



Mercury and methylmercury in a mercury-contaminated agricultural floodplain in Valais, Switzerland

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Agricultural floodplain soils have been identified as having high organic matter content, fluctuating water table levels, and reducing conditions, which can lead to methylmercury (MeHg) production. As a result, mercury (Hg)-contaminated floodplains can provide a source of Hg and MeHg to downstream water bodies, and moreover, a source of Hg and MeHg to agricultural crops and livestock. In this study, we examined Hg and MeHg in soils and plants near the town of Visp, Switzerland, where the historical use of Hg by an industrial plant has resulted in Hg contamination in the soils of the surrounding agricultural floodplain. Our objectives were to determine Hg and MeHg distribution in soils and plants, and to investigate the (bio)geochemical controls on MeHg production. Surface soils (0- 20 cm) and plants were collected from agricultural fields, and soil cores (0 – 50 cm) were collected within tree groves located on the agricultural fields. Soil samples were analysed for total Hg, methylmercury (MeHg), carbon (C), nitrogen (N), sulfur (S), org-CNS, loss on ignition, water content, and total iron (Fe), manganese (Mn), and aluminium (Al) concentrations. In plants, Total Hg concentrations in roots and leaves were generally low (≤ 0.13 mg/kg), and concentration factors were ≤ 1.33 , indicating that Hg transfer from soils to the plants collected was minimal. In the surface soils of the agricultural fields (0-20 cm), Total Hg concentrations were ≤ 1.34 mg/kg, while MeHg concentrations were ≤ 1 $\mu\text{g/kg}$ ($\% \text{MeHg} \leq 0.67$), with two exceptions: MeHg concentrations of 5.7 $\mu\text{g/kg}$ ($\% \text{MeHg} = 2.4$) and 3.7 $\mu\text{g/kg}$ ($\% \text{MeHg} = 0.3$) were observed at two locations. In soils collected from tree groves, Total Hg concentrations were also low (≤ 0.4 mg/kg); however, despite low Total Hg, MeHg concentrations ranging up to 29.6 $\mu\text{g/kg}$ ($\% \text{MeHg} = 17.7$) were observed. Depth profile data (10 cm depth intervals) indicated that MeHg and Total Hg concentrations were highest in the top 20 cm of soil. In the 0-10 cm and 10-20 cm fractions, MeHg was not significantly correlated with Total Hg, org-C, org-N, water content, or C/N ratio, and Total Hg was not significantly correlated with any other parameter. MeHg was negatively and significantly correlated with Fe, Mn, and Al concentrations ($RS \geq 0.83$, $p < 0.05$), suggesting that lower occurrence of Fe and Mn oxides and clay minerals may increase Hg availability for methylation. The Mann-Whitney U test for independence was conducted to compare geochemical parameters from the agricultural field and tree grove soils (0-20 cm). Our data indicated that MeHg concentrations and $\% \text{MeHg}$ were significantly higher in the tree grove soils compared to the agricultural field soils ($p < 0.0001$). Additionally, C/N ratios were lower in tree grove soils ($p < 0.05$), an indication that the org-C was more decomposed, suggesting that org-C composition may be an important factor for Hg methylation. Ongoing work to investigate controls on MeHg production in the agricultural floodplain includes Hg speciation studies, quantification of acid volatile sulfide, and microbial community assays.