Thallium redox speciation in soil Mn concretions by X-ray imaging

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Thallium, a highly toxic trace metal, occurs in the environment as relatively soluble Tl^{I} and, to a lesser extent, insoluble Tl^{III}. Tl^{I} can substitute K in minerals such as illite, but can also be found in metal sulfides. Furthermore, Tl can sorb to Mn oxides via non-oxidative and oxidative uptake mechanisms, the latter occurring on hexagonal vacancy-bearing birnessite [1, 2].

The aim of this study was to use X-ray chemical imaging to gain direct insight into the extent of non-oxidative and oxidative Tl sequestration in soil Mn concretions and its dependence on Tl loading. To this end, we analyzed soil samples from a site in the Swiss Jura mountains that are contaminated with Tl of geogenic origin [3]. The association of Tl with clay minerals and Mn concretions was assessed by analyzing soil thin-sections with micro-focused (μ-) X-ray techniques, including laboratory X-ray fluorescence spectrometry (XRF) as well as synchrotron-based XRF and X-ray absorption spectroscopy (XAS) with a spatial resolution of ~5 μm. The aim of the ongoing data analysis is to derive robust data on the relation between the Tl loading of soil Mn concretions (Tl/Mn ratio) and the fractions of sorbed Tl(III) and Tl(I).

Preliminary results support the hypothesis that an increasing Tl loading of soil Mn concretions is paralleled by an increasing fraction of Tl(I) due to increasing non-oxidative Tl uptake. Furthermore, semiquantitative μ-XRF results on the fraction of soil Tl associated with soil Mn concretions and the respective Tl/Mn ratio are in line with results from chemical extractions. In combination with laboratory studies on the sorption of Tl by Mn oxides and clay minerals [1,2,4], our results gained on natural soil samples allow to better constrain the relevance of different sorbent phases for Tl sequestration in soils.

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