Occurrence of inner-sphere P-O-Fe bonds on natural iron oxides

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The association of organic molecules with mineral surfaces is a major mechanism to stabilize soil organic matter against biodegradation. For the attachment of microorganisms and extracellular polymeric substances (EPS) on Fe oxides, strong inner-sphere iron-phosphate complexes are suggested to play a crucial role, but have not yet been detected in soil.

We used phosphorus spectromicroscopy at the K-edge to prove existence and relevance of P-O-Fe bonds on adsorbed organic substances on synthetic Fe oxides as well as on natural Fe oxides from a Gleysol Bg horizon. NEXAFS-spectra on bulk samples were collected at 11ID-1 of the Canadian Lightsource, while spatially resolved spectra and X-ray fluorescence (XRF) maps were recorded at I08-SXM of Diamond Light Source at a spatial resolution of 0.25 µm. A pre-edge peak at ~2150 eV, assigned to P1s→Fe(2p)-O(2p) transitions (Khare et al., 2007), was taken as evidence for Fe-O-P bonds. A whiteline rise following a Pseudovoigt curve (0.3 Lorentz contribution) was interpreted as the absence of such bonds.

All bulk NEXAFS spectra of adsorbed model substances (inosine monophosphate, phytic acid, extracellular polymeric substances, water extractable soil organic matter) on goethite and/or ferrihydrite showed small pre-edge peaks. XRF maps on the Gleysol Bg horizon showed that P is exclusively associated with Fe oxides, while clay minerals are free of P. Because P and C were strongly correlated, we assume that the Fe oxide-bound P is rather organic P than inorganic free phosphate. In the gleysol, only µNEXAFS measurements on Fe oxides with high P-signals resulted in spectra with acceptable signal/noise ratios. In four out of 10 µNEXAFS spectra we clearly detected pre-edge peaks.

We conclude that for the synthetic adsorption samples as well as for the gleysol, inner-sphere iron-phosphate complexes represent a common adsorption mechanism to bind organic matter on Fe oxides.