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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 ([MeHg]/ [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[1] with ~ 4000 analyses covering more than 6000 Km², 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.

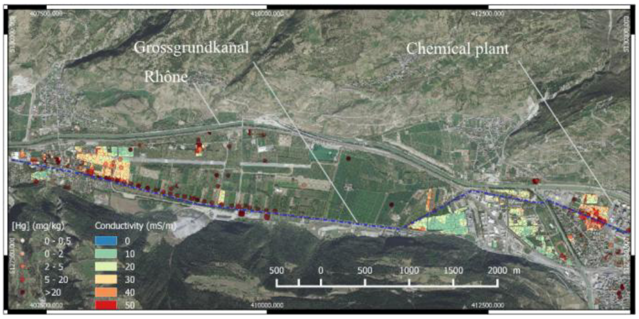

Fig. 1. EM conductivity and topsoil Hg concentration map.

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 µm. 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 monomethylmecury (MMHg) concentration was