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Changes in Redox Properties of Dissolved Organic Matter Sorbed onto Fe(III)-Montmorillonite

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Dissolved Organic Matter (DOM) and Iron (Fe) minerals play major roles in biogeochemical redox processes in soils, sediments and aquifers. While the redox properties of DOM or Fe within clay minerals have been studied individually using mediated electrochemical analysis,[1,2] the effect of sorption to redox active clays on the redox properties of DOM has not been addressed yet. Despite of their inherent complexity, Fe-containing clays are suitable model surfaces to assess changes in DOM redox properties following sorption as they do not release redox active Fe-species into the aqueous phase. Here, we have studied whether changes in the Electron -Accepting (EAC) and -Donating Capacities (EDC) of DOM occur upon sorption to Fe-containing clays as a consequence of DOM fractionation and electron transfer with structural Fe in clays.

Sorption of Pahokee Peat Humic Acid (PPHA) to Na-rich montmorillonite (SWy-2, Fe content 2.3 % wt) was studied at pH 7 in batch experiments for several PPHA/SWy-2 ratios. EAC and EDC were quantified for PPHA stock solution, whole suspensions and filtered supernatants using mediated electrochemical analysis.

Our results show that the Electron Exchange Capacity (EEC = EDC + EAC) of PPHA in filtered supernatants was up to 50 % lower compared to PPHA stock solution, while its redox state was more oxidized after sorption (up to 70 % lower EDC). This can be explained by preferential sorption of molecules with more redox active functional groups in PPHA (e.g. quinones). Suspensions containing PPHA + Fe-clay showed up to 80 % lower EEC (normalized to total batch mass) compared to PPHA stock solution.

These findings demonstrate that both the redox state and the electron exchange capacity of DOM are greatly altered following sorption to redox active clay minerals and, they might help to understand the underlying electrochemical processes contributing to mineral stabilization in the environment.

Literature

[1] Gorski et al. (2012) Environ. Sci. Technol., **46**, 9360-9368. [2] Aeschbacher et al. (2010) Environ. Sci. Technol., **44**, 1, 87-93.