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Probing sorption selectivity of neutral organic compounds to Soil/Sediment Organic Matter through advanced Solid State NMR and nuclear paramagnetic relaxation probes

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One of the widely recognized functions of Soil/Sediment Organic Matter (SOM) is sorption of organic pollutants. SOM-pollutant interaction influences contaminant bioavailability and mobility, which in turn dictates fate and persistence of these contaminants in the environment. Thus, a better understanding of the nature of SOM as well as pollutant retention mechanism is essential in estimating or modeling soil and water systems contamination, pollutant risk assessment and remediation designs. A molecular level understanding of SOM-pollutant interaction is limited.

The main objective of this study is to probe at the molecular level, the question of whether or not there are preferred sites of sorption of organic compounds to SOM. A novel approach was employed, which involved the use of Solid State Nuclear Magnetic Resonance (NMR) techniques and nuclear paramagnetic relaxation probes as sorbates. It takes advantage of the spectral changes caused by the highly efficient relaxation afforded by these relaxation probes near the site of sorption. As a result, line-broadening and reduction of spin-lattice relaxation rate are expected.

Stable organic nitroxyl free radical relaxation probes of different polarities namely, HTEMPO (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine) and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) were used as models for organic compounds. A high organic soil Pahokee Peat and a high organic soft coal Beulah Zap lignite were used as sorbents. In addition, a polystyrene- polyvinylmethylether (PS/PVME) polymer blend was synthesized and used as an example of an intimate blend of aromatic and aliphatic microdomains. Sorption kinetics revealed that pseudo-equilibrium was reached within ∼4 days for all sorbate-sorbent combination. Sorption isotherms were then constructed with an equilibration time of at least 6 days, and with concentrations spanning at least two orders of magnitude. The isotherms were corrected with respect to relaxation probe recovery in order to account for the physisorbed molecules only. Freundlich sorption capacity (K_F) and nonlinearity values (N) for TEMPO were as follows: Pahokee Peat (K_F=1.91, N=0.68); Beulah Zap (K_F=2.62, N=0.54); PS/PVME blend (K_F=1.26, N=0.99). Sorption constants for HTEMPO were as follows: Pahokee Peat (K_F=1.20, N=0.75); Beulah Zap (K_F=1.89, N=0.68). After equilibration, samples were freeze dried and analyzed using ^{13}C Cross Polarization/Total Sideband Suppression (CP/TOSS) Solid State NMR and T2 filter. Peak suppression in terms of percent peak area or peak intensity reduction for TEMPO and HTEMPO in Pahokee Peat and Beulah Zap reveals little to no selectivity with the different SOM functional groups based on ^{13}C chemical shift. Electron paramagnetic resonance as well as partition coefficients of TEMPO and HTEMPO between water and different organic compunds (i.e., n-octanol, anisole, toluene, hexadecane, cellulose) was also determined in order to help explain this phenomenon.

In conclusion, there is little to no selectivity of probes to SOM on the basis of functional group chemistry. This contradicts previous findings on preferential sorption, which were based on functional group correlations with sorption coefficients, i.e., macroscopic data. Furthermore, there seems to be no preference for sorption to the small amount of black carbon present in these SOM samples represented by aromatic region centered at 128 ppm. Thus, the implication of these results is that site selectivity may be due to factors other than functional group composition. This work demonstrates for the first time the use of molecular probes to study sorption specifity.