModFlow modelling

The geochemical code PHREEQC version 3.5.0 (Parkhurst & Appelo, 1999) was used to estimate the aqueous solution speciation of Hg, As and Sb in both water and selected leachate samples. Aqueous phase equilibria were taken into account in the modified *mint-eq.v4.dat* database. Instead, for the calculation of the groundwater flow distribution and transport, the Modflow 6.4.0 software (Langevin et al., 2024) was used. For more information, see Meloni et al. (2024a). In Figure 2, a schematic workflow is reported.

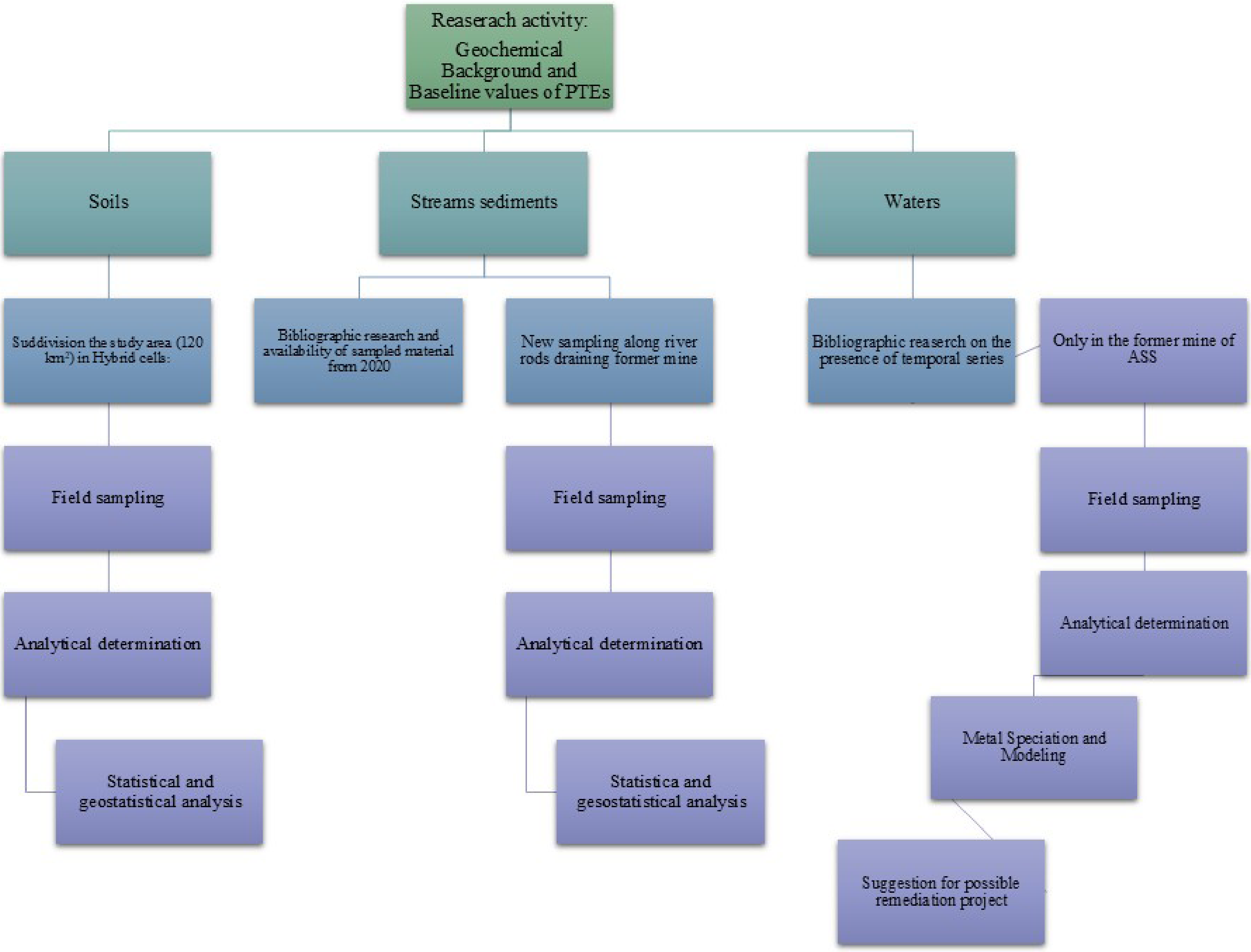

Figure 2 A Schematic workflow of this research.

RESULTS AND DISCUSSION

Mercury speciation by thermal desorption and laboratory experiments

Meloni et al. (2024b) have highlighted that the different geological matrices can affect the Hg-speciation in soils and stream sediments by the Thermal Desorption (TD) technique. Therefore, it is important to characterize the Hg compounds by mixing different matrices to understand the correct Hg temperature (*T*) release. According to this assumption, in contaminated soils, it becomes pivotal to know the liquid Hg behavior. In Meloni et al. (2024b), it has been highlighted that after 42 days, all liquid Hg in soils is oxidized in a more stable Hg^{2+} form. Observing the release temperatures of Hg in both silicate- and carbonate-rich soils where the experimental runs were conducted, the resulting form of Hg appears to be metacinnabar (β-HgS). Further studies, however, would be necessary to assess this hypothesis. Taking this experiment and Hg release *T* in silicate and carbonate soils into account, in all soils and river sediments where Hg concentrations were found to be > 5 mg/kg, speciation was carried out. The speciation has allowed us to verify that Hg is mostly hosted as insoluble species, i.e. α-HgS (Cinnabar) and β-HgS and no effects are expected to affect the ecosystem, these minerals being recalcitrant to chemical weathering. Thus, Hg availability is to be regarded as low or even negligible. Only a few samples inside the mine areas showed the presence of Hg_2SO_4 or $HgCl_2$.

Mercury distribution in plants, soils and mosses in the Abbadia San Salvatore mine area

From the eight different plants analysed in the former mining area of ASS, the greatest pathway for Hg accumulation appears to be the leaf system. The *Sambucus nigra* species, however, turns out to be the one that accumulates most Hg from the root system. This plant could be tested to create a pilot site for the extraction of Hg from soil (Meloni et al., 2023a).

In addition, non-indigenous biomonitoring through moss bags was carried out in the same area. This turns out to be an excellent tool for understanding the way Hg can be dispersed, transported, and accumulated. From the Hg analysis in the moss bags, the main Hg emissions were associated with the mining area of ASS and the gas vents. The wet deposition resulted to be a key factor for its accumulation on the uncovered mosses, while dry deposition resulted to be important for the covered samples, especially those located within the mining area (Meloni et al., 2024c).

Total and Leached Arsenic, Mercury and Antimony in the Mining Waste Dumping Area of Abbadia San Salvatore (Mt. Amiata, Central Italy)

Two different soil samplings were carried out in the Le Lame dump (Fig. 2). The characterization of these soils resulted to be important for the reclamation of the former ASS mine. The first sampling was conducted in 2017, and the soils analyzed were concerning the topsoil (0-20 cm), while the second sampling was carried out in 2022 and included both the top- (0.8-1.2 m) and sub-soil (1.2-3 m). In both samplings, Hg, As and Sb resulted in high concentrations (Hg up to 1910 mg/kg, As up to 616 mg/kg and Sb up to 1980 mg/kg). This study showed that the highest concentrations of Hg were found in the highest morphological part of the tailing. This turned out to be because waste materials from the Cermark-Spirek furnaces, which were found to be less efficient than the Gould furnaces, were piled up in this area. On the other hand, the Hg concentrations in the leachates were almost always < 1 µg/L (Italian legal limit), except for three samples, highlighting the fact that Hg occurs as a non-soluble or poorly soluble form. A characterization by TD is necessary to highlight which forms of Hg are present in the landfill soils. Differently, the concentrations of As and, in particular, Sb in the leachates were extremely high. Analysis in PHREEQC, however, showed that these two elements are present in the leachate phase in their less toxic form (As^{5+} and Sb^{5+}), limiting the toxicity of these two PTEs. This is also favored by the fact that in this area, no water course or shallow aquifers are present (Meloni et al., 2021).

Geochemical Surveys of Surface and Ground Waters in the Abandoned Hg-Mine of Abbadia San Salvatore (Central Italy): A Preparatory Investigation before Remediation

According to Bain et al (2001), one of the most important aspects to be considered when dealing with the operation and closure activities of a mining site is related to the presence of contaminated surface and groundwater bodies. In this research, ten years of temporal series of waters were studied inside and outside the former mine of ASS for Hg, As e Sb. Mercury in the outside waters resulted to be always < 0.2 µg/L, and As and Sb < 0.1 µg/L. Inside the mine, the Hg concentrations indeed resulted in being much higher (up to 695 µg/L). On the other hand, the content of As and Sb was lower than those reported in the Lgs.D. 152/2006 (10 and 5 µg/L, respectively), after the construction of the bypass channel (2014) inside the mine (Vaselli et al., 2015; Meloni et al., 2024a). Seasonal variations of the geochemical facies were observed, but they were not apparently associated with seasonality. The PHREEQC modelling, as well as for

Table 1 Baseline values as a range of concentrations of PTEs in stream sediments for cluster 1 and cluster 2.

PTEs	Hg	Sb	As	Cr_{tot}	V	Co pop.1	Co pop.2	Ni pop.1	Ni pop.2	Cu pop.1	Cu pop.2
Baseline value cluster 1	5.2-6.3	8.5-10.5	39.7-48.5	43.0-52.6	31.2-38.1	5.9-7.2	19.0-23.2	9.6-11.6	51.5-62.9	3.71-4.54	72.2-88.2
PTEs	**Hg**	**Sb**	**As**	**Cr_{tot}**	**V**	**Co**	**Ni**	**Cu**	-	-	-
Baseline value cluster 2	20.0-24.3	6.9-8.54	6.3-7.72	51.1-62.5	62.4-76.3	26.3-32.2	52.8-64.6	62.1-75.9	-	-	-

the leachates for the Le Lame Dump, showed As and Sb in the less toxic form, and Hg mostly occurring as Hg^0. The analysis of the reduced sulfur species in some waters highlighted that α-HgS and β-HgS turn out to be at equilibrium or oversaturated, and the presence of Fe-bearing oxy-hydroxides can adsorb Hg, thus representing a possible Hg sink. The groundwater flow modelling suggested that the water flow follows the local topography (W-E oriented), while the Hg transport modelling highlighted that the Hg contamination is mainly limited to the former mining area, where the piezometers mostly pump from water pockets, thus limiting the water flow. Two exceptions are represented by two piezometers from which a Hg-rich plume was evidenced, and migrating to the east (Meloni et al., 2024a).

Mercury contamination in an artificial mining lake: geochemical investigations and remediation strategies at the Lake Muraglione (Mt. Amiata, central Italy)

Between the end of 2021 and 2022, 16 sediments from the artificial Muraglione Lake, located in a public park of ASS, were sampled to characterize and test different remediation strategies: TD test, dewatering test, filter press test, and inertization strategy. It was highlighted that the lake sediments had high Hg concentration (up to 900 mg/kg), and the concentration of Hg was higher in the fine (60 μm) fraction. The sediment granulometry is dominated by sand to silty loam. The high amount of organic material (mostly consisting of small twigs and roots) was the main problem that affected all remediation tests. Better results were obtained when inertization tests were applied, although high Hg concentrations were recovered when leaching tests were performed. Therefore, computing GB values of the Le Lame is of pivotal importance to evaluate whether the Hg concentrations of the lake sediments are lower than those recorded in the soils of the dumping area where these sediments are supposed to be stored. In fact, the lake is to be emptied and the sediments removed to return this area to the population once the lake is reclaimed.

GEOCHEMICAL BACKGROUND/BASELINE VALUES IN STREAM SEDIMENTS AND SOILS

Geochemical characterization of stream sediments from the eastern Hg-district of Mt. Amiata (Siena and Grosseto, central Italy): deciphering sources and interaction processes

After an in-depth geochemical study using XRF analysis of the 74 stream sediments and the 11 rock samples, it was possible to classify them into 4 different groups: 1) volcanic group, 2) volcanic-sedimentary group, 3) sedimentary-volcanic group and 4) sedimentary group. Volcanic sediments are enriched in As (up to 311 mg/kg), and they are mainly distributed on the Mt. Amiata volcano and near the hydrothermal zone and gas vents. Mercury resulted in having a relatively homogeneous distribution with the most remarkable concentrations (up to 850 mg/L) measured in the streams intimately connected with the main former mines, i.e. Cornacchino, Solforate, and Morone mines. Antimony resulted to be enriched in the sedimentary zone and depleted in the volcanics. The higher concentrations were recorded close to or within the Morone mine (the only Sb-Hg mine in the zone), with concentrations up to 84 mg/kg. Mercury and Sb results were not correlated with each other, suggesting a different origin for the two elements and likely linked to two distinct periods of mineralization, as reported by Brogi et al. (2011). For the GB calculation, the four previous groups were considered, and they were further grouped into two clusters: *i)* volcanic + volcanic-sedimentary and *ii)* sedimentary-volcanic + sedimentary (Meloni et al., 2025). The results are summarized in Table 1.

Geochemical Background/Baseline in the eastern sector of Mt. Amiata (Siena, Central Italy) and the case study of Abbadia San Salvatore municipality

After grouping the local formations into macrozones (*e.g.*, Volcanic, Limestone and clay, Jasper, Sandstone), EDA and statistical tests (e.g. Kolmogorov-Smirnov test) to validate the normality of the distribution were performed. Since soils and rocks are CoDa, the ilr transfor-

Table 2 Baseline values as a range of concentrations of soils for the 120 km² of study area subdivided according to the lithologies.

	Volcanic top-soil	Volcanic sub-soil	Clay+ limestone top-soil	Clay+ limestone sub-soil	Clay+ sandstone top-soil	Clay+ sandstone sub-soil	Jasper top-soil	Lgs.D. 152/06
Hg	15.7-19.2	16.1-19.7	1.1-1.3	3.0-3.6	5.4-6.6	3.3-4.0	611.9-747.9	1
As	53.8-65.8	78.8-96.3	Lgs.D. 152/06	Lgs.D. 152/06	-	-	23.5-28.8	20
Sb	-	-	12.6-15.5	8.3-10.1	-	-	12.1-14.7	10
Co	-	-	22.6-27.1	24.5-29.9	-	-	43.4-53.0	20
Cr	Lgs.D. 152/06	Lgs.D. 152/06	162.5-198.6	142.9-174.7	-	-	-	150
Cu	-	-	-	-	-	-	243.3-297.3	120
V	82.4-100.8	83.6-102.2	137-167.4	149.9-183.2	168.4-205.8	192.6-235.4	-	90

mation was performed on the dataset to understand whether top- and sub-soils could have been considered as a unique population, using a non-parametric test called log-contrast homogeneity test (lc-test). This test confirmed that top- and sub-soils represent two different clusters and were studied separately afterwards. With the CoDa analysis, a robust PCA was also performed in both top- and sub-soils to highlight the presence of the outliers (*e.g.*, mineralization).

Robust-PCA confirmed the findings of EDA for both top- and sub-soils, *e.g.*, volcanic lithology is enriched in As while limestone+clay and sandstone+clay groups appear to be enriched in Co, Cr, V, Ni, and Cu. The jasper formation, on the other hand, was found to be anomalous in Hg. Once the outliers (including mineralization) were excluded, the GB value in the top- and sub-soils was defined. The results are shown in Table 2. In addition, a more specific study was carried out within the Municipality of ASS to meet the requirements of the current reclamation project of the former ASS mine. The results are described in detail by Meloni et al. (2023b). When a comparison between the data from this study (Table 3) with those obtained from a larger area is made, Hg and As are characterized by slightly different values with respect to those reported in Table 2. This is because the sampling mesh in the Municipality of ASS is more detailed and therefore, the more the available data the higher the quality of the GB values (*e.g.*, Varrica et al., 2024).

CONCLUSIONS

This PhD study has investigated the environmental matrices (water, plants, soils, and streams) from the former Hg-mining areas of Mt. Amiata, evidencing the main criticalities which are mostly, as expected, related to the contamination of Hg, though Sb and As were also found to be occurring at relatively high contents in soils and streams.

Water contamination appears to be limited to the former mining area of ASS. This is an important result in terms of remediation since, if confirmed, economically speaking, two options can be evaluated:

	Volcanic top-soil	Volcanic sub-soil	SFR top-soil	SFR sub-soil	Lgs.D. 152/06
Hg	17.3-21.2	18.5-22.7	6.8-8.3	6.5-7.9	1
As	69.6-85.1	78.2-95.6	Lgs.D. 152/06	Lgs.D. 152/06	10
Co	-	-	22.3-27.2	23.3-28.5	20
Ni	-	-	Lgs.D. 152/06	Lgs.D. 152/06	120
Cr	Lgs.D. 152/06	Lgs.D. 152/06	160.2-195.8	157.2-192.2	120
V	85.7-104.2	85.9-104.9	149.6-182.8	158.3-193.5	90

Table 3 Baseline values as a range of concentrations of soils for the Municipally of ASS subdivided according to the lithologies: SFR represents the Santa Fiora Units corresponding to the clay+limestone of Table 2.

- no water treatment;

- partial abatement of Hg from the most contaminated water by tested techniques such as MC-TOMAC, Capterall®, or ferrate compounds, which have been successfully used during laboratory tests (Borruguero et al., 2018; Baroni, 2022; Lazzaroni, 2022).

The definition of the GBc and GB values plays a key role when dealing with environmental matrices since they can be used, if accepted as in the case of those computed for ASS, to help the local authorities when new houses, garages or commercial areas are to be built. It was also evidenced by the notable role played by the stream sediments since they could be used as tools for capturing contaminated areas.

The Hg speciation applied to soils and sediments has allowed us to verify that Hg is mostly hosted as insoluble species, *i.e.*, α-HgS and β-HgS, and no effects are expected to affect the ecosystem, as these minerals are resistant to chemical weathering. Thus, Hg availability is to be regarded as low or even negligible.

REFERENCES

Aitchison, J. (1986) - The Statistical Analysis of Compositional Data. In: Monographs on Statistics and Applied Probability. Chapman & Hall Ltd., London.

Bain, J.G., Mayer, K.U., Blowes, D.W., Frind, E.O., Molson, J.W.H., Kahnt, R., Jenk, U. (2001) - Modelling the closure-related geochemical evolution of groundwater at a former uranium mine. J. Contam. Hydrol., 52, 109-135.

Baroni, T. (2022) - Ferrate removal of metal contaminants in the environmental remediation field: synchrotron radiation studies applied to the Hg contaminated waters from Abbadia San Salvatore, Amiata Area. (PhD Thesis). University of Florence, p. 236

Borreguero, A.M., Leura, A., Rodriguez, J.F., Vaselli, O., Nisi, B., Higueras, P.L., Carmona, M. (2018) - Modelling the mercury removal from polluted waters by using TOMAC microcapsules considering the metal speciation. Chem. Engin. J., 341, 308-316.

Brogi A., Fabbrini L., Liotta D. (2011) - Sb-Hg ore deposit distribution Controlled by brittle structures: the case of the Selvena Mining district (Monte Amiata, Tuscany, Italy). Ore Geol. Rev., 41, 35-48.

Cicchella, D., Ambrosino, M., Gramazio, A., Coraggio, F., Musto, M.A., Caputi, A., Avagliano, D., Albanese, S. (2022) - Using multivariate compositional data analysis (CoDA) and clustering to establish geochemical backgrounds in stream sediments of an onshore oil deposits area. The Agri River basin (Italy) case study. J. Expl. Geochem., 238, 107012.

Dini, A. (2003) - Ore deposits, industrial minerals, and geothermal resources. Per. Min., 72, 41–52.

Egozcue, J.J., Pawlowsky-Glahn, V., Mateu-Figueras, G., Barcelo-Vidal, C. (2003) - Isometric log-ratio transformations for compositional data analysis. Math. Geol., 35, 270–300.

Gozzi, C., Sauro Graziano, R., Buccianti, A. (2020) - Part-whole relations: new insights about the dynamics of complex geochemical riverine systems. Minerals, 10 (6), 501.

Gozzi, C., Dakos, V., Buccianti, A., Vaselli, O. (2021) - Are geochemical regime shifts identifiable in river waters? Exploring the compositional dynamics of the Tiber River (Italy). Sci. Total Environ., 785, 147268.

Langevin, C.D., Hughes, J.D., Provost, A.M., Russcher, M.J., Niswonger, R.G., Panday, S., Merrick, D., Morway, E.D., Reno, M.J., Bonelli, W.P., Boyce, S.E., Banta, E.R. (2024) - MODFLOW 6 Modular Hydrologic Model version 6.4.4: U.S. Geological Survey Software Release, 7 February 2024.

Lazzaroni, M. (2022) - Investigating Hg dispersion in the environment: the experience from the abandoned mining area of Abbadia San Salvatore (Tuscany, central Italy) between research and remediation activities of natural and anthropic matrices (PhD Thesis). University of Florence, p. 213.

Meloni, F., Montegrossi, G., Lazzaroni, M., Rappuoli, D., Nisi, B., Vaselli, O. (2021) - Total and leached arsenic, mercury and antimony in the mining waste dumping area of Abbadia San Salvatore (Mt. Amiata, Central Italy). Appl. Sci. 11, 7893.

Meloni, F., Farieri, A., Higueras, P.L., Esbrì, M.J., Nisi, B., Cabassi, J., Rappuoli, D., Vaselli, O. (2023a) - Mercury distribution in plants and soils from the former mining area of Abbadia San Salvatore (Tuscany, Central Italy). Environ. Geochem. Health, 45, 8523–8538.

Meloni, F., Nisi, B., Gozzi, C., Rimondi, V., Cabassi, J., Montegrossi, G., Vaselli, O. (2023b) - Background and geochemical baseline values of chalcophile and siderophile elements in soils around the former mining area of Abbadia San Salvatore (Mt. Amiata, southern Tuscany, Italy). J. Geochem. Explor., 255, 107324.

Meloni, F., Montegrossi, G., Cabassi, J., Bianchi, F., Nisi, B., Rappuoli, D., Vaselli, O. (2024a) - Geochemical Surveys of Ground and Surface Waters in the Abandoned Hg-Mine of Abbadia San Salvatore (Central Italy): A Preparatory Investigation before Remediation. Water, 6, 1210.

Meloni, F., Higueras, P.L., Cabassi, J., Nisi, B., Rappuoli, D., Vaselli, O. (2024b) - Thermal desorption technique to speciate mercury in carbonate, silicate, and organic-rich soils. Chemosphere, 365, 143349.

Meloni, F., Calabrese, S., Vaselli, O., Capecchiacci, F., Brusca, L., Bellomo, S., Daskalopoulou, K., Venturi, S., Nisi, B., Rappuoli, D., Cabassi, J. (2024c) - Active moss biomonitoring of mercury in the mine-polluted area of Abbadia San Salvatore (Mt. Amiata, Central Italy). Toxic, 13(1), 2.

Meloni, F., Dinelli, E., Cabassi, J., Nisi, B., Montegrossi, G., Rappuoli, D., Vaselli, O. (2025) - Provenance and distribution of potentially toxic elements (PTEs) in stream sediments from the eastern Hg-district of Mt. Amiata (central Italy). Environ. Geochem. Health, 47(4), 123.

Parkhurst, D.L. & Appelo, C.A.J. (1999) - User's guide to PHREEQC (Version 2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey. Water-Resour. Investig., 312, 99– 4259.

R Core Team (2021) - R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna, Austria, Available online: https://www.Rproject.org/ available on-line 15/01/2022.

SNPA (2017) - Linea guida per la determinazione dei valori di fondo per i suoli e per le acque sotterranee (ISBN 978-88-448-0880-8). (In Italian).

USEPA (2022) - ProUCL: Statistical Software for Environmental Applications for Data Sets with and without nondetect Observations. Version 5.2. https://www.epa.gov/landresearch/prouclsoftware.

Varrica, D., Medico, F.L., Zuccolini, M.V., Miola, M., Alaimo, M.G. (2024) - Geochemical baseline values determination and spatial distribution of trace elements in topsoils: An application in Sicily region (Italy). Sci. Tot. Environ., 955, 176951.

Vaselli, O., Nisi, B., Rappuoli, D., Bianchi, F., Cabassi, J., Venturi, S., Tassi, F., Raco, B. (2015) - Geochemical characterization of the ground waters from the former Hg-mining area of Abbadia San Salvatore (Mt. Amiata, central Italy): criticalities and perspectives for the reclamation process. It. J. Geosci., 134, 304-322.