

DISTRIBUTION OF MERCURY, ANTIMONY AND ARSENIC IN THE SHALLOW GROUNDWATER SYSTEM FROM THE FORMER Hg-MINING AREAS OF ABBADIA SAN SALVATORE (TUSCANY, CENTRAL ITALY)

Presenting Author Orlando Vaselli***, Barbara Nisi**, Daniele Rappuoli***, Francesco Bianchi****, Luciano Giannini***, Jacopo Cabassi***, Franco Tassi***, Stefania Venturi***

**Department of Earth Sciences, Florence, Italy*

***CNR-IGG, Institute of Geosciences and Earth Resources, Italy*

****Union of the Amiata-Orcia Valley Municipalities, Italy*

*****SBC Geologi Associati, Italy*

orlando.vaselli@unifi.it

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Introduction

The study area is located in the about 200 ky old silicic volcanic complex of Mt. Amiata (Tuscany, central Italy), which is mainly characterized by dacitic, rhyodacitic and minor olivine-latic products. In two sites (Bagnore and Piancastagnaio), geothermal fluids are currently exploited to produce electricity, while in the past Mt. Amiata was considered the fourth largest district of mercury in the world, the ore deposit containing 0.6-2% Hg. The most important mining site was located at Abbadia San Salvatore, in the eastern flank of Mt. Amiata. Although cinnabar was used since the Etruscan time, the industrial extraction of metallic mercury only commenced in the last century by using Spirek and Cermak-Spirek, Gould and Nesa furnaces. The mining activity ended in 1982 after about 100 years of exploitation. The abandoned mining structures presently occupy a surface of ~65 ha. In the production area at least 270,000 m³ of waste material (post-roasting products and unprocessed materials, also deriving from other Hg exploitation areas from Mt. Amiata), with an average thickness of 6 m, were stored adjacently the buildings hosting the furnaces to fill a topographic low. A shallow (from about 4 to 16 m below the ground level) multi-aquifer formed inside this “landfill”. The present work shows the analytical results of groundwater samples collected during a 3-years long monitoring (7 geochemical surveys from February 2013 to January 2016) from old and recently drilled piezometers located inside and outside the former Hg-mining area of Abbadia San Salvatore, including a water sample from an about 40 m deep piezometer. The aims were those to: i) evaluate the concentrations and the spatial and temporal variations of the main solutes and those of Hg, and As and Sb (the two latter elements being commonly associated with mercury) and ii) define at what extent a vertical and horizontal contamination plume of these metals distributed. This monitoring activity is prodromal to any remediation action that is expected to occur in a couple of years.

Methods

Physico-chemical analyses (pH, T, ORP and electrical conductivity) were carried out in situ, whilst 4 aliquots were collected for the analysis of (i) the main dissolved species (2 aliquots filtered at 0.45 µm, one of which was acidified with 1% suprapur HCl), (ii) Hg (filtered and transferred into dark glass bottles, preventively cleaned several times with HCl and Milli-Q waters) and (iii) As and Sb (filtered and

transferred into pre-cleaned PE bottles). The main composition was determined by titration (HCO_3), colorimetric (NH_4) and ion-chromatographic methods. The concentrations of As, Hg and Sb were measured by ICP-MS (Agilent 7500CE) without any further treatments, following the procedures reported by the 6020A U.S.E.P.A. method. To verify the Hg partitioning, in one survey this element was measured in filtered and unfiltered water.

Results

The classification of the ground waters from the Abbadia San Salvatore mining area was characterized by three main geochemical facies: a) Ca(Mg)-SO_4 , which was the prevailing chemical composition; b) Ca(Mg)-HCO_3 and c) Na-HCO_3 , the latter being recognized in a few samples. Significant compositional variations were recorded during the 7 geochemical surveys. Apparently, no correlation between the geochemical facies and the concentrations of As, Hg and Sb was recorded, whose contents were up to 20, 853 and 199 $\mu\text{g L}^{-1}$, respectively. It has to be pointed out that, while the As and Sb contents were only occasionally above the Parametric Value (PV) intended for human consumption (10 and 5 $\mu\text{g L}^{-1}$, respectively: Council Directive 98/83/EC), more than 50 % of the 280 analyzed waters had a higher content than that of Hg-VPV, i.e. 1 $\mu\text{g L}^{-1}$. Furthermore, Hg concentrations showed a large variation during the different surveys, although no clear correlations with the minimum and maximum seasonal water level were recognized. Another important aspect is that the comparison between the concentrations of Hg in filtered and unfiltered samples had in most cases produced higher contents in the latter aliquot, suggesting that the $>0.45 \mu\text{m}$ fraction is enriched in Hg.

Conclusion

Despite the relatively small surface of the former-mining area, this study has evidenced a high spatial heterogeneity in terms of both main geochemical facies and As, Hg and Sb concentrations. A significant variability was also observed when the 7 surveys were taken into account, likely due to the heterogeneity and the consequent different permeability of the filling terrains, which are mainly characterized by material associated with the production of mercury, where a local shallow multi-aquifer system is emplaced. The deeper aquifer and the groundwater samples outside the mining area were not apparently affected by any As, Hg and Sb contamination. This suggests that the Hg- and, subordinately, As- and Sb-rich waters are locally confined. The significantly high and noxious Hg concentrations, well above the PV, are not accompanied by high contents of As and Sb likely because As- and Sb-bearing minerals are relatively uncommon in the Hg-rich ore deposits of Abbadia San Salvatore. Hence, As and Sb have a minor environmental impact. Conversely, the presence of high Hg contents is ubiquitous in the ground waters underneath the mining structures and only the peripheral waters show acceptable concentrations ($<1 \mu\text{g L}^{-1}$). It is a matter of fact that a strong release of dissolved mercury to the studied groundwater system is occurring and appropriate actions are to be taken in the framework of a reclamation process. Hence, periodical monitoring should be kept going to verify whether the chemical variations observed from February 2013 to January 2016 are going on. This represents an important pre-requisite before any remediation action takes place. It may be suggested that the best solution for a reclamation plan aimed to remove Hg is that to apply permeable reactive barriers and water treatment. However, Hg removal is a difficult task due to both not yet standardized procedures and the continuous supply of Hg deriving from interaction processes of waters with Hg-rich natural and anthropogenic materials, such as the case of the groundwater system at the Abbadia San Salvatore mining area. This implies that in-situ test sites in some of the investigated piezometers characterized by different Hg concentrations should be carried out before any definitive remediation technique.

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