TO: **Texas Hazardous Waste Research Center**

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SUBJECT: Annual Progress Report

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PROJECT TITLE: Biodiesel Fuels and Groundwater Quality

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Project Description

The impact of biodiesel fuels on groundwater contamination will be assessed. The use of alternative biofuels is growing and there are concerns about the impact of these fuels on the nation's drinking water supplies. A considerable amount of research has been conducted on the impacts of alcohols in gasoline (such as ethanol, which has replaced the important gasoline additive, methyl tertiary butyl ether, MTBE), however there has been limited assessment of the groundwater impacts associated with biodiesel fuels. Biodiesel fuels are widely used in Brazil and Europe, and use in the United States is increasing. Similar to alcohol gasoline fuels (e.g., gasohol) which can cosolubilize hydrocarbons, diesel fuels containing fatty acid methyl esters (FAME) may have a significant impact on the cosolubility of other fuel components of environmental concern (e.g., benzene, toluene, xylenes, and naphthalene) due to the production of long-chain fatty acids associated with abiotic hydrolysis and bio-transformation processes as well as free fatty acids present as impurities in the unweathered biodiesel fuel. In addition to cosolubility, another major concern is the redistribution of pre-existing fuel contamination due to lowering of fuel-water interfacial tension associated with the transformation products of FAME.

The following activities are expected: (1) measurement of phase equilibria properties for biodiesel fuels containing FAME (fatty acid methyl esters) including quantification of cosolubilization of BTEX and other hydrocarbons, (2) and spill experiments in 2-dimensional model aquifers, and (3) numerical modeling of the multiphase flow characteristics to both quantitatively analyze the experimental results as well as extend the results to a wide range of spill and aquifer conditions. This project is a two-year study.

Objectives

The ultimate goal of this research is to provide useful predictions of source concentrations of fatty acid methyl esters, fatty acids, BTX and other hydrocarbons and NAPL distribution resulting from spills of biodiesel fuels in order to predict near-source plume behavior. The purpose of this proposed research is to investigate the impact of biodiesel fuels over a range of FAME composition in biodiesel (20 to 100 vol.% FAME). In addition to physical chemical property measurements, experiments will be conducted in a continuous flow, unconfined aquifer, 2-dimensional physical model that simulates spills of these biodiesel fuels. Another important goal of this research is to quantitatively model the flow characteristics of these processes. The 2-D experiments will emphasize the behavior of both capillary zone and saturated zone processes for biofuels of different FAME composition.

More specific goals of this research are:

(i) Determine the impact of biodiesel containing FAME on groundwater quality for a range of fuel composition (20% to 100% FAME) and FAME type.

(ii) Determine source zone groundwater impacts and NAPL migration and distribution using 2-D model aquifer experiments that simulate spills of biodiesel fuels.

(iii) Analyze experimental data with a multiphase flow model that can then be used assess groundwater impacts of biodiesel for a wider range of scenarios (spill size, aquifer permeability, etc.).

Methodology

<u>Research Plan:</u> A three-step approach is being taken:

(Task 1) <u>Phase equilibria for fatty acid/water/biodiesel systems.</u>

(Task 2) <u>2-D Bench-scale model aquifer spill experiments</u> for direct measurement of pore water concentrations and for visualization of NAPL migration and redistribution near sources of spills. These experiments allow for both subsurface visualization of source behavior as well as quantification of groundwater impacts.

(Task 3) Multiphase fluid flow numerical simulations to quantitatively describe the 2-D model aquifer experimental results and to extend the analysis of biodiesel fuel impacts to a broader range of scenarios (e.g., spill size, soil permeability, etc.)

Accomplishments

(Task 1: Equilibria properties): In year 1 we have focused on developing new analytical methods to measure solute concentrations in the aqueous phase to be used for both the equilibrium studies for Task 1 and for the pore water measurements in Task 2. A direct injection, gas chromatography method was developed using a GC capillary column and a flame ionization detector. In addition to fatty acids, the method includes quantification of aromatic hydrocarbons (benzene, toluene, m-xylene, 1,2,4 trimethylbenzene) and isooctane. Preliminary experiments have been conducted to determine the solubilization of benzene, toluene, m-xylene, 1,2,4 trimethylbenzene in the presence of these components in FAME (fatty acid methylesters) and the aqueous/FAME partitioning properties of fatty acids. These experiments are being conducted in 40-ml EPA VOA (Volatile Organic Analyte) glass vials with Teflon-lined caps. These experiments will continue into Year 2 to provide data that establish the equilibrium cosolubilization properties of FAME due to the presence of fatty acids.

(Task 2: 2-D Aquifer experiments): A dedicated continuous flow 2-D glass cell (dimensions 40 cm x 40 cm x 1.5 cm) was fabricated at UH for this work. This cell, developed to model an aquifer, is designed for a continuous flow of water in the saturated zone, and it also has an unsaturated zone. Tracer experiments with fixed-volume pulses of a solution of sodium bromide for quantitation as well as fixed-volume pulses of a solution of a dyed tracer for visualization were conducted to establish flow patterns in the cell and to determine optimum sample locations downstream of the spill injection points. In addition preliminary spill experiments with fixed volumes of fuel mixtures (injected into the capillary fringe) were conducted. These initial experiments were used to visualize how the NAPL sources are formed from the fuel spills how they migrate/distribute from the spill injection point and also to visualize the flow patterns of the dissolved plumes from these sources. Experiments were conducted with a fine sand suitable for visualization studies using a dual-dye system (hydrophobic Sudan IV and hydrophilic Fluorescein). Fixed volume releases of the fuel mixtures were injected into the capillary fringe.

(Task 3: Modeling): In Year 1, UTCHEM simulations were initiated to simulate the conditions for the fixed-volume fuel releases in the 2-D physical model experiments. Simulations were conducted using phase equilibrium data available in the literature for a preliminary assessment of NAPL migration/distribution. A sensitivity analysis was conducted by assessing the effect of key physical-chemical properties such as interfacial tension, fluid viscosity, and media permeability on spill behavior.

Future Work

(Task 1: Equilibria properties): Phase equilibria experiments will continue in Year 2 to provide data that establish the equilibrium cosolubilization properties of FAME due to the presence of fatty acids. These data will be used in the modeling studies in Task 3.

(Task 2: 2-D Aquifer experiments): In Year 2, 2-D physical model laboratory experiments will be conducted for biodiesel fuels over a range of FAME composition (from 20 to 100% fatty acid methyl esters) and spill size.

(Task 3: Modeling): In Year 2, multiphase flow simulations using UTCHEM will be conducted to quantitatively describe the results of the 2-D model aquifer experiments. These simulations will incorporate new phase equilibria data from the Task 1 studies. The results of these experiments will then be extended by conducting additional simulations for a broader range of spill conditions (e.g., spill size, soil permeability, etc.).

List of Publications and Presentations

A presentation on this work is anticipated for either EPA's annual national TANKS conference in Fall 2015 or the Battelle conference in summer 2015. A manuscript on the results of this study will be submitted in the summer of Year 2 for publication following the results of experiments through the spring of Year 2.