



Project Summary

Laboratory Investigation of Residual Liquid Organics from Spills, Leaks and the Disposal of Hazardous Wastes in Groundwater

John L. Wilson, Stephen H. Conrad, William R. Mason, William Peplinski, and Edward Hagan

Organic liquids that are essentially immiscible with water migrate through the subsurface under the influence of capillary, viscous, and buoyancy forces. These liquids originate from the improper disposal of hazardous wastes, and the spills and leaks of petroleum hydrocarbons and solvents. The laboratory studies described in this report examined this migration, with a primary focus on the behavior of the residual organic liquid saturation, referring to that portion of the organic liquid that is *trapped* by capillary forces in the soil matrix. Residual organic saturation often constitutes the major volume of the organic liquid pollution, and acts as a continual source of dissolved or vapor phase organics.

Four experimental methods were employed. First, quantitative displacement experiments using short soil columns were performed to relate the magnitude of residual organic liquid saturation to fluid properties, the soil, and the number of fluid phases present. Second, additional quantitative displacement experiments using a long soil column were performed to relate the mobilization of residual organic liquid saturation in the saturated zone to wetting fluid flow rates. Third, pore and blob casts were produced by a

technique in which an organic liquid was solidified in place within a soil column at the conclusion of a displacement experiment, allowing the distribution of fluid phases within the pore space to be observed. The columns were sectioned and examined under optical and scanning electron microscopes. Photomicrographs of these sections show the location of the organic phase within the porous soil matrix under a variety of conditions. Fourth, etched glass micromodels were used to visually observe dynamic multi-phase displacement processes in pore networks. Fluid movement was recorded on film and videotape.

It was found that the spatial distribution and saturation of organic liquid within the porous media depends on a variety of factors, including: (1) the fluid properties of interfacial tension, viscosity, and density; (2) the soil structure and heterogeneity; (3) the number of fluid phases present; and (4) the fluid flow rates. Photomicrographs on a pore scale show that the residual organic liquid appears as blobs, films, rings, and wedges of microscopic size, depending on these factors. The size, shape, and spatial distribution of these blobs, films, rings and wedges affects the dissolution of organic liquid into the water phase,



volatilization into the air phase, and the adsorption and biodegradation of organic components. These four processes are of concern in the prediction of pollution migration and the design of aquifer remediation schemes.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Many hazardous waste sites, and most leaking underground storage tanks, involve non-aqueous phase organic liquids. Usually released at or near the surface, these organic liquid contaminants move downward through the vadose zone toward the water table. Migrating as a liquid phase separate from the air and water already present in the vadose zone, some of the organic liquid is immobilized within the pore space by capillary forces. The remainder passes on, and if the volume of organic liquid is large enough it eventually reaches the water table. If it is less dense than water the organic liquid spreads laterally along the water table (see right side of Figure 1). If the organic liquid is more dense than water, it continues to move downward into the saturated zone (the left side of Figure 1). In both cases the organic liquid usually migrates down-gradient with the ambient groundwater flow, although dense organic liquids may migrate in other directions as they encounter dipping barriers. In the saturated zone, which is mostly below the water table and includes the capillary fringe, more organic liquid is immobilized by capillary forces. Here the immobilized organics remain as small, disconnected pockets of liquid, sometimes called *blobs*, no longer connected to the main body of organic liquid. The immobilized volume is called the *residual oil saturation* in petroleum reservoir engineering and is measured as the volume of organic liquid trapped in the pores relative to the volume of the pores. The final report refers to the immobilized organic liquid as *residual organic liquid*. Organic liquid at residual saturation can occupy from 15% to 50% of the pore space in petroleum reservoir rocks under conditions that are equivalent to those in the groundwater saturated zones. At a spill or hazardous waste site the entire

volume of organic liquid can be exhausted by this immobilization, although if the volume of organic liquid is large enough, it continues to migrate down-gradient where it becomes a threat to the safety of drinking water or agricultural water supplies. As described in detail in sections 9 and 10 of the final report, the actual spatial distribution of the residual saturation within the pore space is completely different in the vadose and saturated zones.

The organic liquid phase is sometimes referred to as being immiscible with water and air. Although that expression is used here, it is important to realize that small concentrations of the various components of the organic phase volatilize into the air phase and dissolve into the water phase. A *halo* of dissolved organic components precedes the immiscible phase in its migration (Figure 1). Even when the so-called immiscible organic liquid has been immobilized by capillary trapping, the passing groundwater dissolves some of the residual. In effect, the organic liquid phase acts as a continuing source of dissolved organic pollutants. Similarly, in the vadose zone, the residual organic liquid that volatilizes into the air phase migrates by gaseous diffusion and advection, becoming a source of organic contaminants to air or water and a possible explosion hazard. In large spills and leaks it is apparent that most of the liquid organic remains as a liquid, some is volatilized, and a little is dissolved. However small in volume, the volatilized or dissolved components are usually the ones that cause problems. The liquid organic phase acts as a reservoir of additional organic to replenish the air and water phases with dangerous and/or toxic material. Clearly, the source of the dissolved or gaseous organic constituents—the liquid organic phase—must be removed or isolated in order to restore a polluted aquifer.

There is no wholly effective mechanism to remove the residual organic liquid. Waiting for the residual to dissolve can take several decades. In the vadose zone, induced volatilization may help reduce the residual volume for lighter organics, but is not effective for heavier ones. Engineered removal is usually attempted hydraulically, by sweeping the organic liquid out with water, or biologically, by encouraging the consumption of the organic constituents by the soil microbial community. This last process, biodegradation, is the focus of current research and several recent restoration efforts. It is seldom tried

alone, for the microbes generally consume only the dissolved organics. Moreover, some organic chemicals are extremely resistant to biodegradation. PCBs, for example, may biodegrade very slowly, or not at all in the subsurface.

Hydraulic sweeps remain a major component of any attempt to remove organic liquids although, commonly, hydraulic sweeps fail to remove all the liquid organic phase, often leaving a significant quantity of residual organic liquids behind. There is, of course, another removal option often used for small pollution events: excavate the site and dispose of or treat the contaminated soil. For large sites this alternative is unfeasible. Since there is no panacea for the removal of organic liquids, containment is often adopted as part of a restoration strategy. Hydraulic containment, often in combination with structural barriers such as a slurry wall, is becoming standard practice.

Scope of Previous Work

Development of improved technologies to clean up organic pollutants depends in large part on developing an ability to understand and predict the migration of liquid, vapor, and dissolved organics. Liquid organics move through a water and sometimes air filled porous soil, as a separate phase, under the influence of viscosity, gravity, and capillary forces. Dissolved organics move in the water phase and are subject to advection, dispersion, biodegradation, and adsorption onto soil particles. Organic vapors in the air phase are subject to similar mechanisms. A few of these major transport mechanisms are fairly well understood today, principally those associated with the behavior of dissolved organics.

In contrast, the organic liquid phase transport mechanism has been virtually ignored by the research community in the United States, although it has been the subject of empirical studies in Europe. Recently, however, American researchers have obtained some laboratory results.* Several investigators ran gravity drainage experiments on a long column to relate organic liquid retention in the vadose zone with grain size and sorting. Others used a short soil core centrifuging method to measure residuals in the vadose zone, or

* The final report provides complete references for all studies and experiments.

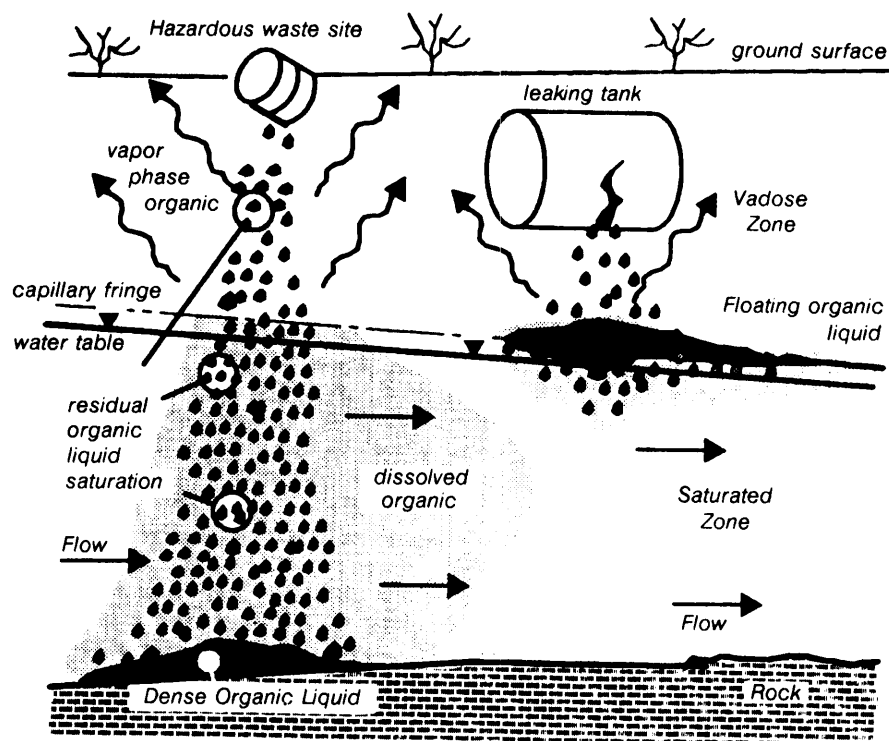


Figure 1. Migration pattern for an organic liquid more dense than water (left), and less dense than water (right).

employed gamma radiation attenuation and bulk soil electrical resistivity to measure three-phase fluid saturations at various times and at various elevations above a water table following a simulated petroleum spill. The experimental procedure allowed a petroleum spill to be tracked as it moved through the vadose zone to the water table. Experiments have been performed to test the ability of multiphase flow theory to predict the infiltration and redistribution of wetting and non-wetting fluids. They met with limited success. American researchers have also used theoretical three-phase saturation-pressure relationships to estimate the volume of oil in soils given observed fluid levels in monitoring wells.

Some simple numerical simulations of multi-phase transport have been developed. These focus on immiscible transport of continuous phases. Residual organic liquids, trapped by capillary forces, are often ignored, although they are sometimes treated as a source of dissolved contamination. This research effort mirrors the state of the art of petroleum engineering's *black oil* models. A few researchers have looked into interphase transfer, including the volatilization and solution of organic

components, using computer simulations. This again reflects the state of the art in petroleum engineering, where so-called compositional models are used to examine enhanced recovery techniques. One study discussed in the final report proposed a model to estimate the functional relationships between fluid pressures, saturations, and permeabilities of two- or three-phase porous media systems, and these functional relationships have been implemented in a multi-phase numerical flow model. The model has since been extended to include the effects of hysteresis and non-wetting phase trapping. The results of concurrent laboratory work were used to validate the model.

Petroleum engineering's long history of research into improving recovery from petroleum reservoirs may be applied to rehabilitating fresh-water aquifers polluted by organic liquids. Through over forty years of experimentation, petroleum engineering has amassed considerable expertise in multi-phase transport, the mechanics of oil phase capillary trapping, and oil recovery. To date, relatively little of this technology has been applied to recovering organic hazardous wastes and petroleum hydrocarbons released in the

near-surface environment. The petroleum literature on residual oil saturation is reviewed in papers referenced in the final report. In groundwater hydrology we too are concerned with the capillary trapping of residual saturation, and with its removal. However, unlike petroleum engineers, we are also concerned with the mechanisms that initially brought the *oil* into the aquifer in the first place.

Motivation for this Study

Residual organic liquid saturation often constitutes the major volume of the organic pollution, and acts as a continual source of dissolved or vapor phase organics. In particular, there is a need to understand how the residual organic liquid is trapped and how it can be hydraulically mobilized or otherwise removed. As shown in Sections 9 and 10 of the full report, the residual organic liquid appears to form blobs, films, wedges and rings of microscopic size, depending on the presence of other fluids, the pore geometry, the surface wetting of the solids, and soil heterogeneity. The term wetting refers to the relative affinity of the solid surface for

the available fluids. Water is normally the wetting fluid in most soils. Organic liquid is normally non-wetting relative to water, and wetting relative to soil gas. The size, shape, and spatial distribution of these blobs, films, wedges and rings affects the dissolution of organic liquid into the water phase, volatilization into the air phase, and the adsorption and biodegradation of organic components. The presence of residual organic liquid also affects the relative permeability versus saturation curves used in numerical simulation codes of fluid movement and pollution migration. A paucity of experimental results regarding these issues makes site characterization conjectural, predictive modeling unreliable, and remediation design of organic liquid leak or waste sites less effective than might be possible.

Objectives

The goal of this study was to better understand the basic physical mechanisms controlling the movement, and especially the capillary trapping, of organic liquids in soils and groundwater. Emphasis was on relating the various mechanisms to the issues of contaminant movement, characterization, and remediation. This broad goal was broken down into two sets of specific research objectives, addressing issues relevant to the saturated and vadose zones, respectively:

The Saturated Zone

Assuming that water is wetting and the organic liquid is non-wetting, our research objectives for saturated zone conditions were to:

- conduct a literature review of basic concepts, including non-wetting phase capillary trapping and mobilization mechanisms, and petroleum experience;
- conduct experiments that permit the visualization of two-phase fluid flow and capillary trapping, and record the visualizations on film and videotape;
- perform a detailed study of two phase flow capillary trapping and non-wetting phase residual saturation in a typical unconsolidated soil, testing the hypothesis that its behavior can be predicted from previously published results from the petroleum engineering literature;
- compare non-wetting phase residual saturations for various organic liquids,

testing the hypothesis that residual saturation is largely independent of organic liquid composition for expected conditions in hydrology;

- compare non-wetting phase residual saturations for various soils, testing the hypothesis that residual saturations should be similar in soils that have a similar grain size distribution;
- investigate how the rate of initial invasion of a non-wetting organic liquid may influence irreducible water saturations and, later, organic residual saturations.
- investigate the possible hydraulic mobilization of non-wetting phase residual organic liquid, by increasing groundwater velocities, testing other researchers' conclusion that this is largely an unrealistic aquifer remediation alternative unless interfacial tensions are reduced significantly; and
- test the hypothesis that porous media heterogeneity can dominate displacement and trapping mechanisms.

The Vadose Zone

Our research objectives for vadose zone conditions were to:

- conduct a literature review of basic concepts, including capillary trapping mechanisms, mobilization issues, and petroleum experience;
- conduct experiments that permit the visualization of multi-phase fluid flow and capillary trapping, testing the hypothesis that spreading organic liquids typically form a film between the water and air phases;
- perform a detailed study of capillary trapping and residual saturation in a typical unconsolidated soil, testing the hypothesis that organic liquid residual saturations are significantly lower in the vadose zone than they are in the saturated zone; and
- conduct experiments that permit the visualization of capillary trapping for non-spreading organic liquids, testing the hypothesis that non-spreading organic liquids behave differently than non-spreading organic liquids.

Experimental Approach

The problem was approached experimentally in four ways:

1. **Quantitative displacement experiments using short columns** were performed to relate the magnitude of residual organic liquid saturation to fluid and soil properties, and to the number of fluid phases present (i.e., both saturated and vadose zone conditions).
2. **Quantitative displacement experiments using long columns** were performed under two-phase saturated zone conditions, yielding water and organic liquid relative permeabilities. In these experiments, reductions of residual organic saturation were correlated to the pressure gradient applied in hydraulic sweeps, and the potential for hydraulic mobilization of residual blobs was investigated.
3. **Pore and blob casts** were produced for saturated zone conditions by a technique in which the organic liquid was solidified in place within a soil column at the conclusion of a displacement experiment, allowing the distribution of organic liquid to be observed. The polymerized organic phase was rigid and chemically resistant. Following polymerization, the water phase was removed and replaced by an epoxy resin. The solid core, composed of soil, solidified styrene (the organic phase), and epoxy resin (the water phase), was cut into sections to show the organic liquid phase in relation to the soil and the water phase. The sections were photographed under an optical microscope. Although polymerization only gave a *snapshot* of the displacement process, it offered the advantage of seeing organic liquid in its *natural habitat* (i.e. within a soil) as compared to that observed in etched glass micromodels. Sometimes, instead of replacing the water with epoxy resin, the solid matrix of the soil column was dissolved with hydrofluoric acid, leaving only the hardened organic liquid. The solidified organic phase was then observed under a scanning electron microscope (SEM) and photographed. For vadose zone conditions, styrene and epoxy liquids were sequentially applied, drained and hardened in an attempt to simulate proper fluid distributions above the water table. The resulting pore casts were photographed under an optical microscope.
4. **Etched glass micromodels** were used to observe dynamic multi-phase displacement processes. Micromodels

provide two-dimensional networks of three-dimensional pores. They offer the ability to actually see fluids displace one another in both a bulk sense and also within individual pores. Although displacements are known to be dependent upon a variety of factors, this report describes micromodel experiments that focused on only three: (1) the fluid flow rate, (2) the presence of heterogeneities, and (3) the number of fluid phases present. The experiments were photographed and videotaped.

To interpret the experiments in heterogeneous material, we also developed a new but simple theoretical model of multiphase flow and capillary trapping. The model is based on the interplay between viscous and capillary forces.

Organization of the Final Report

Following the introduction are two sections (2 and 3) that summarize the report conclusions and recommendations. The next five sections (4 through 8) detail fluid and soil characteristics, and

the experimental methodology, used for each of the experimental approaches outlined above. These sections contain detailed information that may be used by future investigators wishing to verify or extend the results of this study. The reader more concerned with results than methods can probably skip them. The last two sections (9 and 10) describe experimental results for saturated zone and vadose zone conditions, respectively. These sections contain a large number of photomicrographs that visualize multiphase flow and residual saturation.

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Jerry Jones is the EPA Project Officer (see below)

The complete report, entitled "Laboratory Investigation of Residual Liquid Organics from Spills, Leaks and the Disposal of Hazardous Wastes in Groundwater," (Order No. PB90-235 797/AS; Cost: \$31.00, subject to change) will be available only from:

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