Hg release and Hg nanoparticle formation upon flooding of an agriculturally used fluvisol.

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Soils in legacy sites of chlor-alkali and acetaldehyde production are point sources of mercury (Hg) to downstream eco-systems. Flooding and agricultural activities may influence the fate of Hg by altering redox conditions, microbial activity and carbon budgets. However, the complex interplay between these parameters is still not well understood. The aim of this work was to better understand the effect of flooding and fertilisation on the release/sequestration of Hg in a polluted floodplain soil.

We conducted a flooding-draining incubation experiment on two Hg polluted fluvisols (2.4 ± 0.1 and 44.8 ± 0.5 mg.kg⁻¹ Hg). The soils originated from an agriculturally used floodplain situated in the Rhone Valley (Valais, Switzerland) and were exposed to Hg pollution by an acetaldehyde producing plant until the 1970's. They were incubated in triplicates for each treatment. During 56 days the soils were alternately flooded and drained in intervals of 14 days. For flooding, we used an artificial rain water and a 1:1.5 soil:water ratio. The influence of agricultural activites was studied by adding 0.6% (w/w) of liquid manure in a separate treatment. We monitored pore water Hg_{total}, Eh, pH, DOC and relevant metals in daily time intervals. Further, the sampled pore water was filtered in distinct intervals (10µm / 5µm / 0.45µm / 0.020µm) at specific time points and analyzed for Hg_{total}. Additionally, the 0.45µm fraction was sampled to study the evolution of colloidal Hg with AF4-ICP-MS.

We observed differences between soil treated with or without manure. In the microcosms (MCs) treated with manure, we observed a Hg_{total} release along with reductive dissolution of Mn-oxides peaking (Hg_{total}: 20.8 µg.L⁻¹) after 5 days of flooding. Subsequently, pore water Hg_{total} decreased with a simultaneous decrease in pore water SO₄²⁻. This is likely due to the onset of sulfate reduction. Additionally, we observed the increase of inorganic colloidal Hg in the range of 10nm hydro dynamic diameter in manure treated MCs with higher contaminated soil during the first 2 and 10 days of incubation.

In the MCs without manure addition, the onset of reductive dissolution of Mn oxides was 2 days later. Pore water Hg_{total} peaked only after 7 days of flooding (19.76 µg.L⁻¹ Hg) and remained at the same levels until the end of the first flooding period. This is likely due to a lower microbial activity and a lower labile carbon pool in the untreated compared to the treated soils.
Flooding of our polluted fluvisol releases Hg after few days. The additional manuring accelerates this process. However, it as well accelerates the subsequent decrease of $\text{Hg}_{\text{total}}$ in the pore water. This is among others due to the formation of Hg nanoparticles. We plan to use electron microscopy in order to draw conclusions about the nature of these Hg nanoparticles.