

Changes in redox properties of humic acids upon sorption to alumina

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1. Introduction

A prominent role of Natural Organic Matter (NOM) in biogeochemical processes is its ability to act as an electron shuttle, accelerating rates between a bulk electron donor and an acceptor. The underlying processes are reversible redox reactions of quinone moieties.¹ This shuttling effect has been studied in two major areas: transformation of redox active pollutants and microbial respiration.²⁻³ Previous studies primarily compared effects in the presence or absence of NOM without addressing the redox properties of NOM nor its speciation. The interaction between humic acids (HA) and minerals might change properties and reactivity of organic matter. Specifically, we investigate whether changes in the redox properties of a HA occur upon sorption to redox inactive minerals. Since fractionation and conformational rearrangements of NOM moieties upon sorption are likely to happen, the redox properties of the NOM fractions upon sorption might differ as well.

2. Materials and methods

Elliot Soil Humic Acid (ESHA), Pahokee Peat Humic Acid (PPHA) and Suwannee River Humic Acid (SRHA) were used as received from IHSS. Aluminum oxide (Al_2O_3) was suspended in 0.1M KCl. Sorption was studied at pH 7.0 in duplicate batch experiments for several HA/ Al_2O_3 ratios. For the suspension (mineral + sorbed HA, plus dissolved HA), the filtrate ($0.45\mu\text{m}$) and the HA stock solution, the electron donating and accepting capacities (EDC and EAC) were determined following established procedures.⁴

3. Results

All studied HA- Al_2O_3 systems showed similar behavior with regard to changes in redox properties. There was a significant increase in the EDC of the whole suspension compared to the stock solutions and the non-sorbed HA in the filtrate (up to 300% for PPHA). This effect was more pronounced with increasing amounts of sorbed HA in the suspension. Although ESHA had the highest sorption capacity on Al_2O_3 (~ 6 times higher than PPHA & SRHA), it showed the smallest changes in redox properties upon sorption. Considering the total electron exchange capacities, significant changes were found mainly at higher amounts of sorbed PPHA and SRHA.

4. Conclusions

Overall, our results suggest a change in the redox properties of sorbed HA but not for the dissolved fraction. The sorbed fraction showed a higher redox capacity than the stock samples. Given the absence of redox transfer between the HA and the redox inert aluminum oxide, such changes might be due to conformational changes in the humic substances.

5. References

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