Thallium sorption onto birnessite

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The contamination of soil, sediment or water with toxic thallium (Tl) may pose a serious threat to environmental and human health. In the environment, Tl commonly occurs as monovalent Tl^{I} and, to a lesser extent, as trivalent Tl^{III}. Micaceous clay minerals and Mn-oxides are key sorbents for Tl in soils [1]. With respect to Mn-oxides, hexagonal birnessite can sequester Tl^{I} by sorption and oxidation to Tl^{III}, whereas triclinic birnessite binds Tl^{I} without oxidation [2, 3]. However, the underlying molecular basis for these differences in sorption capacity and affinity and their impact on Tl solubility over wide ranges in Tl loading have not been examined to date. We combined batch sorption experiments (1 day equilibration time) with X-ray absorption spectroscopy to study Tl sorption onto synthetic δ-$Mn^{IV}O_2$ (hexagonal sheet symmetry with vacancies, turbostratic stacking), triclinic birnessite (no vacancies, structural $Mn^{III/IV}$-content, higher stacking order), and δ-MnO_2 that was partly reduced by reaction with organic compounds.

Up to Tl loadings of ~0.015 Tl/Mn (~30'000 mg/kg), δ-$Mn^{IV}O_2$ sorbed dissolved Tl^{I} exclusviely as Tl^{III}. At higher Tl loadings up to ~0.15 Tl/Mn, oxidative Tl uptake reaches a maximum at ~0.06 Tl^{III}/Mn and an increasing fraction of Tl^{I} becomes bound via a non-oxidative uptake mechanism. No Tl oxidation was observed when Tl^{I} was sorbed to triclinic birnessite, and the dominant sorption process appeared to be cation exchange at all loadings. At low Tl loadings (Tl/Mn ~0.005), these differences in uptake mechanisms result in an about four orders of magnitude higher affinity of Tl for sorption onto δ-$Mn^{IV}O_2$ than triclinic birnessite. Partial reduction of δ-MnO_2 led to the inhibition of oxidative Tl uptake, probably due to the blocking of vacancy sites by Mn^{III}. Our results confirm that the uptake mechanism of Tl on Mn-oxides depends on the structure and Mn oxidation state of the oxide as well as on Tl loading. Therefore, these factors must be considered when assessing the impact of Mn-oxides on Tl solubility and sequestration in soils.

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