

**CHARACTERIZATION OF ORGANIC MATTER AT THE SOIL-WATER  
INTERFACE BY HIGH RESOLUTION MAGIC ANGLE SPINNING (HR-MAS)  
NMR: IMPLICATIONS FOR CONTAMINANT SORPTION PROCESSES**

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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 (Bonin and Simpson, 2007). In addition, our 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 (Feng et al., 2006; Simpson et al., 2006). To investigate this hypothesis further, a number of soil samples were characterized by both solid-state  $^{13}\text{C}$  Cross Polarization Magic Angle Spinning (CPMAS) NMR and  $^1\text{H}$  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  $^1\text{H}$  which is more sensitive than  $^{13}\text{C}$ ). 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.

Figure 1 shows the solid-state  $^{13}\text{C}$  NMR spectrum and the  $^1\text{H}$  HR-MAS spectra of a grassland soil. The  $^1\text{H}$  HR-MAS NMR spectrum of the soil swollen in water ( $\text{D}_2\text{O}$ ) is dominated by signals from alkyl and O-alkyl structures but signals from aromatic protons are negligible (the peak at  $\sim 8.2\text{ppm}$  is attributed to formic acid). When the soil is swollen in  $\text{DMSO-d}_6$ , 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  $^{13}\text{C}$  solid-state NMR data confirms that aromatic carbon is present in substantial amounts (estimated at  $\sim 40\%$  of the total  $^{13}\text{C}$  signal) therefore, the lack of  $^1\text{H}$  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. Analysis of two other soil samples and one humin sample shows a similar trend. The NMR data indicates that the mineral component of soils governs the physical conformation of OM at the soil-water interface. Consequently, when assessing carbon chemistry for explanations of sorption processes, 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.

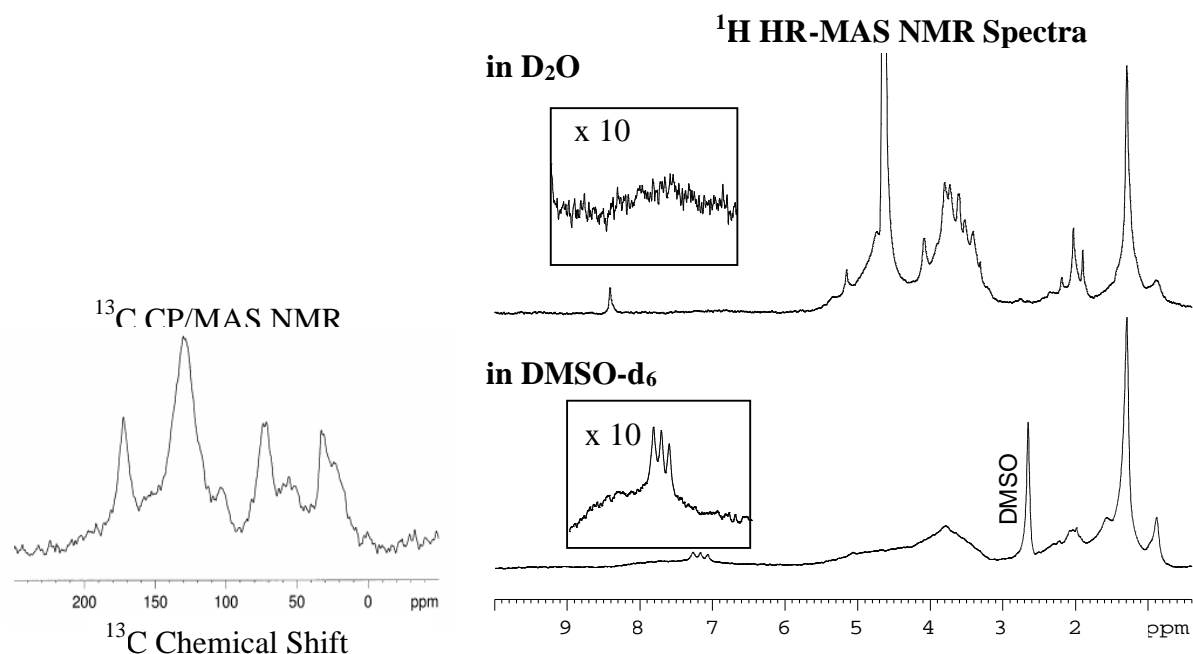


Figure 1. Solid-state  $^{13}\text{C}$  CPMAS NMR spectrum (acquired at a  $^1\text{H}$  frequency of 300MHz) of a HF treated grassland soil (Black Chernozem) and  $^1\text{H}$  HR-MAS NMR spectra (acquired at a  $^1\text{H}$  frequency of 500MHz) of the same soil (untreated) swollen in two different solvents ( $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$ ). Aromatic regions are expanded in the HR-MAS spectra.

## REFERENCES

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