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Relative Contributions of Soil Humic Acid and Humin to the Adsorption of Toluene onto an Aquifer Solid

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Previous investigators (Schwartzenbach and Westall 1981; Voice, et al. 1983; Karickhoff 1984; Uchrin and Mangels 1987) have demonstrated soil organic matter content as the major factor controlling organic substance adsorption in soil/water systems. Aiken, et al. (1985) described soil organic matter (humus, humic substances) "...as a general category of naturally occurring, biogenic, heterogeneous organic substances that can be generally characterized as being yellow to black in color, of high molecular weight, and refractory." Humic substances can be delineated into three fractions as determined by the solubility of each fraction in water. Fulvic acid is soluble in both alkaline and acidic conditions, whereas humic acid is soluble in alkaline solutions but forms a precipitate under acidic conditions. Humin is soluble in neither acidic nor basic conditions (Waksman 1936; Aiken, et al. 1985; Tate 1987). Humin exists as a high molecular weight polymer which is often associated with sesquioxides and silicates.

In ground water (saturated) systems, it is expected that the least soluble constituents will remain within the soil matrix wheras the most soluble will leach and be carried along with the water flow. In cases where organic pollutants are bound to the solids matrix, it is important to determine whether pollutants will move through an aquifer with the soluble constituents or spatially remain localized with an insoluble constituent (Chiou, et al. 1986). The fate of a pollutant is thus dependent on which organic fraction it is adsorbed since not all fractions are active in sorption (Garbarini and Lion 1986).

This study focused on assessing the roles that the humic acid and humin contribute to adsorption in a

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particular system. Batch experiments using toluene as the sorbate and a material from the Cohansey aquifer outcrop (N.J.) identified humic acid as the prime adsorption factor.

MATERIALS AND METHODS

The solids material used in this study was extracted from a Cohansey aquifer outcrop near Chatsworth, NJ. This material is classified under the soil order Spodosol (Donahue, et al. 1983) as a coarse acid sand typical of cranberry bogs and is named a "Lakewood Soil" (Tedrow 1978). Relevant properties are listed in Table 1. Organic matter content was determined by the Walkley and Black modification of the rapid dichromate oxidation technique (Nelson and Somers 1982) with organic carbon content defined as 58% of the organic matter content.

Table 1. Properties of Cohansey aquifer material.

Sand (%)	90.0
Silt (%)	8.0
Clay (%)	2.0
Organic Matter (%)	4.4
pH	3.8
Cationic Exchange Capacity (meq/l)	5.1
Texture	Sand

Analyses performed by the Soils Analysis Laboratory, Cook College, New Brunswick, NJ 08903

Toluene, a primary constituent of gasoline and paint products, is one of the most frequently detected ground water contaminants. Analyses for toluene were performed using direct aqueous injections into a Gow-Mac 750P gas chromatograph (GC) with a flame ionization detector. A 6 ft long, 0.64 cm OD, 2 mm ID glass column was packed with 80/100 Carbopack C/0.1% SP-1000 and 10% SP-1000 on Supelcoport 80/100 stationary phase obtained from Supelco Analytical, Inc. Fine glass wool treated with phosphoric acid provided support for the packing. Standard aqueous solutions of 100, 50 and 25 mg/L were formulated and analyzed at the set chromatographic parameters. Standards were regularly checked throughout each experimental run with coefficients of variation not exceeding 5%.

The fractionation of soil was performed similar to the procedures described by Black (1965) and Swift (1985). Extractions were performed in 100-ml teflon-lined screw cap glass bottles. The bottles were first filled with 25 g of the Cohansey solids, 50 ml distilled water and 10 drops of 6N NaOH. The bottles were then sealed, continuously agitated for a period of at least eight hours using a reciprocating wrist shaker, and the mixture then centrifuged (International Centrifuge, 500 rpm, 4275xG) for 15 minutes. The resultant supernatant, comprised of the humic and fulvic acid fractions, was then decanted and placed in another 100 ml bottle and the pH adjusted to less than 3 by the addition of 10 drops of concentrated HCl. An additional 50 ml distilled water and 10 drops 6N NaOH were added to the solids and the slurry agitated by the wrist shakers. After 24 hours, the mixture was again centrifuged, the supernatant decanted and placed with the previous supernatant and its pH readjusted to approximately 1 by the addition of excess concentrated HCl. Since fulvic acid is soluble in both acid and alkaline conditions and humic acid is soluble only under alkaline conditions (Black 1965; Stevenson 1982; Tate 1987), the humic acid settles. The mixture was allowed to settle for a period of at least 24 hours, whereupon the fulvic acid supernatant was decanted. The remaining humic acid fraction was lyophilized utilizing a New Brunswick Scientific Lyophilizer, Model B-66, at -125^{O}F, and the solids analyzed for a mass balance. The remaining sand/clay/humin fraction (insoluble at any pH) was air dried and each individual sample weighed to determine consistency among samples and for mass balance purposes.

Batch equilibrium studies were performed to determine the net sorption of toluene to the various organic components of the Cohansey solids. These experiments have been designed to minimize loss due to volatilization and takes advantage of the use of direct water injection GC analysis. A series of 60-ml crimp top glass vials were filled with varying masses of solid humic acid or sand/clay humin. Several vials were left empty for use as controls. The solids in the vials were then presaturated with 10 ml distilled water to eliminate any air within the solid matrix. The toluene/distilled water solution was then added to the vials using an automatic pipette dispenser thus ensuring fast and accurate transfer of solution to the vials. The control (solid free) vials were also filled in this manner. Each vial was immediately capped with an aluminum cap fitted with a teflon coated seal/septum. Blank vials (containing only solids and distilled water) were also used to check for any external contamination from glassware, instrumentation, or the solids. Immediately after capping, each vial was sampled and analyzed for toluene by piercing the teflon septum with a 10-ul syringe and extracting a 4 ul aliquot for direct GC analysis. For the batch kinetic studies, the vials were agitated periodically and samples withdrawn for analysis at specific times over a 72 hour period. Batch equilibrium studies involved only initial liquid phase concentrations and

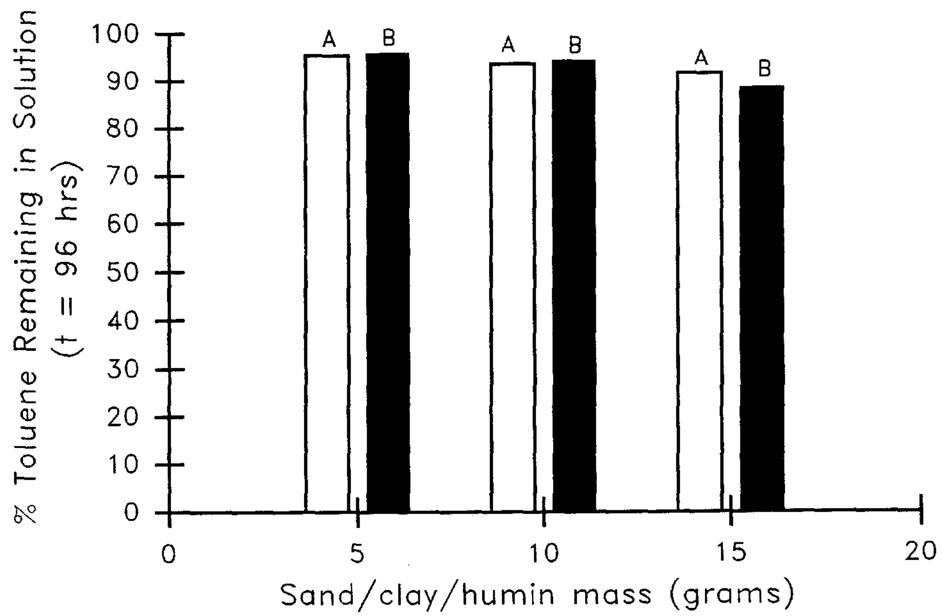

Figure 1. Batch equilibrium results indicating minimal sorption of toluene to humin.

concentrations after 72 hours.

RESULTS AND DISCUSSION

Thirty, 25-g, samples of the Cohansey solids were separated and the mass of each component determined and compared. The mean mass of the sand/clay/humin fraction of the soil was 23.47 g, with a standard deviation of 0.444 g and a coefficient of variation of 6.1%. Considering the heterogeneity of soil organic matter, these results are exceptionally consistent. The remaining 1.038 g required to complete the mass balance can be assumed to be comprised of the fulvic acid component or losses due to the transfer of the fine powders. It was, however, noted that a consistent (35 ml) volumn of supernatant was removed after the humic acid was allowed to settle. In addition, batch adsorption experiments to the liquid fulvic acid showed no discernable reduction of toluene concentration.

Batch adsorption experiments were performed on the air dried sand/clay/humin solids. Results for replicates A and B are displayed in Figure 1. Although toluene adsorption appears to increase with increasing soil mass, the quantity of toluene adsorbed by these solids is minimal (not significant at 95% confidence).

Batch kinetic experiments were performed on the humic acid fraction to determine how rapidly the toluene

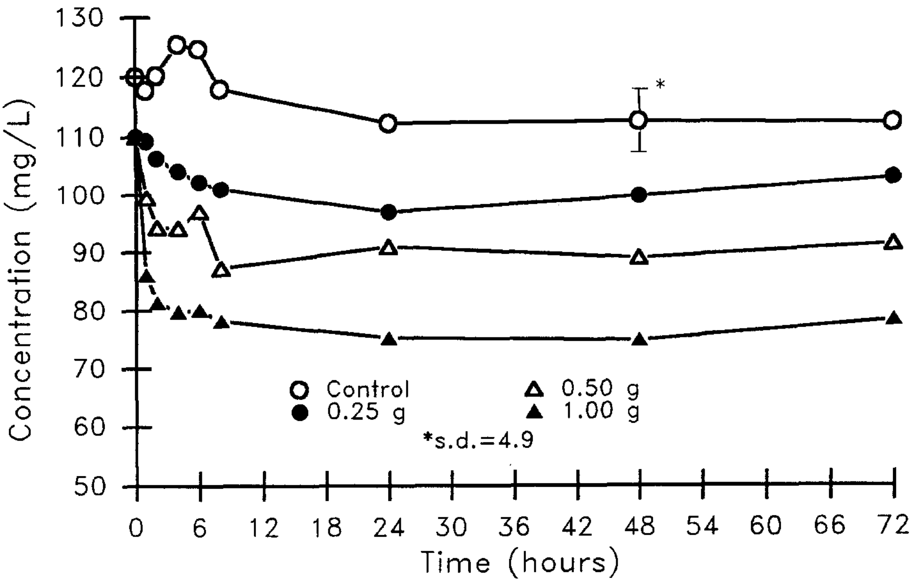

Figure 2. Batch kinetic study of toluene to humic acid.

associates with the solid matrix and the time to steady-state (assumed equilibrium). Figure 2 shows that toluene adsorbs rapidly to the humic solids, reaching a virtual steady-state within 24 hours. The difference in starting concentrations between the control and the three experimental sets reflects the effect of presaturating the solids with distilled water. Studies by Haas and Kaplan (1985) showed similar time to equilibrium results.

A series of batch equilibrium experiments were performed at different humic acid masses and different solute concentrations. The mass of toluene adsorbed per unit mass of humic acid was calculated and plotted as a linear function of the resultant liquid phase equilibrium concentration. The resultant linear isotherm displayed in Figure 3 has a distribution coefficient (slope) equal to 29.0 ml/g and a correlation coefficient (r^2) of 0.933. The solid point on this figure represents a sample where no adsorption was detectable. This sample contained 0.25 g humic acid and 100 mg/l toluene in solution. Because of the high concentration and low soil mass, any adsorption may have been masked due to an overwhelming (or quenching) of the system with toluene. This point was thus considered an outlier and not used in calculation of the distribution coefficient. Williams (1990) reported a distribution coefficient of 5.08 ml/g for toluene to the Cohansey solids.

It is important to note that adsorption results

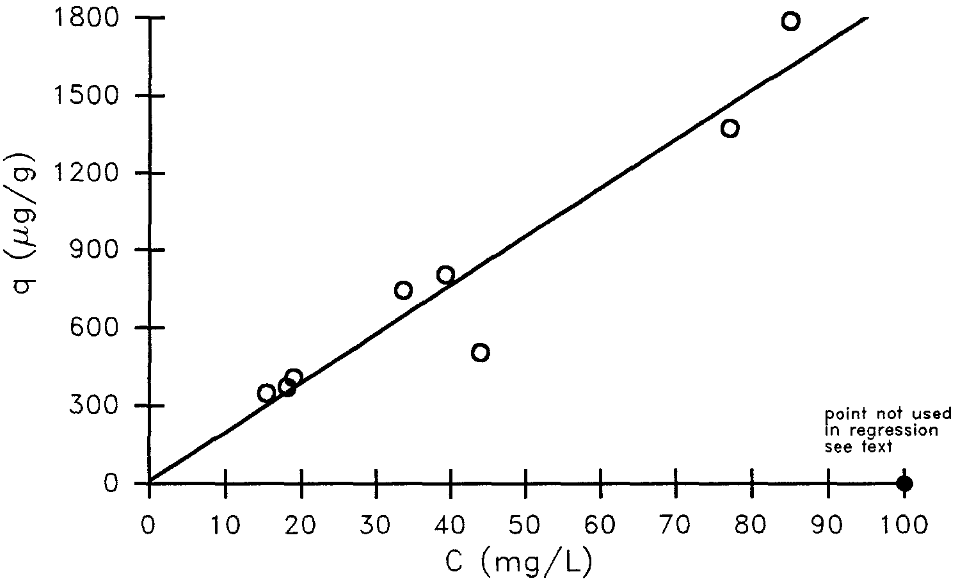

Figure 3. Linear isotherm for toluene to humic acid.

presented in the literature are obtained from mass reduction experiments, thus what is attributed to adsorption may result from other phenomena including photochemical oxidation and biodegradation. To minimize the potential of photochemical oxidation, all experiments were performed in the dark. The harshness of the extraction procedures employed including the raising and lowering of pH to extremely basic (10) to extremely acidic (1) would preclude significant biochemical activity.

The harshness of the extraction procedure raises another concern. Tan (1985) reported that the methods employed for preparation of humic substances for testing altered considerably the structure of the macromolecule. At high sample concentration, low pH, or at medium to high organic strength, humic acid was believed to behave as rigid spherocolloids but otherwise as a flexible linear colloid. Other investigators (Swift 1985; Stevenson 1985) also stated that simply air drying the solids affected their structure and suggested less extreme extraction procedures using buffers and diluted extractants. These factors were considered in this work. However, due to the strong base neutralizing capacity of the Cohansey solids, milder extractants than those used were unable to completely remove the humic and fulvic acids from the solids matrix. Also, the use of buffers, such as potassium salts, would have affected the sorption processes. Sodium hydroxide was chosen as the initial extractant for its strong neutralizing ability and the small effect it has on sorption processes.

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