Speciation and fractionation of geogenic thallium in soils from the Swiss Jura mountains

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Thallium (Tl) is a highly toxic trace element. We investigated the speciation and fractionation of Tl in soils from the Swiss Jura mountains that developed from a Tl-As-Fe-sulfide mineralization hosted within carbonate rocks [1]. Within a zone of about 200×100 m^2, the topsoil contained 100-1000 mg/kg Tl, the subsoil up to several 1000 mg/kg Tl.

Using micro-focused X-ray fluorescence spectrometry and X-ray absorption spectroscopy (XAS) at the Tl L_3-edge, we identified four Tl species: (i) Avicennite (Tl_2O_3) and Tl(I)-substituted jarosite as weathering products of the primary mineralization. (ii) Tl(III) associated with Mn-concretions and Tl(I) bound to illite as pedogenic Tl species. The analysis of whole soils by XAS showed that Tl(I) uptake by illite was the most relevant sequestration mechanism in topsoils.

For topsoil samples containing dominantly Tl(I) bound to illite, 1 M NH_4-acetate extractions suggested that a major fraction of the Tl(I) may be fixed in the illite interlayers rather than sorbed at edge sites. The concentration of Tl in 10 mM $CaCl_2$ extracts ranged from ~10 to ~1000 μg/L. The log-transformed concentrations of Tl in the extracts correlated with the log-transformed soil Tl contents, but did not show any detectable variation as a function of soil Tl speciation.

This study provided first spectroscopic evidence for the effective sequestration of Tl by illite in contaminated soils. In ongoing work, we therefore investigate the sorption of Tl by illite and its effect on the solubility of Tl in soils. Further work is concerned with the detailed characterization of secondary Tl- and As-bearing minerals.

[1] Voegelin et al. (2015) *Thallium speciation and extractability in a thallium- and arsenic-rich soil developed from mineralized carbonate rock*. Environ. Sci. Technol. 49, 5390-5398.