Thallium sorption onto soil minerals

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Thallium (Tl) is a highly toxic trace element with a diverse biogeochemical behavior. In the environment, Tl occurs mainly as Tl^{I} and, to a lesser extent, as Tl^{III}. The Tl^{+} cation can substitute K^{+} in K-bearing minerals such as mica due to its similar ionic radius. Elevated levels of Tl may also be found in Mn-oxides [1]. Using X-ray absorption spectroscopy (XAS), it was shown that birnessites, depending on their structure, can sorb Tl as Tl^{+} or as Tl^{3+} via an oxidative mechanism [2]. Based on the general geochemistry of Tl, sorption of Tl onto illite and birnessite have long been hypothesized to be key retention mechanisms for Tl in soils.

Using micro-focused and bulk XAS to speciate Tl in geogenically Tl-rich soils, we obtained spectroscopic evidence for the importance of Tl^{+} uptake by illite and the association of Tl^{3+} with Mn-oxides in soil [3]. In laboratory experiments, we further examined the adsorption of Tl^{+} onto purified Na-, Ca-. K-, and NH_4-exchanged illite [4]. Adsorption isotherms covering large ranges of dissolved Tl^{+} concentration could be adequately modelled by extending a generalized 3-site cation exchange model for the uptake of Cs^{+}, Rb^{+}, NH_4^{+}, K^{+} and Na^{+} by illite. XAS data supported the mechanistic interpretation of the model sites in terms of their association with the planar surfaces and frayed edges of illite.

In ongoing work, we use the parameterized adsorption model for Tl on illite in combination with adsorption and extraction data obtained on geogenic Tl-containing soil samples to assess the effect of illite on the solubility of Tl in soils. Recently, we started to study the adsorption of Tl onto different Mn-oxides, linking macroscopic adsorption data with spectroscopic information to determine the quantitative relevance of different uptake mechanisms as a function of Mn-oxide structure and solution chemistry.

With our work, we aim to contribute to a better quantitative and mechanistic understanding of the uptake of Tl onto soil mineral colloids and its control on the solubility, mobility and bioavailability of Tl in environmental systems.

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