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Monitoring, assessment, and possible remediation in the abandoned Hg-mine of Abbadia San Salvatore (central Italy)

Study area: Abbadia San Salvatore Hg mine

Abbadia San Salvatore (ASS) mine was the most important mine of the Mt. Amiata Hg district (central Italy) classified as the fourth largest producing Hg district

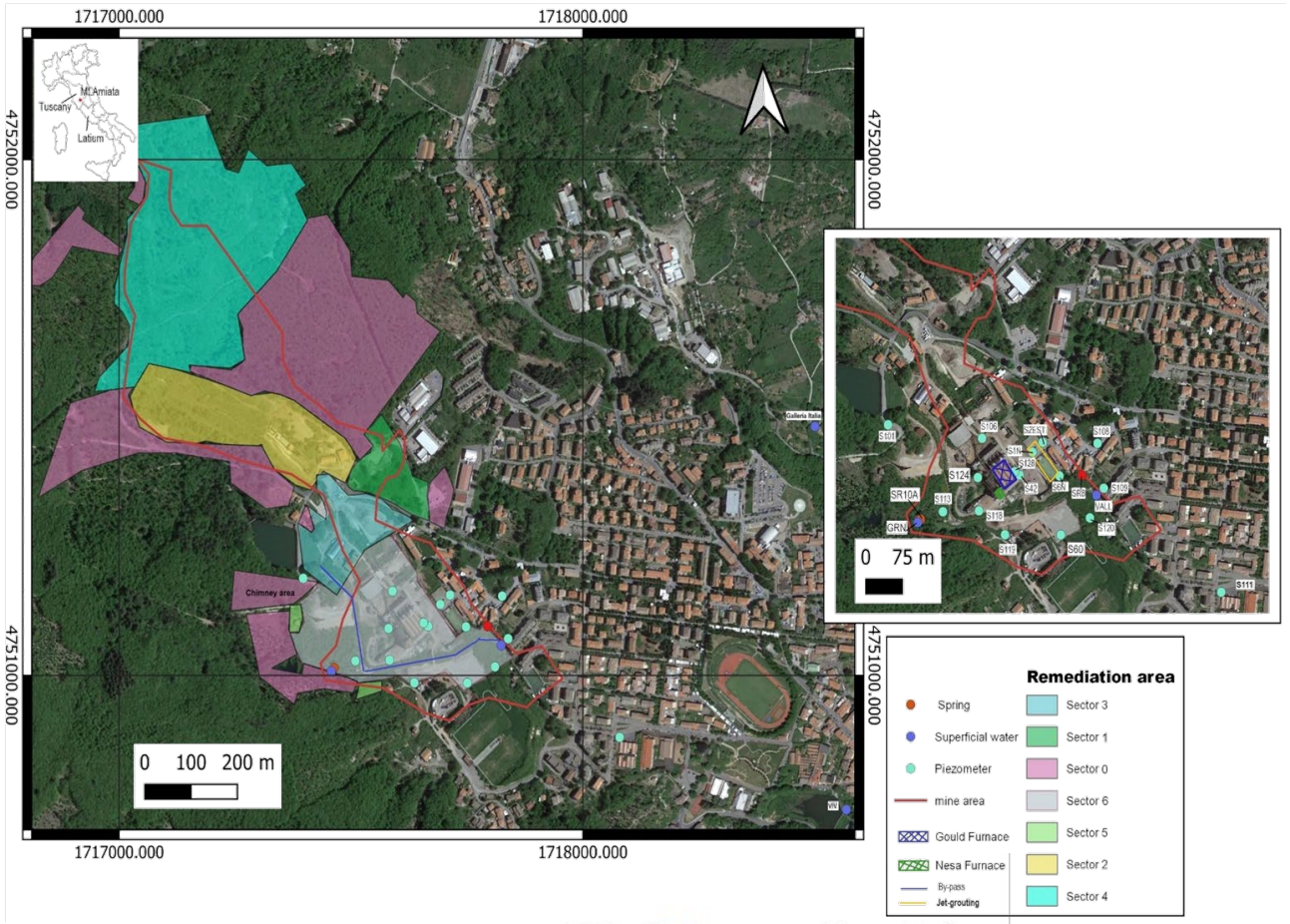
For the remediation activity, ASS mining area was divided into 7 different sectors

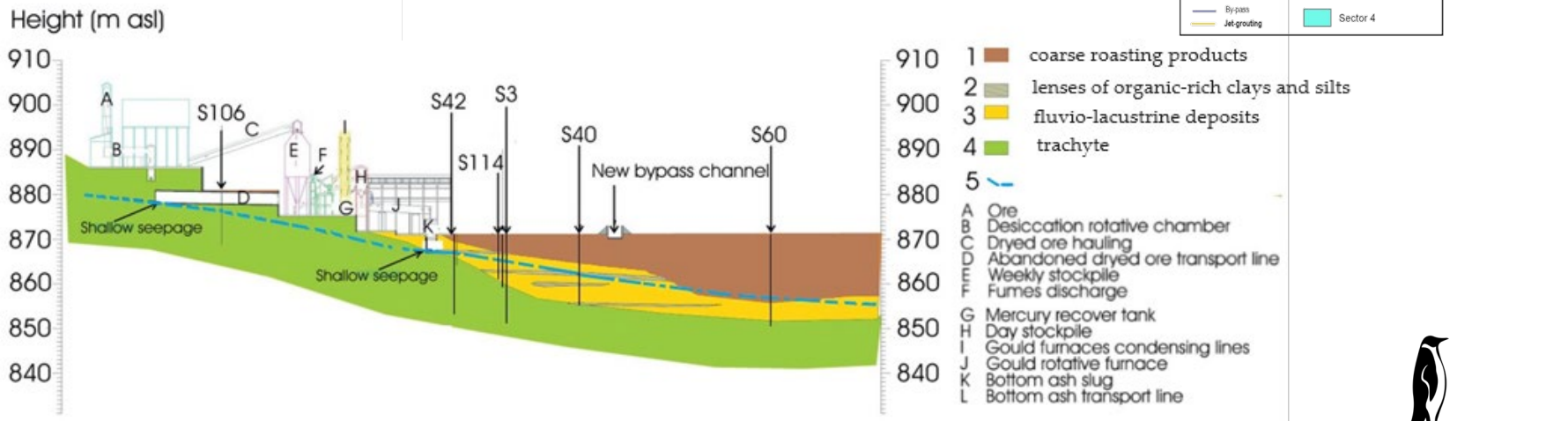
2007: a physical barrier was built with an impermeable cover that extended down to 15 m depth using the jet grouting technique on a small area (roughly 4,500 m^2)

15 piezometers were drilled inside and outside the mining area

2013: remediation activities took place:

- construction of a bypass channel to convoy the meteoric waters to decrease the interaction with the contaminated soils
- a periodical geochemical survey to verify the quality of the groundwater system and the degree of contamination by Hg, As and Sb was established.





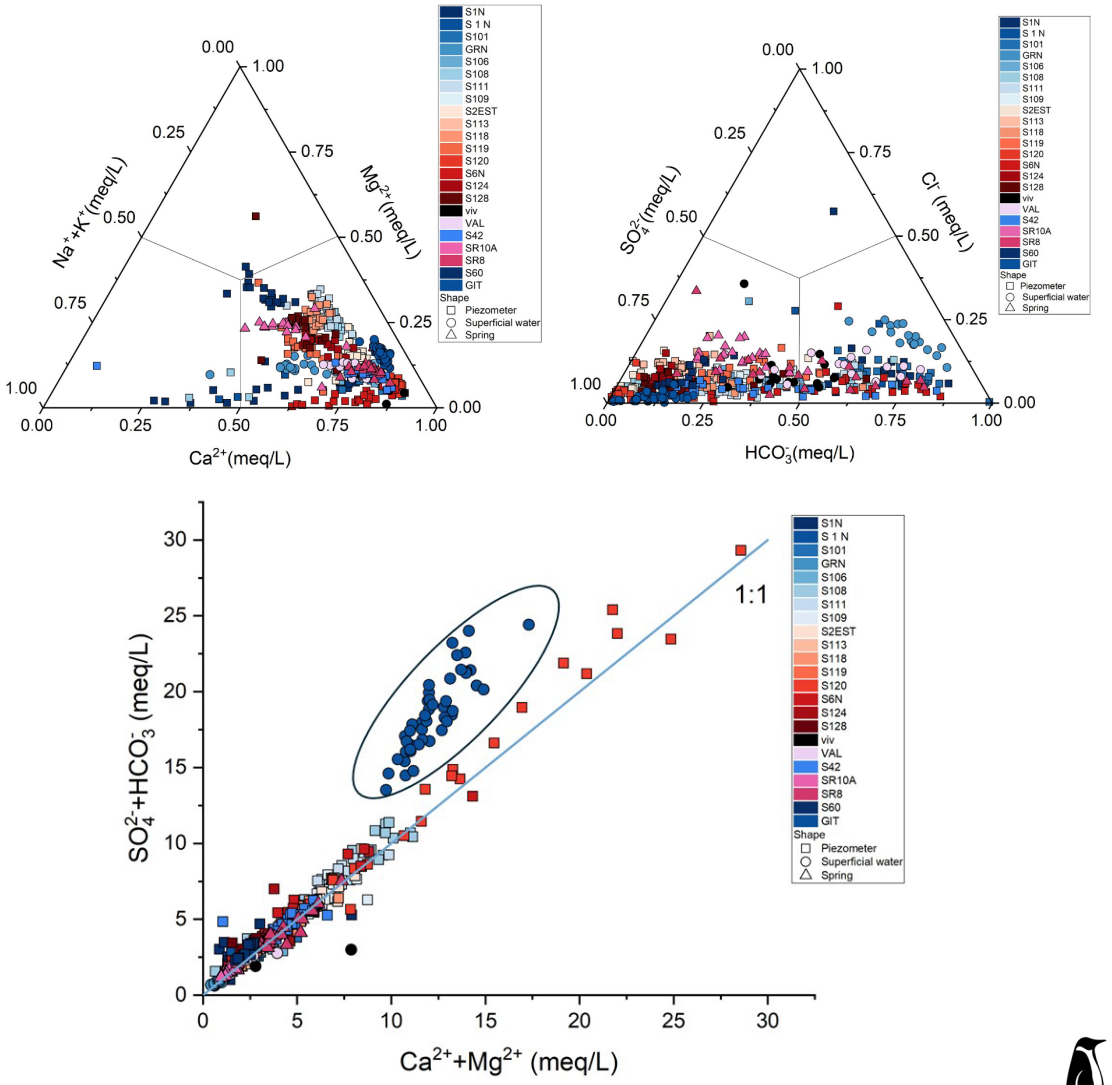
Aims

- Geochemically characterize the surface and ground waters, after 10 years of surveys
- Speciate Hg, As, and Sb by a geochemical modeling with PhreeQC software and determine whether the three chalcophile elements were preferentially partitioned in solution or co-precipitating with other minerals
- Present a water flow and Hg transport model, preparatory to the remediation actions to be undertaken.

Water geochemistry, Boundary Conditions (BC) and simulation

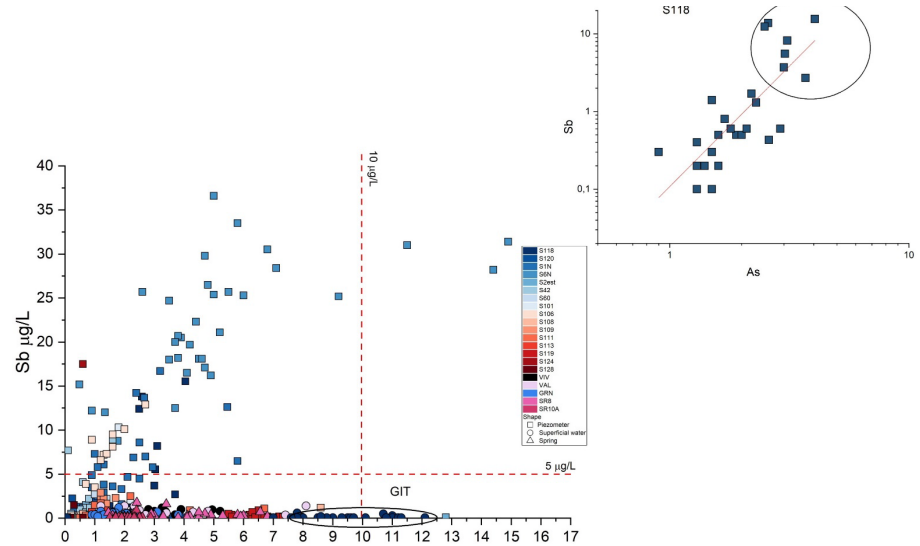
- Three main geochemical facies:
- Ca(Mg)-SO_4
- Ca(Mg)-HCO_3
- (Na+K)-HCO_3

- Season variations of the geochemical facies were observed, though not apparently related to meteoric precipitation

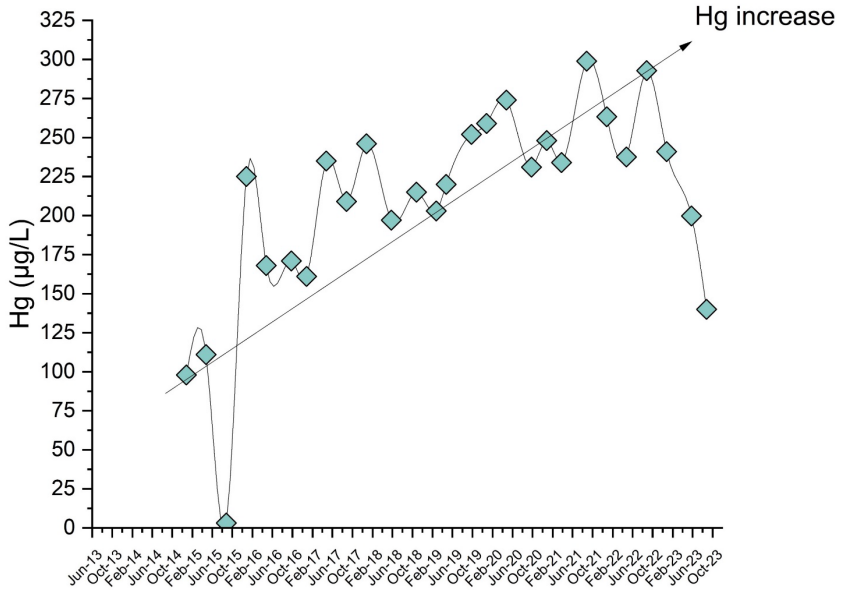


Water geochemistry, Boundary Conditions (BC)

- Concentrations of **As** and **Sb** dramatically decreased after the construction of the bypass canal



- **Hg** concentrations in the water inside the mine were: **> 1 µg/L** (EC) up to **695 µg/L** in S6N. In some waters (e.g. S124), the Hg content decrease after the complete of some remediation works (e.g. removed partly of the pipelines and partly was covered with foam (end of 2022) to avoid any interaction with the meteoric waters)



Water geochemistry, Boundary Conditions (BC) a

Using the pe value **As** and **Sb** in solutions were occurring as As^{5+} and Sb^{5+}
The three main species were $HAsO_4^{2-}$, $H_2AsO_4^-$, $CaAsO_4^{2-}$ and SbO_3^-, $Sb(OH)_6^-$ and $CaSb(OH)_6^+$

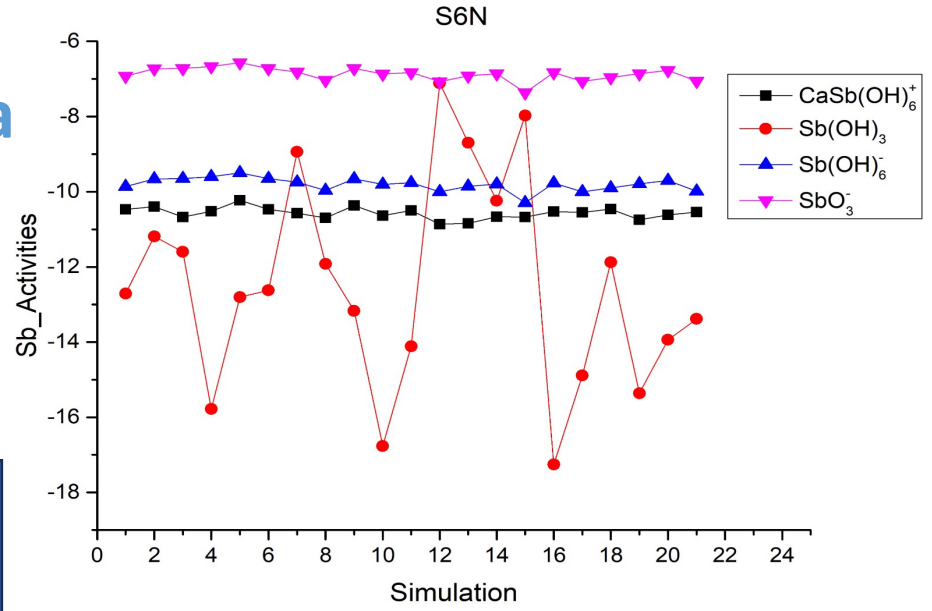
From January 2020 to September 2021 the redox conditions drastically decreased and the pH clustered around 7 or even weakly acid. The As an Sb main species were $H_3AsO_3^0$ and $Sb(OH)_3^0$

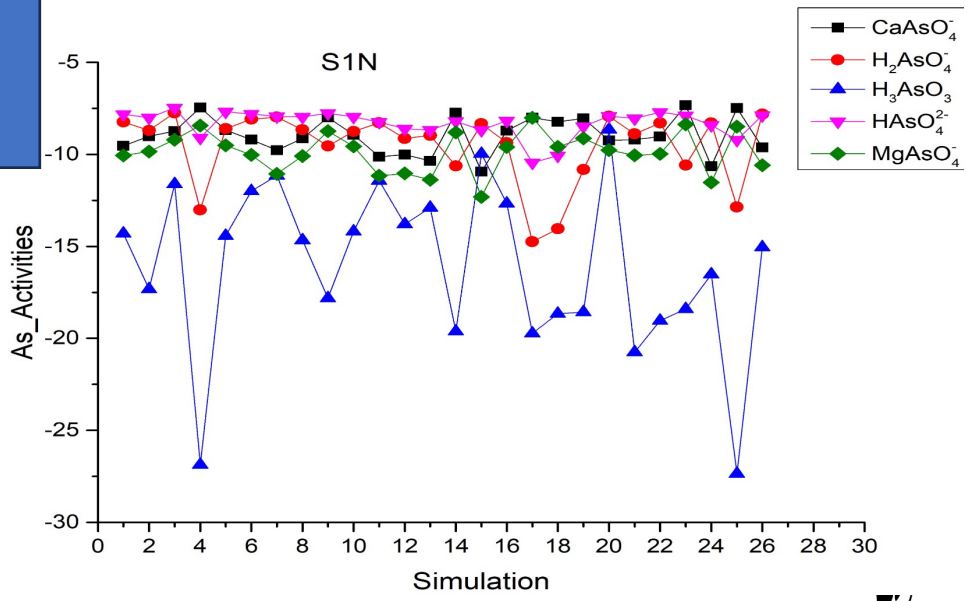
Sb was at equilibrium or oversaturated as Sb_2O_4 or when Fe was present, as Schafarzikite or Tripuhyite. When pH> 10.5, Romeite was stable.

The main **Hg** species was $Hg^0(aq)$

Limited mobility

Migrating with the groundflow





Water geochemistry, Boundary Conditions (BC) and simulation

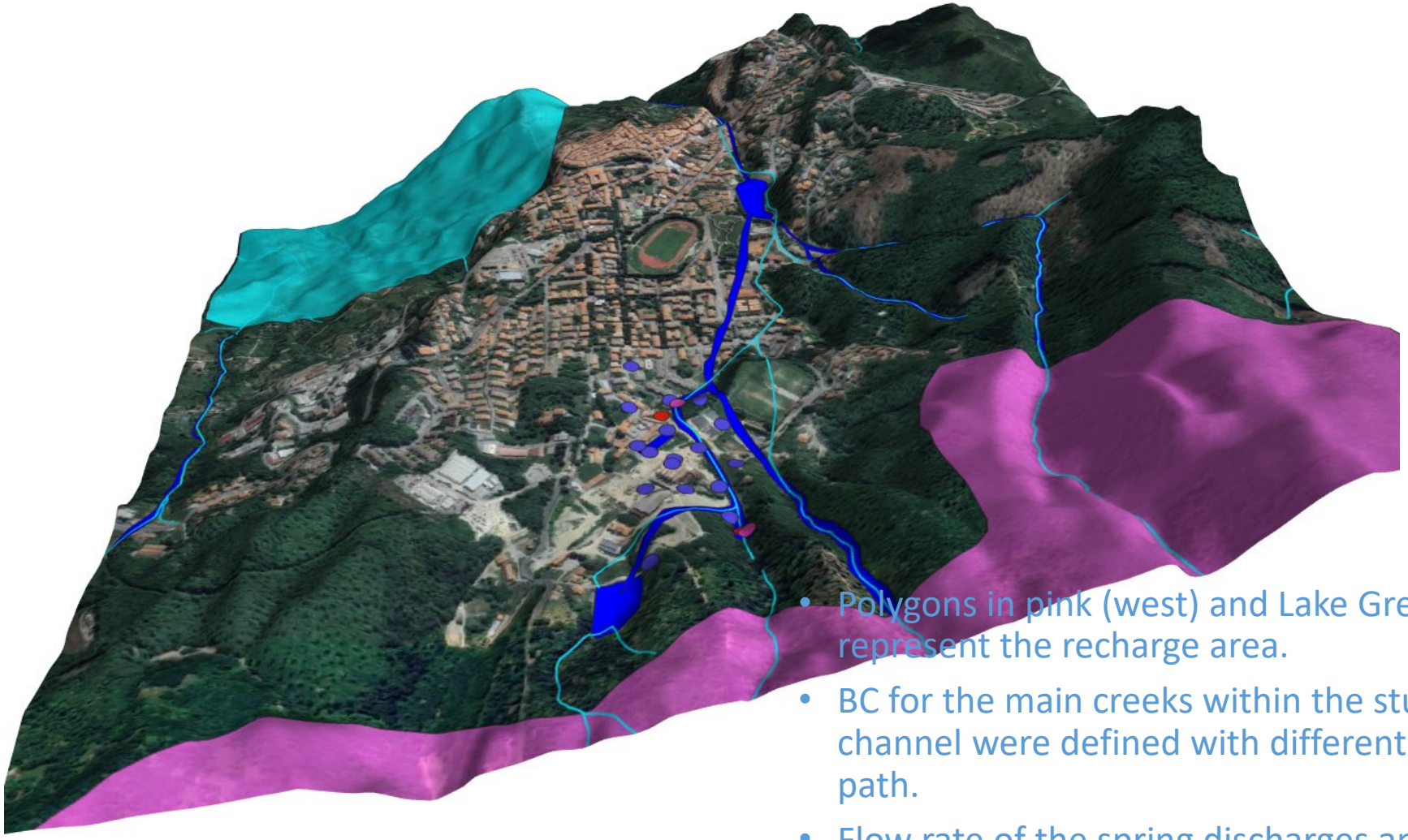
- On the four waters with the highest Hg concentrations, the amount of HS- was analysed, according to Montegrossi et al. (2006), so that the redex pair S^{-2}/S^{-6} could be used in PhreeQC.

- The main Hg species turns out to be $Hg^{0}_{(aq)}$ although, except in S118, α-HgS and β-HgS turns out to be at equilibrium or oversaturated.

- Orpiment, Pyrite, Grigite, Mackinawite result to be oversatured.

Adsorption on Fe-bearing oxy-hydroxides is a possible sink for Hg, while the origin of Hg is due to leaching of mine waste deposits, leading to a tracer source/sink transport model.

Water geochemistry, Boundary Conditions (BC) and simulation



- Grid cell size 10
- Cell number: 213*274
- Kx: $2*10^{-6}$
- Ky=Kx
- Kz=Kx/10
- Initial concentration: 0.1
- Porosity: 0.1
- Longitudinal disperisivity: 9.13

- Polygons in pink (west) and Lake Green to the north of the mine represent the recharge area.
- BC for the main creeks within the study area and the by-pass channel were defined with different hydraulic heads along the flow path.
- Flow rate of the spring discharges and surface waters was not directly determined, an average flow rate of 0.1L/s was attributed according to the field observation.

Water geochemistry, Boundary Conditions (BC) and simulation

- The simulation considered three periods:

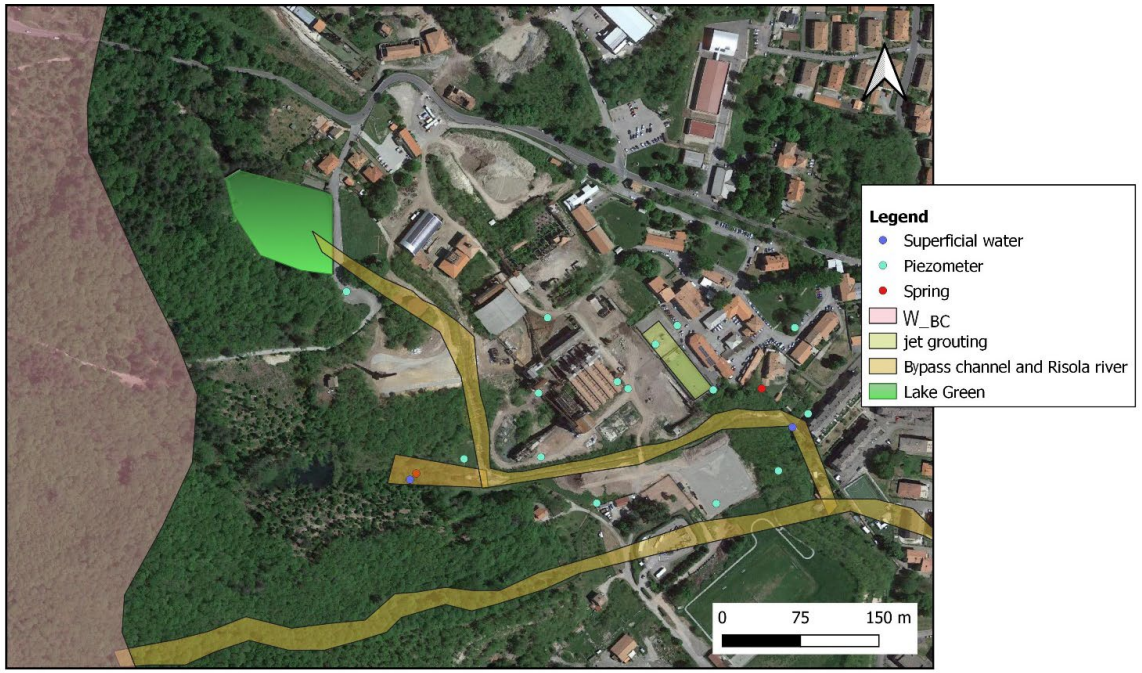
i) steady state;

ii) a 6-month transient: wet period

iii) a 6-month transient: dry period.

Transmissivity (T) of soil = 2×10^{-6} m/s

T of jet grouting = 8.2×10^{-7} m/s (15 m thick)



The concentration of Hg measured in the piezometer (dry and wet season) are used.

A background value of 0.1 µg/L was assigned to the modeled area and BC.

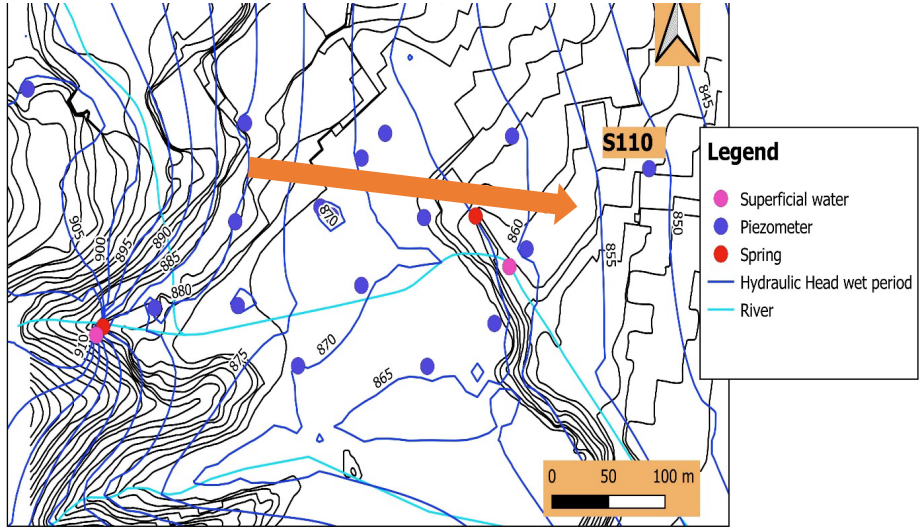
Lake Green BC had a constant value of 0.1 µg/L.

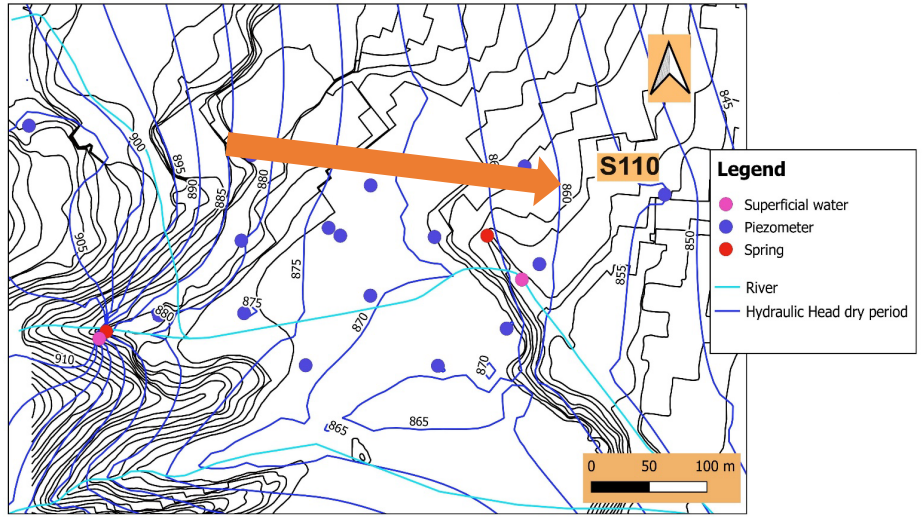
Note: 0.1 µg/L is the minimum detection limit for Hg

Results and Discussion: Modflow modeling

- The flow is computed by ModFlow 6 with ModelMuse interface, allowing the hydraulic model to be verified by comparing the measured water levels of the piezometers with those calculated in both wet and dry season

- Groundater flow is W-E-oriented, following the local topography.





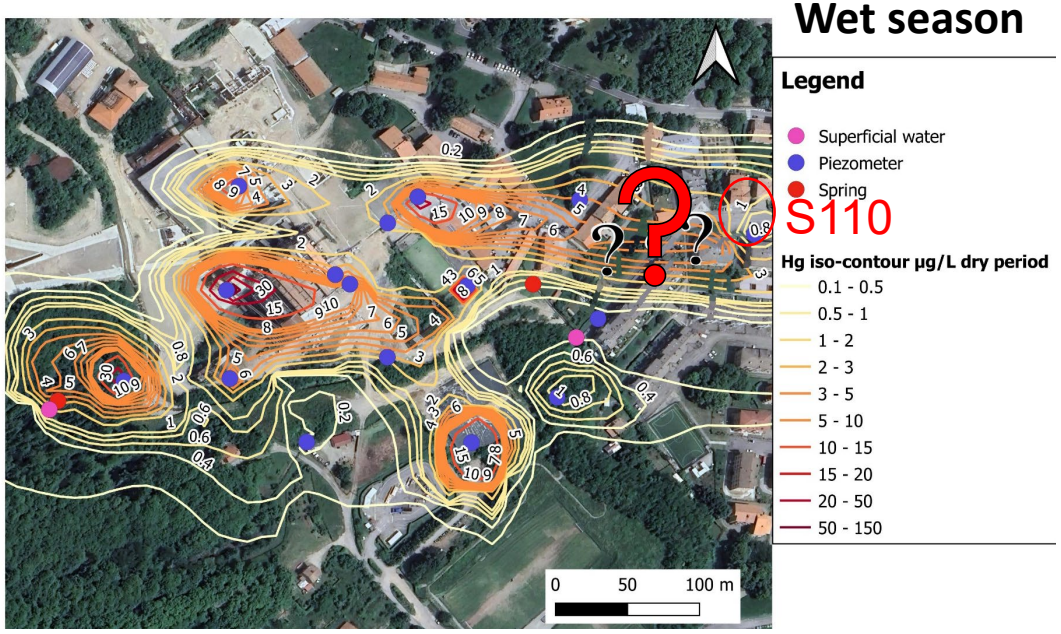
Results and Discussion: Modflow modeling

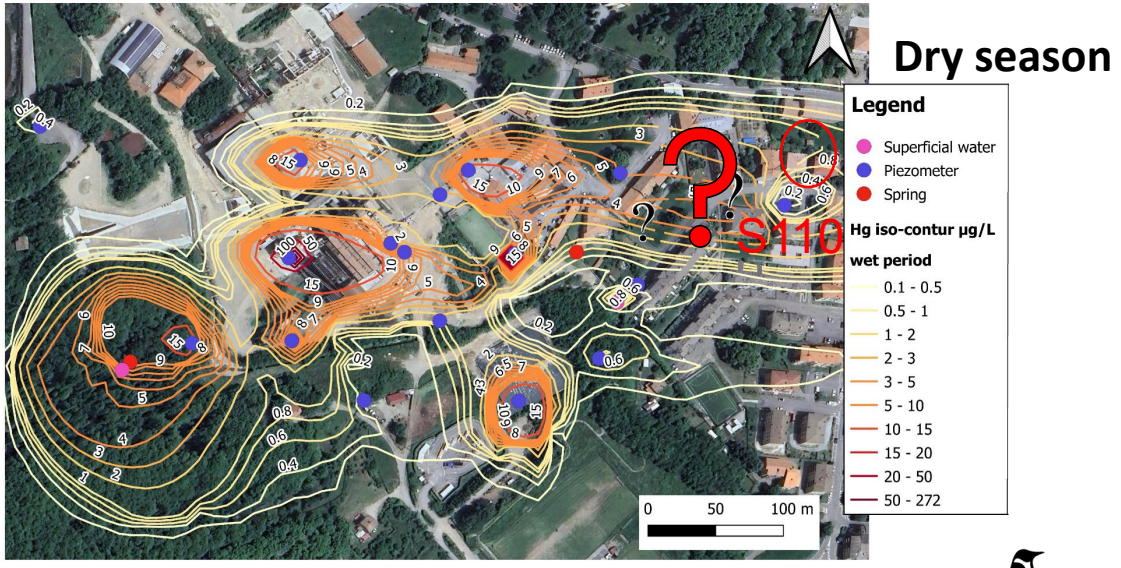
The Hg concentrations of the last survey (2023) confirmed that the contamination was mainly limited to the former mining area, except for piezometers S6N and S2EST from which a plume is generated and migrate to the East

The piezometer S110, drilled in 2014, was included in the model and sampled in March 2024 (Hg =0.11 µg/L).

The Hg plume generated by the S6N and S2Est waters reduces in both the wet and dry periods

No specific information is available on the shallow aquifer between the S108 and S110 piezometers. This poses some difficulties in defining whether the Hg-plume is affecting the the areas external to the former Hg-mine.



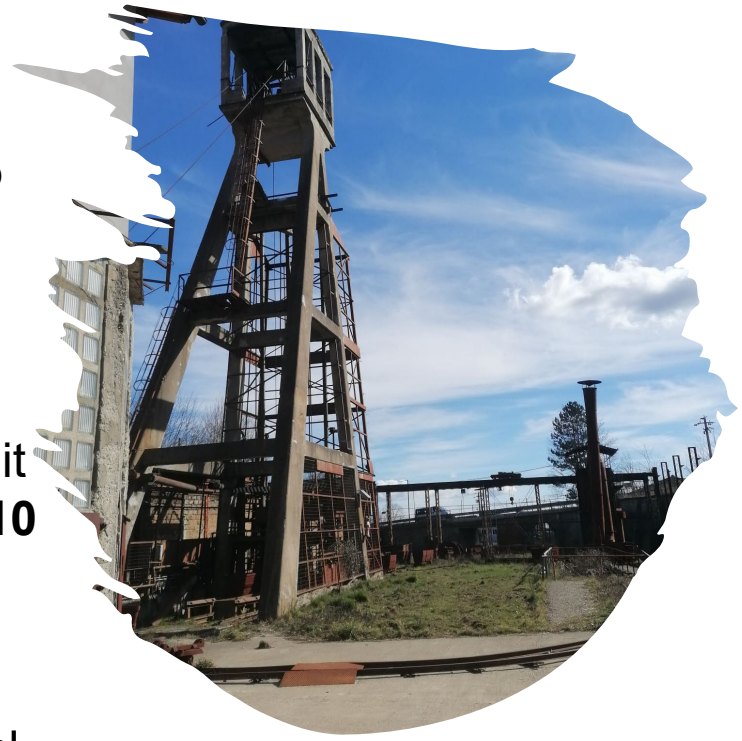


Conclusions

The **Hg contamination as well as that of As and Sb appears to be limited to the mining area**. This would strongly facilitate any technique to be adopted for the removal of mercury.

The criticalities evidenced by the Modflow model and related to a possible extension of a Hg-plume outside the mining area is presently hypothetical since it need to be confirmed by **drilling new piezometers downstream S108 and S110**

The Modflow model is suggesting that the shallow aquifer of the mining area should not be regarded as a single aquifer but characterized by multiple water **"pockets"**. This would facilitate the remediation operations aimed at the removal of mercury notwithstanding that a physicochemical approach is expected to be applied.



water

MDPI

Article

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

Federica Meloni [1,2,*], Giordano Montegrossi [2], Jacopo Cabassi [2], Francesco Bianchi [3], Barbara Nisi [2], Daniele Rappuoli [4,5] and Orlando Vaselli [1,2,*]