



Changes in redox properties of Humic Acid (HA) upon sorption to alumina

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The interaction between humic substances and soil minerals may change important properties and reactivity of the organic matter. In particular, we are interested whether changes in the redox properties of a HA (namely total electron exchange capacity and redox state) occur upon sorption to redox inactive minerals.

Sorption of Pahokee Peat humic acid to Al_2O_3 was studied at pH value of 7.0 in batch experiments, at several HA/oxide ratio. All experiments were conducted in anoxic environment. The required equilibration time was determined by taking aliquots of the suspension at several time intervals and registering the UV-vis spectra of the supernatant; apparent sorption equilibrium (no decrease in UV-vis signal) was achieved after 5 days approximately. Both the suspension (mineral+sorbed HA, plus supernatant) and the supernatant after centrifugation were analyzed using mediated electrochemical techniques, and the electron donating and accepting capacities (EDC and EAC, respectively) were determined. In addition, SUVA was calculated for each batch. These preliminary results show a slight increase in the SUVA of the supernatant upon sorption, which would indicate a preferential sorption of more aliphatic fractions. Interestingly, the total electron exchange capacities (EEC) of the supernatants showed no significant differences to that of the stock HA, whereas the EEC of the whole suspension showed values up to twice the one from the stock HA. The EDC/EAC (which can be interpreted as a measure of the redox state of the sample) also showed same values for stock and supernatants, being the values of the whole suspensions towards the reduced side. Therefore, such preliminary results would indicate not a change in the redox properties of the dissolved HA, but only for the sorbed one. The sorbed fraction seems to present higher redox activity (higher EEC) and a more reduced state than the stock HA. Given the absence of redox transfer between the HA and the oxide, it could be inferred that such change is a consequence of conformational changes in the humic: due to the sorption, a higher amount of redox active groups would be exposed and detected by the electrochemical techniques here used, and they would be enriched in hydroquinone content, rather than quinone one.