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Uptake of Methyl Tertiary Butyl Ether (MTBE) by Groundwater Solids

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Oxygenates, such as methyl tertiary butyl ether (MTBE) are added to gasoline to reduce carbon monoxide and hydrocarbon emissions through reductions in aromatic content, heat of vaporization, and boiling point (Piel and Thomas, 1990). MTBE is widely used because it blends easily in gasoline and can be transported through existing pipelines (Suflita and Mormile, 1993: Suflita and Mormile, 1994).

MTBE is a synthetic compound prepared from the addition reaction of methanol to isobutylene, which is a reversible, endothermic reaction (Izquierdo, et al. 1992). MTBE has a high water solubility, ranging from 23.2 to 54.4 g/L (Squillace, et al. 1996). It is soluble in water, alcohols, and ethers (Von Burg, 1992). Oxygenated gasoline can contain up to 15% MTBE (Barreto, et al. 1995: Palassis, et al. 1993).

Groundwater can be contaminated by MTBE resulting from an underground gasoline storage tank leak. MTBE readily dissolves in water and can rapidly travel beyond the site of gasoline contamination ethers (Von Burg, 1992). It is expected to have little or no adsorption to soil due to its high water solubility. MTBE is usually the first contaminant detected in groundwater following a gasoline spill (Barreto, et al. 1995: Mihelcic, 1990). The median concentration of MTBE which has been measured in shallow urban groundwater in the United States is 0.2 µg/L (Squillace, et al. 1996).

This paper presents research results focusing on the sorptive and degradative characteristics of MTBE in three soil/water systems.

MATERIALS AND METHODS

The soil materials used in this study were a Cohansey sand, an acid washed sand, and a Neshaminy clay. The Cohansey sand was extracted from the surface horizon of the Cohansey formation, located at the Rutgers University Cranberry Culture Experiment Station near Chatsworth, New Jersey. The soil was sieved through a 2 mm screen and air dried (Fischer, 1995). The acid washed sand (RediCrete All Purpose Sand, Flanders, New Jersey) was sieved through a 2 mm screen and treated with a 1.0 *N* Hydrochloric acid solution (Fischer, 1995). The Neshaminy clay was excavated from a location near Princeton, New Jersey. The consolidated material was crushed with a 30

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Table 1. Soil Properties

SOIL	COHANSEY	ACID WASHED SAND	NESHAMINY
% SAND	94	92	17
% SILT	2	5	46
% CLAY	4	3	37
% ORGANIC CARBON	1.44	Not Detectable	0.34
BULK DENSITY (g/mL)	1.60	1.68	1.22
POROSITY	33.4	34.1	50.5
AIR PERMEABILITY (cm^2)	$3.59x10^{-7}$	$6.02x10^{-7}$	$6.53x10^{-9}$
% MOISTURE (air)	0.24	0.12	1.9

pound roller and sieved through a 2 mm screen (Fischer, 1995). Soil properties are listed in Table 1.

MTBE analyses were performed using a Hewlett Packard 5890 Series II Gas Chromatograph (GC) equipped with an HP-1 fused silica capillary column and a flame ionization detector.

Batch studies were conducted under both oxic and anoxic conditions as described by Wojtenko, et al. (1996). A 15 gram mass of soil and a 30 mL of deionized, autoclaved, water were added to a series of 60 mL autoclaved vials. The liquid phase and the head space of each of the anoxic vials were purged with nitrogen gas. The vials were capped with teflon seals and aluminum crimp tops and spiked by syringe with 1 µL of MTBE. Control vials, which did not contain soil, were prepared using the same procedure. The vials were sampled by extracting 50 µL of head space by syringe at specific times over a 72 hour period. The samples were analyzed by injection into the GC. Samples were run in triplicate. Liquid phase concentrations were computed using Henry's Law.

Oxic and anoxic samples for each soil were analyzed for biological activity of MTBE. Four milliliters of nutrient broth were added to a series of test tubes and the test tubes were covered with aluminum foil. The test tubes and pipettes were autoclaved and approximately 1 mL from each sample vial was added to the test tubes. Each test tube was recovered with aluminum foil. The controls, which did not contain any sample, were used to determine if a sterile procedure was followed. The biological activity tests were conducted under aerobic conditions.

The Cohansey sand was also examined for adsorption equilibrium by varying the initial concentration of MTBE in each sample. Fifteen grams of irradiated Cohansey soil and 30 mL of deionized water were added to a series of vials. The liquid phase and the head space of each sample were purged with nitrogen

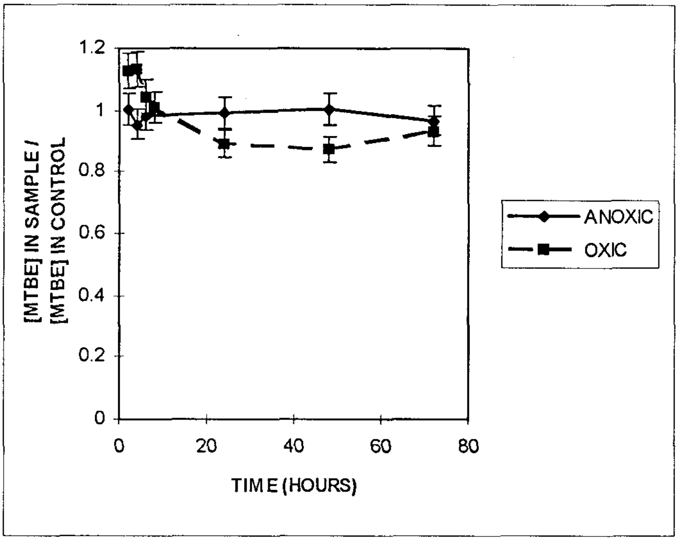

Figure 1. Uptake of MTBE by Acid Washed Sand

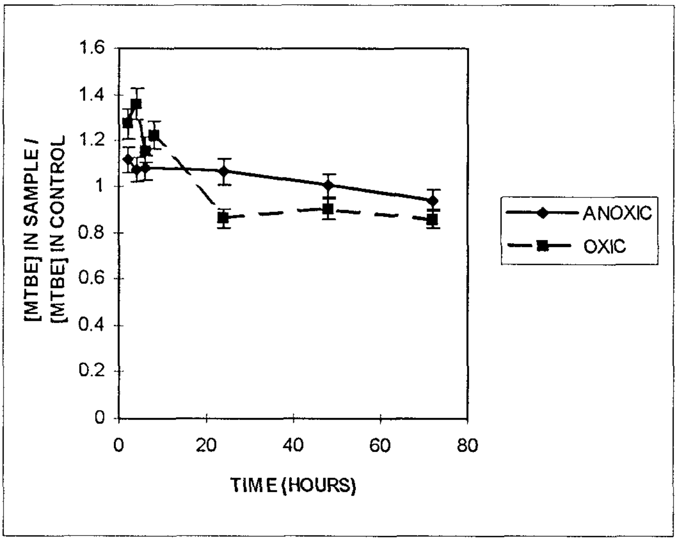

Figure 2. Uptake of MTBE by Neshaminy Clay

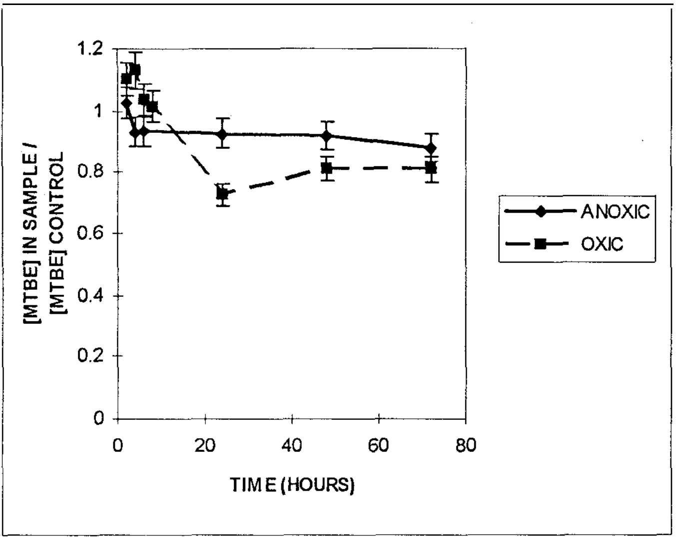

Figure 3. Uptake of MTBE by Cohansey Sand

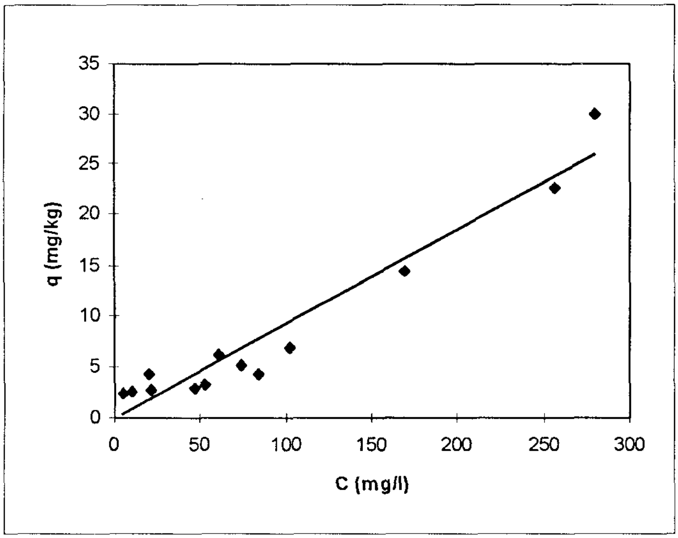

Figure 4. Linear Isotherm of Adsorption of MTBE to Cohansey Sand

gas and then the vials were capped with teflon seals and aluminum crimp tops. Controls, which did not contain any soil were filled using the same procedure. The vials were spiked with different initial quantities of MTBE, ranging from nominal liquid phase concentrations of 6 mg/L to 500 mg/L. Vials were allowed to equilibrate for 72 hours and then sampled and analyzed as described before. Soil concentrations were computed by difference calculation.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 display the time variable uptake for the acid washed sand, Neshaminy Clay, and Cohansey soil/water systems, respectively. Relative concentration, obtained by dividing the liquid phase concentration of MTBE sample in the soil/water system to the control, was plotted as a function of the elapsed time of the experiment. It can be noted that under oxic conditions, all three systems exhibited uptake of the MTBE and the relative concentrations were less than unity. This was not expected for the acid washed sand as it should have acted as a non-adsorbing medium (Fischer and Uchrin, 1994).

Also displayed in Figures 1, 2, and 3 are the results from the anoxic, nitrogen purged systems. It can be noted that in both the acid washed sand and Neshaminy systems, the relative concentrations were near unity, suggesting that the uptake noted in the oxic systems might have been due to aerobic activity. The anoxic Cohansey system continued to exhibit uptake, but less than in the oxic experiments. This uptake is attributed to sorption as the Cohansey soil readily adsorbs to other gasoline components (Uchrin, et al., 1992).

Both anoxic and oxic samples for each of the soil systems were analyzed for biological activity. After 48 hours, the nutrient broth for each sample was cloudy, indicating biological activity. The controls remained clear, thus the test was conducted under sterile conditions. These results demonstrate that the uptake observed in the oxic experiments can be attributed to aerobic biological activity.

Results from the equilibrium adsorption study for MTBE in the Cohansey system are displayed in Figure 4. The adsorbed (solid) phase concentration is plotted versus the liquid phase concentration. The resultant data can be fitted with a line through the origin, a so-called linear isotherm. Liquid phase concentrations greater than 300 mg/L were not considered, as these approached the liquid phase solubility limits of MTBE in water. The slope of the isotherm, often referred to as the solid/liquid phase partition coefficient, K_p, was computed to be 0.0925 and the r^2 as 0.936. In comparison to other gasoline components with the Cohansey soil, this value for K_p is very small, thus one would expect MTBE to appear first in a contamination scenario where the gasoline components would separate chromatographically (Uchrin, et al., 1992).

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