

Thallium sorption onto illite

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Thallium (Tl) is a highly toxic trace element. In the environment, Tl occurs predominantly as Tl^I. The Tl^I cation can substitute K⁺ in K-bearing minerals due to its similar ionic radius. In analogy to the highly specific uptake of Cs⁺ at the frayed edges of the clay mineral illite, sorption of Tl^I onto illite has long been hypothesized to be a key retention mechanism for Tl in soils and sediments. In a recent spectroscopic study on geogenically Tl-rich soils, we confirmed this hypothesis [1]. Sorption data for Tl on illite are lacking to date.

In this study, we investigated the sorption of Tl^I on purified homoionic Na- and K-exchanged illite (Illite du Puy). Sorption of Tl from pH 3 to 11 at trace concentration ($\sim 5 \cdot 10^{-8}$ M) and sorption isotherms at neutral pH at dissolved Tl concentrations from 10^{-10} to 10^{-2} M in KNO₃ and NaCl electrolytes was analysed. Radioactive ²⁰⁴Tl was used to quantify Tl sorption. Changes in the mode of Tl uptake were assessed by X-ray absorption near edge structure (XANES) spectroscopy. The sorption data were modelled by extending a generalized 3-site cation exchange model for the uptake of Cs⁺, Rb⁺, NH₄⁺, K⁺ and Na⁺ by illite [2].

Our results confirm that trace amounts of Tl^I are very effectively sorbed by illite, with a sorption affinity between Cs⁺ and Rb⁺, a strong sorption competition with K⁺, and a slight pH-dependence. Using the generalized sorption model with fixed capacities for cation exchange sites at the frayed edge and on the planar surface of illite, the sorption data could be adequately described by adjusting the Tl-Na and Tl-K selectivity coefficients. XANES data are in line with a transition from specific sorption of dehydrated Tl^I at frayed edge sites to less-specific sorption of hydrated Tl^I on planar sites of illite with increasing Tl loading.

In continuing work, we plan to use the parameterized sorption model for Tl on illite in combination with sorption and extraction data on Tl-containing soil samples to elucidate the impact of Tl uptake by illite on the solubility of Tl in soils and, more generally, the mobility and bioavailability of Tl in environmental systems.

[1] Voegelin A. et al., Environ. Sci. Technol. 49, 5390–5398, 2015. [2] Bradbury M. H. and Baeyens B., J. Contam. Hydrol. 42, 141-163, 2000.