♻EPA ENVIRONMENTAL RESEARCH BRIEF

COMPLEX MIXTURES AND GROUNDWATER QUALITY

M.L. Brusseau*

INTRODUCTION

The occurrence of organic chemicals in soil and groundwater has become an issue of great interest and import. Concomitantly, research on the transport and fate of organic contaminants in subsurface environments has expanded greatly in recent years. Much of this research has been focused on dissolved constituents in aqueous systems. However, the behavior of "complex mixtures" is beginning to receive increased attention. By complex mixture we mean any system other than the simple system of water containing a single solute. Examples of pertinent problems involving complex mixtures include the transport of oxygenated gasoline in the subsurface, the dissolution of diesel fuel and coal-tar, and the use of chemical agents such as surfactants or solvents to enhance the removal of contaminants by pump-and-treat remediation. A discussion of these few selected examples will serve to highlight some of the issues associated with complex mixtures, with a focus on potential groundwater contamination and remediation.

COMPLEX MIXTURES AND SUBSURFACE CONTAMINATION

Miscible Organic Liquids and Alternative Fuels

Concern about air pollution and the dependency on foreign sources of oil has led to major programs promoting the use of alternative fuels in the U.S.A. Currently, oxygenates, either neat or as additives, appear to be the principal alternative fuel

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candidates (Haggin, 1989). Of the oxygenates, methanol and ethanol are the primary miscible compounds in use (Hanson, 1991). The advent of alternative fuels has fomented increased interest in the transport and fate of miscible organic liquids in the subsurface. It has also increased interest in the effects of these liquids on the transport and fate of other contaminants.

1. Transport and Fate of Miscible Organic Liquids in the Subsurface

The sorption of miscible organic liquids by soil is generally extremely low. Little sorption is expected for compounds such as methanol and ethanol because of their polarity and large (infinite) aqueous solubility. The minimal sorption of alcohols has been widely demonstrated in the chromatography literature. Limited data for soil systems has also shown negligible sorption of alcohols (cf., Garrett et al., 1986; Wood et al., 1990). Hence, these compounds will be minimally retarded and will travel through the subsurface at essentially the velocity of water. This large mobility can be a useful characteristic. For example, alcohols may be useful as an "early warning" sign of the impending arrival of a contaminant plume emanating from a fuel spill. In regard to the use of alcohols for in-situ soil washing, the greater mobility means that an injected pulse of alcohol may be able to overtake a plume of a retarded solute.

Alcohols such as methanol have been reported to be biodegradable under both aerobic and anaerobic conditions (cf., Colby et al., 1979; Lettinga et al., 1981; Novak et al., 1885). However, the concentrations of alcohol at which biodegradation occurred were less than 1%. Large concentrations (> 10%) of alcohol are generally considered to be toxic to most microorganisms and therefore not biodegradable.

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2. Effect of Miscible Organic Liquids on the Subsurface Environment

The addition of a miscible organic liquid, such as methanol, to water results in a reduction of surface tension. For example, surface tension is reduced by approximately one-half in systems containing 5% acetone (Paluch and Rybska, 1991) or 50% methanol (Wells, 1981). Very large reductions in interfacial (liquid-liquid) tension are required to mobilize immiscible liquids trapped in porous media (Puig et al., 1982). Using the surface tension data as a guide, cosolvents will probably not produce such large reductions in interfacial tension. Thus, the presence of a cosolvent is not expected to produce emulsions or to mobilize residuals of immiscible liquids.

The presence of organic liquids has been shown to cause shrinking of clay materials and of soils consisting of large portions of clay. For example, clay materials have been demonstrated to shrink (in relation to status in aqueous system) with the addition of acetone or ethanol (Green et al., 1983; Brown and Thomas, 1987; Chen et al., 1987). This shrinkage can result in an increase in hydraulic conductivity (Brown and Thomas, 1987). Thus, it is possible that the presence of large concentrations of cosolvent could cause shrinking and cracking of subsurface domains containing large fractions of clay. This perturbation may alter the hydraulic conductivity and, thereby, affect fluid flow and solute transport.

The presence of organic liquids can also affect the properties of naturally occurring organic components of the soil. It is well known in polymer science that organic liquids can cause organic polymers to swell. The degree of swelling is dependent upon the properties of the solvent (polarity) and of the polymer (type, structure). The addition of an organic liquid has been shown to cause natural organic materials to swell (Freeman and Cheung, 1981; Lyon and Rhodes, 1991). One potential effect of the swelling of organic matter associated with the subsurface solid phase is a reduction in permeability due to blockage of pores. Given the relatively small content of organic matter associated with most subsurface materials, this effect will probably not lead to a measurable reduction in permeability in most cases. Another potential effect is the dissolution of components (e.g., humic or fulvic acids) from the solid-phase organic matter. A great deal of research has been reported describing the effect of dissolved organic matter on the solubility, sorption, and transport of organic and inorganic compounds. There is a possibility that large concentrations of cosolvents could extract organic material from the soil, and that this dissolved organic matter could affect the transport of contaminants. This effect will probably be of importance for limited conditions, i.e., for systems with high organic-carbon content soils and highly hydrophobic compounds.

Another potential effect of the swelling of organic matter is the enhanced release of organic compounds (contaminants) residing in the matrix of organic matter. It is generally accepted that the organic fraction of soil is the predominant sorbent for low-polarity organic compounds. It is likely that sorbed organic compounds reside in internal as well as external domains of the organic matter. It is quite possible that high concentrations of cosolvents could enhance the release of organic contaminants retained within the organic phase. The swelling of the organic matrix with the addition of a cosolvent allows greater diffusive mass transfer and, thus, enhances the release of sorbed

compounds (Freeman and Cheung, 1982; Brusseau et al., 1991a). This concept is used in analytical chemistry in terms of solvent extraction of contaminated soils. This is discussed in more detail in the following section.

As previously mentioned, large concentrations (> 10%) of alcohol are generally considered to be toxic to most microorganisms. Hence, it is possible that a release of a fuel containing large concentrations of alcohol could deleteriously affect the subsurface biota. The potential effect of large concentrations of alcohols on microbial communities in the subsurface appears to have received minimal attention.

3. Effect of Miscible Organic Liquids on the Transport and Fate of Organic Contaminants in the Subsurface

The influence of an organic liquid (cosolvent) on the solution-phase activity of organic compounds is dependent upon the nature of the solute and of the solvent-cosolvent system. For many of the systems of environmental interest, water is the solvent, the cosolvent is less polar than water, and the solutes are of relatively low polarity. For this case, the addition of a cosolvent tends to increase the amount of solute that can reside in solution under equilibrium conditions. A simple relationship describing the influence of cosolvent on the solubility of a solute in the mixed-solvent system is the log-linear cosolvency model (Yalkowsky et al., 1972)

$$\log S_m = \log S_w + \sigma f_c \qquad (1)$$

where S is the solubility in water (w) and mixed-solvent (m), σ represents the cosolvency power of the cosolvent expressed as the slope of the solubilization profile (i.e., log solubility versus f_c), and f_c is the volume fraction of organic cosolvent.

Given that the sorption of low-polarity organic compounds by soils, sediments, and aquifer materials ("soil") is considered to be driven primarily by an entropic, solute-solvent interaction process, it is expected that the presence of a cosolvent should significantly affect sorption. A log-linear cosolvency model, relating the equilibrium sorption constant (K_p) to the volume fraction of cosolvent, for sorption of organic solutes from binary mixed solvents has been presented in the chromatography and soil science literature (Dolan et al., 1979; Rao et al., 1985). This equation is:

$$\log K_{p,m} = \log K_{p,w} - \alpha\sigma f_c \qquad (2)$$

where $K_{p,m}$ and $K_{p,w}$ are the equilibrium sorption constants (ml g^{-1}) for the mixed-solvent and aqueous systems, respectively, and α is an empirical constant that represents any deviation of the sorption-f_c functionality from that observed for solubilization. The latter term is generally considered to represent solvent-sorbent interactions.

The decrease in K_p caused by addition of a cosolvent results in a reduction in retardation (i.e., retardation factor, R, = 1 + $(\rho/\theta)K_p$ where ρ and θ are soil bulk density and volumetric water content, respectively). The cosolvency effect has been demonstrated by experiment to cause a decrease in the sorption and retardation of many organic solutes (cf., Nkedi-Kizza et al., 1985; 1987; 1989; Fu and Luthy, 1986; Wood et al.,

1990; Brusseau et al., 1991a). An example of this effect is shown in Figure 1, where log K_p values obtained for sorption of anthracene by a sandy soil are plotted versus volume fraction of methanol (Figure 1A). The effect of methanol on the transport of anthracene in a column packed with the sandy soil is shown in Figure 1B.

The discussion of the cosolvency effect presented above was focused on low-polarity organic compounds. A number of environmentally important compounds, however, are ionizable acids or bases (e.g., phenols, amines). The impact of organic cosolvents on the sorption of ionizable organic solutes has received very little attention to date. The decreases in sorption of ionizable solutes, present in the neutral form, obtained with increasing fraction of cosolvent were similar to those observed for nonionizable solutes (Fu and Luthy, 1986; Lee et al., 1991), as might be expected. In these cases, however, the system pH was fixed. The impact of cosolvents on sorption of ionizable solutes in systems where pH is not controlled is of great interest, considering the effect organic cosolvents can have on the pH of the system and on the pK_a of the solute. The pK_a of an ionizable solute changes with the composition of the solvent because of the so-called medium effect, which results from differences in solvent-solvent and solute-solvent interactions (cf., Bates, 1969). The pK_a value of an organic acid will increase with increasing fraction of cosolvent (cf., Parsons and Rochester, 1975; Rubino and Berryhill, 1986), while that of an organic base will decrease (cf., Gowland and Schmid, 1969). Observe that for both cases, the shift in pK_a promotes formation of the neutral species. This shift in speciation could significantly affect the nature and magnitude of sorption.

To illustrate the impact of cosolvent on transport of ionizable solutes, breakthrough curves obtained for pentafluorobenzoate in water and methanol systems are compared in Figure 2. Note

that no sorption is observed for the aqueous system and that the retardation factor is, therefore, 1. No sorption of pentafluorobenzoate is expected since it is in the anionic form under the experimental conditions. The fact that sorption is essentially nonexistent for many organic acids under conditions typical to the subsurface ($pK_a \ll pH$; net negative surfaces) has fomented the use of these organic acids as groundwater tracers. In contrast, R is greater than 1 for the methanol system. This change in R would negate the use of pentafluorobenzoate as a tracer to delineate the velocity of fluid flow. The increase in retardation with addition of an organic cosolvent has also been observed for other acids such as dicamba, 2,4-dichlorophenoxyacetic acid, and chlorophenols (Hassett et al., 1981; Brusseau, 1990; Lee et al., 1993). This phenomenon may be important at waste-disposal sites, where ionogenic chemicals may co-exist with organic solvents.

In comparison to the amount of research devoted to the effect of cosolvents on solubility and equilibrium sorption of organic contaminants, there has been little work reported on the impact of cosolvents on nonequilibrium sorption of organic solutes. A decrease in the asymmetry of breakthrough curves with increasing volume fraction of cosolvent was reported by Nkedi-Kizza et al., (1987), who were investigating the transport of two herbicides (diuron and atrazine) in columns packed with a sandy soil. Breakthrough-curve asymmetry, which was attributed by the authors to nonequilibrium sorption, decreased with increasing cosolvent content suggesting that the rate of sorption is greater in the presence of a cosolvent. The sorption of dioxins by soils from water/methanol mixtures was observed to be more rapid at higher methanol contents (Walters and Guiseppi-Elie, 1988). The desorption rate constant (k_2) has been observed to increase with increasing fraction of cosolvent (Nkedi-Kizza et al., 1989; Shorten and Elzerman, 1990; Brusseau et al., 1991a; Lee et al., 1991).
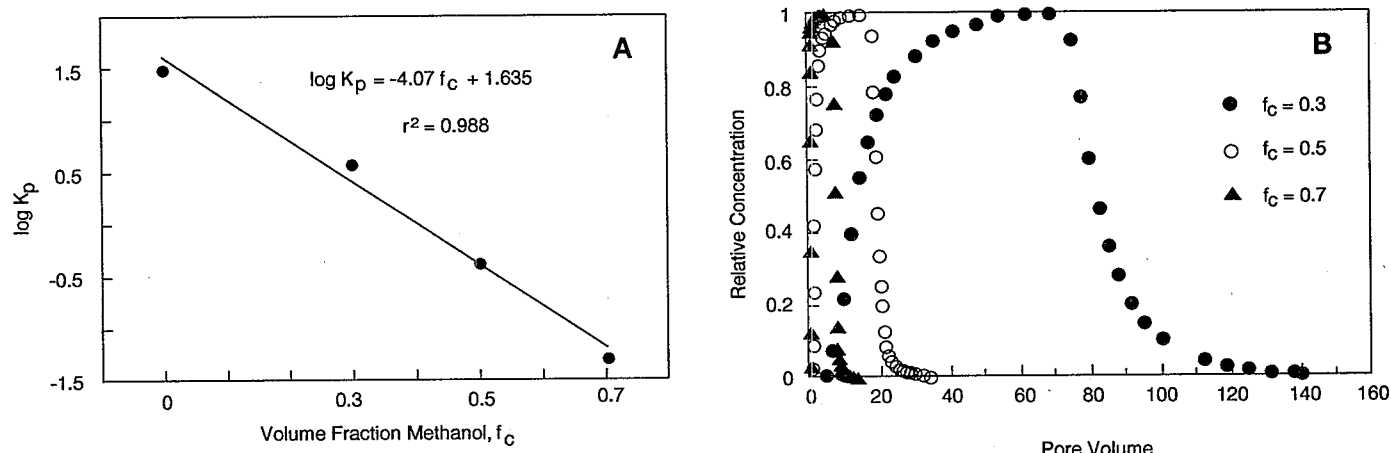

Figure 1. The influence of methanol on the sorption and transport of anthracene in a Eustis sand; A) the log-linear relationship between the equilibrium sorption constant (K_p) and volume fraction of cosolvent (f_c). B) The influence of cosolvent on the retardation and transport of anthracene. Data from Brusseau et al., 1991a.
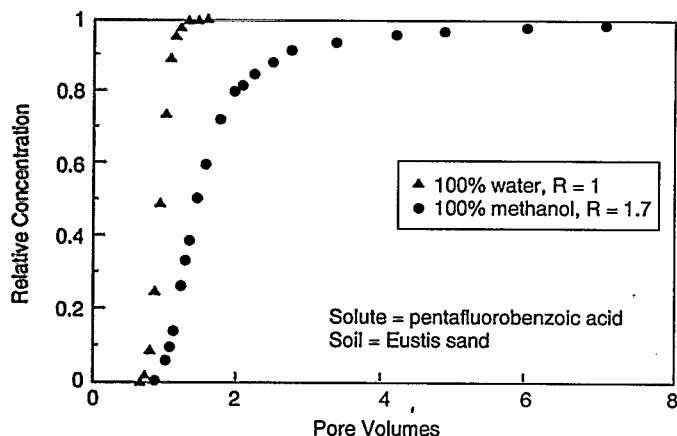
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Figure 2. The effect of methanol on the transport of an organic acid (pentafluorobenzoate) in a sandy soil; data from Brusseau 1990.

A quantitative investigation of the impact of organic cosolvents on nonequilibrium sorption of organic solutes was presented by Brusseau et al. (1991a). They presented a model that predicts a log-linear relationship between k_2 and f_c:

$$\log k_{2,m} = \log k_{2,w} + \phi f_c \qquad (3)$$

where $k_{2,m}$ and $k_{2,w}$ are the reverse sorption-rate constants for the mixed-solvent and aqueous systems, respectively; $\phi = a\alpha\sigma$; and a is the slope of the linear relationship between $\log k_{2,w}$ and $\log K_{p,w}$. The validity of this model was substantiated using experimental data. Examples of their results are presented in Figure 3. The mechanism responsible for the cosolvency effect on sorption kinetics was postulated to involve changes in conformation of the organic carbon associated with the sorbent. These conformational changes were induced by the changes in solvent polarity that resulted from the addition of a cosolvent.

The concentrations of cosolvent required to produce substantial enhancement in solubility and reduction in sorption are relatively large (% level) for many solutes of interest. Thus, it has been difficult to envision scenarios wherein cosolvency could be important. The use of oxygenated and alternative fuels, however, has presented cases where cosolvency could be very important. For example, the presence of the cosolvent in alternative fuels (e.g., 50% methanol, 50% gasoline) could enhance the transport of the gasoline constituents contained in the fuel, thus increasing the potential for groundwater contamination resulting from a spill. In any case, the effect would probably be limited to the region near the spill (i.e., the near-field domain).

Immiscible Liquids: Multi-Component Systems, Dissolution Kinetics, and Transport of Co-Solutes

The disposition of immiscible organic liquids in the subsurface is of interest to environmental scientists, hydrologists, environmental/civil engineers, and petroleum engineers. The vast majority of research performed by these groups has focused on the movement, entrapment, and displacement of the liquid (cf., Marle, 1981; Schwille, 1988). This reflects concerns associated with petroleum-reservoir engineering as

well as remediation of solvent- and petroleum- contaminated sites. Other aspects that have begun to receive attention are the dissolution of residual immiscible phases, including the partitioning behavior of multi-component liquids and the rate of mass transfer to the aqueous phase, and the effect of immiscible liquids on the transport of co-solutes.

1. Transport, Entrapment, and Dissolution of Immiscible Organic Liquids in the Subsurface

The movement, entrapment, and mobilization of immiscible organic liquids in porous media has been the focus of a tremendous research effort. Entire volumes have been published on this subject and there is no need to reproduce this material. Instead, the dissolution of immiscible organic liquids, a topic that has received less attention, will be briefly discussed.

Mass transfer of a constituent between two liquids can be represented by (Cussler, 1984):

$$\partial C_r/\partial t = k_r (K_r C_m - C_r) \qquad (4)$$

where C_r and C_m are the concentrations of the solute in the residual and aqueous phases, respectively; K_r is the liquid-liquid partition coefficient; k_r is the mass-transfer constant (1/T); and t is time (T). The appropriate driving force for mass transfer is the difference between the actual solute concentration in the residual phase and that attained at equilibrium ($K_r C_m$) (Cussler, 1984). Equation 4 is based on a macroscopic approach and the mass transfer term is a global parameter. Microscopic approaches where mass transfer across individual interfaces is explicitly simulated have also been developed. This latter approach, however, is constrained by the difficulty of specifying the nature and magnitude of the interfaces present in the system.

Consideration of the kinetics of dissolution of residual phases of immiscible organic liquids is a departure from the majority of models developed for multi-phase systems, which are based on instantaneous attainment of equilibrium between residual and water phases. The results of several laboratory experiments have suggested that mass transfer between immiscible liquid and water is relatively rapid (cf., van der Waarden et al., 1971; Fried et al., 1979; Schwille, 1988; Miller et al., 1990). Other investigations, however, have shown that liquid-liquid transfer can be significantly rate-limited, especially under conditions that may be found in the field (cf., Hunt et al., 1988; Powers et al., 1991; Brusseau, 1992a). Thus, the use of the equilibrium assumption for mass transfer in the development of mathematical models is still open to question. Much additional research is needed in this area to identify the conditions under which dissolution will be rate limited and the local equilibrium assumption is not valid. Liquid-liquid mass transfer in heterogeneous porous media is of special concern.

2. Partitioning of Multi-Component Liquids

While some of the most widely studied immiscible liquids are composed of a single component (e.g., trichloroethene), many others (e.g., gasoline, diesel fuel, coal tar) are multi-component liquids. Knowledge of the partitioning behavior of multi-component liquids is essential to the prediction of their impact on groundwater quality. The partitioning of components into
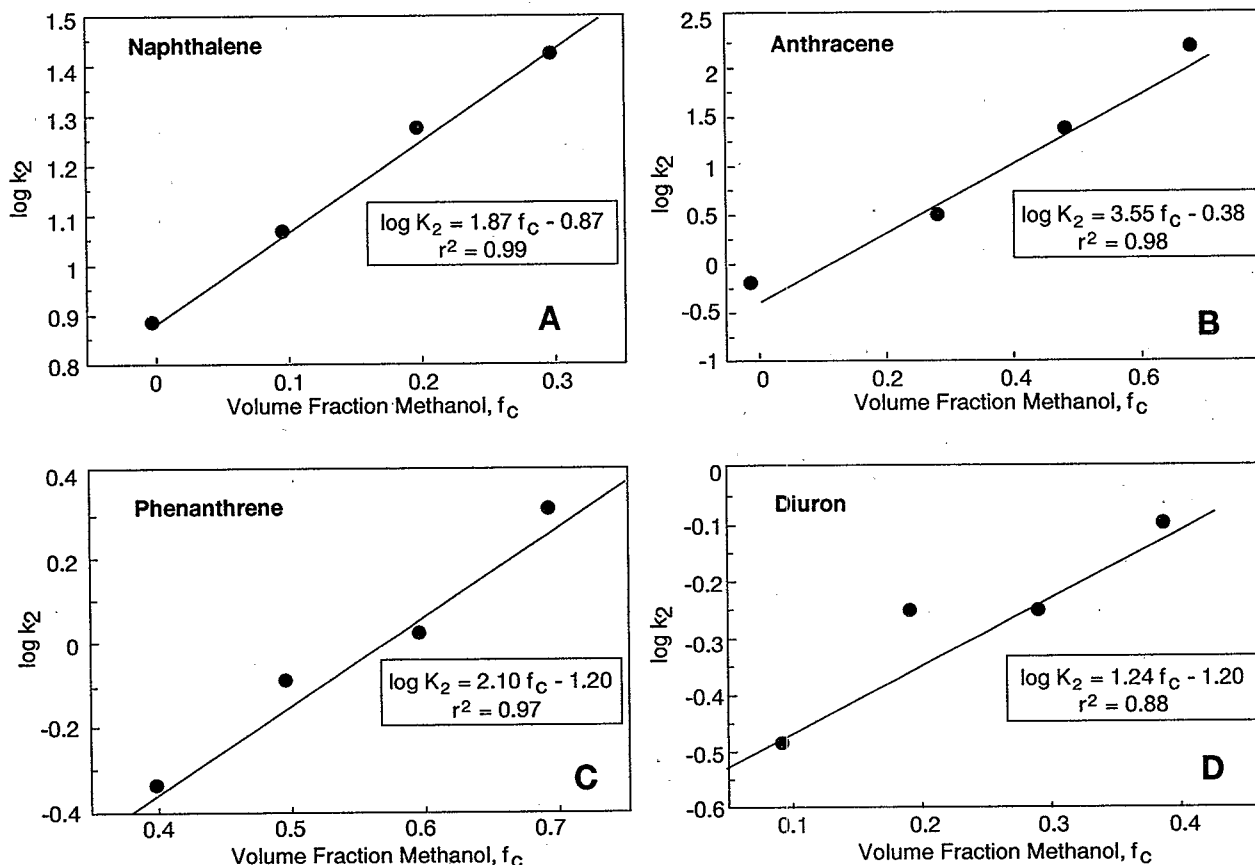
Figure 3. The effect of methanol on the reverse sorption rate coefficient (k_2); figure adapted from Brusseau et al., 1991a.

water is controlled by the aqueous solubility of the component and the composition of the liquid. A simple approach to estimating partitioning involves an assumption of ideal behavior in both aqueous and organic phases and the application of Raoult's law:

$$C^w_i = X^o_i S^w_i \qquad (5)$$

where C^w_i is aqueous concentration (mol/l) of component i, S^w_i is aqueous solubility (mol/l) of component i, and X^o_i is mole fraction of component i in the organic liquid. The liquid-liquid partition coefficient, K_i, is given by:

$$K_i = C^o_i/X^o_i S^w_i \qquad (6)$$

where C^o_i is concentration (mol/l) of i in the organic liquid and where C^o_i/X^o_i is equivalent to the inverse of the molar volume of the organic liquid. The Raoult's law-based approach has been used successfully to predict aqueous-phase concentrations of gasoline (or partition coefficients) for gasoline (Cline et al., 1991), diesel fuel (Lee et al., 1992a), and coal-tar (Lee et al., 1992b) systems (see Figure 4). One result of this and other work (Banerjee, 1984; Picel et al., 1988; Vadas et al., 1991) is that it appears that many multi-component liquids can be approximated as ideal mixtures.

3. Effect of Immiscible Liquids on Solute Transport.

The impact of immiscible liquids present as a separate phase on the sorption and transport of organic solutes was evaluated by Brusseau (1990). An analysis of experimental data obtained from systems where an immiscible liquid (e.g., toluene) was the mobile phase showed that the retardation of organic solutes (e.g., benzene) was near unity and much lower than that which would be obtained with water as the solvent. This enhanced transport by mobile immiscible liquids is to be expected based upon the relative solubilities of low-polarity organic solutes in organic liquids and water.

The opposite effect is observed, however, when the immiscible liquid is present as a fixed residual phase. The residual phase serves as a sink for organic solutes, resulting in enhanced retention and retardation. For example, the presence of a residual phase of aviation gas was observed to increase retention of petroleum constituents (e.g., toluene) in columns packed with an aquifer material (Bouchard et al., 1989). The presence of residual petroleum or PCB oils was shown to increase the sorption of pentachlorophenol, toluene, and 2-chlorobiphenyl (Boyd and Sun, 1990). A large increase in retardation of naphthalene was observed when a residual phase of tetrachloroethene was emplaced in a column packed with
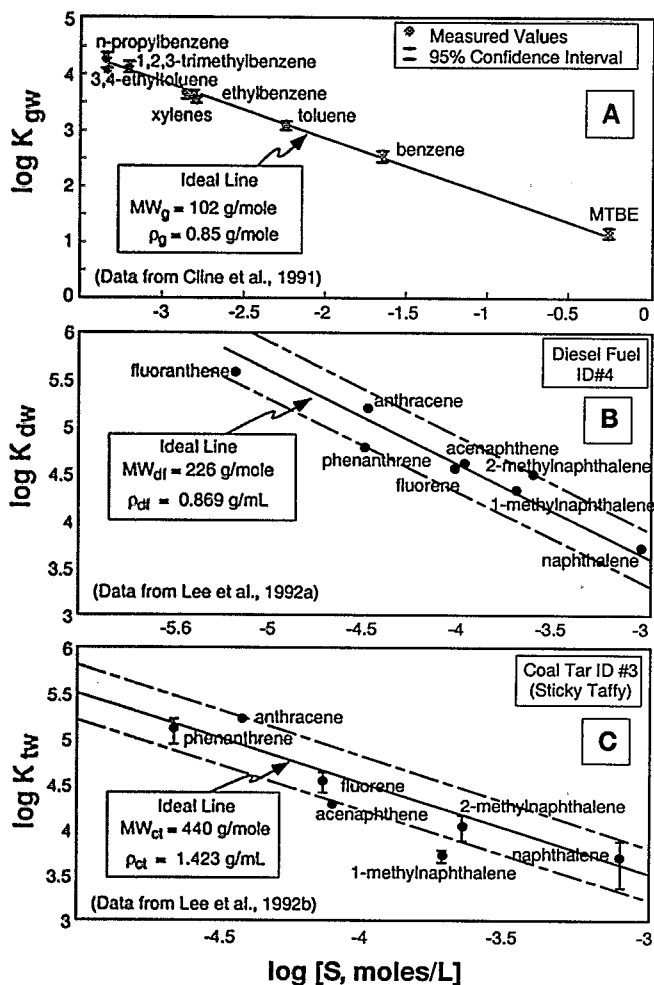
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Figure 4. Comparison of data obtained from multi-component partitioning experiments to ideal behavior predicted by use of Raoult's Law. A) Gasoline system, data from Cline et al., 1991; B) Diesel Fuel system, data from Lee et al., 1992a; C) Coal Tar system, data from Lee et al., 1992b. S is aqueous solubility of the compound, K_{tw}, K_{dw}, and K_{gw} are the equilibrium partition coefficients of the compounds for distribution between the organic and aqueous phases.

When multiple contaminants are present in solution, a primary question to be addressed is the occurrence of antagonistic or synergistic interactions among the solutes, and between the solutes and the solid and aqueous phases. The presence of a cosolute at high concentrations can affect the behavior of organic compounds in several ways, resulting in the following three phenomena: (1) competitive sorption; (2) cooperative sorption; and (3) cosolvency. The first and third phenomena reduce sorption and thus enhance the transport of solutes, whereas cooperative sorption has the opposite effect. A potential source of these multi-contaminant solutions is the dissolution of immiscible liquids into water residing in or entering the subsurface. the relatively slow movement of water in the subsurface creates the possibility of relatively high solute concentrations (e.g., near X^o_i S^w_i limit) in the vicinity of the immiscible liquid phases.

Competitive sorption, where sorption of a solute is reduced by the presence of a co-solute, has been investigated by several researchers and their results have generally shown no competition for nonionic, low-polarity organic solutes such as naphthalene and chlorinated benzenes (cf., Karickhoff et al., 1979; Chiou et al., 1983). Indeed, non-competition is considered a defining characteristic of the sorption of nonionic, low-polarity organic solutes by a "partitioning" mechanism (Chiou et al., 1983). However, some researchers have reported relatively small decreases in sorption resulting from competition (MacIntyre and deFur, 1985; Abdul and Gibson, 1986; McGinley et al., 1989). The vast majority of studies on sorption in multi-solute systems have used sorbents with relatively high organic-carbon contents (i.e., greater than 0.1 %). Conversely, few studies have been reported for systems comprised of sorbents containing small organic-carbon contents, which are representative of many sand aquifers. The sorption of trichloroethene and p-xylene from single and binary solute solutions by two organic-carbon-poor aquifer materials was examined by Lee et al. (1988). They observed no difference in sorption between the single and binary systems. The sorption of trichloroethene by a sandy aquifer material in single and ternary solute systems was observed by Brusseau and Rao (1991) to be essentially identical.

Cooperative sorption, where sorption of nonionic, low-polarity organic solutes is enhanced by the presence of other nonionic, low-polarity organic solutes, has been studied by few researchers. Brusseau (1991) investigated the effect of a nonionic, low-polarity cosolute (tetrachloroethene) on the sorption of three nonionic, low-polarity organic chemicals (naphthalene, p-xylene, 1,4-dichlorobenzene) by two aquifer materials with small organic-carbon contents (< 0.03 %). In all cases, the sorption of the primary solute was enhanced by the presence of high concentrations of tetrachloroethene. Equilibrium sorption constants measured in binary-solute systems were 1.5 to 3 times larger than those measured for the single-solute systems. Hence, tetrachloroethene had a synergistic (i.e., cooperative), rather than an antagonistic (i.e., competitive), effect on the sorption of the primary solutes. The enhanced sorption was postulated to result from sorbed tetrachloroethene increasing the effective organic carbon content of the sorbent. Enhanced sorption was observed by Onken and Traina (1991) in recently reported experiments that used synthetic organo-clay complexes. They examined the sorption of pyrene by $CaCO_3$ treated with humic acid to obtain an organic carbon content of 0.003%. The sorption of pyrene in a binary

aquifer material (Brusseau, 1990). A mathematical model describing the effect of immobile immiscible organic phases on the transport of solutes was presented by Brusseau (1992a). The model was used to predict the transport of toluene in a column packed with an aquifer material contaminated with a residual of aviation gas (data reported by Bouchard et al., 1989). The simulated prediction produced with the model provided a good description of the data (see Figure 5). Based on these investigations, it appears possible that residual phases of immiscible organic liquids can serve as long-term sinks and sources for organic solutes.
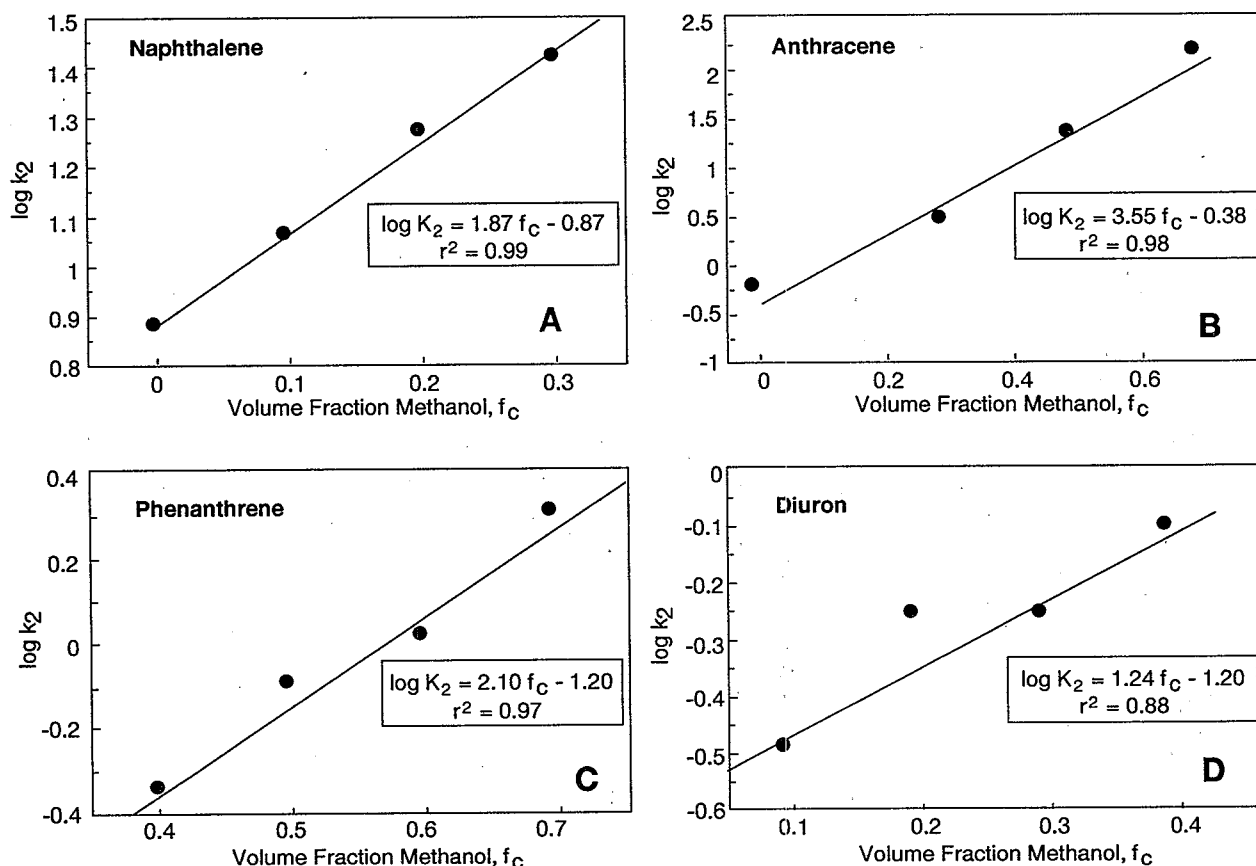
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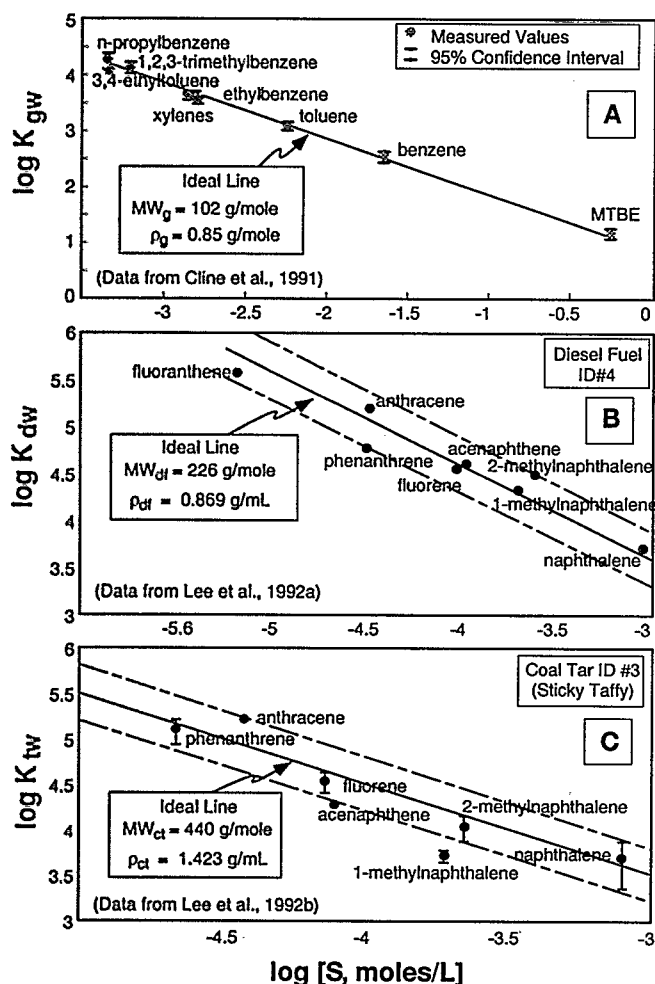
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When multiple contaminants are present in solution, a primary question to be addressed is the occurrence of antagonistic or synergistic interactions among the solutes, and between the solutes and the solid and aqueous phases. The presence of a cosolute at high concentrations can affect the behavior of organic compounds in several ways, resulting in the following three phenomena: (1) competitive sorption; (2) cooperative sorption; and (3) cosolvency. The first and third phenomena reduce sorption and thus enhance the transport of solutes, whereas cooperative sorption has the opposite effect. A potential source of these multi-contaminant solutions is the dissolution of immiscible liquids into water residing in or entering the subsurface. the relatively slow movement of water in the subsurface creates the possibility of relatively high solute concentrations (e.g., near X^o_i S^w_i limit) in the vicinity of the immiscible liquid phases.

Competitive sorption, where sorption of a solute is reduced by the presence of a co-solute, has been investigated by several researchers and their results have generally shown no competition for nonionic, low-polarity organic solutes such as naphthalene and chlorinated benzenes (cf., Karickhoff et al., 1979; Chiou et al., 1983). Indeed, non-competition is considered a defining characteristic of the sorption of nonionic, low-polarity organic solutes by a "partitioning" mechanism (Chiou et al., 1983). However, some researchers have reported relatively small decreases in sorption resulting from competition (MacIntyre and deFur, 1985; Abdul and Gibson, 1986; McGinley et al., 1989). The vast majority of studies on sorption in multi-solute systems have used sorbents with relatively high organic-carbon contents (i.e., greater than 0.1 %). Conversely, few studies have been reported for systems comprised of sorbents containing small organic-carbon contents, which are representative of many sand aquifers. The sorption of trichloroethene and p-xylene from single and binary solute solutions by two organic-carbon-poor aquifer materials was examined by Lee et al. (1988). They observed no difference in sorption between the single and binary systems. The sorption of trichloroethene by a sandy aquifer material in single and ternary solute systems was observed by Brusseau and Rao (1991) to be essentially identical.

Cooperative sorption, where sorption of nonionic, low-polarity organic solutes is enhanced by the presence of other nonionic, low-polarity organic solutes, has been studied by few researchers. Brusseau (1991) investigated the effect of a nonionic, low-polarity cosolute (tetrachloroethene) on the sorption of three nonionic, low-polarity organic chemicals (naphthalene, p-xylene, 1,4-dichlorobenzene) by two aquifer materials with small organic-carbon contents (< 0.03 %). In all cases, the sorption of the primary solute was enhanced by the presence of high concentrations of tetrachloroethene. Equilibrium sorption constants measured in binary-solute systems were 1.5 to 3 times larger than those measured for the single-solute systems. Hence, tetrachloroethene had a synergistic (i.e., cooperative), rather than an antagonistic (i.e., competitive), effect on the sorption of the primary solutes. The enhanced sorption was postulated to result from sorbed tetrachloroethene increasing the effective organic carbon content of the sorbent. Enhanced sorption was observed by Onken and Traina (1991) in recently reported experiments that used synthetic organo-clay complexes. They examined the sorption of pyrene by $CaCO_3$ treated with humic acid to obtain an organic carbon content of 0.003%. The sorption of pyrene in a binary
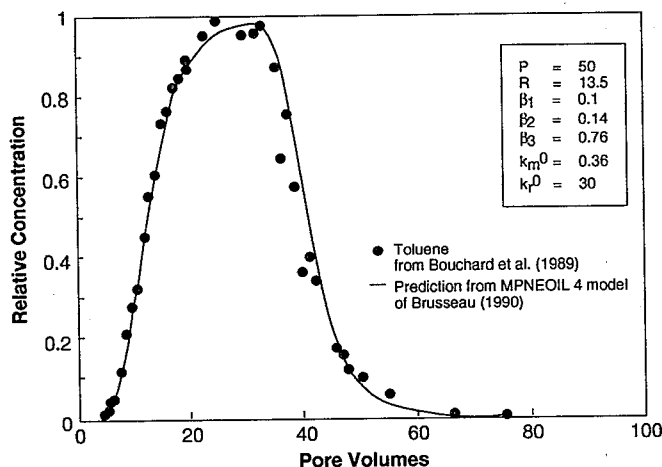
Figure 5. The effect of a residual phase of immiscible organic liquid on the transport of toluene in an aquifer material; figure adapted from Brusseau 1990, 1992a.

solution with anthracene as the cosolute was greater than that measured with no anthracene. The potential for competitive or cooperative interactions associated with large concentrations of solute dissolving from immiscible liquids requires further study, especially for systems consisting of solids with small organic-carbon contents.

Competitive and cooperative sorption result primarily from solute-sorbent interactions. In contrast, cosolvency, where the cosolute is considered a cosolvent, results from solute-solvent interactions. Interest in cosolvency is focused on the impact of the cosolvent on the physicochemical properties of water and the resultant effects on solute behavior in the mixed-solvent system. The vast majority of research on cosolvency has involved miscible liquids, as discussed above. It might be expected that the cosolvency effect of immiscible liquids present at concentrations below phase separation will generally follow the behavior of miscible cosolvents, with two major differences. First, the immiscible liquids are generally of lesser polarity than are the miscible solvents. By this measure, the immiscible cosolvent should have a greater effect on the solubility and sorption of a low-polarity organic solute. However, the lower polarity of the immiscible cosolvent also limits the amount of cosolvent that can reside in the aqueous phase. Thus, the volume fraction of many immiscible cosolvents may be limited to less than 1%. These small volume fractions may not be sufficient to induce a significant cosolvency effect.

The cosolvency of water-immiscible liquids was investigated by Pinal et al. (1990) and Rao et al. (1990). They found that, while the impact of immiscible cosolvents on solubility and sorption of hydrophobic organic solutes depended upon the polarity of the cosolvent, the general trends were similar to those observed for miscible cosolvents. However, for some immiscible liquids, the presence of a miscible cosolvent was required to enhance the solubility of the immiscible liquid to levels such that the immiscible cosolvent had an appreciable cosolvency effect. Much more research is needed on the potential cosolvency effect of solutes dissolving from immiscible liquids.

COMPLEX MIXTURES AND REMEDIATION OF CONTAMINATED SOIL AND GROUNDWATER

"Pump-and-treat" is one of the most commonly used techniques for attempting to remediate contaminated groundwater. In fact, approximately 68% of Superfund Records of Decision list pump-and-treat as the primary remediation technique (Travis and Doty, 1990). Confidence in and popularity of pump-and-treat is beginning to wane as its effectiveness has proven to be questionable. In a recent analysis of 19 active or completed pump-and-treat operations, it was concluded that, although groundwater extraction is an effective method for containing plumes, it is not practicable to rely solely on pump-and-treat to achieve health-based cleanup objectives (Haley et al., 1991). It was recommended that methods to enhance extraction effectiveness and efficiency be considered. In order to design enhanced removal techniques, the factors responsible for poor performance of pump-and-treat must be understood.

Two phenomena relating to poor performance of pump-and-treat systems have been observed at many sites. The first is the so-called "tailing" phenomenon, wherein the rate of reduction in contaminant concentration in water declines greatly after a relatively short phase of rapid reduction. This behavior results in an asymptotic concentration-time profile and greatly delayed cleanup times. The second phenomenon has been popularly termed "rebound" and is characterized by an increase in contaminant concentration after cessation of pumping. Both of these phenomena greatly reduce the efficacy of pump-and-treat remediation systems.

Factors Influencing the Efficacy of Pump-and-Treat Remediation

The tailing and rebound phenomena discussed above are indicative of nonideal contaminant transport. The fact that transport nonideality can have a significant impact on the effectiveness of pump-and-treat remediation is just beginning to be acknowledged (cf., Hall, 1988; Brusseau and Rao, 1989; Keely, 1989; MacKay and Cherry, 1989). Of primary concern for this technique is the removal efficiency associated with a given pumping regime or, in other words, the amount of time and water required to flush the aquifer to a specified contaminant-concentration level. The concentration/time function is sensitive to nonideal transport. In general, most nonideality factors will increase the time and the volume of water required to effect remediation.

Some of the major factors that can cause nonideal transport are briefly discussed.

1. Flow in heterogeneous porous media: Aquifers are heterogeneous in nature; hydraulic conductivity and sorption capacity are generally the two most significant properties. The hydrodynamics of fluid flow in heterogeneous systems causes nonideal solute transport. For example, the existence of low-conductivity media (e.g., silt/clay lenses) within a sandy aquifer creates domains through which advective flow and transport are minimal in comparison to the surrounding sand. Contaminant associated with the silt/clay lenses, or the "non-advective" domain, is released to flowing groundwater primarily by pore-water diffusion. Increasing the flow rate can increase the state of

disequilibrium between the advective and non-advective domains and result in delayed removal (i.e., "tailing"). The effects of variable velocity fields caused by hydraulic conductivity heterogeneity can also be caused by sorption capacity variability.

2. Sorption/desorption kinetics: Recent research has revealed that adsorption/desorption of organic solutes by aquifer materials can be significantly rate limited (Lee et al., 1988; Ball and Roberts, 1991; Brusseau and Reid, 1991; Brusseau et al., 1991b). The rate-limiting mechanism apparently involves constrained diffusion within the sorbent matrix (Ball and Roberts, 1991; Brusseau et al., 1991c). The validity of the local equilibrium assumption is dependent, in part, upon the hydrodynamic residence time of the contaminant in the system, which is a function of, among other factors, pore-water velocity. Increasing the velocity, as is done in pump-and-treat, can cause or enhance nonequilibrium conditions as a result of reduced residence time. Nonequilibrium will produce aqueous-phase concentration values lower than those obtained under ideal, equilibrium conditions. Thus, tailing will occur and removal by flushing will take longer.

3. Immiscible liquid dissolution kinetics: In many cases, residual phases of immiscible organic liquids may exist in portions of the contaminated subsurface. It has been shown that very large pore-water velocities (i.e., hydraulic gradients) are required to displace residual saturation (Wilson and Conrad, 1984; Willhite, 1986; Hunt et al., 1988). Hence, the primary means of removal will be dissolution into water and volatilization into the soil atmosphere. The immiscible liquid, therefore, serves as a long-term source of contaminant. As discussed above, the dissolution of immiscible liquid into water may be rate limited and, in such cases, would be dependent upon pore-water velocity. Increased velocity would enhance nonequilibrium conditions and, thus, result in tailing and delayed removal.

4. Contaminant Aging: Recent research has shown that contaminants that have been in contact with porous media for long times are much more resistant to desorption, extraction, and degradation. For example, contaminated soil samples taken from field sites exhibit solid:aqueous distribution ratios that are much larger than those measured or estimated based on spiking the porous media with the same contaminant (e.g., adding contaminant to uncontaminated sample) (Steinberg et al., 1987; Pignatello et al., 1990; Smith et al., 1990; Scribner et al. 1992). In addition, the desorption rate coefficients determined for previously contaminated media collected from the field have been shown to be much smaller than the values obtained for spiked samples (Steinberg et al., 1987). These field-based observations are supported by laboratory experiments that show desorption rate coefficients to decrease with increasing time of contact prior to desorption (Karickhoff, 1980; McCall and Agin, 1985; Coates and Elzerman, 1986; Brusseau et al., 1991c). These phenomena are significant not only because of the delayed removal they can cause, but also because the aged contaminants appear to be highly resistant to degradative processes (cf., Steinberg et al., 1987; Scribner et al., 1992). Thus, these aged contaminant residues may be resistant to remediation, except perhaps by use of an enhancement technique.

5. Other Factors: Other factors, such as nonuniform flowpaths and stagnation zones, can contribute to observed nonideal phenomena such as tailing during a pump-and-treat remediation. The effects of these factors are, however, much more a function of well-field dynamics than contaminant-media interactions and, as such, would not be affected by chemical enhancements.

It is apparent from the above discussion that several factors influencing contaminant transport can have deleterious effects on the efficacy of pump-and-treat remediation. These effects can create conditions where the expected, desirable result of large decreases in remediation time is not obtained when pumping is initiated or increased. These factors must be considered when designing pump-and-treat remediation systems.

Unfortunately, there has been very little quantitative analysis of the impact of nonideal transport on aquifer flushing. An example taken from one of the few such analyses is presented in Figure 6 (adapted from Brusseau, 1993). The data presented in the figure were obtained from a pilot-scale aquifer flushing system wherein a two-well injection-withdrawal couplet was used to evaluate the effect of injecting clean water into a contaminated aquifer (Whiffen and Bahr, 1984). These, as well as other, data were used by Brusseau (1992b) to evaluate the ability of a multi-factor nonideality model to predict field-scale solute transport. The data were subsequently used to quantitatively evaluate the effect of porous-media heterogeneity and nonequilibrium sorption on the effectiveness of pump-and-treat (Brusseau, 1993). The predicted removal curve for the case of uniform aquifer properties and instantaneous sorption/desorption is shown in Figure 6. It is evident that the prediction greatly underestimates the volume of water required to remove the contaminant. The predicted simulation obtained for the case of variable hydraulic conductivity and rate-limited sorption/desorption matches the field data extremely well (see Figure 6). A comparison of this prediction to the one obtained for ideal conditions clearly illustrates the effect that nonideal transport factors can have on aquifer flushing.

The predicted removal of contaminant for the case of spatially variable hydraulic conductivity and instantaneous sorption/desorption is also shown in Figure 6. While this prediction does not match the early field observations, at large pore volumes the simulated curve approaches the curve obtained by including the combined effects of variable conductivity and rate-limited sorption/desorption. This suggests that, while both factors contribute to nonideal transport, spatially variable conductivity may be the more important factor constraining the efficacy of aquifer flushing in this system. The knowledge of which factor or factors is the major cause of nonideal transport is essential in the design of an effective method for enhancing the efficiency of a pump-and-treat operation.

Chemical Enhancement of Pump-and-Treat Remediation

Several chemical-based techniques for enhancing contaminant removal in the subsurface are under investigation (e.g., addition of surfactants, cosolvents, complexing agents), and each has advantages and disadvantages. A detailed discussion of chemical enhancement techniques was presented by Palmer and Fish (1992). However, several aspects relating to the
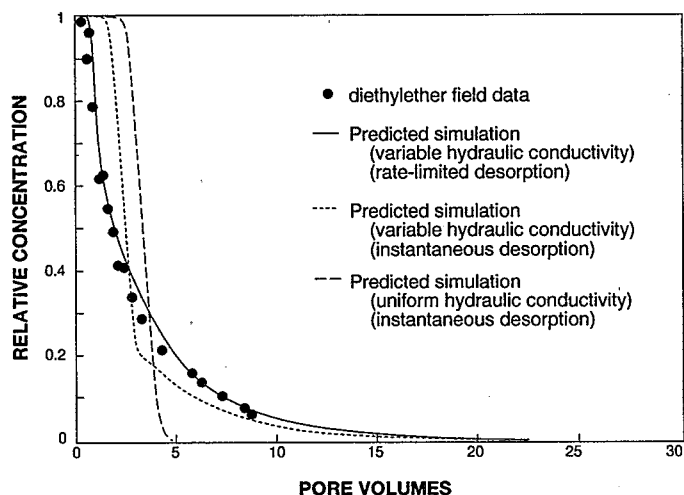
Figure 6. The effect of nonideal transport on removal of organic contaminants from aquifers by flushing. Field data from Whiffen and Bahr, 1984; model used for simulations from Brusseau et al. 1989. Figure adapted from Brusseau 1993.

impact of nonideal transport phenomena on the efficacy of chemical enhancement were not discussed.

Surfactants are currently the focus of the research effort on chemical enhancements and, based on preliminary laboratory data, appear to have promise for enhancing pump-and-treat remediation in some situations. The use of dissolved organic matter (DOM) and of cosolvents is also being investigated, albeit at a smaller scale. Miscible cosolvents, such as methanol, reduce the net polarity of the mixed solvent when added to water and thereby increase the quantity of a nonionic organic compound that can dissolve in the mixed solvent. This increase, in turn, results in a smaller equilibrium sorption constant and less attendant retardation. Thus, the addition of a cosolvent can reduce the volume of water required to flush a contaminant from porous media by altering the equilibrium phase distribution. A similar result is obtained with surfactants and DOM, although by different mechanisms. Hence, surfactants, DOM, and cosolvents act to increase the aqueous-phase concentration of organic compounds, the so-called "solubilization" effect. This effect is of special interest for the removal of residual phases of immiscible liquids. The other major method of removing trapped residual phases, mobilization, will not be considered in the present discussion.

A comparison of the relative degree to which aqueous-phase concentration of contaminant is enhanced by the various additives favors the surfactants. However, a comparison of this type can be very misleading without considering such factors as potential interactions between the additive and the porous media. It is well known, for example, that surfactant molecules (cf., Ducreux et al., 1990; Kan and Tomson, 1990; Jafvert and Heath, 1991) and DOM (cf., Dunnivant et al., 1992; Moore et al., 1992) can sorb to surfaces of solids, thereby reducing the concentration of additive available for dissolving the contaminant. In addition, surfactants and DOM may precipitate under certain conditions. In contrast, most subsurface solids have a low affinity for miscible solvents such as methanol. Thus, it is possible that, whereas the "active" mass of a surfactant or DOM may be significantly less than the total mass injected into the subsurface, that of a solvent may be essentially the same.

A comparison of the impact of several potential chemical additives on the apparent solubility of selected organic compounds was developed by collecting and synthesizing data reported in the literature (see Table 1). The effect of sorption and precipitation of the additives was taken into account. The results of the analyses are presented in Figure 7a-c. For all three solutes, the nonionic surfactant (Triton), with low assumed sorption, produced the greatest enhancement. The cosolvent (ethanol) produced the lowest degree of enhancement for all three solutes. The solubilization effect of ethanol increases dramatically at cosolvent concentrations above those used in these analyses. It is readily apparent that the relative enhancement effect will vary by solute, and by other factors such as the nature of the sorbent. The comparison of the effectiveness of various additives under a range of conditions is a topic requiring more research.

The primary criterion upon which chemical enhancement additives are judged is their solubilization potential. The impact of interactions between the additive and the solid phase on this enhancement is an important factor to consider, as discussed above. However, there are several other factors that should also be considered when selecting an enhancement agent. In this regard, cosolvents have several benefits that surfactants and DOM do not.

First, the addition of a cosolvent increases the magnitude of the desorption rate coefficient (not to be confused with an increase in the rate of desorption), thereby reducing the time required to attain equilibrium. This reduction in the degree of nonequilibrium would result in reduced tailing during pumping. This, in turn, would decrease the volume of water and the time required to remove the contaminant by flushing. As previously discussed, rate-limited desorption may impose a significant constraint on the efficacy of pump-and-treat remediation. If so, the ability of a cosolvent to reduce the degree of nonequilibrium would be a major attribute. There is no reason to expect surfactants or DOM to increase desorption rate coefficients.

Second, cosolvents may be able to "extract" the highly retained, aged contaminants that have been observed in field studies (see discussion above). There is no reason to suppose that surfactants or DOM could act in an "extractive" manner. Conversely, there is good reason to suppose that cosolvents could enhance the release of aged contaminants, based on the results of solvent extraction techniques used in the analysis of contaminated soils (cf., Sawhney et al., 1988) and on the results of experiments that evaluated the effect of cosolvents on the desorption of organic compounds (Freeman and Cheung, 1981; Nkedi-Kizza et al., 1989; Brusseau et al., 1991a).

Third, cosolvents may be able to access contaminant that is residing in low hydraulic-conductivity domains such as clay lenses. During a pump-and-treat remediation, as discussed above, contaminant in these domains is probably removed primarily through diffusion. The clay particles provide a large surface area with which a surfactant or DOM may interact and thereby reduce its availability for enhancing contaminant
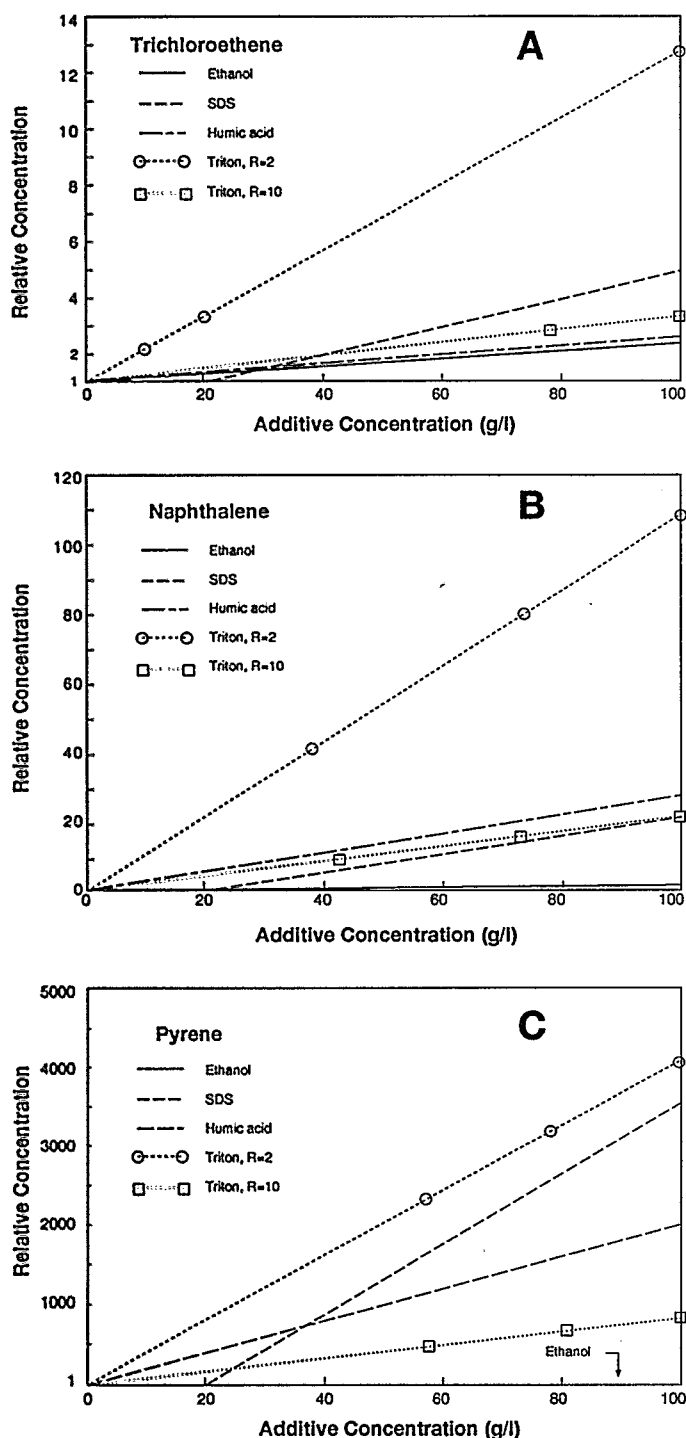
Figure 7. The effect of several additives on the aqueous-phase concentration of (A) trichloroethene, (B) naphthalene, and (C) pyrene.

removal. In addition, the sorption of the surfactant or DOM can enhance the retention of the organic solutes by providing an increase in stationary organic carbon. Surfactant micelles and larger DOM particles may possibly be excluded from the smaller pore-size domains, which would limit accessibility. Cosolvents such as methanol do not sorb significantly to solid surfaces and, because of their small size, would not be excluded from any pore domains in which contaminants would be found. In addition, as discussed above, cosolvents have been found to cause cracking of clayey materials. This cracking results in larger permeabilities, which could enhance the rate of contaminant removal from the lenses. Thus, in comparison to surfactants and DOM, cosolvents may have a much greater potential for enhancing the release of contaminants trapped in fine-grained media.

Fourth, cosolvents have the potential for being used in an integrated, chemical-biological remediation technique. For example, methanol is the initial intermediate in the oxidation of methane by methanotrophic bacteria. The addition of methanol to the groundwater environment at low concentrations may stimulate useful cometabolic transformations, causing the destruction of otherwise refractory contaminants such as trichloroethene. Under (locally) anaerobic conditions, cosolvent addition may also drive reductive dehalogenation, particularly of compounds such as tetrachloroethene (cf., DiStefano et al., 1991; Gibson and Sewell, 1992). It is possible to envision situations where addition of cosolvents such as methanol or ethanol may initiate transformations that result directly or indirectly in degradation to non-toxic products. The negative effects of high concentrations of cosolvent on the subsurface microbial community may initially preclude the development of biodegradative activity. However, such activity could occur following dilution of the cosolvent during transport.

Considering the preceding discussion, cosolvents may have specific properties that make them useful for enhanced pump-and-treat. However, given these same properties, it is likely that the use of cosolvents will be limited to smaller scale problems. The clean-up of near-field contamination problems is probably where cosolvents can be put to best use.

CONCLUSION

Experience has shown that many soil and groundwater contamination problems involve complex mixtures of chemicals. As discussed in this monograph, these mixtures may affect contaminant behavior through a variety of mechanisms. Because many of these mechanisms are not well understood, approaches for dealing with complex mixtures in the subsurface often involve direct application or untested extrapolation of knowledge derived from relatively simple aqueous systems. Not surprisingly, the results are frequently less than satisfactory.

The primary purpose of this paper is to identify and discuss, in a generic sense, some of the important processes which must be considered when dealing with complex mixtures in the subsurface, and to illustrate how these may impact groundwater quality. From the discussion, it is apparent that complex mixtures may play a role in groundwater reclamation as well as degradation of groundwater quality. Equally apparent, however, is the need for improved scientific understanding of the processes associated with the transport of complex mixtures and of the

Table 1. Enhanced Solubilization Data Collected From the Literature

Additive	Compound	Sorption of Additive[#]
SDS	TCE (Shiau et al., 1992)	R = variable (Jafvert and Heath, 1991)
SDS	Naphthalene (Gannon et al., 1989)	R = variable "
SDS	Pyrene (Jafvert, 1991)	R = variable "
Triton	TCE (West, 1992)	R = 2,10 (Kan and Tomson, 1990)
Triton	Naphthalene (Edwards et al., 1991)	R = 2,10 "
Triton	Pyrene (Edwards et al., 1991)	R = 2,10 "
Ethanol	TCE (Morris et al., 1988)	R = 1 (Wood et al., 1990)
Ethanol	Naphthalene (Morris et al., 1988)	R = 1 "
Ethanol	Pyrene (Morris et al., 1988)	R = 1 "
Humic Acid	TCE (Garbarini and Lion, 1986)	R = 2 (Dunnivant et al., 1992)
Humic Acid	Naphthalene (McCarthy and Jiminez, 1985)	R = 2 "
Humic Acid	Pyrene (Gauthier et al., 1987)	R = 2 "

SDS = sodium dodecyl sulfate; TCE = trichloroethene; Triton = triton X-100; Humic Acid = Aldrich humic acid; [#]Retardation factor, R, of an additive in a hypothetical soil was estimated from data reported in the references cited in this column.

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