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PROGRESS DURING FIRST EIGHTEEN MONTHS

The research project has been ongoing from July 1, 1989 through the present. The upcoming Fall semester is considered as part of the initial funding phase; two research assistants will be supported on remaining initial-phase funds.

Two publication have been forthcoming from the research (Amy, and Liu, 1990; Amy, Conklin, Liu, and Cawein, 1990). We also intend to present a poster at the seminar "Concepts in

Manipulation of Groundwater Colloids for Environmental Restoration" to be held in Mateo, North Carolina during October, 1990.

A general summary of our progress associated with batch and column experiments follows.

Batch Experiments. During the period of July 1, 1989 through the present, we have emphasized batch experiments to study the partitioning between one PAH, phenanthrene, and each of two sources of groundwater natural organic matter (NOM) in the presence and absence of a model mineral surface ($a-Al_2O_3$). The behavior of a soil-derived fulvic acid sorbed to the mineral surface has also been investigated. The NOM sources were used as "bulk" (unfractionated) and fractionated into different molecular weight (MW) fractions by ultrafiltration (UF), and into humic and non-humic fractions by XAD-8 resin adsorption.

Three techniques have been evaluated for differentiating between aqueous PAH and NOM-bound PAH: fluorescence quenching (FQ), reverse phase (Sep-Pak) separations, and dialysis bags. We have found that the FQ and Sep-Pak methods yield comparable results and have selected the FQ technique as the method of choice due to its analytical ease and reproducibility.

We have conducted batch experiments to study the three binary systems; PAH-NOM, PAH-$a-Al_2O_3$, and NOM-$a-Al_2O_3$; and the ternary system, PAH-NOM-$a-Al_2O_3$.

Groundwater sources have been found to vary in their ability to bind PAHs; binding was also found to vary with different samples of groundwater derived from a given source. Moreover, various fractions of NOM exhibited different binding properties; our results indicated stronger binding occurred between PAHs and higher MW NOM; the humic fraction of NOM exhibited stronger binding than the non-humic fraction.

Sorption of NOM onto a mineral surface, alumina, has been evaluated from the perspective of providing a model of soil organic matter. As anticipated, NOM sorption onto alumina varied as a function of source, with greater sorption at lower pH.

Preliminary batch results for the ternary system indicate that residual dissolved NOM (i.e., the fraction that does not sorb onto $a-Al_2O_3$) exhibits a very weak affinity for phenanthrene in relation to both aquatic and soil-derived NOM. This result is attributed to the higher MW/humic (i.e., stronger PAH-binding) NOM fractions sorbing to the mineral surface, leaving the lower MW/nonhumic NOM fractions in solution. When NOM-coated $a-Al_2O_3$ is introduced into a phenanthrene solution, minimal binding the PAH occurs: this decreased ability for the sorbed NOM to bind phenanthrene may be due to a configurational/steric change occurring when NOM sorbs to the surface of $a-Al_2O_3$. Our results suggest that aqueous-phase partition coefficients are not applicable for mineral-bound NOM, and that aquatic NOM sorbed to a mineral surface is not a good model for soil organic matter.

Column Experiments. We have recently completed column experiments and generated breakthrough curves for the ternary system consisting of (i) a mineral phase, silica (quartz), (ii) a colloid phase, NOM from each of two sources, and (iii) an aqueous phase. The PAH of interest has been phenanthrene. The two NOM sources evaluated are Orange County groundwater (OCGW) and Biscayne Aquifer groundwater (BAGW). Quartz (60 um) has been used as a mineral packing, with a specific gravity of 2.65 and a porosity of 0.35. Both PAH and NOM breakthrough curves have been developed.

Breakthrough curves have been generated for binary systems; NOM-mineral, PAH-mineral; and the ternary system comprised of pre-equilibrated [PAH + NOM] passed through the mineral phase. As expected, the breakthrough curve for either of the NOM sources resembles that of the conservative tracer; there is virtually no sorption of NOM onto the acidic mineral surface of the silica. In the absence of NOM, there is significant interaction between the PAH and the silica surface, with a concomitant retardation observed. However, this attenuation of PAH transport is diminished when NOM is present, thus suggesting NOM-facilitated transport.

We are modelling the above results to quantify retardation factors and partition coefficients. We are also commencing work involving a mineral phase of a more basic character, alumina, for which significant sorption of NOM will occur. In this system, dissolved NOM will facilitate transport of the PAH while mineral-bound NOM will retard transport; the relative abundance of these two NOM phases will control the overall transport of the PAH.

Contributions to Subprogram Goals. This research project, funded by the Subsurface Science Program, falls within the subprogram entitled "Geochemical Transport Processes/Colloids Subprogram". Our contribution to specific subprogram goals are summarized below:

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