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Analysis of organic matter at the soil-water interface by NMR spectroscopy: Implications for contaminant sorption processes

M. J. Simpson and A. J. Simpson
University of Toronto, Toronto, Ontario, Canada (email: myrna.simpson@utoronto.ca)

Contaminant sorption to soil organic matter (OM) is the main fate of nonionic, hydrophobic organic contaminants in terrestrial environments and a number of studies have suggested that both soil OM structure and physical conformation (as regulated by the clay mineral phase) govern contaminant sorption processes. A great deal of this evidence has come from macroscopic observations with contaminants and soil fractions as well as a recent mass balance approach where the sum of the parts exceeded the whole suggesting that the physical arrangement of OM in organo-mineral complexes may be more important than OM structure in sorption processes (1). In addition, recent studies with constructed organo-mineral complexes have suggested that aliphatic OM is preferred over aromatic moieties and suggests that clay minerals play an indirect role by governing the sorption of organic contaminants by controlling the surface accessibility of OM at the soil-water interface (2,3). To investigate this further, a number of soil samples were characterized by both solid-state 13C Cross Polarization Magic Angle Spinning (CPMAS) NMR and 1H High Resolution Magic Angle Spinning (HR-MAS) NMR. HR-MAS NMR is an innovative NMR method that allows one to examine samples that are semi-solid using liquid state NMR methods (ie: observe 1H which is more sensitive than 13C). With HR-MAS NMR, only those structures that are in contact with the solvent are NMR visible thus one can probe different components within a mixture using different solvents. The 1H HR-MAS NMR spectrum of a grassland soil swollen in water (D2O) is dominated by signals from alkyl and O-alkyl structures but signals from aromatic protons are negligible (the peak at 8̃.2ppm is attributed to formic acid). When the soil is swollen in DMSO-d6, a solvent which is more penetrating and capable of breaking hydrogen bonds, aromatic signals are visible suggesting that the aromatic structures are buried within the soil matrix and do not exist at the soil-water interface. The 13C solid-state NMR data confirms that aromatic carbon is present in substantial amounts (estimated at 4̃0% of the total 13C signal) therefore, the lack of 1H aromatic signals in the HR-MAS NMR spectrum indicates that aromatic structures are buried and that the soil-water interface is dominated by aliphatic chains, carbohydrates, and peptides. The NMR data indicates that the mineral component of soils governs the physical conformation of OM at the soil-water interface. Consequently, one must consider that one-dimensional NMR methods provide an excellent overview of all the structures that are present but they do not provide direct information regarding which structures are available or accessible at the soil-water interface for contaminant interactions.

References: (1) Bonin J.L. and Simpson M.J. 2007 Environmental Science & Technology 41:153-159. (2) Feng X., Simpson A.J., and Simpson M.J. 2006. Environmental Science & Technology 40:3260- 3266. (3) Simpson A.J. et al. 2006. Langmuir 22:4498-4503.