TO: **Texas Hazardous Waste Research Center**

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SUBJECT: Final Report

PROJECT NUMBER: 513UHH0034H

PROJECT TITLE: Biodiesel Fuels and Groundwater Quality

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Project Description

This project provided a preliminary assessment of the impact of biodiesel fuels on groundwater contamination. 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), diesel fuels contain components (triglycerides/fatty acid methyl esters) that may have an impact on the source zone NAPL foot print of the fuel contamination associated with biodiesel and on the groundwater impact of other fuel components of environmental concern (e.g., benzene, toluene, xylenes, and naphthalene).

Objectives

The ultimate goal of this research is to provide useful predictions of source effects of biodiesel including NAPL distribution and potential effects on concentrations of BTX and other compounds that may impact groundwater resulting from spills of biodiesel fuels. The purpose of this proposed research was to investigate the impact of biodiesel fuels over a range of composition. Experiments were conducted in a continuous flow, unconfined aquifer, 2-dimensional physical model that simulates spills of these fuels. Another important goal of this research is to develop a model of the flow characteristics of these processes. The 2-D experiments emphasize the behavior of both capillary zone and saturated zone processes for biofuels of different vegetable oil based content.

More specific goals of this research are:

(i) Determine source zone NAPL migration and distribution and potential groundwater impacts using 2-D model aquifer experiments that simulate spills of biodiesel fuels for a range of fuel composition and type.

(ii) Develop a multiphase flow model that can then be used that can used to describe NAPL distribution and flow that can potentially be used to assess impact for a wide range of spill and aquifer conditions.

Experimental methods

(1) 2-D Bench-scale Model Aquifer Experiments: The impact of oil type and composition was addressed in 2-D bench-scale experiments that allows for studying characteristics (NAPL mobilization and potential groundwater impacts) for a range of fuel compositions for vegetable oils in the fuel mixtures. The experiments were conducted in a 2-D (1.5 cm in thickness) continuous flow glass cell (Figure 1). 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. These 2-D experiments were carried out at 25 ^{o}C. A fine-grained sand was used for these experiments: Ottawa-Federal Fine (U.S. Silica; Ottawa, Illinois) sand. Ottawa sand, which is light in color, is used to enhance the visualization of the capillary zone and also for better definition of dye that will be used to track the migration of NAPL (hydrophobic Sudan-IV) as well.

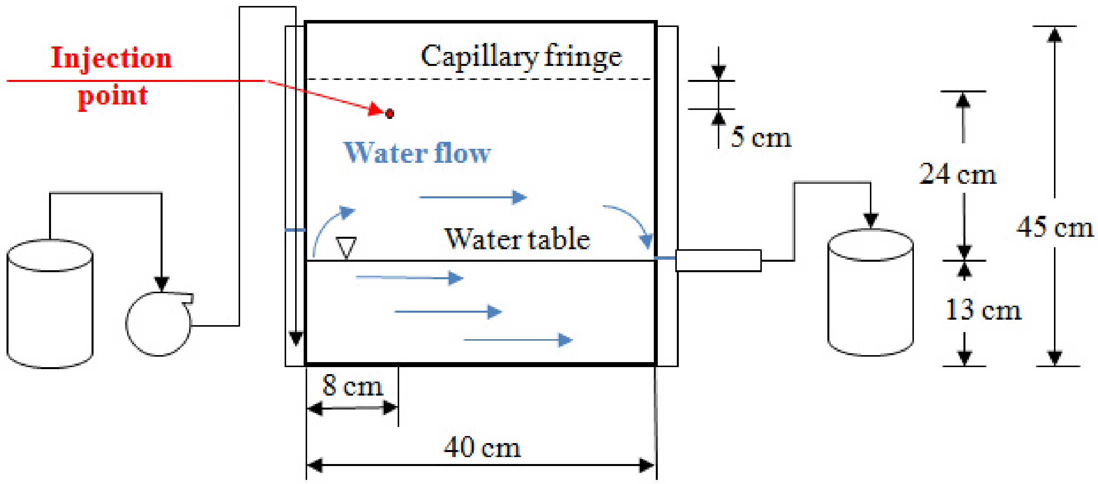


Figure 1. Two-dimensional (1.5 cm wide) cell experimental design for a bench-scale release of biodiesel fuels with continuous flow in the saturated zone. For this diagram, fuel blends of varying composition were injected in the capillary fringe.

Results/Accomplishments

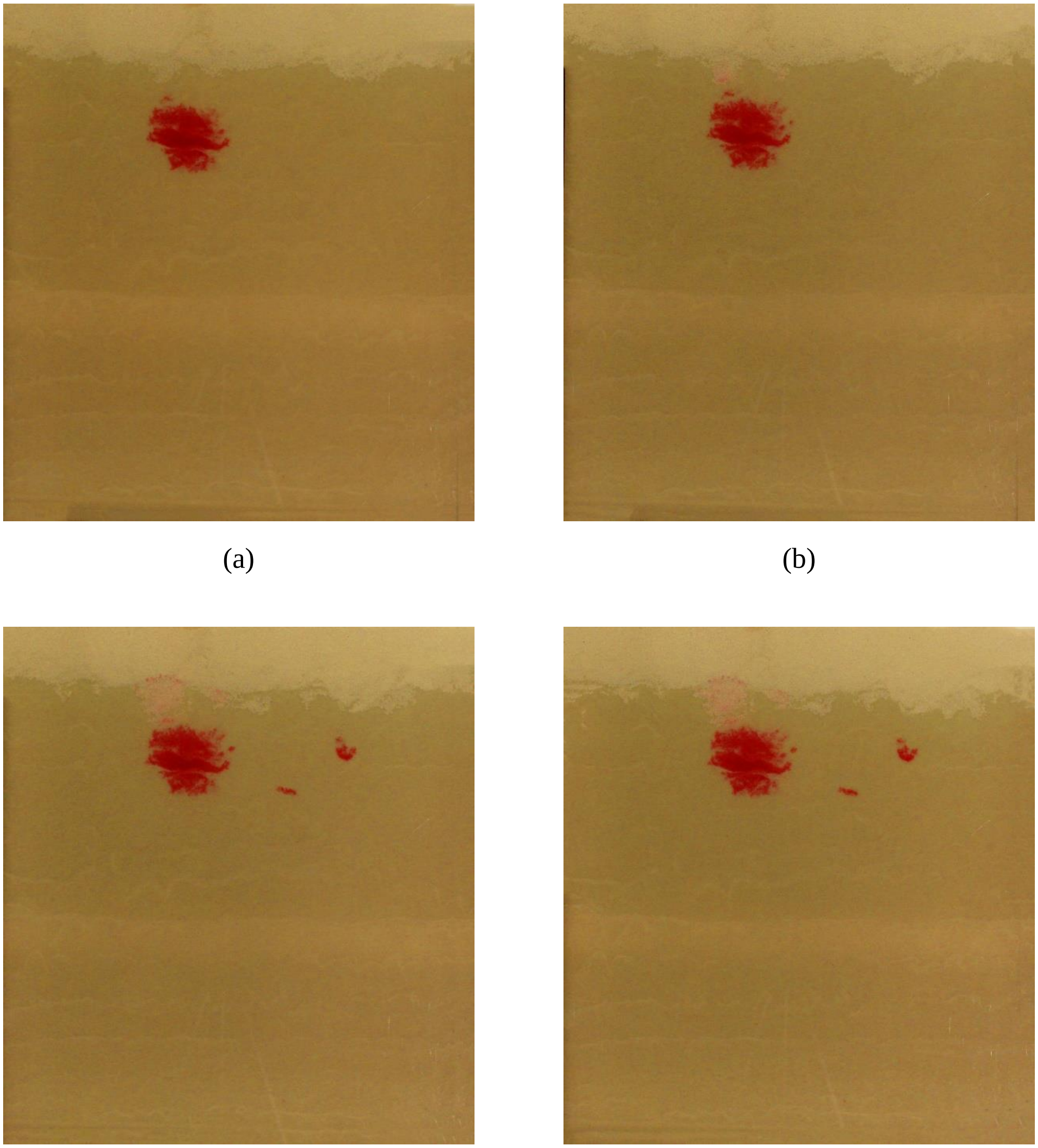
(2-D Aquifer experiments): Spill experiments with fixed volumes of fuel mixtures (injected into the capillary fringe) were conducted. These experiments were used to visualize how the NAPL sources are formed from the fuel spills how they migrate/distribute from the spill injection point and also to visualize the flow patterns of the dissolved plumes from these sources. Each of the experiments was conducted with Ottawa-Federal Fine sand suitable for visualization studies using the dual-dye system (hydrophobic Sudan IV and hydrophilic Fluorescein). Fixed volume releases of the fuel mixtures were injected into the capillary fringe. Tracer experiments with fixed-volume pulses of a dyed tracer for visualization were then conducted to establish flow patterns in the cell and to assess the effect of NAPL on flow distribution.

Experiments were conducted for blends of a mixture of aromatic and aliphatic hydrocarbons with different vegetable-based oils. For these experiments the following two oils were used: soybean oil and olive oil. These oils were chosen due to their high concentrations of triglycerides comprised of oleic and linoleic acids. Soybean oil is representative of a vegetable oil feed stock used in some biodiesel fuel mixtures. Olive oil (not commercially used) was also studied for comparison to see the effect of triglycerides that contain higher concentrations of oleic acid. The vegetable oils were blended with a NAPL mixture containing benzene, toluene, m-xylene, 1,2,4-trimethylbenzene, and isooctane. For the alkane portion of the NAPL mixture, isooctane was used vs. a higher molecular weight alkane that would be more representative of diesel range hydrocarbons. This allowed for more direct comparisons of the effect of the oils on NAPL generation and migration in soils with NAPL mixtures of gasoline fuels containing alcohols. Results from these experiments show that fuels that contain triglycerides produce NAPL footprints that are more similar to petroleum based fuels (e.g., gasoline and diesel fuels) that do not contain alcohols, such as ethanol. This directly impacts the short and long term source concentrations in groundwater that emanate from these sources of contamination. (Representative experimental results for the injection of 30-mL of a 15 vol.% soybean/85 vol.% petroleum hydrocarbon mixture are shown in Figure 1. Representative post tracer results following the injection of 30-mL of a 15 vol.% soybean/85 vol.% petroleum hydrocarbon mixture are shown in Figure 2.)

(Modeling): Multi-phase flow numerical model simulations (using UTCHEM) were initiated in complementary work to simulate the conditions for fixed-volume fuel releases in a 2-D physical model experiments. Simulations were conducted to assess NAPL migration/distribution and groundwater flow near the source region. 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. When further developed the model will allow for predicting behavior for a wide variety of spill and aquifer conditions.

Publications and Presentations

A manuscript on the results of this work is in preparation.



(a) (b) (c) (d)

Figure 1. 2D visualization for a 30-ml release of a 15 vol.% soybean/85 vol.% petroleum hydrocarbon mixture in the capillary fringe with continuous flow in the saturated zone: (a) 0 h, (b) 1 hr, (c) 1 day and (d) 1 week after the release..

(a)

(b)

(c)

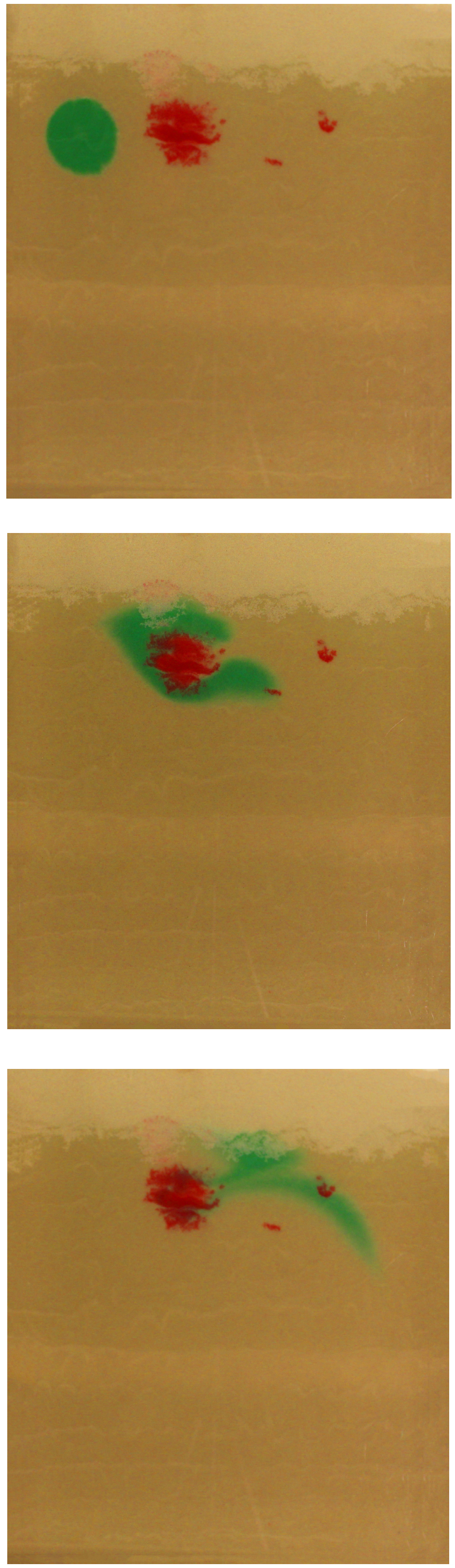


Figure 2. Post-tracer experiment following a 30-ml release of a 15 vol.% soybean/85 vol.% petroleum hydrocarbon mixture in the capillary fringe with continuous flow in the saturated zone: (a) 0 h, (b) 1 hr, (c) 1 day and (d) 2 days after injection of the tracer.