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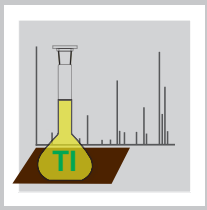

Highlights of Analytical Sciences in Switzerland

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Exploring the Geochemistry of Thallium in Soils by X-ray Absorption Spectroscopy and Chemical Soil Extractions

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Thallium (Tl) is a toxic trace element. From Tl-contaminated soils, Tl may enter the food chain or leach into groundwater, and may therefore also threaten human health. However, mechanistic studies on the geochemical behavior of Tl in soils are still scarce. In the Swiss Jura mountains, on the Erzmatt near the village Buus (BL), soils with high Tl contents have developed on carbonate rock that hosts a hydrothermal mineralization.

In a first study, we used synchrotron-based X-ray absorption spectroscopy (XAS; Tl L_{III}-edge) to show that Tl in topsoil horizons was mainly monovalent Tl(I) associated with micaceous clay minerals (illite and muscovite) and only to a minor extent trivalent Tl(III) associated with manganese (Mn) oxides. In subsequent work, we examined the extent and mechanisms of Tl sorption onto illite and Mn oxides. In our most recent study, we used XAS to characterize the speciation of geogenic Tl in numerous topsoil samples from the Erzmatt, and performed chemical extractions to determine the concentrations of Tl in soil porewater and the amounts of exchangeable and Mn oxide-associated Tl, using inductively coupled plasma-mass spectrometry (ICP-MS) for solution analysis. From our results, we derived the following conclusions: (i) Most of the geogenic Tl in topsoils from the Erzmatt (~95%) is fixed in the structure of micaceous clay minerals. (ii) Only ~3% of the total Tl is adsorbed onto micaceous clay minerals in readily exchangeable form, and the solubility of this fraction can be described with a model for Tl adsorption onto illite. (iii) About 2% of the total Tl is associated with Mn oxides.

Our results allow to explain the observation of the local authorities that Tl transfer from soils to plants on the Erzmatt is limited and to better predict the effects of variations in soil chemical conditions on the solubility of Tl in soils. **In conclusion, synchrotron-based XAS together with chemical soil extractions is a powerful approach to advance the mechanistic understanding of the behavior of potentially toxic elements in soils.**

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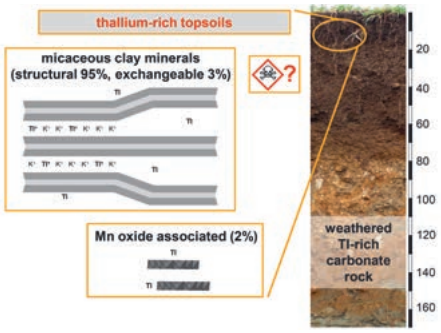
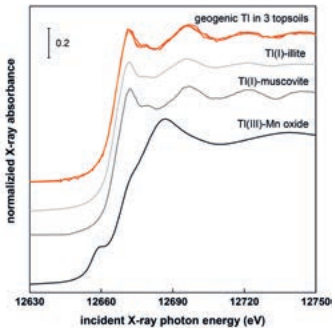
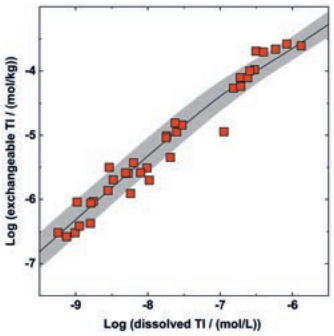


Geogenic Tl in topsoils from the Erzmatt (Buus, BL).



X-ray absorption spectra (at the Tl L_{III}-edge) of Tl in 3 topsoil samples with ~10 to 1000 mg/kg geogenic Tl in comparison to reference spectra of Tl(I) adsorbed onto illite, Tl(I) incorporated into muscovite, and Tl(III) sorbed onto Mn oxide.



Exchangeable soil Tl (1 M NH_4-acetate extract) dissolved Tl in soil solution (0.01 M $CaCl_2$ extract) (red squares), compared to the relationship predicted using a cation exchange model for Tl adsorption onto illite (black line, gray area).

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