

# Water Geochemistry in the Former Hg-Mining Area of Abbadia San Salvatore: a Review

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## Abstract

The mercury (Hg) district of Mt. Amiata (Tuscany, central Italy) has been one of the most famous mining areas to produce liquid mercury from cinnabar (HgS)-bearing ore deposits and the mining site of Abbadia San Salvatore was by far the largest exploiting and productive center of the whole district. In this work, we reviewed a large dataset of geochemical parameters, including As, Hg and Sb, using about 40 geochemical surveys of surface and ground waters from the mining areas and surroundings to provide evidence of the most important contaminants and to suggest remediation actions.

**Keywords:** Mercury mines, Hg contamination, Abbadia San Salvatore, remediation

## Introduction

Contamination of surface and ground waters represents one of the most important criticalities in decommissioned and active mines where poly-metallic sulfides have been or are exploited. This is due the fact that the interaction between meteoric waters and sulfides causes so-called acid mine drainage which is normally characterized by high concentration of potentially toxic elements (PTEs) and pH down to 2 (Nordstrom 2011a). However, mines showing circumneutral waters are also affected by anomalous concentrations of PTEs (Nordstrom, 2011b; Gandy *et al.* 2015; Vriens *et al.* 2019). The former mercury (Hg)-mining area of Abbadia San Salvatore (central Italy) is indeed showing pH values that very sporadically are clustering around 5, while most of them are between 6.3 and 7.3. Despite these pH values, arsenic (As) and antimony (Sb) concentrations are commonly found to be  $>10 \mu\text{g L}^{-1}$  while those of Hg largely exceed  $1 \mu\text{g L}^{-1}$ , the latter being the targeted value for uncontaminated

ground- and surface waters (Vaselli *et al.* 2015; 2021; Lazzaroni *et al.* 2022; Meloni *et al.* 2024).

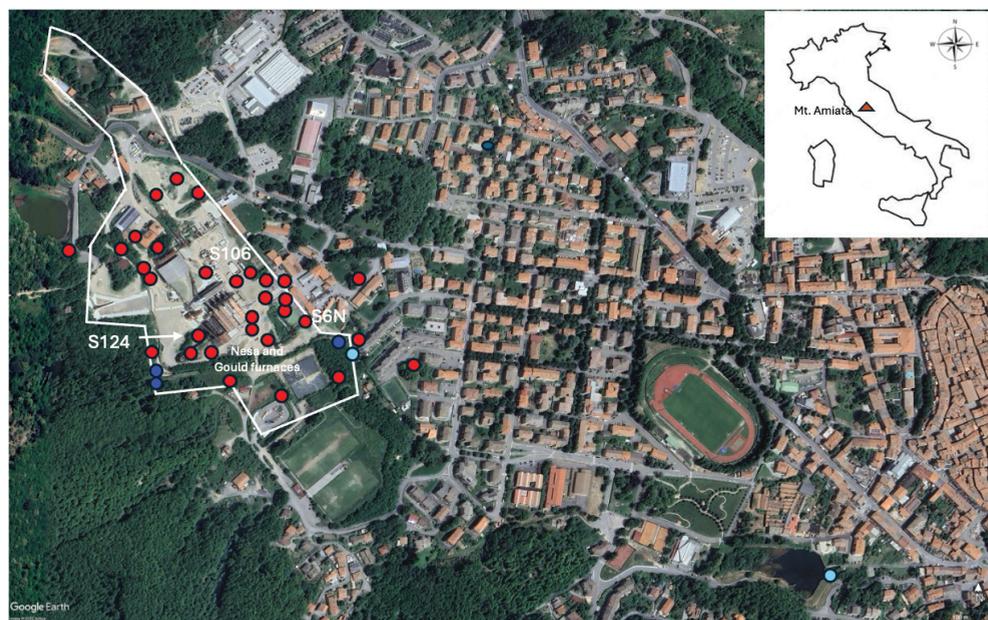
This study reviews the ground- and surface water geochemistry of the Abbadia San Salvatore mine and its environs. The dataset includes dissolved major, minor and trace (As, Hg and Sb) concentrations of waters collected and analyzed since 2013 and new original data collected in 2024 as part of a collaboration between the local municipality and the Department of Earth Science at the University of Florence, Italy. This study's primary goal is to identify the geochemical facies, As, Sb, and Hg concentrations, as well as their seasonal variations, in order to reduce the remarkably high Hg concentrations and, to a lesser extent, As and Sb concentrations. These elements are considered rather dangerous since they have negative effects on the ecosystems and human health, therefore, minimizing their concentrations in aquatic environments is necessary (Fu *et al.* 2010). As reported by Vaselli *et al.* (2015), several approaches have been proposed

to remove Hg from water, but no well-assessed methods are commercially available since most abatement systems are still at laboratory scale. Here, we report the main results related to two experimental methods, carried out at laboratory scale, where the initial concentration of dissolved Hg in groundwaters collected from the Abbadia San Salvatore Hg-mine was successfully and quantitatively reduced.

### The study area

The Abbadia San Salvatore Hg-mine (Fig. 1) is part of the Mt. Amiata, a 300–200 ka old volcano, mining district that has been one of the most important sites worldwide for the exploitation of Hg from cinnabar (HgS) that lasted for more the 150 years (1846–1982). About 117,000 tons of liquid Hg were produced (Segreto 1991). It has been estimated that about 70% of the total production of Hg was from the Abbadia San Salvatore Hg-mine (Cipriani and Tanelli 1983; Rimondi *et al.* 2015). In contrast to As and Sb, which were found to be more dispersed and primarily related to tailings and calcines derived from

roasting processes of ore deposits treated at Abbadia San Salvatore but exploited from other Mt. Amiata mines (e.g. Meloni *et al.* 2023), particularly high abundances of Hg were determined within the mining area and nearby (Vaselli *et al.* 2013; Rimondi *et al.* 2019). The initial phases related to the remediation of the Abbadia San Salvatore Hg-mine dates back to 2010, and due to the large variety of criticalities encountered (Vaselli *et al.* 2019), the operations have been extended up to the early 2020. Finally, at the end of 2025 the ground of the mining area is expected to be completed. The difficulties related to the removal of dissolved Hg from the surface and ground waters are still to be decided and are still a matter of debate. This is due to different problems, including: i) the Hg concentrations are extremely variable, and sometimes  $>100 \mu\text{g L}^{-1}$ , from piezometer to piezometer, although they are located a few tens of meters from each other (Vaselli *et al.* 2015), similar behavior is also shown by As and Sb, though to a minor extent; ii) there is not continuous shallow aquifer. According to Meloni *et al.* (2024), hydrological investigations did indicate that



**Figure 1** The Abbadia San Salvatore mining area. The white line surrounds the main mining structure (including the Gould and Nesa furnaces). Red circles: piezometers; Blue circles: spring; Light blue: surface waters. The sampling points refer to the geochemical survey activity carried out since 2013. Over time, some piezometers were covered due to the remediation operations while others were drilled. The water samples used for the laboratory tests related to the removal of Hg are reported (see text).



there are a few isolated subterranean water pockets with low transmittivity, meaning that the hydraulic connection is rather poor; iii) the shallow aquifer in the mining area was formed when a small paleo-valley was filled with material derived from the mining activity, as observed during piezometer drillings that also showed the presence of drops of liquid Hg (Vaselli *et al.* 2015); iv) groundwaters located along the water flowlines and outside the mining area showed concentrations of Hg, As and Sb of <1, 10 and 5  $\mu\text{g L}^{-1}$ , respectively (Meloni *et al.* 2024).

## Methods

The sampling sites (collected in January/February, May/June and September/October) are shown in Fig. 1. The limits of the Hg-contaminated site are indicated with a white line that also defines the area where the main mining structures, such as edifices, Gould and Nesa furnaces, mineral conveyor belts, dryers and condensers, are hosted. It must be pointed out that since 2013 onward some piezometers were destroyed during the remediation activities and others were drilled to cover as much as possible the former mining area. All the chemical analyses were carried by titration ( $\text{HCO}_3^-$ ), molecular spectrophotometer ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ), ion chromatography (main cations and  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ ,  $\text{F}^-$  and  $\text{NO}_3^-$ ) and inductively coupled plasma-mass spectrometry (As, Hg and Sb) or by cold vapor with a Lumex device (Hg). Temperature, pH and electrical conductivity were measured in the field. All water samples were filtered at 0.45  $\mu\text{m}$  prior analysis. Other trace elements were also determined but their concentrations did not show any specific peculiarity and thus, they will not be considered in this work. In order to provide suitable solutions to reduce the concentration of dissolved Hg in the Abbadia San Salvatore mine, laboratory tests were conducted by using two different approaches: i) Borraquero *et al.* (2018) proposed the use of highly Hg-selective microcapsules (MC-TOMAC) characterized by trioctyl-methylammonium-chloride and applied to three waters with different Hg concentrations: from 1.4 to 257  $\mu\text{g L}^{-1}$ ; ii) Capterall® is an industrial patented product by Solvay industries. Capterall® is a synthetic bio-apatite used for

wastewater treatments. It was tested in three different water samples with different amount of Hg: 21, 46.6 and 252  $\mu\text{g L}^{-1}$ . In this three different waters, three different typologies (Mix 1, Mix 2, Mix 3) of Capterall® with 2 distinct dosages (D1: 0.4 and D2: 0.8 g/L, respectively) were given by the manufacturer. The pH of the water was stabilized at 7.5 with NaOH. The waters were left reacting with the three Mix products using the two distinct dosages overnight by means of a horizontal shaker. The samples were filtered afterwards with a Sartorius® filtering device.

## Results and Discussion

Temperature was strictly dependent on the season, particularly for the surface waters (down to 4.8 °C and up to 17 °C). Groundwater temperatures ranged from 11 °C in the winter to up to 17 °C in the summer. The electrical conductivity ranged from 60 to 1800  $\mu\text{S/cm}$ , and the pH was circumneutral, ranging from 5.5 (only four samples) to 7.9. The Ca(Mg)- $\text{SO}_4$  composition was mostly dominant and characterized most studied waters. This composition was linked to the water-rock interaction with gypsum, which is a gangue mineral that was probably employed during the roasting process of HgS. The Ca(Mg)- $\text{HCO}_3^-$  and (Na+K)- $\text{HCO}_3^-$  facies were identified as secondary. It should be noted, though, that seasonal differences were noted in water geochemistry. This was interpreted as being related to remediation actions carried out over time, such as construction of an artificial channel to convey the meteoric waters to minimize the interaction with the contaminated soils and the made-made material (such as concrete, bricks, tuff, tiles) of the mining area where concentrations of Hg as high as 73,000 and 46,000  $\text{mg kg}^{-1}$  were measured, respectively (Vaselli *et al.* 2017). High concentrations of Hg in soil were found in front of the Gould and Nesa furnaces where the mining materials were stored whereas those related to the construction material were related to the long-lasting contact with an Hg-rich atmosphere (up to >50,000  $\text{ng m}^{-3}$ ) (Vaselli *et al.* 2017; Lazzaroni *et al.* 2020). Table 1 summarizes the minimum, maximum, mean, and median concentrations of As, Hg, and Sb.

**Table 1** Minimum and maximum concentrations ( $\mu\text{g L}^{-1}$ ) for As, Hg and Sb. These abundances refer to the seasonal surveys carried out from 2013 to 2024 in the waters from the former Hg-mining areas of Abbazia San Salvatore.

Sampling period	Arsenic $\mu\text{g L}^{-1}$	Mercury $\mu\text{g L}^{-1}$	Antimony $\mu\text{g L}^{-1}$
Winter 2013–2024	<0.1–18.1	<0.1–853	<0.1–31.0
Spring 2013–2014	<0.1–18.4	<0.1–695	<0.1–31.4
Autumn 2013–2014	<0.1–30.4	<0.1–440	<0.1–199

To simplify, the three chalcophile elements' mean, minimum, and maximum values are listed by considering their contents on an annual seasonal basis.

Samples ranging from 22 to 42 were gathered throughout each survey. Only a few samples had very high levels of As and Sb, since most of them had values within the 10 and 5  $\mu\text{g L}^{-1}$ , respectively, limits suggested by the European Community. Remarkably different is the situation concerning Hg. In fact, its abundance spanned over 4 orders of magnitudes and reached up to 853  $\mu\text{g L}^{-1}$  (January 2014). The concentrations of Hg are not preferentially distributed in a specific area since they are mostly scattered throughout the mining site. The highest concentrations are indeed found in the eastern and western part although notable concentrations were also found close to the building hosting the Gould and Nesa furnaces (Fig. 1). When the current measured amounts need to be carefully reduced in the future, the randomly distributed Hg may cause some challenges. According to the new hydrogeological conceptual model and the geochemical data, the Hg-contamination seems to be presently limited to the mining area (Meloni *et al.* 2024) while the deeper aquifer appears to be not affected by Hg concentrations  $>1 \mu\text{g L}^{-1}$  (Vaselli *et al.* 2015).

The two different approaches test for Hg removal in waters have given excellent results. The MC-TOMAC approaches, at the current pH values, the laboratory results indicated that up to  $99 \pm 2.0\%$  of the initial Hg was successfully removed.

The application of a commercial product, named Capterall®, to the water samples characterized by variable and increasing Hg contents provided satisfactory results. As

previously mentioned, three different typologies of Capterall® with two distinct dosages were tested, containing bioapatite although the complete industrial receipt was not provided.

The results are reported in Table 2 for the S6N, S106 and S124 water samples (Fig. 1). Note that the initial concentrations of Hg are in  $\mu\text{g L}^{-1}$  whereas those after the application of Capterall® are in  $\text{ng L}^{-1}$ . The removal of Hg appears to be effective. In fact, in only two cases the concentration of Hg is about 1  $\mu\text{g L}^{-1}$  whereas in most cases the remaining Hg in solution after the Capterall® is clustering around 1% of the original concentration.

## Conclusions

A large variability of concentrations of As, Hg and Sb was observed in the former Hg-mining area of Abbazia San Salvatore. However, from an environmental perspective, As and Sb do not pose a serious problem since a very low number of samples showed concentrations higher than those expected for surface and ground waters. Dissolved Hg is thus the main issue in this site where remediation operations at the ground level in the mine are about to be completed at the end of 2025. The laboratory runs, conducted with two different approaches (MC-TOMAC and Capterall®), have produced satisfactorily results. The next step is to set up a pilot site that is planned by the end of 2025 to test the encouraging laboratory results although economic evaluations to select one of the two approaches are required.

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**Table 2** Laboratory tests carried out using different mixing products of Capterall® and dosages (D1 and D2). The second and third columns refers to the concentrations of the original content of Hg ( $\mu\text{g L}^{-1}$ ) and those measured after the application of Capterall® ( $\text{ng L}^{-1}$ ). The three samples (S6N, S106 and S124) were collected from the former Abbadia San Salvatore Hg mine (Fig. 1).

Sample	Initial concentration (Hg)	Final concentration (Hg)
	$\mu\text{g L}^{-1}$	$\text{ng L}^{-1}$
S6N Mix1 d1	252	595.2
S6N Mix2 d1	252	1516
S6N Mix3 d1	252	638.4
S106 Mix1 d1	21	811.6
S106 Mix2 d1	21	464.4
S106 Mix3 d1	21	676.4
S124 Mix1 d1	46.6	379.6
S124 Mix2 d1	46.6	267.6
S124 Mix3 d1	46.6	355.6
S6N Mix1 d2	252	402
S6N Mix2 d2	252	450
S6N Mix3 d2	252	282
S106 Mix1 d2	21	710
S106 Mix2 d2	21	1668
S106 Mix3 d2	21	443.2
S124 Mix1 d2	46.6	275.2
S124 Mix2 d2	46.6	193.6
S124 Mix3 d2	46.6	263.2

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