Fractionation and competitive adsorption of DOM components at the water-goethite interface

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Mineral-organic associations (MOAs) play an important role in the long term stabilization of soil C. MOAs form via interactions between dissolved organic matter (DOM) and reactive soil mineral phases [1]. The adsorption capacity of these mineral surfaces is not infinite [2], and as a consequence competitive adsorption among DOM components occur. Thus, DOM components with high surface affinity will displace more weakly adsorbed species, causing fractionation [3]. The dynamics and mechanisms behind these processes are largely unkown.

In this study, we applied in-situ infrared spectroscopy to study the fractionation and displacement of DOM components on goethite as a function of reaction time. These processes were examined in a pH range between 4-9 using OM extracted from forest litter by hot or cold water, or by direct leaching of intact litter material in presence of mineral particles. The displacement of adsorbed OM was investigated by continously adding DOM. Spectral data sets were analyzed using multivariate curve resolution alternating least squares (MCR-ALS).

The time-dependent IR spectral changes revealed predominance of carboxlyate, phenolic and carbohydrate fractions that displayed different adsorption kinetics. Continous addition of DOM to goethite surfaces saturated with DOM components resulted in the displacement of weakly adsorbed OM by components of high surface affinity. The overall results elucidated that 1) adsorption and fractionation was pH-dependent and affected by the method used to extract the DOM; 2) different adsorption mechanisms of the major DOM components were distinguished by differences in adsorption kinetics; 3) phenolic rich components were preferentially retained on the goethite surfaces and the average protonation state of carboxyl groups also had an impact on the competitive ability among DOM components.

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