

## **Fractionation of humic acids upon sorption to redox inert sorbents and its effect on redox state**

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Interactions among Natural Organic Matter (NOM) and minerals trigger changes in its properties and reactivity. Since NOM is an extremely heterogeneous mixture of countless organic compounds with different properties, the type and extent of interactions between individual components of NOM and mineral surfaces are complex as well. Given that fractionation and conformational changes of Humic Acid (HA) upon sorption to minerals are likely to happen, the chemical composition and redox properties of the HA fractions upon sorption might differ as well. Sorption isotherms of three IHSS HA standards to aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and a hydrophobic resin (DAX-8) were studied at pH 7. The electron donating and accepting capacities (EDC and EAC, respectively) were measured for both the suspension and the filtered (non-sorbed) HA following mediated electrochemical analysis. Additionally, High-field FTICR mass spectra were acquired to non-sorbed HA samples after solid phase extraction with methanol using PPL cartridges. Our major findings are that the redox properties of humic acids changed both with the extent of sorption as well as with the sorption mechanism (polar-Al<sub>2</sub>O<sub>3</sub> vs. non-polar-DAX-8). We propose that the changes in electron exchange capacity of sorbed HA to redox inert sorbents might be associated to conformational re-arrangements of the humic moieties. Conversely, FTICR mass spectrometry analysis showed clear evidence of fractionation in filtered HA although the EDC and EAC of HA stock and filtered were comparable. Our results suggest that sorption phenomena considerably affect the chemical and redox properties of humic acids. Since a large fraction of NOM in soil and groundwater is present in sorbed state, these findings are crucial for an improved understanding of electron transfer processes involving NOM.