

Cobalt Sorption to Ferrihydrite and Ferrihydrite-Humic Composites

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Cobalt is a potentially toxic trace metal and radionuclide that is present in many contaminated soils. Its environmental mobility is primarily controlled by sorption to charged mineral surfaces and organic substrates. An understanding of Co sorption behaviour to these phases, and mineral-organic composite phases is therefore required to predict Co environmental behaviour. Here, Co sorption to pure ferrihydrite, humic acid (HA), and ferrihydrite coated with HA is investigated as a function of pH, ionic strength and Co concentration using batch sorption experiments, synchrotron X-ray absorption spectroscopy (EXAFS) and thermodynamic surface complexation modelling (SCM). For all sorbent phases Co sorption increases with increasing pH. However, for three ferrihydrite-HA composites (containing 5, 10, and 17 wt% C) Co sorption is intermediate to end-member ferrihydrite and HA phases, displaying enhanced sorption at pH values where sorption to the pure ferrihydrite end-member is negligible (pH <6.5). This is in good agreement with the sorption behaviour of other heavy metals with ferrihydrite-organic composites [1, 2]. For the first time, EXAFS analysis indicates that Co is sorbed to ferrihydrite via inner-sphere surface complexes (or Co(OH)₂ surface precipitates), and to HA via loosely bound complexes, and to ferrihydrite-HA composites via complexation to both ferrihydrite and HA functional groups. This molecular-level sorption information is implemented in a new SCM for Co sorption to ferrihydrite, HA, and ferrihydrite-HA composites, in which Co sorption to the composites cannot be modelled assuming linear additivity of Co sorption to the end-member ferrihydrite and HA phases. As such Co sorption to ferrihydrite-organic composites is non-additive, and deviation from additivity increases with increasing organic mass fraction.

[1] Moon & Peacock (2012), *Geochimica et Cosmochimica Acta*. 92, 203-219. [2] Moon & Peacock (2013), *Geochimica et Cosmochimica Acta*. 104, 148-164.