WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Laboratory Scale Model of the Fate and Transport of Methyl tert-Butyl Ether (MTBE) in Groundwater Systems

Graduate Student Name: Daniel Lefkowitz

Degree Sought: Ph.D.; Department of Environmental Sciences

Institutional Address: Environmental Sciences, 14 College Farm Rd. New Brunswick, NJ 08903-8551

Thesis Advisor: Dr. Christopher G. Uchrin

Address: Environmental Sciences, 14 College Farm Rd. New Brunswick, NJ 08903-8551

Amount Requested: $3,000.00

Priority Issue(s) Addressed by Research

The proposed research focuses on the development of a laboratory fate and transport model which will be critical for predicting concentration levels of the gasoline additive, Methyl tert-butyl ether (MTBE), in groundwater systems. Based on the data generated on fate and transport from an experimental laboratory model, it is possible to develop a mathematical model on the movement of MTBE to human receptors in a variety of soil types. Furthermore, the physical model developed here, and/or a subsequently developed mathematical model could be the focal point of risk assessments or exposure studies done on the MTBE. These risk/exposure studies cover both effects on human and environmental health. For example, a critical element in calculating the Lifetime Average Daily Exposure (LADE) to MTBE from drinking water, is the concentration. The model can provide estimations of that concentration downgradient of an MTBE source, such as a leaking underground storage tank. The advantage of the proposed model is that important parameters can be validated in the laboratory system which reduce uncertainty in the mathematical model.

In 1990, the Clean Air Act mandated the use of new reformulated gasolines containing increased oxygen levels in areas in the United States that fail to meet the carbon monoxide standards. Then in 1992, the Clean Air Act Amendments required oxygenates to be added in reformulated gasoline in nearly 40 carbon monoxide nonattainment areas (Kirchstetter et al. 1996). The primary gasoline oxygenate is MTBE, due mainly to its low cost, ease of production and favorable transfer and blending characteristics (Garret, Moreau and Lowery, 1996).

Despite its use in mitigating CO emissions, MTBE has some unexpected deleterious effects. MTBE is highly soluble in water, but unlike many compounds associated with gasoline spills or leaks, it is relatively recalcitrant. It can move very quickly via groundwater in the subsurface, and can travel further than plumes without MTBE. These plumes can and have reached drinking water supplies. In fact, because of these characteristics, MTBE use has been eliminated in Maine, will be eliminated in California by 2002, and remains an extremely controversial issue New Jersey.

The New Jersey DEP and DWQI have identified MTBE in drinking water wells in NJ. From 1989 to 1993, MTBE was found in 120 nonpublic wells, 50 public noncommunity wells and 60 public community wells (NJDWQI, 1994). Levels of up to 10 ppm were reported in private wells. In the period of 1982-1994, the maximum level reported for a drinking water well in NJ was 40 ppm, a level exceeding limit of the EPA Health Advisory (20-200 ug/L). According to the NJDWQI study, approximately 10% of nonpublic wells had detectable levels of MTBE, and 10% of these had concentrations exceeding 70 ppb. Also, about 60 of 630 public community water supplies reported detectable levels of MTBE.

Thus, MTBE is considered a problem in New Jersey, and more work needs to be done on its fate and transport, both to predict concentration levels critical to further study, and to model subsurface movement in order to select appropriate treatment/management strategies.

New Jersey institutions are at the forefront of current MTBE research on risk assessment, and investigating potential exposure levels. Lioy et al. (1994) examined human exposure to MTBE associated with automobile use and found low levels in the automobile microenvironment during a 1-hour commute. Mohr et al. (1994) determined the health effects of MTBE on garage workers in New Jersey. Their measurements indicated that at least some of the workers received significant exposure, even in the non-oxyfuel season.

Currently a project is underway at EOHSI investigating the human risk assessment of inhalation exposure to MTBE. Unfortunately, no studies are being done on the risk assessment of the ingestion of MTBE contaminated water. The model developed by this project could be critical in determining the levels of concentration that would be realistic for further study.

Objectives

The primary objective of this project is to develop a physical laboratory scale model to determine the fate and transport characteristics of the gasoline additive methyl tert-butyl ether (MTBE) in groundwater systems. Specifically, it is our intention to investigate the major transport and loss mechanisms of MTBE in the saturated, unsaturated, and capillary zones of various aquifer solids. We hypothesize that some of these mechanisms will include volatilization, advection/dispersion, and to a limited extent adsorption and biodegradation.

Research Methods and Experimental Design

In order to model the fate and transport of MTBE in groundwater systems three dimensionally, we will conduct a number of experiments. These experiments will each deal with particular elements of the model. Upon completion of these elements, we will attempt to piece them together to build the three dimensional model. To study all of the transport and loss mechanisms, the following experiments will be conducted: an extensive adsorption batch study on all of the different aquifer solids, an extraction study where a method is developed for the extraction of MTBE from soil, and flow through column studies that attempt to account for volatile loss, soil moisture effects, and biodegradation.

The first study to be done is a batch study. A batch study involves placing a known amount of soil, water, and MTBE into a sealable vial of known volume. The soil only partially fills the vial leaving free space above the soil, called the headspace. The headspace can be analyzed for MTBE (which volatilizes into the headspace from the liquid) by using a syringe to draw out gaseous sample and then injecting it into a Gas Chromatograph (HP 5890, with Flame Ionization Detector). Typically, only a gaseous sample is injected, and then the liquid/soil concentrations are back calculated using Henry's Law. However, we have developed a method using a Suppelcowax column in the Gas Chromatograph (GC) which allows us to inject both gaseous and liquid samples. The basic premise behind a batch study is to determine the soil concentration, that is, MTBE that has sorbed onto the solids. This is accomplished by using a simple mass balance: the difference between the MTBE in the headspace + liquid concentration and the initial liquid concentration, is the mass on the solids. Initial results and previous studies have shown that MTBE can a will adsorb to some high organic matter soils.

A number of different soil types will be used in this study, which were selected to give a representation of the general soil series found in New Jersey. The first soil used in most of the experiments is Cohansey sand. This is a well-studied sand with a relatively high organic matter content (1.44%). A description of more detailed characteristics can be found in Shaffer and Uchrin, 1997. Other soils will include: Neshaminy sand (also found in Shaffer and Uchrin), an undetermined shale soil, a farm soil, an acid washed sand, and glacial till taken from the overburden of a fractured rock aquifer in Sussex county.

The next experiment is to develop and conduct an extraction method that is relatively easy, inexpensive and quick. Once we have shown that MTBE can adsorb to solids, we must now show that the soil samples we take are free of the compound. To do this, we have developed an extraction procedure using octanol. octanol was chosen because after trying many other solvents it produced both the best separation and recovery. The other solvents tested were: methylene chloride, water, ether, hexane, and toluene. A relatively simple extraction procedure was developed: 20 mg of soil was placed in a 20ml vial, followed by 5ul of MTBE. Then 10ml of octanol is added, and the vial is capped. Then the vial is shaken using a Vortex, for 1 minute, and let to stand for 15 minutes. Finally, some supernatant liquid is siphoned off using a Pasteur pipette and put into a GC-vial and injected into the GC. Due to the relative ubiquity of MTBE in New Jersey, all soils used in this experiment will undergo or have undergone this extraction procedure to ensure no detectable MTBE can be found.

The final experiment proposed by this research is a flow through column study. This phase actually consists of several experiments. The first experiment is an attempt to model the vapor movement of MTBE through the soil atmosphere. Here, four glass columns are set up of 3 different heights: 4', 6', and 8' (two six foot columns are set up, one acting as a control). An example of one of these columns is pictured in Figure 1. MTBE is injected into the base of the column (through the bottom sealable port), and samples are taken over time using a syringe from the top of the column (through sealable port at the top) and immediately injected into the GC.

The column studies proposed by this research will also include an investigation of aqueous flow through various aquifer solids. In this case, the flow will be top to bottom, as the system is gravity fed. This study will be done under both aerobic and anaerobic conditions, and at differing soil moistures. Here we will attempt to show both adsorption and biodegradation to a limited extent in a flow-through system. An anaerobic condition is obtained by flushing the column with N_2 gas, which will purge the system of all oxygen. This method has been shown to be effective in minimizing aerobic decomposition of organics in soil/water systems in long-term experiments (Wojitenko et al. 1996). The soil moisture can be adjusted by adding varying amounts of water to the column, and measuring the moisture using a series of tensiometers.

Expected Results

With the data generated from these series of experiments, concluding information should be definitive about the fate and transport of MTBE in a groundwater system. As stated in the literature, MTBE is not known to be degraded anaerobically (Suflita and Mormille, 1993). Thus, we expect the primary loss mechanisms or transport of MTBE from the saturated zone to be either volatile loss, vertical dispersive/advective transport in either the liquid or aqueous phases (which will have reached a steady-state), aerobic biodegradation, and adsorption

Future Work

Using the laboratory scale model developed by this proposed research, it will be possible to construct a three dimensional, finite difference groundwater plume model. The mathematical model we are currently favoring for the study is Visual MODFLOW, which is a quasi-three dimensional finite difference model. The results from this, once validated, can be used to simulate the fate and transport of MTBE in groundwater from a point source to a human receptor.

Progress Since Last Year

Last year we received a funding award of $3,000 from the NJWRRI. This money was used to begin many of the experiments outlined in this proposal. Last year's focus was on constructing a laboratory physical model (a flow through tank with controllable head). Much work was done to discover that this was not necessarily the ideal way to represent the flow of MTBE. The tank had leaks, was difficult to maintain a mass balance, contained an unmanageable amount of soil, made controlling variables near impossible, and did not quite represent the column heights that are represented in the field. Therefore, we have decided to investigate the different processes one piece at a time, thereby allowing us to control for any variable.

Since last year, we have conducted much of the batch study, and have preliminary data on vapor diffusion through a column filled with Cohansey sand. We have also developed the octanol extraction procedure, which we hope to publish by the end of this year.

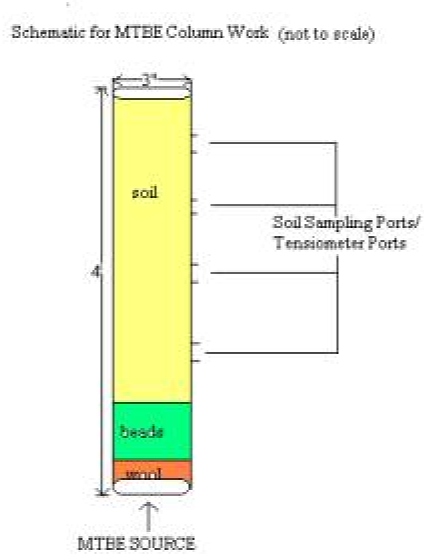

Figure 1. A Representation of a Soil Column Used to Investigate MTBE Fate and Transport.

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