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Understanding the mechanisms of organic-mineral and organic-colloid interactions will help determine under which conditions organic contaminants will be bioavailable or sequestered. This project combines spectroscopic (*i.e.*, ATR-FTIR = Attenuated Total Reflectance Fourier-Transform Infrared) and microscopic (*i.e.*, HRTEM = High-Resolution Transmission Electron Microscopy) studies with molecular modeling, in order to help elucidate the mechanisms of organic-mineral interaction and binding. The overall goal of this research is to predict biological environmental effects from chemical knowledge of contaminated sites. Interactions of several key chemical parameters can either enhance or decrease the environmental impact of a given contaminant concentrations. Thus, this research leads to better risk assessment capability and savings in sediment management costs.

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Contract Information

Contract Number	N00014-97-WX-20416
Title of Research	Molecular Modeling of Natural Organic Matter Interactions with Cations, Mineral Surfaces and PAHs
Principal Investigator	James D. Kubicki
Organization	Dept. of Geosciences - The Pennsylvania State University

Technical Section

Technical Objectives

This section will describe the objectives of the contract

Understanding the mechanisms of organic-mineral and organic-colloid interactions will help determine under which conditions organic contaminants will be bioavailable or sequestered. This project combines spectroscopic (*i.e.*, ATR-FTIR = Attenuated Total Reflectance Fourier-Transform Infrared) and microscopic (*i.e.*, HRTEM = High-Resolution Transmission Electron Microscopy) studies with molecular modeling, in order to help elucidate the mechanisms of organic-mineral interaction and binding. The overall goal of this research is to predict biological environmental effects from chemical knowledge of contaminated sites. Interactions of several key chemical parameters can either enhance or decrease the environmental impact of a given contaminant concentrations. Thus, this research leads to better risk assessment capability and savings in sediment management costs.

Specifically, this research is attempting to understand the long-range structure of the important components of natural organic matter: soot, fulvic acids, humic acids and lignin. The interactions of organic contaminants with these components controls to a large degree their fate and bioavailability. In addition, fulvic and humic acids can strongly bond to aqueous cations (e.g., metals) and mineral surfaces. This bonding affects their long-range structure and their interactions with organic contaminants.

Technical Approach

This section will describe the Technical Approach taken by the contractor.

The approach taken in this project is to examine simple systems that represent important components of more complex sediment-water systems. Probable bonding mechanisms are generated from previous studies in the literature. The mechanisms deemed most important for controlling environmental fates of contaminants are then studied experimentally with analogous systems of simple compounds. The spectroscopic data of these experiments are then interpreted with molecular orbital model calculations on several possible bonding mechanisms. The results of these simplified systems are then used to help understand results on more complex experiments involving numerous natural components. Larger-scale molecular simulations of the complex systems can also be performed.

The combination of experimentation, spectroscopic analysis and molecular simulations allows one to take advantage of the strengths of each technique. For example, infrared spectra provide clues as to bonding mechanisms between natural organic matter and metals or mineral surfaces. Interpretation of these spectra is not unambiguous, however. Molecular simulations allows for more detailed and reliable interpretation of spectra. In turn, molecular simulations on their own are subject to modeling unrealistic systems. Using experimentation and spectroscopy as benchmarks for the model systems provides "ground truth" to the computational research.

Progress

This section will describe the accomplishments for Fiscal Year 2000 for the contract

Research for the Fiscal Year 2000 has focused on three main thrusts. First, field studies and experiments (Gustafsson and Gschwend, 1997) have revealed that a relatively small component of natural organic matter can control the behavior of PAHs in the environment. This component is known as "soot" or "black carbon." Field and experimental studies of soot are hampered by the fact that most soils and sediments contain only a small concentration of soot and that soot occurs as very fine-grained particles (< 1 micron). Molecular simulations have been able to take 2-D structural models of soot and produce 3-D models of long-range soot structure (Kubicki, 2000a). These models also explain the strong adsorption and sequestration of PAHs associated with soot on a molecular level (Kubicki, 2000b).

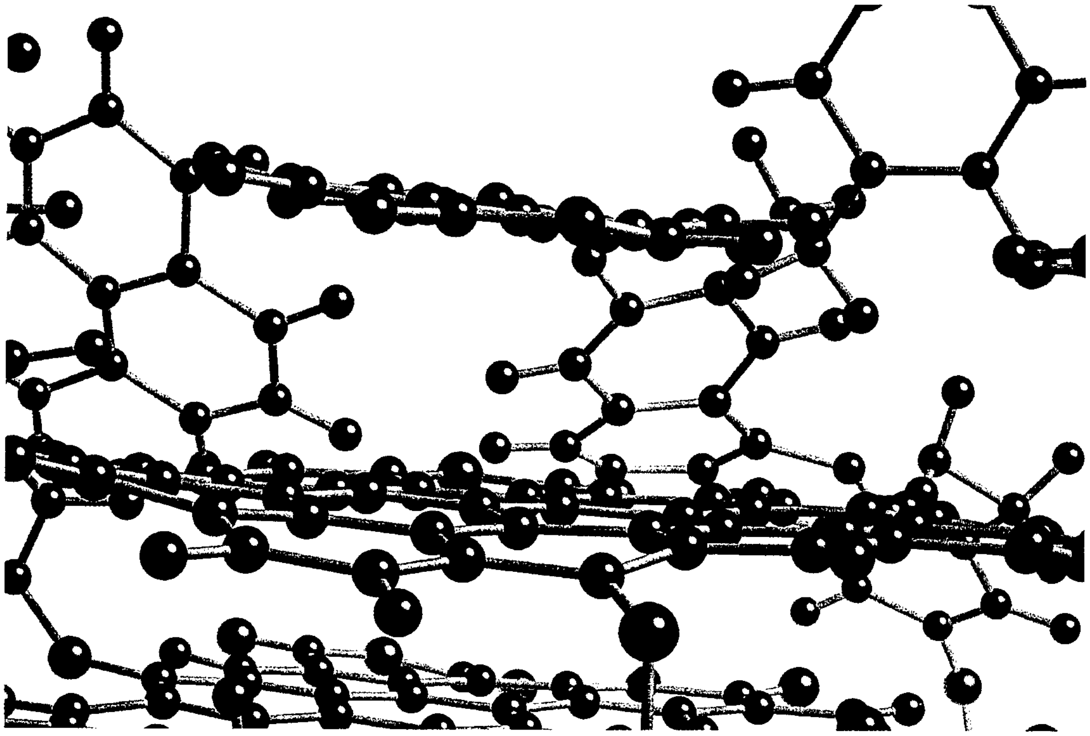

Figure 1 - Top molecule is a PAH (pyrene) that is strongly adsorbed to the surface of a soot molecule (lower layers). The pyrene-soot interaction is the same as that between layers of soot explaining the strong partitioning of PAHs from water onto soot. Simulations of PAH molecules within micropores of the soot structure demonstrate that diffusion out of a soot particle is very slow in agreement with studies that conclude sequestration and reduced bioavailability of PAHs associated with soot or similar types of natural organic matter.

The second research thrust has been to develop accurate and realistic models for mineral-water interfaces. The approach has been to use highly accurate quantum mechanical calculations on clusters and mineral surfaces to derive force field parameters that describe bonding on a hydrated surface (Kubicki et al., 2000). These force fields can then be used to model larger scale systems than can be handled with the computationally demanding quantum mechanical calculations. The structure of the mineral surface and water near mineral surfaces are critical in determining the behavior of PAHs, especially when natural organic matter contents in a sediment are low. Furthermore, an accurate picture of the mineral-water interface must be developed before effective modeling of natural organic matter binding to a mineral surface can be simulated.

Third, simulations of fulvic and humic acids in aqueous solutions have begun. The components of natural organic matter dissolve in water and can lead to enhanced solubility and transport of otherwise sparingly soluble organic contaminants. The long-range structure or conformations of fulvic and humic acids is thought to influence how much contaminant can be solubilized and the stability of the sorption. However, little is known about the conformational behavior of fulvic and humic acids in solution. Research in this group has tested the techniques necessary to realistically model dissolved organic matter as a function of solvation, pH and interaction with aqueous cations. All of these have been found to influence the long-range structure of the model fulvic and humic acids significantly and must be accounted for during simulations of interactions with organic contaminants.

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