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Association of organic matter and ferrihydrite: adsorption versus coprecipitation

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Ferrihydrite (Fh) - even if present at low concentrations - may control the available surface area and therefore, the behaviour of nutrients and pollutants in soils. Its precipitation often takes place in the presence of dissolved organic matter (OM). This involves processes such as adsorption, but also coprecipitation, flocculation/coagulation and poisoning of crystal growth. In this study, we compare coprecipitation of organic matter and ferrihydrite with pure adsorption of OM on ferrihydrite. We therefore prepared an adsorption series and a coprecipitation series using (i) water extractable organic matter from a forest topsoil and (ii) sulfite extractable lignin from paper. Products were investigated by N₂-adsorption, XRD and FTIR.

In coprecipitation experiments with both types of OM we observed a strong interference of the organic molecules with crystal growth leading to smaller Fh crystals, increased lattice spacings and a lower crystallinity. The highest achieved C loadings were found at approximately 200 mg C per g Fh for the adsorption and coprecipitation of the soil extract as well as for the adsorption of lignin. Coprecipitation of lignin, in contrast, resulted in a much higher maximum loading of 360 mg C per g Fh. The FTIR spectrum of the unreacted soil extract is mainly characterized by carboxyl C and polysaccharide C, with a smaller contribution of phenolic C. Spectra of the adsorbed or coprecipitated soil extract reveal weaker bands and lowered wave numbers indicating removal from solution followed by the formation of chemical bonds between the organic species and Fh by inner-sphere surface complexes. The FTIR spectrum of the lignin material shows a strong contribution of carboxyl C, polysaccharide C, and several aromatic C species. Again, all of these C species seem to form surface complexes after reaction with Fh in adsorption and coprecipitation experiments. Interestingly, at low initial C concentrations in all experiments the sorption of carboxyl C is strongly favoured compared to the sorption of aromatic compounds and polysaccharides. In conclusion, in the case of the soil extract, the significantly altered crystallinity of the coprecipitates affected neither the loading capacity of Fh for OM nor the composition of the associated OM. When using lignin, we observed an almost doubled maximum loading of organic C. Here, we assume that roughly half of the associated OM is not adsorbed but encapsulated due to the coprecipitation processes.