Modeling the Transport of Ethanol Fuel Blends with the Combined HSSM and MT3D Models

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Introduction

Releases of gasoline move as a distinct liquid from water in the environment. This applies both to surface and subsurface releases. Much of the unique character of gasoline leaks results from its flow as a separate phase liquid. Despite remaining distinct from water, the components of gasoline can partition into the water phase and create the subsurface contaminant that is the object of LUST site remediation. A simplified conceptualization of this process is shown in Figure 1. Here the gasoline is shown as migrating to the water table and accumulating in a mound. Components of the gasoline can dissolved and be transported with the flowing ground water.

The Hydrocarbon Spill Screening Model (HSSM) was designed to follow this conceptual model. The model accounts for the dissolution and transport of two species into flowing ground water. From experience in running the model it's clear that typical time scales for transport to the water table, mound formation and decay and transport in an aquifer increase in this sequence from days to months to years, given a limited-duration release. Consequently most of the emplacement of product occurs rapidly relative to transport in the aquifer. At most LUST sites this occurs prior to site investigation and the opportunity to collect data documenting this phase of transport.

The ground water model within HSSM is limited in that it simulates only transport of non-interacting species using an analytical solution to the transport equation. A consequence of this approach is that the model does not represent heterogeneous aquifers, flow towards pumping wells, realistic hydrologic boundaries (i.e., rivers, lakes, etc.), or reacting components of gasoline.

A variety of problems have been found that depend on transport of multiple components of gasoline:

•both aerobic and anaerobic biodegradation depend on concentrations of electron donors (i.e., BTEX) and electron acceptors (oxygen, nitrogen, ferric iron, manganese and carbon dioxide)

•methyl tert-butyl ether (MTBE)-laden gasoline may contain tert-butyl ether (TBA) which is also a transformation product of MTBE

•preferential degradation of ethanol may allow BTEX plumes to expand further if the gasoline contains ethanol.

HSSM Evaluation

A release of oil into a laboratory-scale physical model is shown in Figure 2. The release occurred from a gasoline source with a constant level into a course sand. This could correspond to an idealized tank with a certain fixed depth of gasoline over a hole or crack. The elapsed time is indicated for each contour. These results indicated that the oil (in this case Soltrol 220; viscosity of 4.5 cP, density of 0.803 g/ml) migrated downward in a somewhat irregular pattern. For most of the upper part of the flow system, the Soltrol moved laterally beyond the boundaries of the release. This was due to the constant head of the source driving the flow laterally. At greater depth, the width narrowed and was more nearly similar to the source size. In the capillary fringe the oil spread laterally and formed a lens. A two-dimensional version of HSSM's OILENS module was used to simulate the lateral transport. This was needed because OILENS itself allows the oil to move radially from the source. In the physical model, the side walls restrict radial motion to occur only parallel to the walls. Thus the model exaggerates the height of the lens and limits its lateral extent. The results in Figure 3 show reasonable matches between the model, given various source conditions. Similarly there was reasonable agreement between the lens heights, although the model requires uniform oil content in homogeneous media. The actual oil content and media may not be as homogeneous as in the model simulations.

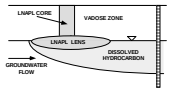

Figure 1 Schematic of a gasoline release showing simplified conceptualization of flow through the vadose zone, accumulation on the water table and transport to a receptor well.

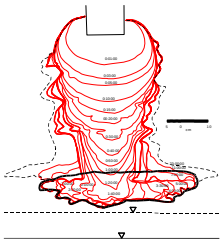

Figure 2 Results showing infiltration and redistribution of an oil in a laboratory physical model (courtesy Randall J. Charbeneau, Univ of Texas).

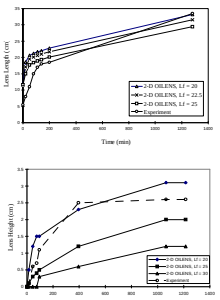

Figure 3 Comparison between a 2D version of HSSM and the lens size, left and lens height, right. Lf is a parameter representing three different sources.

Model Design

For the current work, the objective was to combine vadose zone transport of gasoline with reactive-transport simulation capability in realistic aquifers. Thus the vadose zone and lens-forming parts (known as KOPT and OILENS) portions of HSSM with a modified version of MT3D. Since MT3D is a transport model for dissolved contaminants, MODFLOW is used to generate ground water flows.

The sequence of use of these models is:
• set up and run MODFLOW to generate ground water velocities
• RUN sequentially HSSM to generate the flux of contaminants to the aquifer and the Modified MT3D to simulate transport and reaction.

Fuel Composition

Gasoline is composed of several hundred identifiable petroleum hydrocarbons (e.g.,, benzene, toluene, octane) , proprietary additives that serve several purposes (e.g.,, detergents, corrosion inhibitors, etc.) and other blending components (e.g., alkylate, ethanol). Simulating all of these compounds is neither practical nor necessary. Only a limited number of compounds need to be simulated, because of their inherent interest or their impact on transport of other compounds. Because the fuel may release more compounds than just these to the ground water, the overall impact of the fuel is modeled when all compounds are included in some fashion.

Under the assumption that a relatively small number of surrogate fractions can be used to represent the physical and chemical properties of gasoline in the environment a limited number of surrogate compounds were developed for use in the simulations. These include five aliphatic fractions, five aromatic fractions (with benzene and toluene each representing a single fraction), three additives (ethanol, MTBE, TAME), and one additive which is also a metabolite (TBA).

Transformation Reactions

Briefly, transformations are simulated by considering:

• stoichiometry of gasoline component biodegradation by multiple electron acceptors,
• mass conservation equations for electron donors and electron acceptors,
• reaction rates for electron donors,
• reaction rates for electron donor utilization by sequential electron acceptors and transformation to methane, and
• generalized relations between electron donor degradation and electron acceptor consumption/degradation product formation.

Special treatment is used for iron. Ferric iron (solid phase) is treated as a property of the aquifer. Reaction with iron occurs until either the ferric iron or the gasoline is depleted.

Example Simulation

An example simulation was made with the release of 0.8235 m3 of gasoline that occurred in a catastrophic release that lasted one day. The water table was located 21 m below the ground surface. The unconfined aquifer averaged 25 m thick with an average gradient of 1.9% and hydraulic conductivity of 200m/d. The model domain consisted of 161 rows and 161 columns and grid blocks of 10 m^2.

Simulations were made for two different gasolines: the first represented a pre-2006 reformulated gasoline (RFG) that contained MTBE (benzene 1%, MTBE 10%, and a single surrogate 89%); the second represented a reformulated E10 ethanol gasoline (benzene 1%, ethanol 10%, surrogate 89%).

The aquifer background concentrations of each of the three compounds was 0 mg/L. The background electron acceptor concentrations were 10 mg/L of oxygen, nitrate and sulfate. The background transformation products, ferrous iron and methane were 0.001 mg/L and 0.0001 mg/L, respectively.

Results

The simulation of the pre-2006 RFG in the highly conductive aquifer is shown in Figure 4, 723 days after the end of the release. This figure shows a pattern of similarly-sized plumes for benzene, MTBE and the surrogate, with corresponding regions of oxygen, nitrate and sulfate depletion and production of ferrous iron and methane. The breakthrough curves (Figure 5) show a very slightly declining concentration of benzene and the surrogate, and the release of MTBE as a pulse. There is a rapid loss of oxygen and nitrate with a spike in ferrous iron. A relatively small methane pulse passes the receptor between 500 and 900 days.

The corresponding simulation of E10 RFG (Figure 5) shows extensive degradation of ethanol and corresponding elongated plumes of benzene and the surrogate. The breakthrough curves (Figure 5) show roughly similar concentrations of benzene and the surrogate and an ethanol pulse that is greatly reduced in comparison to the MTBE pulse. The major differences in electron acceptors/degradation products are slightly more usage of sulfate and an increased methane peak.

The simulation time for the pre-2006 RFG was 32 minutes (on a Duo 2 3.0 GHz CPU). The time was 827 minutes for the E10 RFG. Much smaller time steps were required for the E10, because of its very rapid degradation rate.

Conclusions

Inclusion of gasoline as a separate phase in simulation of LUST site releases provides the means to account for partitioning from the gasoline to the ground water and various gasoline compositions. Simulation of a pre-2006 reformulated gasoline containing MTBE and a reformulated E10 gasoline show the expected elongation of the benzene plume and enhanced production of methane. Simulation of these problems, however, is fairly computation intensive.

Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy

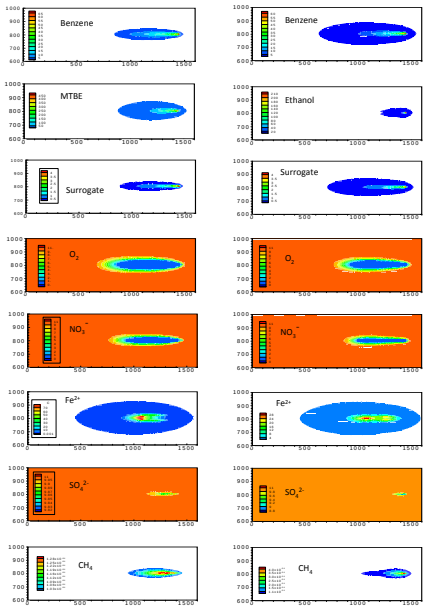

Figure 4 Simulation results at 500 days, left MTBE gasoline, right ethanol gasoline.

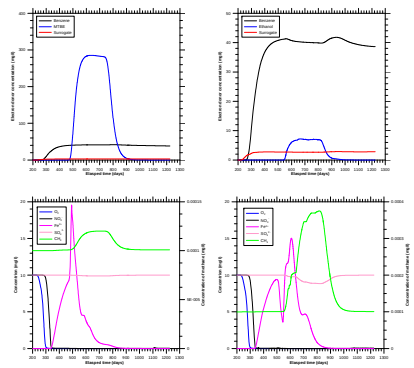

Figure 5 Breakthrough curves at a location 50 m from the source, left MTBE gasoline, right ethanol gasoline.