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## Industrial mercury pollution in a mountain valley: a combined geophysical and geochemical study

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### Abstract

Many alpine valleys have inherited strong industrial remnants. Chemical and metallurgical companies were set up in these narrow glacial valleys at the beginning of the industrial era to benefit from cheap labor and hydroelectricity. Regulations concerning solid and liquid waste handling did not exist, and contaminated sediments were often used as soil amendment to improve soil texture, spreading the contamination, which local Authorities have now to deal with.

In the present study we report on mercury contamination in the narrow alpine valley known as canton of Valais valley. Waste materials and contaminated sediments were deposited in the valley for many years. An electromagnetic conductivity survey allowed a definitive mapping of the extent of such practices because an EM conductivity contrast was clearly detectable between the added silty-clay material and the natural silty-sand soil. High EM conductivity correlates quite well with high Hg surface soil content. Cores drilled at hotspots and along the canal were analyzed for total mercury, methyl mercury, and core sedimentary features recorded. While up to 70 cm thick, dredged, Hg-contaminated material was found to lay above the original sandy soil in housing areas, the mercury contamination extends down to 1.5 m depth, i.e. down to the water table, probably caused by the high sediment material organic content (OC), and OC-Hg enhanced transport. Methylation reductive conditions were observed, together with high MeHg relative abundance ( $[\text{MeHg}] / [\text{HgT}] > 0.1\%$ ), in two environments, namely the zone of fluctuating water table and the canal water/sediment interface. Groundwater quality was not impacted, because of large groundwater fluxes observed in these glacial alpine valleys.

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**Keywords:** Mercury contamination; anthropogenic soils; methyl mercury; aquifer; watertable fluctuation; reductive conditions

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## 1. Introduction

In the present study, we investigate mercury pollution occurring in a narrow glacial alpine valley. The contamination is from an anthropogenic source, mostly attributed to a chemical plant where mercury was used as catalyzer for acetaldehyde production in the early 1920's. After the 1930's, the chemical industry used a drainage canal (the 10 km long GrossKundKanal) for industrial waste effluent discharge. Up to the late 1970's, i.e. before the construction of a water treatment plant by the chemical industry, mercury was released in the canal, and thus the sediment accumulated mercury at levels up to 100 times background (0.05 ppm). Between the 1930's and the 1970's, canal dredged material and industrial waste were used as civil engineering backfill, e.g. for road construction along the canal where high Hg levels are found, see Fig. 1. Canal sediment was further spread over the agricultural fields as soil amendments, the local soils being very sandy. Before allowing housing and freeway construction in the valley, the Authorities launched a large sampling campaign to evaluate soil and food chain contamination. Prior to the present study, a large topsoil (0-40 cm) sampling and Hg analysis was done by the BMG company<sup>1</sup> with ~ 4000 analyses covering more than 6000 Km<sup>2</sup>, see Fig. 1.

The present study, part of an interdisciplinary multi-University program, combines geophysics and geochemical investigations. An electromagnetic (EM) conductivity field survey using standard geostatistics produced a map of the canal sediment and other waste material spread on soil. Because of textural differences between canal sediment and topsoil sediment – thin sandy clay and sandy silt, respectively, the EM conductivity could distinguish top soil Hg contamination. Hg hotspot areas were drilled to describe vertical mercury distribution and sedimentary logs (6 cores) to evaluate the vertical extent of Hg soil contamination (i.e. backfilling thickness & possible Hg transfer) and possible mercury methylation in depth. Groundwater was sampled in 17 piezometers to measure physicochemical properties and total dissolved mercury concentration.

## 2. Material and methods

The EM survey was carried out in summer after a long dry period using a Geonics EM31-MK2 with GPS antenna and data-logger. The future housing areas were investigated with 5 m apart EM measurement transects. The recording intervals along the transects and the running operating frequency were set equal to 0.5 s and at 9.8 kHz, respectively. The output data, reformatted by DAT31W code, gave a ground EM conductivity (mS/m) integrated over the soil top 5 m. Standard krigging procedures and SURFER code were used to produce EM conductivity maps, see Fig. 1.

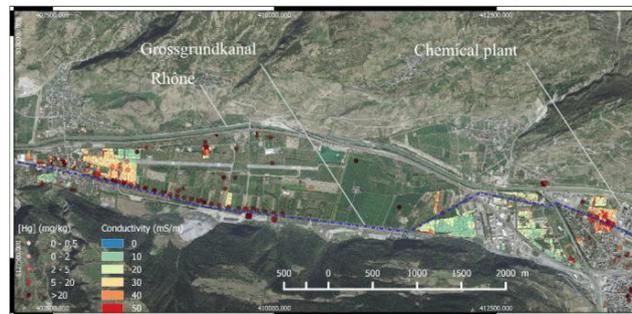


Fig. 1. EM conductivity and topsoil Hg concentration map.

Six cores were drilled in Hg contamination hotspots with a motorized percussion corer. Back to the laboratory, cores were sectioned into two halves. The first half was used for sedimentary and color features. The second half was sub-sampled for solid-phase total mercury and methyl mercury analysis. All sub-samples were freeze-dried, 1 mm mesh sieved, and ground to < 0.63  $\mu$ m. The total solid-phase mercury concentration was measured by Altec AMA 254 atomic absorption spectrophotometer, with an absolute detection limit equal to 0.2 pg, soil samples were diluted with a quartz sand ( $Hg_T$  solid = 0.0027 ppm). Solid-phase monomethylmercury (MMHg) concentration was

determined after derivitization by purge and trap-gas chromatograph-atomic absorption spectrophotometry (MEX System, Brooks Rand®).

Groundwater was sampled during two field campaigns (July and October 2015) in 17 piezometers. Piezometers were first purged<sup>2</sup>, and groundwater sampled and filtered using for total mercury analysis ultraclean techniques<sup>3</sup> and a TEFLON® pump, as well as a standard submersible pump for physico-chemical properties. Fe(II) and S(-II) concentrations were analyzed with a HACH spectrophotometer. Alkalinity was obtained by the second derivative of titration data. The dissolved organic carbon (DOC) concentration was measured on a TOC-VCSN Shimadzu analyzer. The total dissolved liquid phase mercury concentration was determined by Cold Vapor Atomic Fluorescence Spectrometry technique (CVAFS) using a Tekran analyzer (model 2500).

### 3. Results and Discussion

#### 3.1. EM-31 conductivity vs. Hg top soil content

The first conductivity study was obtained on known Hg-rich canal and natural backfilled zone to calibrate the EM results. With the help of value interpolation (Kriging method), Hg-rich and natural backfill were found to equal 30 and 20 mS/m, respectively. Calibration results are in agreement with the textural properties of the prospecting zone: higher for the zone backfilled with sediment rich in clay (i.e. rich in dissolved/adsorbed ions). Globally, see Fig. 1, the survey suggests that conductivity variations are likely associated with burial of Hg-rich sediments. However, sandy clay texture of natural backfill occurring below 150 cm (study cores result) may interfere as Hg-rich sediment backfilled. Note that steel materials (e.g. buried, fence, etc.) alter the interpretation of the conductivity result and make it inoperable for small field areas enclosed by steel materials.

#### 3.2. Sedimentary survey result

Mercury profile distributions in sediment cores are shown in Figure 2. The maximum concentration observed in the cores was about 70 ppm. Lithological evidence showed two different Hg-rich sediments – sandy silt and coarse sand with gravels – found in the upper 80 cm. Potential Hg transfer in deeper core horizons vary from core to core, and is apparently negligible down to 70 cm (see Fig. 2). Such differences in potential transfer from place to place are still not fully explained. In core “a” (Fig. 2a) a significant Hg concentration (6.5 ppm) is found at 150 cm depth, just 10 cm above the water table (~ 10 cm), and this would suggest a facilitated Hg transfer. In most cores, MMHg analysis showed typical relative abundance (0.1%) of total mercury. However, three samples showed higher MMHg relative abundance (> 0.1%). The first one is found in core “a” at 175 cm deep (see Fig. 2a, red symbol).

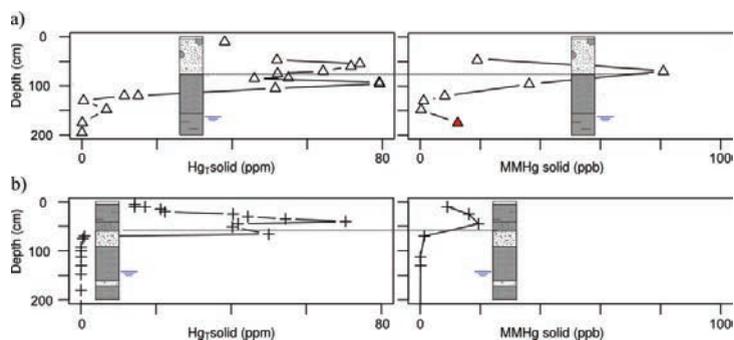


Fig. 2. Core sedimentary features with Hg and MMHg concentration profiles for two cores: (a) core with top thick coarse sandy to gravel textured Hg-rich layer of unknown origin and (b) core with thick Hg-rich sandy clay to silt texture, presumed originating from GrossKundkanal dredged sediment. Red triangle depicts, sample with MMHg to total Hg relative abundance of > 0.1%.

Two other ones are found in samples coming from the Hg contaminated canal (data not shown). The entire canal core sediment showed a high MMHg relative abundance (+ 0.1 %), attributed to the large organic matter content and to anoxic reductive conditions prevailing in these sediments.

### 3.3. Groundwater geochemical results

Groundwater table was usually located at 1.5 m depth (see Fig. 2) when sampled (at the heart of the dry season). Neutral to alkaline pH (7- 8) and alkalinity (median ~ 4mmol/L) values were observed. Typical sedimentary fill conductivity values were observed (median ~ 500  $\mu$ S/cm), except for some piezometers located along the main road, where very high conductivities (> 2000  $\mu$ S/cm) were attributed to de-icing salt spray. The Eh values vary from -230 mV to 220 mV and indicate different redox environments. The Fe(II) concentrations indicate two sub-oxic environment areas<sup>4</sup> (~1 km in length) along the main river (Rhône) and the GrossKundkanal, which could potentially favor Hg methylation<sup>5</sup>. However high MMHg solid content was usually found at the fluctuation water table depth. Most DOC concentrations were significantly higher (median ~ 10mg/L) than typical groundwater DOC content (0.7 mg/L) and were attributed to the continuous leaching of OM contained in sediments. However this organic content leaching did not contribute to groundwater Hg contamination probably due to a dilution effect. Indeed, all filtered liquid-phase total mercury concentrations were below the detection limit (0.04 ng/L).

## 4. Conclusion

The present study demonstrates a link between (i) EM conductivity of top 5 m soil horizons (ii) surface soil Hg content, and also between Hg vertical distribution in anthropogenic soils, sedimentary features and methylation prone subsurface conditions. The groundwater has an alkaline pH, a high DOC content (~ 10 mg/L), very low dissolved Hg concentrations (< 0.04 ng/L). Two groundwater zones, along the main river and the GrossKundkanal, showed the prevalence of reductive environments depicted by high Fe(II) concentrations. Sedimentary features and Hg distribution in soil showed that (i) Hg-rich anthropogenic surface horizon could have two different textures (sandy clay/silt and coarse sandy with gravels) and depth (up to 80 cm), and that (ii) mercury transfer could occur on long vertical distances (70 cm). Two methylation prone horizons were found: (i) in the Hg-rich sediment canal, and (ii) in depth at the groundwater/unsaturated zone interface. The EM data shows that canal Hg-rich sediment has been spread in agricultural fields and housing areas. The areas characterized by a higher conductivity than natural alluvial soils (+10 mS/m) could thus have received canal sediment backfilling. The spatial distribution of Hg-rich surface soils is therefore facilitated by cheap (compared to Hg analysis) EM data survey.

The combined information give a better understanding of the complex industrial inherited pollution and should be of helpful for post-pollution management. First, extended reductive groundwater areas were found (water table interface and canal sediment) that could favor mercury methylation but are little reflected in aqueous phase analysis. This risk was, however, experimentally determined by the high relative abundance of MMHg in one core, drilled in one of the Hg hotspots, at the groundwater interface. Second, two different anthropogenic sediments were found to be contaminated by mercury and used as backfill and in one case a significant Hg transfer down to the water table was observed. Finally, the Hg-rich sediment originating from the canal was found to have higher than natural conductivity and could be mapped in agricultural fields and housing areas by EM conductivity survey.

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