

Sorption to Aliphatic Plant Biopolymers

The mobility, chemistry and bioavailability of pollutants in natural waters, soils and sedimentary systems are influenced by their interactions with dissolved and solid-phase organic matter and organic matter associated with mineral particles. Our ability to predict pollutant behavior is limited mainly by the lack of established techniques capable of probing the relevant molecular interactions of the pollutants with natural organic matter (NOM). Sorption of pollutants to soils is believed to occur by a combination of a partitioning process (absorption) and a hole-filling mechanism that is site-specific (adsorption). Partitioning is more common in the amorphous or 'rubbery' phases of NOM, whereas adsorption is believed to be significant in the condensed or 'glassy' phases. As the contact time between the pollutant and the soil increases, the pollutant becomes increasingly more difficult to extract with organic solvents, and its bioavailability also goes down, which is commonly described as 'pollutant aging'. The most common mechanisms proposed to describe the 'aging' process in soil are diffusion to reactive sorption sites in micropores (<20 Å in size) that interact strongly with the pollutant or physical entrapment into porous components of the soil organic matter. Due to the high degree of chemical heterogeneity in humic matter, limited information is available on the specific chemical functionalities involved in pollutant aging.

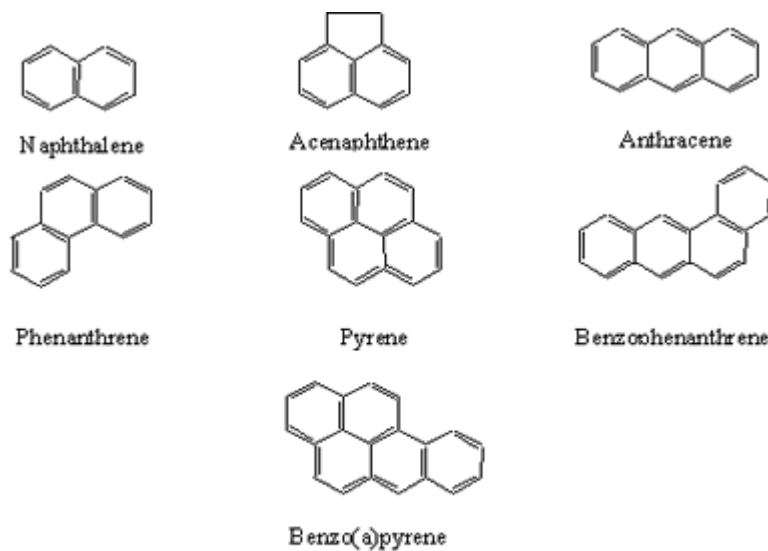


Figure 1. Polycyclic aromatic hydrocarbons (PAHs)

Many investigators have reported strong correlations between organic carbon normalized sorption coefficients (K_{oc} values) and the amount of aromaticity in the sample and some suggest that aromaticity can be used as a parameter to predict pollutant K_{oc} values. In our laboratories, we found that there is a poor correlation between aromaticity and pyrene K_{oc} for substrates with varying aromaticity and aliphaticity. However there is a good correlation between aliphaticity and K_{oc} values, which demonstrates that aliphatic moieties play an important role in pollutant sorption and undermine the current paradigm of aromaticity regulating the sorption processes.

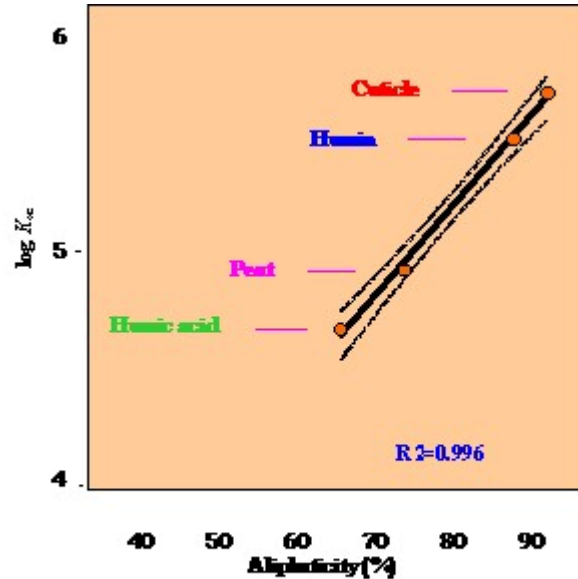


Figure 2. Correlation between aliphaticity and $\log K_{oc}$

Hypothesis: Aliphatic functionalities in macromolecular organic matter in soils and sediments, play a significant role in pollutant sorption and eventual transformations.

Objectives: Biologically and chemically resistant aliphatic biopolymers such as those found in plant materials and other organisms, contribute significantly to soil and sedimentary organic matter. The observation that aliphatic components of NOM can contribute significantly to pollutant sorption, coupled with the recent recognition that NOM in soils and sediments is predominantly aliphatic rather than aromatic and is derived from aliphatic plant biopolymers, points to the fact that pollutant sorption to NOM could be largely controlled by aliphatic structures.

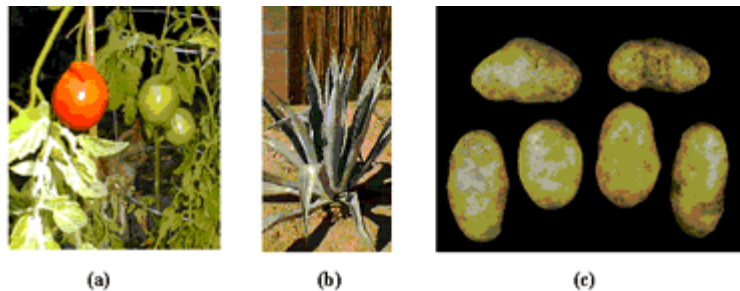


Figure 3. (a) Tomato fruit cuticle (cutin); (b) *Agave americana* leaf cuticle (cutan); (c) Potato skins (suberin)

The objective will be to characterize and identify the nature of sorption of PAHs to diagenetically resistant aliphatic biopolymers derived from plants, which could serve as proxies for aliphatic soil organic matter.

Research Plan: Plant biopolymers such as cutin, cutan, suberin, and lignin, as well as organic matter fractions (humic acid and humin) and bulk organic matter samples will be characterized using advanced analytical techniques such as high resolution magic angle spinning (HR-MAS) NMR, ^{13}C cross-polarization magic angle spinning (CPMAS) NMR, pyrolysis GC-MS, and TMAH-thermochemolysis GC-MS, and other techniques available to us.

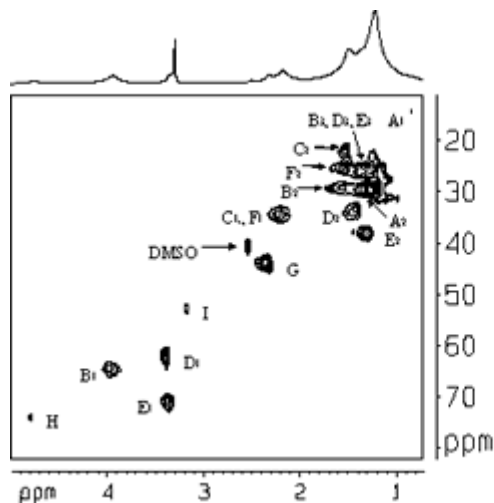
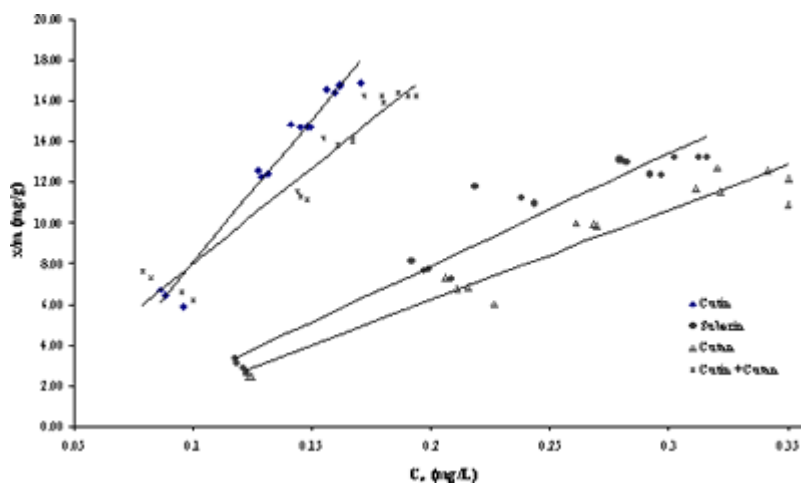
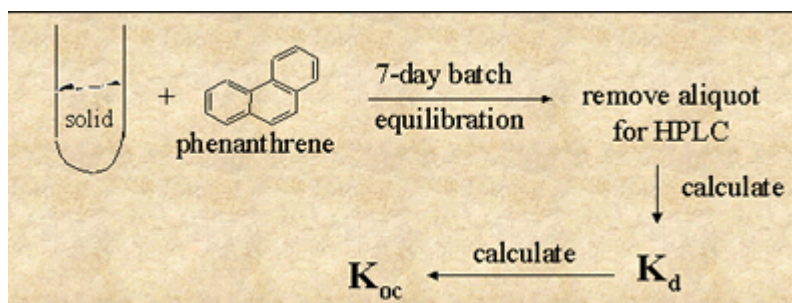


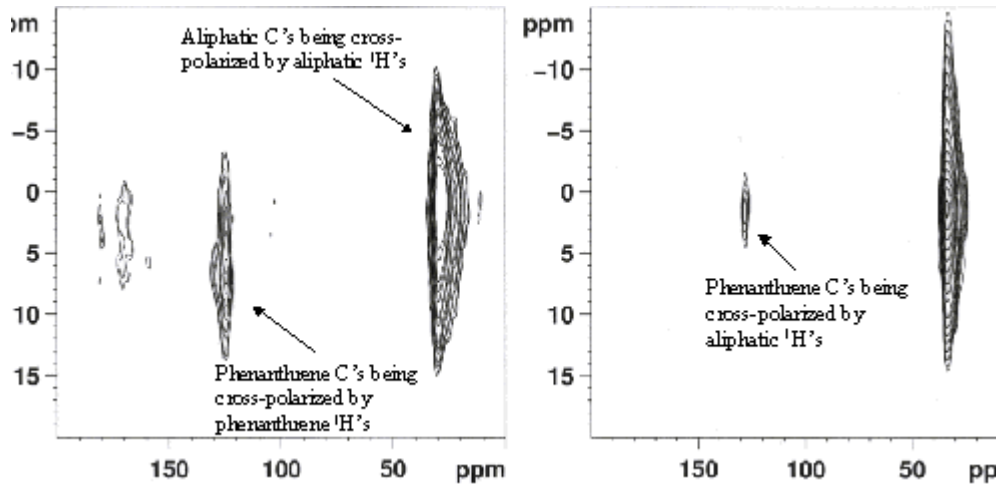
Figure 4. Tomato cutin ^1H - ^{13}C Heteronuclear Single Quantum Coherence (HSQC) NMR Spectroscopy

These organic matter samples will be used in batch equilibration studies with phenanthrene and pyrene, and K_{oc} values will be determined and correlated to the structural makeup of aromatic and aliphatic constituents within the organic matter matrix.



^{13}C - or labeled polycyclic aromatic hydrocarbon (PAH) pollutants will be used for studying the properties of the sorbed PAHs. Spin-lattice relaxation time (T_1) measurements and chemical shift anisotropy studies will allow us to probe the type of environment the PAH molecules are in. Two-dimensional heteronuclear correlation

experiments can shed light on the type of carbon functionalities in the biopolymers that the PAH molecules are getting associated with.



Experiments using ¹²⁹Xe NMR spectroscopy will help us in studying microporosity in the NOM. Artificially aged NOM samples will be prepared and comparisons will be made with freshly sorbed samples.