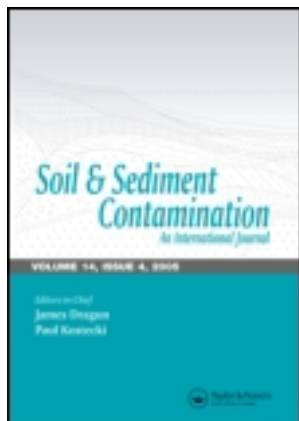


This article was downloaded by: [Institutional Subscription Access]

On: 08 August 2011, At: 02:27

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Soil Contamination

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/bssc19>

Microemulsion-mediated removal of residual gasoline from soil columns

R. S. Mansell^a, R. D. Rhue^a, Y. Ouyang^a & S. A. Bloom^a

^a Soil and Water Science Department, University of Florida, Gainesville, FL, 32611-0290

Available online: 02 Dec 2008

To cite this article: R. S. Mansell, R. D. Rhue, Y. Ouyang & S. A. Bloom (1996): Microemulsion-mediated removal of residual gasoline from soil columns, *Journal of Soil Contamination*, 5:4, 309-327

To link to this article: <http://dx.doi.org/10.1080/15320389609383533>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan, sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Microemulsion-Mediated Removal of Residual Gasoline from Soil Columns

R. S. Mansell,* R. D. Rhue,
Y. Ouyang, and S. A. Bloom

Soil and Water Science Department,
University of Florida, Gainesville, FL 32611-
0290

In situ pumping of micellar solutions of surfactant (S) and cosurfactant (CoS) in water (W) through contaminated soils or aquifers offers potential for enhanced remediation of residual nonaqueous-phase liquids (NAPLs). Extremely low interfacial tension generated between a W/S/CoS mixture and residual NAPL in soil pores may initially mobilize the NAPL, which is then transported temporarily as a separate phase by immiscible displacement. The NAPL is then solubilized by microemulsification as the W/S/CoS mixture forms a stable W/S/CoS/NAPL microemulsion that undergoes miscible displacement through the pore space. This remediation technique was tested under laboratory conditions by sequentially flushing a saline solution and a W/S/CoS mixture through columns of a sandy soil recently contaminated with residual leaded gasoline (LG). Prior to the flushings, the soil was initially contaminated by applying a W/S/CoS/LG microemulsion. A simple conceptual transport model with kinetic clogging of soil pores adequately described breakthrough curves for gasoline and organolead in the soil columns.

KEY WORDS: microemulsions, soil remediation, gasoline, surfactant, cosurfactant, in situ soil flushing, tetraethyl lead.

* Corresponding author.

INTRODUCTION

INFILTRATION of hydrophobic nonaqueous-phase liquids (NAPLs) such as gasoline into water-unsaturated soil presents serious problems for contaminating the soil matrix, the soil solution, and potentially for underlying groundwater. Consequent percolation of rain water through the vadose zone partially dissolves hydrocarbon components of the residual gasoline and transports them to underlying groundwater. Contaminants considered "insoluble" above parts per million nevertheless migrate, but more slowly (Nash and Traver, 1989). Organic contaminants have been reported to be the most common health-threatening chemicals detected in groundwater, and NAPLS comprise much, if not most, of this contamination (Imhoff *et al.*, 1994).

Repeated spillage and/or leakage of leaded aviation gasoline (LG) into soils poses a special problem by introducing tetraethyl lead (TEL, $(C_2H_5)_4Pb$) and associated chemical and microbial degradation products (Ou *et al.*, 1995a, b; Rhue *et al.*, 1993), all of which are toxic when present in groundwater used for drinking purposes. In aqueous solution and in the presence of light, TEL undergoes a sequential loss of ethyl groups to form ionic triethyl lead (TREL, $(C_2H_5)_3Pb^+$), diethyl lead (DEL; $(C_2H_5)_2Pb^{2+}$), and inorganic lead (IL, Pb^{2+}). In contrast to hydrophobic TEL, each of the dissociation cations (TREL, DEL, and IL) are soluble in water (Mansell *et al.*, 1992).

Many conventional remediation methods such as pump-and-treat technology have proven both expensive and generally inefficient (Abelson, 1990; Fetter, 1992). Pump-and-treat technology typically involves pumping contaminated groundwater to the surface, where it is treated to remove organic contaminants. If some of the NAPL is mobile, it may be captured by pumping, but considerable amounts of immobile residual NAPL commonly remain even if the mobile NAPL is temporarily removed (Fetter, 1992). This method is basically inefficient because the primary focus is removal of contaminants from the mobile aqueous phase of NAPL without direct removal of the typically larger immobile residual phase entrapped within pores of the soil or aquifer. Because NAPLs and NAPL components may also diffuse into zones with smaller pores and lower permeability, pump-and-treat techniques are not efficient in contaminant removal, as most of the water being pumped will come from the most permeable zones of the aquifer (Fetter, 1992). If contaminants in the aqueous phase sorb onto mineral or organic surfaces in soil, kinetic desorption may occur very slowly as the groundwater is pumped from the porous media. Although pump-and-treat technology has been shown to gradually lower concentrations of contaminants in the groundwater for specific sites over long pumping periods, contaminant levels have been observed to actually increase during subsequent periods of extended flow interruption (Abelson, 1990). Six years of pump-and-treat (1978 to 1984) at the IBM Dayton hazardous waste site in New Jersey lowered the concentrations of perchloroethylene (PCE) (Abelson, 1990) in the groundwater 61-fold (from 6132 to 100 ppb);

however, 4 years after terminating pump-and-treat remediation, the concentration increased 125-fold (from 100 to 12,558 ppb).

Because of the limited solubility of gasoline and other NAPLs in water, considerable effort has been devoted to assessing the suitability of aqueous solutions of micelle-forming surfactants (water/surfactant or W/S) for *in situ* washing of hydrophobic organic contaminants from the subsurface environment (Abdul and Gibson, 1991; Taylor and Hawkins, 1992). Micelles are aggregates of 50 to 200 surfactant molecules (Harwell, 1992) that have a tendency to solubilize hydrophobic molecules. Results from those investigations indicate that W/S solutions can enhance the removal of hydrocarbons from soils over aqueous solutions by as much as 50 to 86%. Although such surfactant-facilitated removal of hydrocarbons is more efficient than conventional pump-and-treat technology, it may not reduce the contaminant concentrations in the aqueous phase below limits proposed by the U.S. Environmental Protection Agency (EPA) for most hydrophobic compounds. Effective and inexpensive remediation methods is a recognized need for cleaning up NAPL-contaminated subsurface environments for hazardous waste sites (Abelson, 1990).

Harwell (1992) discussed a number of major factors that affect surfactant performance in groundwater remediation applications. When selecting a surfactant or mixture of surfactants for soil remediation, five major processes must be considered: (1) ability of surfactant micelles to solubilize organic contaminants, (2) ability of surfactants to mobilize residual contaminant liquids by producing ultralow interfacial tensions (0.001 mN/m^1 or less) with trapped phases in the porous media, (3) ability of surfactants to retain their activity in the environment of the porous media, (4) ability to minimize the dispersion of clay minerals, and (5) ability to undergo biodegradation. Contaminants can be solubilized at three locations within a surfactant micelle: within the hydrophobic core, the polar surface, and the transition "palisade layer". Solubilization of hydrophobic, nonpolar contaminants such as dodecane may be expected to occur in the hydrophobic core of the micelle, thus increasing the core diameter.

In order to maintain conditions favorable for emulsification, the initial concentration of a surfactant in influent applied to contaminated soil must exceed the critical micelle concentration (CMC). However, surfactant concentrations in the aqueous phase of porous media can be decreased by processes such as precipitation, liquid crystal formation, formation of a coacervate phase, partitioning into trapped residual phases, biodegradation, and adsorption onto solid surfaces. Adsorption of surfactants to soil surfaces may result in dispersion of clay particles, which decreases flow by clogging soil pores.

Avoiding surfactants with unfavorable phase behavior (instability, anisotropy, multiple phases, high viscosity, etc.) is more easily accomplished when solubilization is the enhanced remediation mechanism because solubilization does not require a close matching of the structures for both the surfactant and the solubilize (Harwell, 1992), leaving room for selection of a surfactant structure with favorable phase behavior. Use of biodegradable, nontoxic surfactants and cosurfactants is an

important environmental consideration for remediation of contaminated soils and aquifers (Shiau *et al.*, 1994).

In order to achieve the ultralow interfacial tensions needed for the mobilization mechanism, microemulsification is required. Microemulsion formation requires the adsorption of a dense surfactant film at the interface between two immiscible liquids such as water and NAPL. Droplet diameters within microemulsions (range, 0.01 to 0.1 μm) are generally larger than molecular solutions ($<0.001 \mu\text{m}$) but smaller than colloidal dispersions of polymers or clays (range, 0.1 to 2 μm) (Martel *et al.*, 1993). Oil-in-water microemulsions are generally transparent, isotropic, clear, and thermodynamically stable. Macroemulsions behave more like a dispersion, whereas microemulsions behave more like a true solution. Thus, microemulsions would be expected to undergo miscible displacement in the pore space of soils and aquifers more effectively than macroemulsions.

“Middle phase” microemulsions as defined by De Bruyn *et al.* (1989; West and Harwell, 1992) are a special category that offer some potential for the removal of NAPL from contaminated porous media. Unfortunately, “middle phase” microemulsions have been shown to be very sensitive to changes in environmental conditions (Shiau *et al.*, 1994). Compared with “middle phase” microemulsions, the microemulsions addressed here are richer in water and more stable with respect to changes in salinity, temperature, surfactant/cosurfactant composition, and amount and type of oil emulsified.

In situ flushing with surfactant-cosurfactant mixtures offers potential for more cost-effective removal of residual NAPL than commonly used strategies such as pump-and-treat for aquifers or by *in situ* flushing with simple W/S solutions. Cosurfactants (low-molecular-weight amphiphilic cosolvents with high water solubility such as isopropanol) are often introduced in order to decrease the tendency of ionic surfactants to be lost by precipitate formation. Solubilization of an amphiphilic molecule such as the cosurfactant pentanol occurs in the palisade layer of surfactant micelles and thus lowers the CMC of the surfactant (Harwell, 1992). The hydrophobic moiety of the cosurfactant increases the solubility of the hydrophobic moiety of the surfactant monomer, thereby increasing the solubility product K_{sp} (Harwell, 1992). Other advantages for microemulsion-enhanced remediation of contaminated soil include NAPL removal with minimal pore volumes of influent, utilization of alcohols such as pentanol with relatively low water solubility and high mobilization efficiency as cosurfactants, and much lower concentrations of alcohol are required than cosolvent flushing technologies (Rao *et al.*, 1991; U.S. EPA, 1991) with water-soluble alcohols.

The quantity of NAPL which can be incorporated by a given W/S/CoS system varies with the specific surfactants and cosurfactants used, the type of NAPL, and the ambient temperature. The composition and extent of the microemulsion regions can be described using a phase diagram such as reported by Martel *et al.* (1993) in which boundaries between microemulsion regions (clear, transparent mixtures) and multiphase regions (turbid NAPL and water mixtures present as macroemulsions) are delineated.

Cosurfactant/surfactant-enhanced remediation of soils utilizes the formation of oil-in-water microemulsions and their subsequent miscible displacement through the pore space. In contrast, most research on aquifer cleanup by surfactant washing has involved macroemulsions and immiscible displacement of oil in water (Martel *et al.*, 1993). Hydrophilic and lipophilic groups of surfactant molecules must be balanced such that the solubility of the surfactant is not too high in either of the immiscible liquids (Harwell, 1992). When solubilization is the enhanced remediation mechanism of choice, one can afford to focus on minimizing surfactant losses when optimizing the selection of a surfactant; however, when mobilization is the enhanced remediation mechanism, developing ultralow interfacial tensions and minimizing surfactant losses must be considered simultaneously. Because most soil mineral surfaces are negatively charged, anionic and nonionic surfactants tend to undergo lower levels of adsorption than cationic surfactants of the same size hydrophobic moiety.

In this investigation, pulses of gasoline-in-water microemulsions were steadily injected into soil columns in order to develop residual levels of gasoline. Microemulsions of leaded (W/S/CoS/LG) and unleaded gasoline (W/S/CoS/UG) were utilized. The recently contaminated soil columns were then sequentially flushed with pulses of saline (NaCl) solution and a water/surfactant/cosurfactant mixture (W/S/CoS) in order to recover the residual LG. *In situ* remediation with a W/S/CoS mixture has the distinct advantage of producing stable, favorable-phase microemulsions of NAPL with very low interfacial tension. Such microemulsions can be miscibly displaced through soil pore space with minimal loss of soil permeability due to clogging of pores.

The objectives for this investigation were fourfold: (1) to examine residual gasoline levels in water-saturated columns of sandy soil following steady injection of gasoline-in-water microemulsions, (2) to evaluate the effectiveness of an aqueous low salt, anionic surfactant/cosurfactant mixture (W/S/CoS) for washing the recently entrapped gasoline and TEL from columns of sandy soil during steady, saturated flow, (3) to investigate the relative behavior of breakthrough curves (BTC) for anionic surfactant, TEL, and gasoline during microemulsion flow through columns of sandy soil, and (4) to evaluate a conceptual view of microemulsion-mediated recovery of gasoline using a simple, empirical convective dispersive (CDE) transport model with a kinetic capture-release mechanism (mobilization) for describing W/S/CoS/UG and W/S/CoS/LG microemulsion transport from gasoline-contaminated soil columns.

EXPERIMENTAL METHODS

Selection/Preparation of a W/S/CoS Mixture and Gasoline In-Water Microemulsions

Although many potential W/S/CoS mixtures are available, the specific one chosen for this work was prepared by mixing 4.3 g of the anionic surfactant sodium

dodecyl sulfate (SDS), 8.7 g of the cosurfactant *n*-pentanol (C₅OH), and 87 g of deionized water. Because the surfactant concentration of 0.15 mol/l exceeded the CMC of 0.00810 mol/l (Heimenz, 1987) by more than 20-fold, losses of SDS by sorption, etc. are not likely to lower concentrations below the CMC in the aqueous phase of the soil. Properties for SDS and *n*-pentanol are presented in Table 1.

A leaded gasoline-in-water (LG/W) microemulsion was prepared using 2 g of leaded aviation gasoline and 98 g of the W/S/CoS mixture. The LG/W microemulsion contained 2% by weight of leaded gasoline. A similar formula was used for making unleaded gasoline-in-water (UG/W) microemulsion except that LG was replaced by UG.

An Optimum Surfactant/Cosurfactant Mixture for Gasoline Recovery from Contaminated Soil

Phase diagrams have been used to optimize the composition of a water/surfactant (SDS)/cosurfactant (*n*-pentanol) mixture designed for the recovery of NAPL (Shiau *et al.*, 1994). Martel *et al.* (1993) have shown that the combination of a surfactant and a cosurfactant (alcohol) is more effective than the use of alcohols or surfactants separately. S/CoS mixtures can be used to solubilize light oils (e.g., gasoline) and chlorinated solvents (e.g., PCE). A schematic pseudoternary diagram (percent by weight of water, oil, and CoS/S ratio) can be used to locate the largest monophasic or microemulsion zone in the water-rich region of the diagram (Martel *et al.*, 1993). The transition from monophasic (microemulsion) to multiple phase or macroemulsion zones is often gradual. Optimum compositions are then selected from within the monophasic or microemulsion zone. Martel *et al.* (1993) state that concentrations and amounts of surfactants in influent injections for site cleanup must be large enough to account for surfactant losses due to adsorption, precipitation, and biodegradation, surfactant dilution (dispersion) at the moving front, and

TABLE 1
Properties of Sodium Dodecyl Sulfate Surfactant (S)
and *n*-Pentanol Cosurfactant (CoS) Used in a W/S/CoS Mixture

Parameter	Surfactant (S)	Cosurfactant (CoS)
Ionic nature	Anionic	Neutral
Formula	CH ₃ (CH ₂) ₁₀ CH ₂ OSO ₃ Na	CH ₃ (CH ₂) ₄ OH
Molecular weight	288	88.15
Critical micelle concentration (CMC)		
In water (mol/l) ^a	0.00810	
In 0.1 M NaCl (mol/l)	0.00139	

^a From Heimenz, 1987.

optimal contact time considering groundwater flow velocity in the water-saturated porous media. Influent concentrations of a specific surfactant should be sufficiently large to maintain local aqueous-phase concentrations greater than the CMC.

In order to choose a specific W/S/CoS mixture, we experimentally determined a pseudoternary phase diagram for water/SDS/pentanol/gasoline systems. The specific mixture was chosen from a water-rich, monophasic region. An SDS/pentanol ratio of 1:2 on a mass basis was maintained.

Flow of LG/W Microemulsion in a Column of Astatula Soil

A glass cylinder with a 4.8-cm inner diameter was used to contain a hand-packed 15.75-cm-long column of Astatula fine sand (Typic Quartzipsamments). The column was placed in a vertical position and initially saturated with a 0.1 M NaCl solution using an upward-flow mode. The saline solution was utilized to prevent the dispersion of clay minerals within the soil. A peristaltic pump was then used to establish steady-state water flow.

When liquid flow in the soil column reached steady state, one pore volume of LG/W microemulsion was pumped through the soil column. This was followed by flushing first with 4.5 pore volumes of a 0.1 M NaCl solution and then with 3.5 pore volumes of a W/S/Co mixture to remove any residual gasoline remaining in the soil column from the LG/W microemulsion. Effluent samples from the column were collected by an automatic fraction collector to analyze gasoline (UV-active components such as aromatic and unsaturated bonds), surfactant, and TEL contents, using a spectrophotometer and a gas chromatograph, respectively. The investigation was performed in a semidark area to avoid the photodecomposition of TEL. Experimental parameters are reported in Table 2.

After flow through the column was terminated, the soil in the column was extracted with hexane and the extracts analyzed for gasoline and TEL residues.

Sorption of SDS in Astatula Soil

In addition to precipitation reactions, sorption onto soil solids may also occur, particularly with hydrous oxides of Fe and Al, which can carry a positive charge at pHs below the PZC. The Astatula C horizon material we used is a coated quartzipsamment, meaning that the quartz sand grains have clay coatings that are cemented with hydrous oxides of Fe and, to a lesser extent, Al. The soil is acidic (pH ~4.5), and its cation exchange capacity is dominated by exchangeable Al. Thus, it was of interest to determine the sorption characteristics of this soil material at concentrations below the CMC.

A sorption isotherm for SDS surfactant was obtained by equilibrating 5 g of oven-dried soil with 10 ml of SDS solution for 24 h. Aqueous suspensions were

TABLE 2
Experimental Parameters for the Displacement
of LG/W and UG/W Microemulsions and
Subsequent Flushings with NaCl and
W/S/CoS Through Soil Columns of 15.75 cm Length

Parameter	Unit	LG/W emulsion	UG/W emulsion
Bulk density (ρ)	mg/m ³	1.6	1.6
Soil water content (ρ)	m ³ /m ³	0.3	0.3
Pore volume (V_0)	cm ³	81.1	82.0
Pore water velocity (v)	m/s	2.303×10^{-5}	1.842×10^{-5}
Gasoline concentration in emulsions (C_{g-in})	kg/m ³	13.26	17.38
Pulse width for Emulsions (P_{em})	PV ^a	1.0	0.95
NaCl concentration in flush ($C_{salt-in}$)	kg/m ³	3.885	3.885
Pulse width for NaCl flush (P_{salt})	PV ^a	4.5	4.5
Surfactant concentration in flush (C_{s-in})	kg/m ³	90.19	90.19
Pulse width for surfactant flush (P_s)	PV	3.5	3.5

^a Pore Volumes.

then centrifuged and the SDS concentration in the supernate analyzed for SDS using the procedure of Motomizu *et al.* (1982). The initial SDS concentrations ranged from 0 to 2.5×10^{-5} M, well below the CMC.

Flow of UG/W Microemulsion in a Column of Astatula Soil

Experimental procedures for the flow of the UG/W microemulsion were similar to that of the LG/W microemulsion flow experiment. A single soil column was used. Experimental conditions for this treatment are given in Table 2.

Concentrations of SDS in effluent samples from the soil columns were determined using the procedure of Motomizu *et al.* (1982).

CONVECTIVE-DISPERSIVE TRANSPORT MODEL FOR MICROEMULSION-MEDIATED TRANSPORT OF GASOLINE IN ASTATULA SOIL

A simple convective-dispersive mathematical model was used to describe the one-dimensional transport of gasoline during steady displacement of a LG/W

microemulsion through water-saturated soil and removal of residual gasoline from soil during flushing with a W/S/CoS mixture. Microemulsion flow was assumed to occur by miscible displacement. A kinetic capture-release or clogging-unclogging mechanism was assumed for gasoline droplets flowing through the soil pore space. Convective-dispersive transport of dispersed gasoline droplets in the microemulsion was described using the differential equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{\rho}{\theta} \frac{\partial(S)}{\partial t} \quad (1)$$

where C represents the concentration of gasoline in the emulsion (kg/m^3), S represents gasoline captured in the soil matrix (kg/kg), v is the Darcy flow velocity (m/s), θ is the volumetric water content (m^3/m^3), ρ is the soil bulk density (kg/m^3), D is the dispersion coefficient (m^2/s), t is time (s), and z is distance (m). The rate of capture-release of gasoline droplets is given as a simple second-order reaction of the Langmuir type

$$\rho \frac{\partial S}{\partial t} = K_1 \left[1 - \frac{S}{S_{\max}} \right] \theta C - \lambda K_2 \rho S \quad (2)$$

where K_1 is the forward rate coefficient (s^{-1}) for clogging of soil pores by gasoline, K_2 is the backward rate coefficient (s^{-1}) for unclogging of pores, S_{\max} is the maximum capture of gasoline droplets for the soil (kg/kg), and λ is a dimensionless empirical parameter with a range from 0 to 1. The condition

$$\lambda = 0 \quad \text{if } C_{\text{surf}} = 0 \quad (3)$$

is imposed, where C_{surf} is the concentration of surfactant (kg/m^3). Otherwise,

$$\lambda = \left[1 - \frac{C}{C_{\text{surf}} R_m} \right] \quad \text{if } C_{\text{surf}} \neq 0 \quad (4)$$

where R_m is the optimum ratio of C/C_{max} (dimensionless) that gives maximum mobilization of gasoline. The transport of Cl and SDS surfactant were treated as conservative solutes in our experimental system, and Equation 1 was altered by removing the third term on the right side.

The boundary condition at the input end of the soil column was

$$C_0 = C - \frac{D}{v} \frac{\partial C}{\partial z} \quad (5)$$

where C_0 is the influent concentration. The boundary condition at the output end of the column was

$$\frac{\partial C}{\partial z} = 0 \quad (6)$$

Equations 1 through 5 provide an empirical mathematical description of three major aspects of our conceptual view for microemulsification-mediated remediation in contaminated soil. These aspects are kinetic behavior of the capture-release of gasoline droplets, the rate of release is directly influenced by the surfactant concentration in the aqueous phase, and the rate of capture is not unlimited. In Equation 2, the forward and backward rate coefficients, K_1 and K_2 , are dynamically modified by the critical ratios S/S_{\max} and C/C_{surf} , respectively.

A Crank-Nicolson finite difference technique was used to numerically solve Equations 1 and 2, subject to the conditions expressed in Equations 3 through 6.

RESULTS AND DISCUSSION

An experimental pseudoternary phase diagram for a water/SDS/pentanol/gasoline system in which the SDS/pentanol mass ratio was 1:2 (Figure 1) was used in this investigation to describe salient features of (1) microemulsions likely to result from the injection of a SDS-pentanol mixture into soil contaminated with gasoline and (2) the flow of gasoline-in-water microemulsions applied to soil columns. This diagram also provided an inexpensive means to select an optimum W/S/CoS mixture for the remediation of soils contaminated with gasoline. The water-rich, monophasic region in the lower left corner of Figure 1 represents microemulsions with favorable phase properties and is of particular interest for *in situ* remediation of soils contaminated with NAPLs. In that region, gasoline occurs as very small droplets ($<0.1 \mu\text{m}$) dispersed in the aqueous phase at concentrations up to several weight percent. The W/S/CoS mixture used here provided LG/W and G/W microemulsions of gasoline-in-water that occur in that region. Actual weight fractions of emulsified NAPL were particularly sensitive to changes in the W:S:CoS ratios.

Adsorption of surfactant molecules onto surfaces of soil particles is one of many mechanisms (Harwell, 1992) by which surfactant concentrations in soil solution can decrease. Sorption of anionic SDS on Astatula soil in the absence of pentanol is shown in Figure 2 for a range of equilibrium concentrations well below the CMC. The term sorption is used here to indicate any mechanism that results in the transfer of SDS molecules from the aqueous phase to the sorbed or immobile phase. The data were fitted to the Freundlich isotherm, $S = KC^n$, by linear regression. The superscript n value was 0.81, and the distribution coefficient K

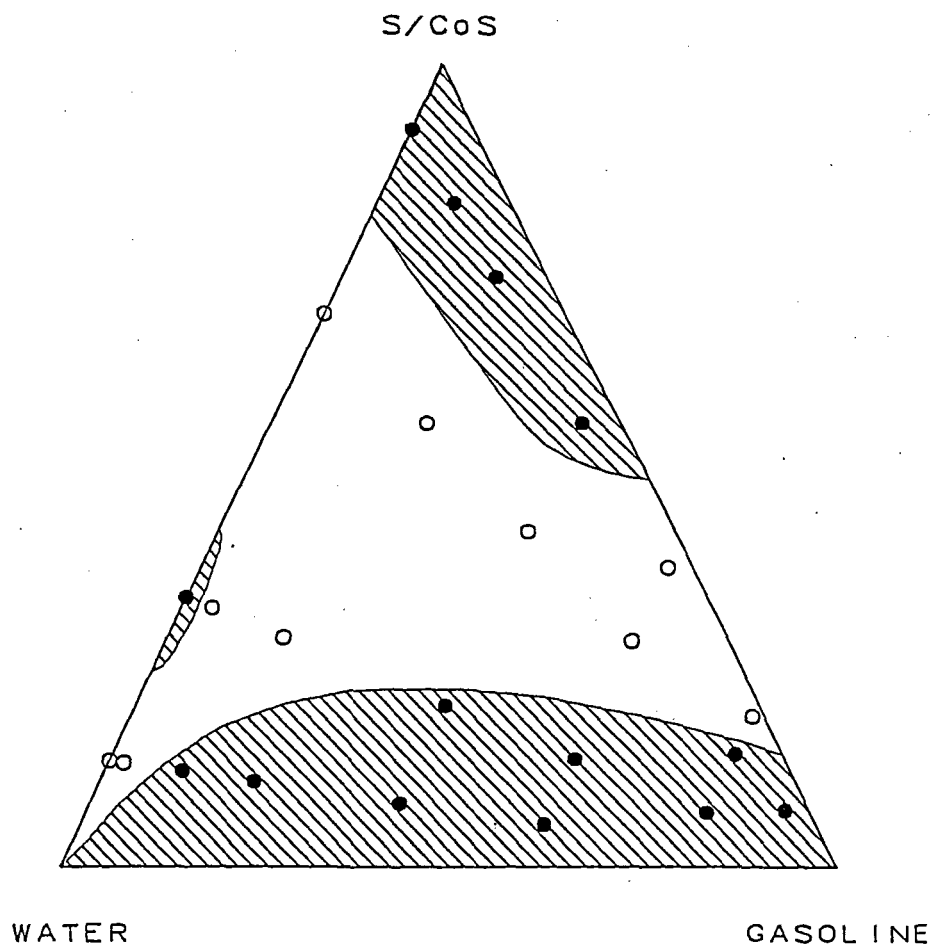


FIGURE 1

Pseudo-ternary phase diagram for a water/SDS/pentanol/gasoline system. Solid and open circles represent data obtained for turbid, multiphase mixtures and transparent microemulsions, respectively. Shaded areas represent monophasic regions. The SDS/pentanol ratio was 1:2 on a weight basis.

value was 3.7 ml/g, with an R^2 of 0.998. The slight convex shape of the isotherm implies that sorption buffering for SDS molecules was greatest at low concentrations in the aqueous phase and increased with increasing concentration. Because the initial SDS concentrations (C_0) for the influent injected into Astatula soil columns was very large compared with the CMC, sorption losses of SDS molecules during steady flow in the columns were not expected to lower local concentrations (C) below the CMC, thus inhibiting microemulsification as the advancing SDS front moved through the relatively short soil columns. The presence of

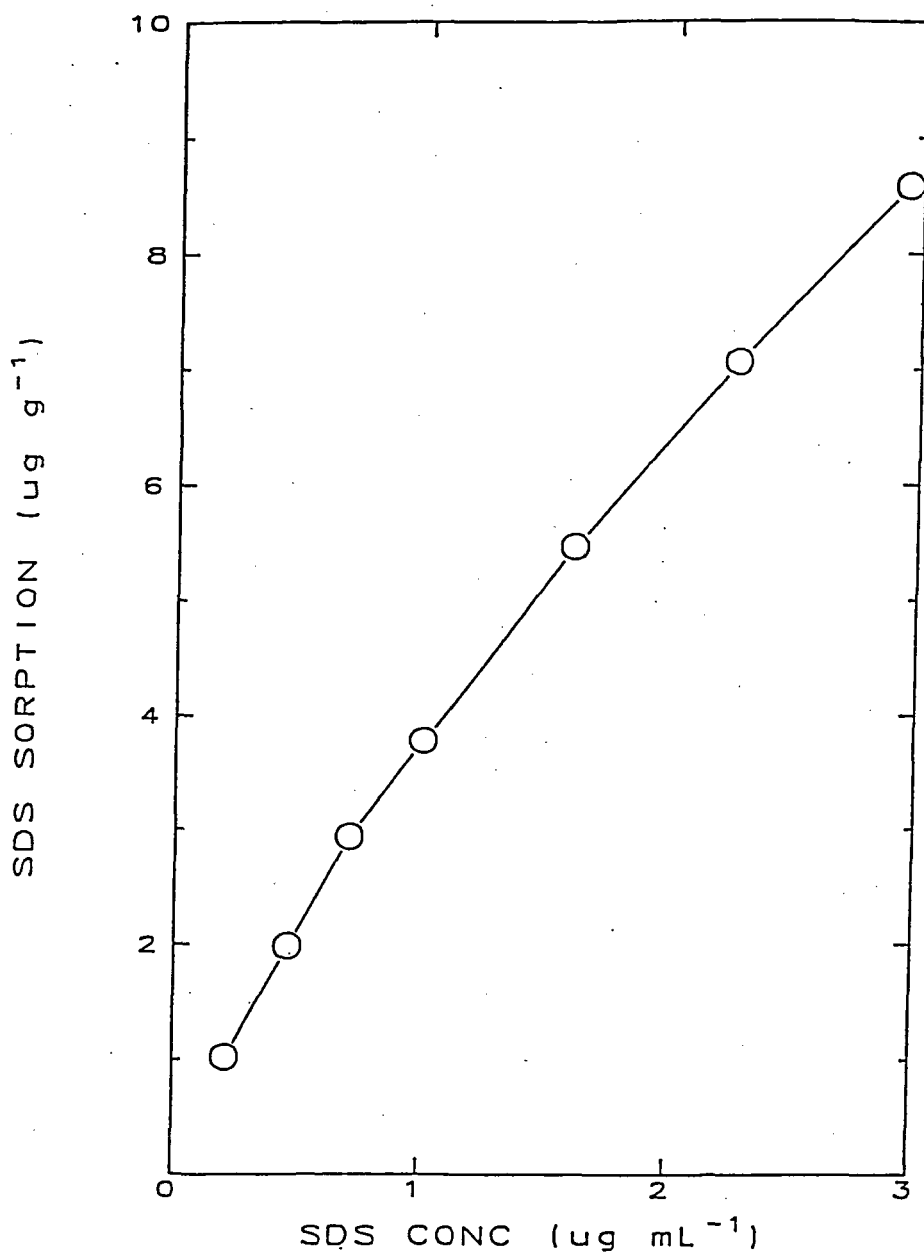


FIGURE 2

SDS surfactant sorption isotherm for Astatula fine sand for a low range of aqueous phase concentrations of SDS.

pentanol reduces the sorption of SDS below that shown in Figure 2, presumably by lowering the surfactant CMC (West and Harwell, 1992).

Equilibration of a W/S/CoS solution containing 5 g of SDS and 5 g of pentanol with Astatula soil at a soil (g):solution (ml) ratio of 1:2 did not result in detectable losses of SDS from solution. Thus, losses of SDS by sorption from W/S/CoS mixtures should have minimal impact upon microemulsification efficiency in this soil.

A convection dispersion equation (CDE) with a rate-limited clogging (capture) and unclogging (release) kinetic process was used to predict breakthrough curves (BTCs) for gasoline (Figures 3 and 4). The relative magnitudes of forward and backward rate coefficients used for the entrapment of gasoline droplets in soil pores (Table 3) implied that unclogging was favored over clogging for the coarse-textured Astatula soil. This would probably not be true for finer-textured soils with a large fraction of the pore space occupied by very small pores.

Observed and model-simulated BTCs for gasoline during displacement of a UG/W microemulsion through the soil column are presented in Figure 3. Using a value for the dispersion coefficient obtained by fitting the BTC for Cl in the column effluent (Table 3), the CDE model predicted the gasoline BTC reasonably well (Figure 3). Values for the input parameters k_1 , k_2 , and S_{\max} (Table 3) for the model were obtained by calibrating the simulation with the observed BTCs. The first gasoline BTC represents gasoline droplets in the column effluent due to simple miscible displacement of gasoline-in-water microemulsion by the 0.1 M NaCl solution. Approximately 94.1% of the gasoline applied in the UG/W microemulsion was detected in the column effluent by the initial flushing with saline solution, leaving only 5.9% as residual gasoline in the soil matrix. The maximum gasoline concentration in the effluent exceeded 90%. This clearly indicates that most of the G/W microemulsion droplets were easily miscibly displaced through most of the sequences of soil pores without major retention by soil surfaces for the Astatula soil used. However, size constrictions in some of the pore sequences resulted in entrapment of probably the largest of the droplets in the microemulsion.

Displacement of the saline solution from the soil column with the W/S/CoS mixture removed all of the entrapped residual gasoline. The second BTC in Figure 3 represents gasoline droplets removed by the W/S/CoS solution. The effective removal of residual gasoline from the soil by flushing with the W/S/CoS solution was attributed to miscible displacement of the resulting microemulsion. Because of the strongly hydrophobic nature of gasoline and very low water solubility for most of its components, gasoline applied to water-saturated mineral soil tends to become entrapped by capillary forces in small pores and sorbed by active soil components such as organic matter and clay minerals. After the residual gasoline has been microemulsified, the small dispersed gasoline droplets with a net negative surface charge can then be readily transported through the large soil pores. Entrapped gasoline underwent solubilization into the hydrophobic core of surfactant micelles to form a stable gasoline-in-water microemulsion. Thus, the processes of solubilization and mobilization during microemulsification resulted in complete removal of the residual gasoline.

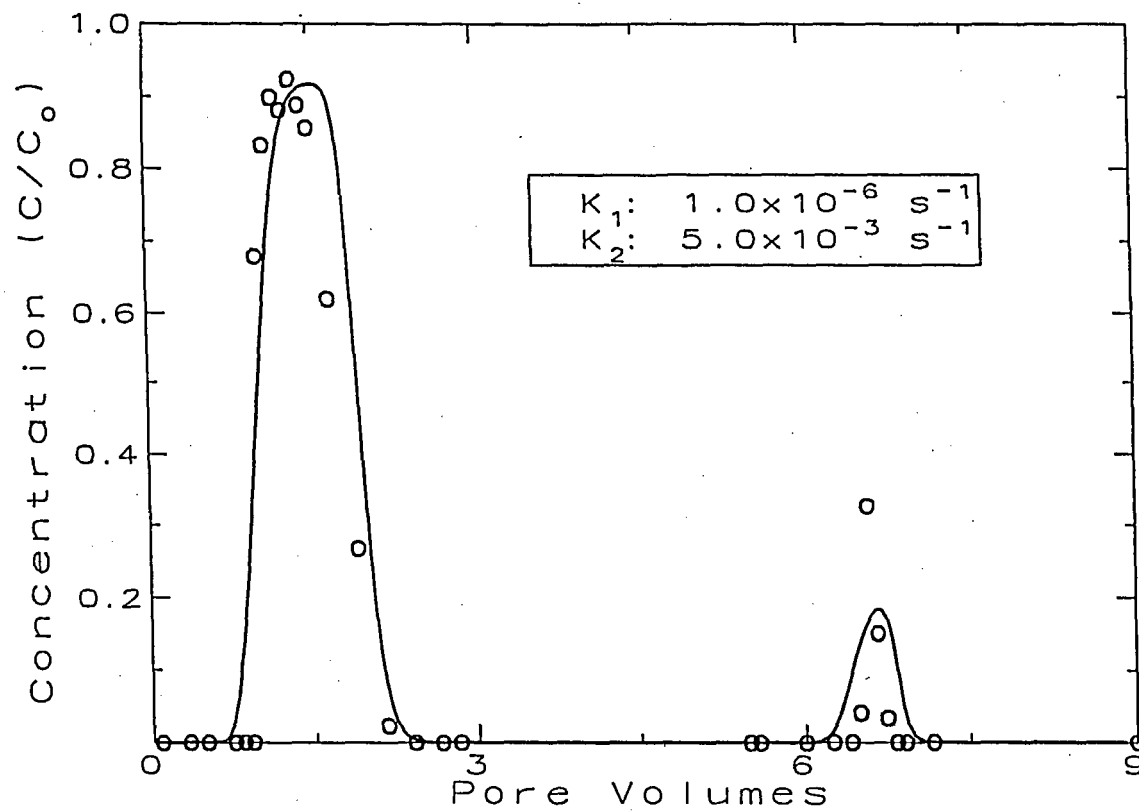


FIGURE 3

Observed and simulated gasoline BTC corresponding to pulsed consecutive flushings with NaCl solution and a W/S/CoS mixture following displacement of a pulse of UG/W microemulsion through a soil column.

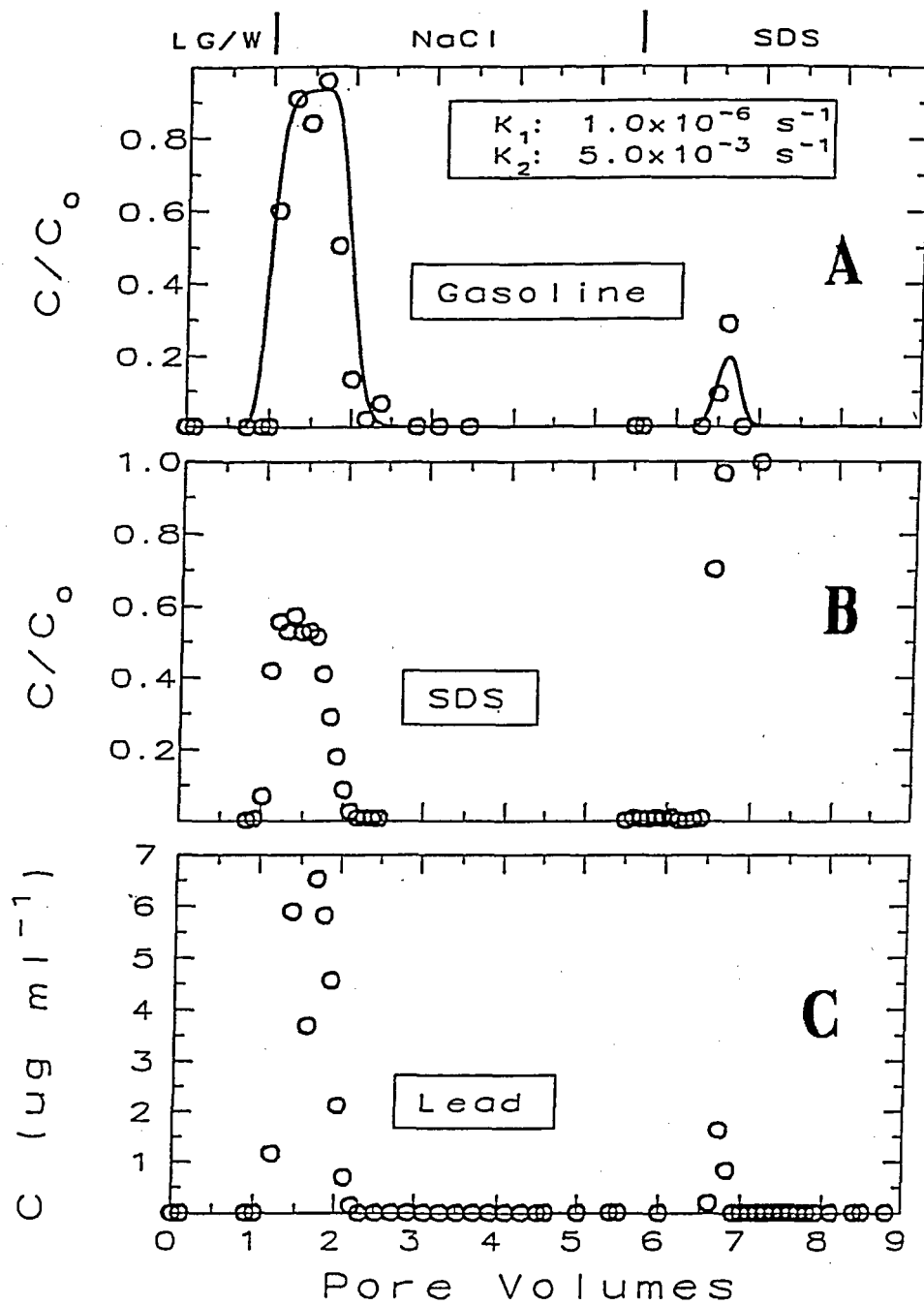


FIGURE 4

Simulated and observed breakthrough curves for gasoline, Pb, and surfactant (SDS) corresponding to sequential flushings with NaCl solution and a micellar W/S/CoS solution following displacement of a pulse of LG/W microemulsion through a soil column.

TABLE 3
Input Parameters for Model Simulations for the Displacement of
LG/W and UG/W Microemulsions and Subsequent Flushings
with NaCl and W/S/CoS Through Soil Columns of 15.75 cm Length

Parameter	Unit	LG/W emulsion	UG/W emulsion
Dispersion coefficient (D)	m ² /s	3.33 × 10 ⁻⁸	3.33 × 10 ⁻⁸
Maximum clogging (S _{max})	kg/kg	100	100
Coefficient for pore clogging (K ₁)	s ⁻¹	1.0 × 10 ⁻⁶	1.0 × 10 ⁻⁶
Coefficient for pore unclogging (K ₂)	s ⁻¹	5.0 × 10 ⁻³	5.0 × 10 ⁻³
Maximum C _{gas} /C _{surf} ratio (R _m)	None	0.04	0.04

Simulated and observed BTCs for gasoline during initial displacement of an LG/W microemulsion by saline solution through the soil column are presented as the first curve in Figure 4. Saline flushing removed approximately 91.6% of the gasoline applied as a LG/W microemulsion, leaving only 8.5% as residual gasoline. As in the UG/W experiment, no residual LG remained in the soil column after flushing with the W/S/CoS mixture.

The gasoline BTC (Figure 4) reveals that the microemulsion produced by the W/S/CoS mixture was able to remove the entrapped gasoline that resisted wash-out by the NaCl solution. Removal of entrapped gasoline from the soil was attributed to uptake by the hydrophobic cores of surfactant micelles to form a gasoline-in-water microemulsion when the S/CoS mixture was applied. As expected, similar gasoline BTCs were obtained for the LG/W (Figure 4) and UG/W (Figure 3) flow experiments.

Initial flushing of a pulse of LG/W microemulsion with saline solution resulted in Pb concentrations as high as 6.5 µg/ml in the column effluent (Figure 4). Pb in the effluent was attributed to the transport of TEL within droplets of leaded gasoline. The BTCs for Pb show that Pb in the LG/W microemulsion solution was removed from the soil column completely. When the column was flushed by the micellar W/S/CoS solution, only small concentrations of Pb were observed in the column effluent and no TEL was found in the soil at the end of the experiment. Areas under the BTCs in Figure 4 indicate that only about 30% of the TEL applied in the LG/W emulsion was recovered by the consecutive flushings with saline and micellar solutions. This low recovery was attributed to sorption and transformation of TEL into the ionic forms, TREL and DEL alkyls and inorganic Pb²⁺ during the experiment (Rhue *et al.*, 1992). Concentrations of the ionic lead alkyls were not determined in the effluent and soil.

The BTC for SDS surfactant in the LG/W microemulsion flow experiment is presented in Figure 4. Location of peaks in the SDS concentration corresponded to NaCl and W/S/CoS flushes and overlapped with maximum concentrations of gasoline and lead in column effluent. The first surfactant BTC corresponds with SDS molecules that were associated with micelles in the applied LG/W microemulsion, while the second surfactant BTC corresponds with the front of SDS applied to the soil as a W/S/CoS solution following the saline flushing.

A simple CDE with a rate-limited clogging and unclogging kinetic process (Table 3) was used to predict the BTC for gasoline. By utilizing a dispersion coefficient obtained from Cl breakthrough curves, the CDE model predicted the gasoline breakthrough curve reasonably well (Figure 4).

SUMMARY

Microemulsification offers a potential means for effective remediation of residual NAPLs from contaminated soils and aquifers. Microemulsions are stable, optically transparent, isotropic systems composed of water, surfactant, cosurfactant, and NAPLs. A properly selected W/S/CoS mixture, when pumped through a porous media containing residual NAPLs, can enhance remediation because the W/S/CoS mixture can microemulsify residual NAPL and transport it by miscible displacement.

The driving force for spontaneous microemulsification is the negative interfacial tension that results from an initial gradient in film pressure across the interface between the two immiscible phases (water and NAPLs). Both the surfactant and cosurfactant orient within the film with their polar groups anchored in the aqueous phase and their hydrocarbon tails extending into the NAPL phase. Curvature of the film occurs until the two film pressures are equal. Droplet diameter in a given microemulsion is quite uniform, generally $<0.1 \mu\text{m}$. In contrast, droplet diameters in a macroemulsion vary widely and can range up to $10 \mu\text{m}$. The smaller droplet diameter and the stability of microemulsions during miscible flow would be expected to impart much less deterioration of soil permeability by the clogging of pores than for the miscible flow of macroemulsions.

A specific microemulsification remediation technique was tested whereby a saline solution (NaCl) and a W/S/CoS mixture was applied sequentially to a soil column for the purpose of removing residual LG and TEL by the formation and miscible flow of a G/W microemulsion. Results from our work show that microemulsification induced by injecting a SDS-pentanol mixture into columns of recently contaminated soil permitted effective recovery of residual gasoline and organolead.

The potential exists for considerably more gasoline or NAPLs in general being microemulsified than can be solubilized by surfactants or cosolvents alone. Microemulsification of dodecane using aqueous mixtures of SDS and water-

insoluble pentanol (P) has been observed to exceed the solubilization of dodecane using either SDS or pentanol alone (Clausse *et al.*, 1987). SDS-pentanol mixtures have been observed to produce microemulsions with a wide range of water and dodecane compositions (Clausse *et al.*, 1987).

The actual success of *in situ* microemulsification under field conditions remains to be tested but will depend on site-specific conditions such as the hydrological/biological properties of the materials used and in-place weathering of residual NAPL. Under field conditions, application of W/S/CoS mixtures to gasoline-contaminated sites should solubilize gasoline in unsaturated soil and move it downward into underlying groundwater. Pumping of the groundwater could then be used to remove the LG/W microemulsion. The SDS surfactant used here has been reported to be nontoxic and microbially degraded rapidly in soils (Anderson *et al.*, 1990).

ACKNOWLEDGMENT

This investigation was partially supported by funds from Tyndall Air Force Base through Environics Task Order Contract No. F08635-90-C-0064 (for Phase 2 of Task 2) entitled "Fate of Lead Alkyls in the Subsurface".

REFERENCES

- Abdul, A. S. and Gibson, T. L. 1991. Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyl from sandy material. *Environ. Sci. Technol.* **25**, 665-671.
- Abelson, P. H. 1990. Inefficient remediation of ground-water pollution. *Science*. **250**, 733.
- Anderson, D. J., Day, M. J., Russell, N. J., and White, G. F. 1990. Die-away kinetic analysis of the capacity of epilithic and planktonic bacteria from clean and polluted river water to biodegrade sodium dodecyl sulfate. *Appl. Environ. Microbiol.* **56**, 758-763.
- Clausse, M., Nicolas-Morgantini, L., Zradba, A., and Touraud, D. 1987. Water/ionic surfactant/alkanol/hydrocarbon systems: influence of certain constitution and composition parameters upon the realms-of-existence and transport properties of microemulsion-type media. In: *Microemulsion Systems*, pp. 15-62. *Surfact. Sci. Ser.* **24**.
- De Bruyn, P. L., Overbeek, J. Th. G., and Verhoeckx, G. J. 1989. On understanding microemulsions: III. Phase equilibria in systems composed of water, sodium chloride, cyclohexane, SDS, and n-pentanol. *J. Coll. Interface Sci.* **127**, 244-255.
- Fetter, C. W. 1992. *Contaminant Hydrogeology*. New York, Macmillan.
- Harwell, J. H. 1992. Factors affecting surfactant performance in groundwater remediation applications. In: *Transport and Remediation of Subsurface Contaminants*, pp. 124-132. (Sabatini, D. A. and Knox, R. C. Eds.) American Chemical Society, Washington, D.C.
- Hiemenz, P. C. 1987. *Principles of Colloid and Surface Chemistry*, p. 815. New York, Marcel-Dekker.
- Imhoff, P. T., Jaffe, P. R., and Pinder, G. F. 1994. An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media. *Water Resour. Res.* **30**, 307-320.
- Mansell, R. S., Ou, L., Rhue, R. D., Cox, R. J., and Tang, S. R. 1992. The Fate and Behavior of Lead Alkyls in the Subsurface Environment. Technical Literature Review (CDRL A013), Final Report

- to Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2693, for Civil Engineering Laboratory, Air Force Civil Engineering Support Agency, Tyndall Air Force Base, FL.
- Martel, R., Gelinis, P. J., Desnoyers, J. E., and Masson, A. 1993. Phase diagrams to optimize surfactant solutions for oil and NDAPL recovery in aquifers. *Ground Water*, **31**, 789-800.
- Motomizu, S., Fujiwara, S., Fujiwara, A., and Toel, K. 1982. Solvent extraction-spectrophotometric determination of anionic surfactants with ethyl violet. *Anal. Chem.* **54**, 392-397.
- Nash, J. H. and Traver, R. P. 1989. Field studies of *in situ* soil washing. In: *Petroleum Contaminated Soils: Volume I. Remediation Techniques, Environmental Fate, and Risk Assessment*, pp. 157-161. (Kostecki, P. T. and Calabrese, E. J., Eds.) Chelsea, MI, Lewis Publishers.
- Ou, L.-T., Jing, W., and Thomas, J. E. 1995a. Degradation and metabolism of tetraethyllead in soils. *J. Ind. Microbiol.* **14**, 312-318.
- Ou, L.-T., Jing, W. and Thomas, J. E. 1995b. Biological and chemical degradation of ionic ethyllead compounds in soil. *Environ. Toxicol. Chem.* **14**, 545-551.
- Rao, P. S. C., Lee, L. S., and Wood, A. L. 1991. Solubility, Sorption, and Transport of Hydrophobic Organic Chemicals in Complex Mixtures. R. S. Kerr, Environmental Research Laboratory, U.S. Environmental Protection Agency. Ada, OK, EPA/600/M-91/009.
- Rhue, R. D., Mansell, R. S., Ou, L.-T., Cox, R., Tang, S. R., and Ouyang, Y. 1992. The fate and behavior of lead alkyls in the environment: a review. *CRC Crit. Rev. Environ. Control*, **22**, 169-193.
- Shiau, B. J., Sabatini, D. A. and Harwell, J. H. 1994. Solubilization and microemulsification of chlorinated solvents using direct food additive (edible) surfactants. *Ground Water*. In press.
- Taylor, K. C. and Hawkins, B. F. 1992. Emulsions in enhanced oil recovery. In: *Emulsions, Fundamentals And Applications in the Petroleum Industry*, pp. 263-293. (Schramm, L. L., Ed.) Washington, D.C., Advances in Chemistry 231, American Chemical Society.
- U.S. EPA. 1991. *In-situ* solvent flushing. EPA/540/2-91/021. Washington, D.C., Office of Emergency Response, U.S. Environmental Protection Agency.
- West, C. C. and Harwell J. H. 1992. Surfactants and subsurface remediation. *Environ. Sci. Technol.* **25**, 2324-2330.