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INDOT Guidance Document
for
In-Situ Soil Flushing

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INTRODUCTION

Organic solvents and other petroleum-based products are known to frequently entered the subsurface as a separate organic phase or non-aqueous phase liquid (NAPL)(Pennell et al., 1993). Organic liquids that are lighter than water are referred to as light non-aqueous phase liquids (LNAPL). Examples of LNAPLs include gasoline and diesel fuel. LNAPLs tend to accumulate above and slightly below the water table (consistent with a fluctuating water table). Organic liquids that are heavier than water are referred to as dense non-aqueous phase liquid (DNAPL). Examples of such liquids include chlorinated solvents and PCB oils. Because they are denser than water, DNAPLs have the potential to migrate to depths well below the water table, and thus, pose special cleanup challenges. It is now widely known that conventional pump-and-treat remediation technologies are ineffective and costly methods of aquifer restoration (MacDonald and Kavanaugh, 1994). In-situ soil flushing with surfactants and cosolvents has been shown to be an effective strategy for solubilization and subsequent removal of NAPLs (Brusseau et al., 1999; Lowe et al., 1999; Wood and Enfield, 1999).

This document is intended to provide a better understanding and practical guidance of this technology for decision makers and users involved in evaluating remediation strategies being recommended by contacted consultants. It contains information from the basic chemistry and mechanisms of cosolvent and surfactant flushing to the key factors that need to be considered during the selection, design and implementation of this technology. It also provides information on several categories of contaminants subject to in-situ flushing. It should be used as a general guidance rather than a design manual. More technical detail can be found in AATDF (AATDF, 1997) and NFESC (NFESC, 2002) reports, and regulatory guidance is provided more comprehensively in ITRC report (ITRC, 2003).

Basics of In-situ Soil Flushing

General Process

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Contrast to soil washing, which involves excavating the contaminated soil and treating it at the surface in a soil washer, soil flushing involves an injection/recirculation process in place. Traditional pump-and-treat methods are ineffective at locations that contain significant amounts of water-immiscible solvents, precipitated metals, contaminants that have diffused into small pore spaces, or those that adhere strongly to soils (NRC, 1994). The classification of surfactant/cosolvent flushing as an emerging technology is based on criteria for experimental, emerging, and proven technologies described by Pankow and Cherry (1996). All *in-situ* technology is consistent for using carriers for delivery and removal. Soil flushing uses surfactant or cosolvent as a carrier. A schematic of in-situ soil flushing system is shown in Figure 1.

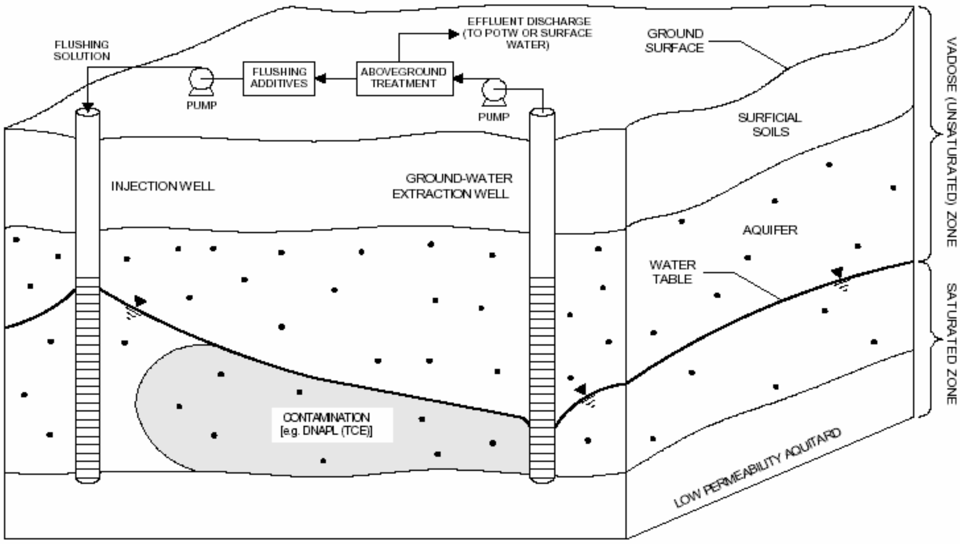

Figure 1. Schematic of an In-Situ Flushing System (Roote, 1998)

The flushing process begins with the drilling of injection and extraction wells into the ground where the contamination has been found. The number, location, and depth of the injection and extraction wells should be decided based on several geological factors and engineering considerations. In addition to placing the wells, other equipment, (e.g., wastewater treatment system) must be transported to or built on the site. The soil flushing equipment pumps the flushing solution into the injection wells. The solution passes through the soil, picking up contaminants as it moves towards the extraction wells. The extraction wells collect the flushing solution containing the contaminants. The solution-contaminant mixture is pumped out of the ground through the extraction wells. The mixture is typically treated by a wastewater treatment system to remove the contaminants and reclaim the flushing solvents whenever possible.

In-situ soil flushing is a source control treatment technology, which is designed to treat soil, sediment, sludge, or solid-matrix wastes (in other words, the source of contamination), but not to treat groundwater directly. According to the EPA 2004 annual report on treatment technologies for site cleanup (USEPA 2004), 863 treatment technologies were selected for source control over fiscal year 1982-2002 and of these, 42% were *in-situ* technologies and 58% were *ex-situ* technologies. Figure 2 provides a cumulative overview of *in-situ* and *ex-situ* treatment technologies selected for source control. For *in-situ* technologies, soil vapor extraction has been most common (25%) and *in-situ* soil flushing represents 2% of total source control treatment.

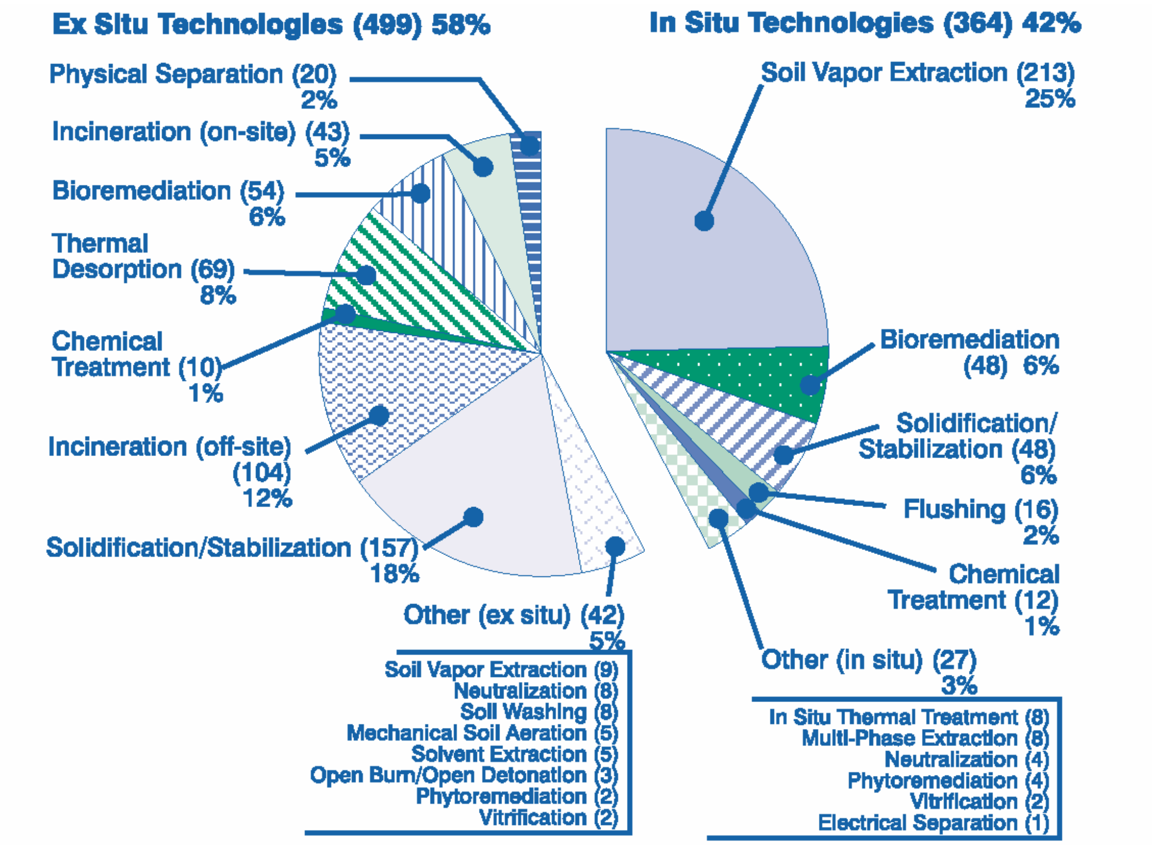

Figure 2. Superfund remedial actions: Source control treatment Projects (1982-2002) (USEPA, 2004).

Mechanisms of residual NAPL removal by cosolvent (solubilization versus mobilization)

Cosolvents are organic compounds with a hydrophobic part, usually hydrocarbon chains, and a hydrophilic functional group, such as hydroxyl, carboxylic, and aldehyde groups. Cosolvents most commonly used in in-situ flushing are alcohols. The amphiphilic and hydrophobic groups enable cosolvents to be miscible in both the aqueous phase and NAPL phase, respectively. For the cosolvency effect to be dominant, the volume fraction used should generally be higher than 10% (Schwarzenbach et al., 2002; Yalkowsky and Roseman, 1981). At this concentration range, the cosolvent-enhanced solubility is exponentially correlated to the volume fraction of the cosolvent in the mixture by the cosolvency power (Banerjee and Yalkowsky, 1988; Schwarzenbach et al. 2002; Yalkowsky et al., 1972a; Yalkowsky et al., 1972b; Yalkowsky and Roseman, 1981) as follows: $C_m^{sat} = C_w^{sat} \bullet 10^{\sigma f}$ where C_m^{sat} is the cosolvent-enhanced solubility (mass or moles/L); C_w^{sat} is the initial aqueous solubility (mass or mol/L); σ is known as the cosolvency power (dimensionless); and f is the cosolvent volume fraction.

Cosolvents enhance removal of NAPLs from porous media by two methods: solubilization and mobilization. Cosolvent-enhanced solubilization of a NAPL can be achieved by a flushing solution with a reduced polarity relative to the resident groundwater (Jafvert, 1996). The mechanisms responsible for mobilizing NAPL contaminants include: (1) creation of a single phase condition, (2) decrease in the water-NAPL interfacial tension, and (3) swelling of the NAPL by solubilization of the cosolvents within this phase. However, addition of cosolvent also causes the interfacial tension to drop, which may lead to NAPL mobilization. Consequently in the case of a DNAPL, downward movement of DNAPL to previously clean regions would result in an increase in environmental risk. Figure 3 shows the decrease of interfacial tension between NAPL and cosolvent/water mixture with the increasing solubility of NAPL as more cosolvent is added (ethyl lactate in this case). These results are important with respect to optimizing for solubilization while minimizing risks of DNAPL mobilization. There should be a maximum level of cosolvent that can be used in a given site where DNAPL solubility is sufficiently increased without a concomitant decrease in interfacial tension below the value that would induce mobilization. Such a system can be designed based with characterization of interfacial tension, density, and viscosity and an estimated trapping number, which will be discussed in detail later.

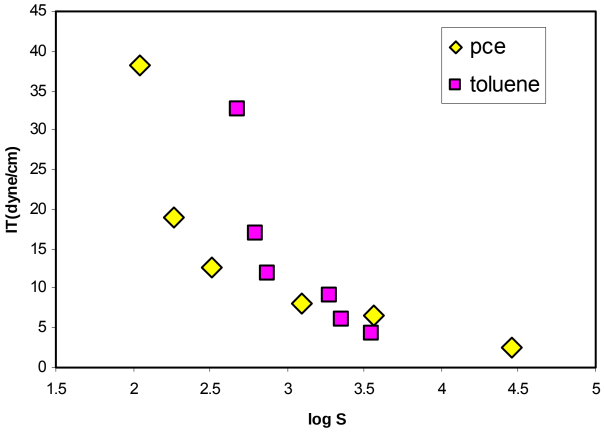

Figure 3. The inverse relationship between interfacial tension and ethyl lactate enhanced solubility.

The presence of cosolvent in a NAPL-water system can alter the physical properties of both water and NAPL by partitioning into both phases. Given sufficient amount of cosolvent, a single phase (i.e., completely miscibility) is formed, which is one of the mobilization mechanisms mentioned above. This process can be illustrated by a **ternary phase diagram** such as the one shown in Figure 4 for IPA-water-PCE system. The **binodal curve** represents the boundary between the one phase region and two phase region. Above this curve, all components exist in one single phase and interfacial tension equals to zero. Below this curve, NAPL and water exist as two phases with each containing some cosolvent. The tie lines under the binodal curve represent constant interfacial tension and phase composition. The relative proportion of each phase can be read from the endpoints of the tie lines where they meet the binodal curve. For each tie line, the endpoint on the left hand side defines the aqueous phase composition and the one on the right hand side defines the NAPL phase composition.

The slope of the tie line reflects the equilibrium partitioning of cosolvent into both phases. For shorter chain alcohols that prefer to stay in the aqueous phase and don’t partition into NAPL phase significantly, the tie lines have a negative slope, known as type II(-) system, like the one shown in Figure 4. Longer chain or larger molecule alcohols are more lipophilic, thus partition more into NAPL phase, with the tie line sloping down toward the water endpoint. Ternary phase diagrams with positive-slope tie lines are knows as type II(+) systems (Falta, 1998).

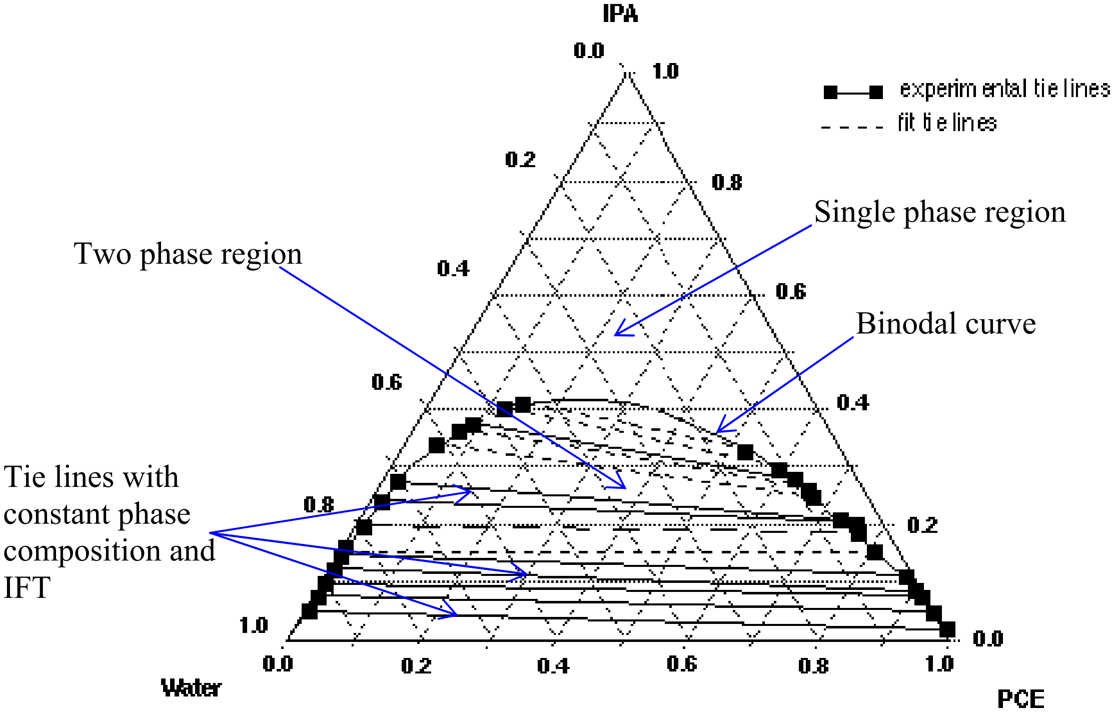

Figure 4. Ternary phase diagram for IPA-water-PCE system (Adapted from AATDF, 1997)

It is obvious that if the cosolvent concentration is above the binodal curve, NAPL removal is mainly through mobilization (miscible extraction). If the cosolvent concentration lies below the binodal curve, the dominant NAPL removal mechanism depends on the cosolvent's preference toward water and NAPL. For more water soluble cosolvents (e.g., methanol, ethanol), the ternary phase diagram has tie lines with negative slopes and is a type II(-) system and the primary NAPL removal mechanism under the binodal curve will be dissolution. Some mobilization may occur if interfacial tension is reduced too much. For cosolvents that partition preferentially into NAPL phase, like tertiary butanol, in type II(+) systems, NAPL mobilization is more likely to occur in response to reduction of interfacial tension and NAPL swelling. Enhanced NAPL dissolution may also occur to a certain degree but not as predominant.

Mechanism of residual NAPL removal by surfactant (solubilization versus mobilization)

Surfactants (surface active agents) are chemical agents with structures that can alter the property at the solution interface. Figure 5 illustrates a typical surfactant molecule structure, which consists of a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail. The hydrophilic head group often includes anions or cations such as sodium, chloride, or bromide as a counter charge balancing ion. The hydrophobic portion of a surfactant molecule is typically a long hydrocarbon chain, with strong affinity to NAPL. This amphiphilic nature leads to the accumulation of surfactant monomers at NAPL-water interfaces, with the hydrophobic tail embedded in the NAPL and the hydrophilic head facing toward the aqueous phase (Figure 6). The molecular weight of surfactants generally used in environmental remediation area ranges from 200 g/mol to 2000 g/mol (AATDF, 1997).

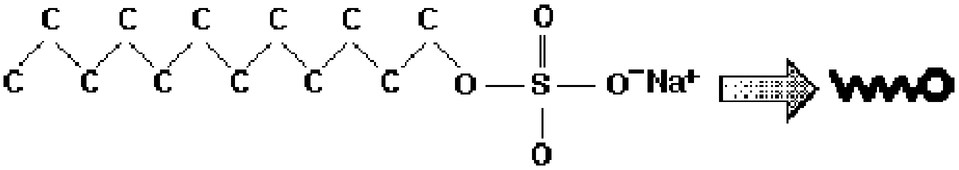

Figure 5. Structure sodium dodecylsulfate, which is a typical surfactant, (AATDF, 1997).

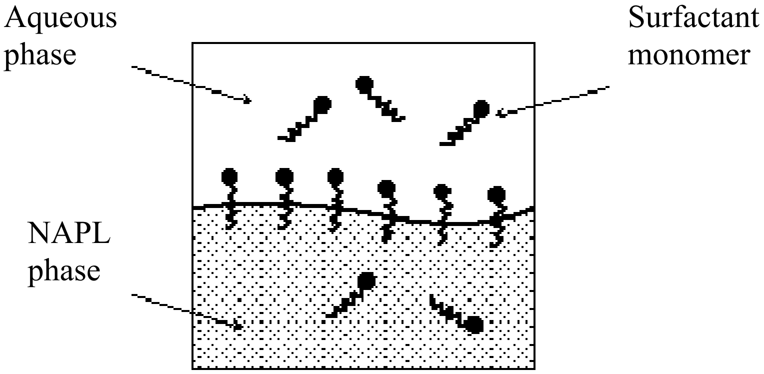

Figure 6. Surfactant accumulation at the NAPL-water interface (From AATDF 1997)

Surfactants are typically classified by the nature of their head group as cationic, anionic, nonionic or zwitterionic (both cationic and anionic group), with the characteristics of each group summarized in Table 1. An amphiphilic nature is a characteristic that surfactants share in common with cosolvents. A unique feature that distinguishes surfactants from cosolvents is the formation of micelle. A surfactant molecule that exists as a single unit is called surfactant monomer. With increasing surfactant concentrations, monomer concentration increases up to the concentration at which micelles form, which is referred to as the critical micelle concentration (CMC). At concentrations at or above the CMC, the number of monomers remains constant and the excess surfactant molecules aggregate to form micelles (Figure 7). Micelles in aqueous solutions will have their hydrophobic tail pointing toward the interior of the micelle and the hydrophilic head oriented toward the aqueous solution. The concentration required to form micelles (CMC) of typical aqueous-based surfactants (Table 2). Surfactants are also characterized by their hydrophile-lipophile balance (HLB), which is an indication of the relative strength of the hydrophilic and hydrophobic portions of the surfactants. A high HLB value indicates a higher water solubility and less affinity for the NAPL (Sabatini et al., 1995). When choosing surfactant to remove a given contaminant composition, one of the factors to consider is that the HLB of the surfactant should be as close as possible to that of the contaminant (Rosen 1989).

The hydrophobic nature inside of the micelle makes it an amenable place for NAPL to reside (Figure 8). This NAPL removal mechanism is defined as *solubilization*, as opposed to *mobilization*. Mobilization occurs mainly by reducing interfacial tension between the NAPL and surfactant. For example, liquid organic contaminants can be trapped in soil pores due to capillary forces that exist in soil, which is typically referred to as residual NAPL. These capillary forces are proportional to the interfacial tension at the NAPL-water interface (West and Harwell 1992). During surfactant enhanced aquifer remediation, surfactants accumulate at the DNAPL-water interface, and the interfacial tension (IFT) is reduced between the two-phases because of amphiphilic nature of surfactant. If buoyancy and viscous forces overcome capillary forces, then the DNAPL migrates in the direction of the net force and the phenomenon is termed mobilization.

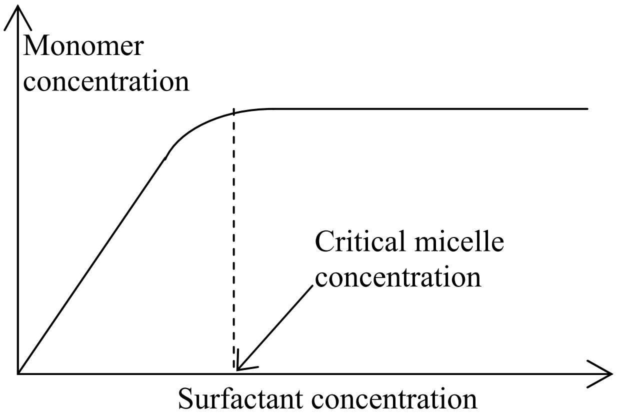

Figure 7. Formation of micelle at the critical micelle concentration

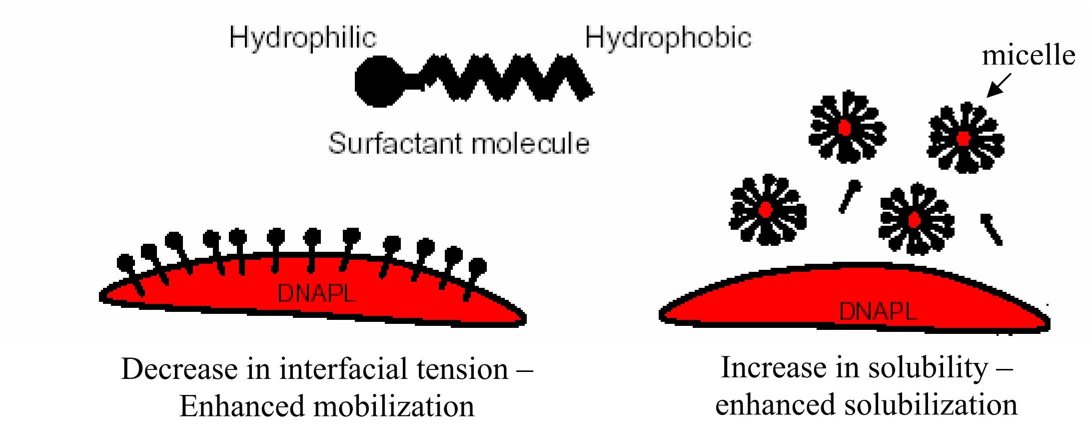

Figure 8. Mobilization versus solubilization of DNAPL by surfactant (from Kullasooriya, I.H. at University of Cambridge)

Table 1. Surfactant classification based on ion charge and their characteristics (summarized based on AATDF, 1997 and Rosen, 1989)

	Anionic surfactants	**Cationic surfactant**	**Zwitterionic surfactants**	**Nonionic surfactant**
Surfactant ion	Negatively charged	Positively charged	Both positive and negative parts	No ionization
Examples	sulfonic acid salts, alcohol sulfates, alkylbenzene sulfonates, phosphoric acid esters, and carboxylic acid salts	polyamines and their salts, quaternary ammonium salts, and amine oxides	β-N-Alkylaminopropionic acids, N-alkyl-β-iminodipropionic acids, N-alkylbetains, sulfobetaines, sultaines	polyoxyethylenated alkylphenols, alcohol ethoxylates, alkylphenol ethoxylates, and alkanolamides
Toxicity	Relatively nontoxic	toxic	Relatively nontoxic	Relatively nontoxic
Sorption to soil	No sorption	Strong sorption	Can be adsorbed	Not significant sorption
Application in environmental area	Good solubilizer, widely used in petroleum oil recovery, contaminant hydrogeology remediation	Not widely used in environmental application	Compatible with other surfactants and therefore can be mixed together as a cosurfactant in petroleum and environmental application	Good solubilizer, can be used as cosurfactant in petroleum and environmental application

Table 2. CMC of Typical Surfactants in Aqueous Solution

Surfactant	**CMC (mg/L)**
Witconol 2722	13[a]
Triton X-100	130[b]
Triton X-114	110[b]
Triton X-405	620[b]
Brij 35	74[b]
Sodium dodecyl sulfate	2100[b]
Synperonic NP4	23.7[c]
Marlophen 86	32.5[c]
Synperonic NP9	48.9[c]
Marlophen 810	55.4[c]
1:1 blend Rexophos 25/97, Witconol NP-100	2000[d]

[a] Pennel et al., 1993; [b] (Kile and Chiou 1989); [c] (Narkis and Ben-David 1985); [d] (Longino and Kueper 1995)

If a surfactant is added to lower the interfacial tension between two immiscible liquids such as oil and water, then the mixing together of the constituents results in one immiscible liquid undergoing multiphase dispersion of very small droplets within the other, thus producing an emulsion (Heimenz, 1986). The performance of a surfactant in the subsurface is not only a function of the surfactant and contaminant chemical properties, but also a function of the soil and geochemical condition of the groundwater (e.g., salts present, pH, temperature). The Winsor phase diagram shown in Figure 9 illustrates how surfactant partitions differently with varying salinity, temperature, and surfactant HLB (i.e., water solubility). At low temperature, low salinity and low water solubility, the surfactant preferentially resides in the aqueous phase with hydrophilic heads facing out of the micelles and the NAPL in the center of the micelle. This scenario is referred to as a Winsor type I system. An optically transparent dispersion of NAPL droplet coated by micelles in a continuous aqueous phase formed in this system is termed as **single phase microemulsion (SPME)**. Increasing salinity or temperature can expel surfactant from the water phase to the oil phase, and decreasing the HLB value has the equivalent effect. This leads to a Winsor type II system, where "reversed micelles" exist with hydrophobic tail exterior and hydrophilic head interior and water molecules in the center, are formed. During the transition from Winsor type I to type II, at appropriate salinity values, temperature, or HLB number, a middle phase composed of water and oil exists. This is classified as Winsor type III system. The middle phase is optically transparent, and referred to as **middle phase microemulsion**. The interfacial tensions (IFTs) between the middle phase and any excess oil or water phases reach extreme low values, much lower than those achieved in Winsor Type I and II systems. These ultralow IFTs make the middle-phase microemulsions an ideal condition for NAPL remediation (Baran et al., 1994; Jawitz et al., 1998b; Sabatini et al., 1996; Shiau et al., 1996). However, the middle-phase microemulsion condition is hard to achieve in a field situation, because there are numerous parameters that must be optimized and maintained. Martel and collaborators (Martel and Gelinas, 1996; Martel et al., 1993) proposed the use of Winsor Type I microemulsions to solubilize NAPLs without mobilization.

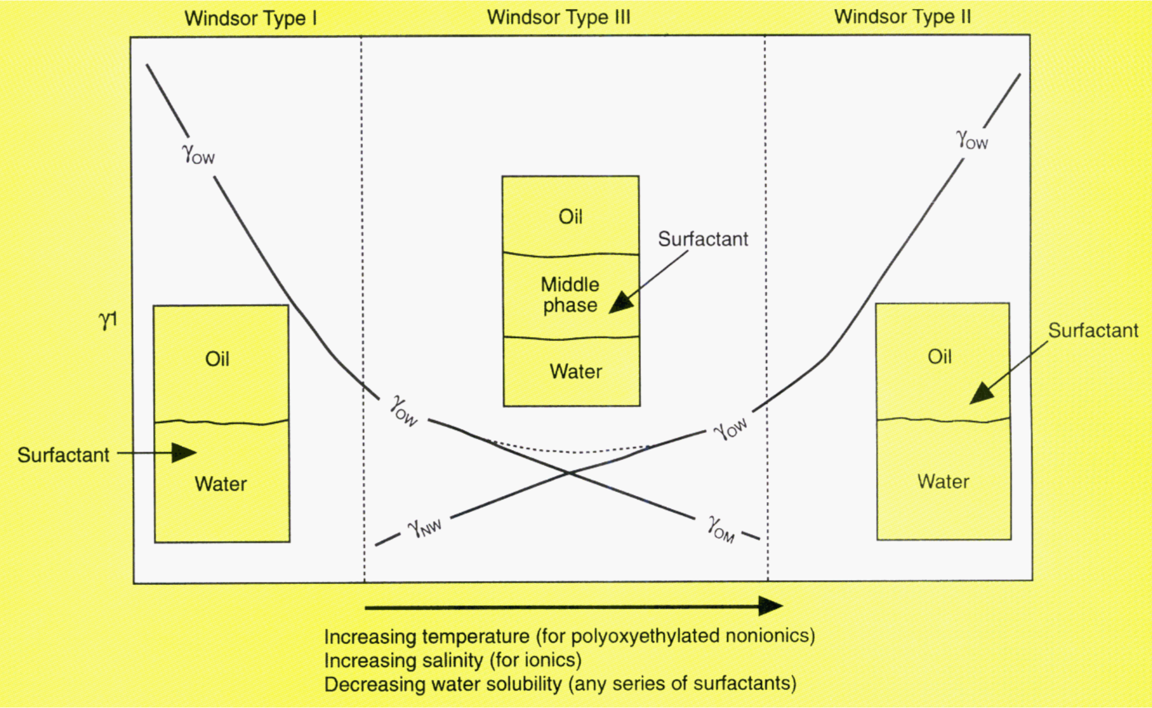

Figure 9. Winsor Phase diagram (From West and Harwell, 1998)

Density Modified Displacement (DMD) method

Significant partitioning of a low-density alcohol cosolvent into DNAPL can cause a DNAPL swelling such that its density is reduced and it is converted to an LNAPL. This process is known as density modified displacement (DMD), which significantly reduces the risk of downward DNAPL movement (Ramsburg and Pennell, 2002). Roeder et al. (2001) reported the conversion of PCE DNAPL to LNAPL by a butanol cosolvent flushing solution containing high density food additives. The swollen NAPL achieved a density of 1.05 to1.16 g/mL, which is an “LNAPL” relative to clean water; however, the high density water-miscible food additives (e.g., sucrose at 1.59 g/mL or glycerol at 1.26 g/mL) preferentially transfer to the aqueous phase, increasing the aqueous-phase density above that of the swollen NAPL. In their 1-D column flushing and 2-D sand box flushing, more than 90% of PCE was recovered in the swept zone.

Recently, alcohol addition has been suggested for use in combination with surfactant flushing to enhance solubilization kinetics and permit DNAPL density control (Taylor et al., 2004). This method introduces a partitioning alcohol and *n*-butane to convert the DNAPL to an LNAPL followed by a low interfacial tension surfactant solution to displace and recover the resulting LNAPL. Ramsburg and colleagues (Ramsburg et al., 2003) used 1.2 pore volume of macroemulsion consisting of 4.7% (vol) Tween 80 + 1.3 % (vol) Span 80 + 15% (vol) 1-butanol as a ‘preflood” solution to convert a TCE DNAPL to an LNAPL, with subsequent 1.2 pore volumes of low IFT surfactant flushing consisting of 10% (vol) Aerosol MA + 6% (vol) 1-butanol + 15 g/L NaCl + 1 g/L $CaCl_2$ through a 2-D flow cell. The combined 2.4 pore volumes of density conversion and low-IFT solutions recovered 93% of the introduced TCE to the 2-D cell. It was verified that the use of macroemulsion flooding strategies coupled with the density modified displacement method holds great promise for remediation of DNAPL source zones.

NAPL mobilization

Two types of NAPL mobilization can occur during surfactant or cosolvent flushing. NAPL globule entrapped in the porous media can be carried away by injected fluid due to increased viscosity and decreased interfacial tension. This can be characterized by a total trapping number (Pennell et al. 1996). NAPL flows in the same direction as the injected fluid in this type of mobilization. The other type is the vertical penetration of the DNAPL pool through the underlying fine layer as a result of a cosolvent or surfactant-induce decrease in interfacial tension, which subsequently causes a decrease in entry pressure of the fine strata.

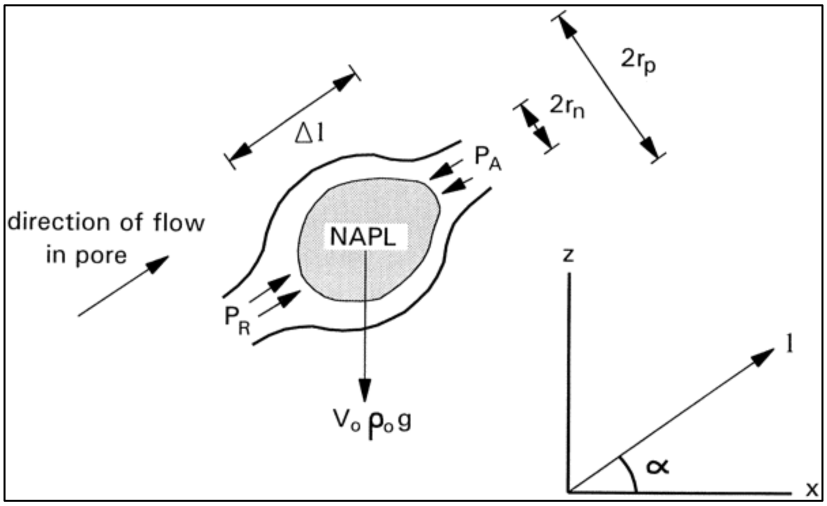

Figure 10. Schematic diagram of the pore entrapment model and corresponding coordinate system (From Pennell et al., 1996)

The total trapping number apporach considers the forces acting on a single NAPL "globule" as illustrated in Figure 10. The pore is oriented in a direction l, which makes an arbitrary angle, α, with the horizontal axis. Pressure and gravity forces, tend to mobilize the globule, which are balanced by capillary forces acting to retain the NAPL globule. Shear forces relevant to this system would be a function of the viscosity contrast between the aqueous and NAPL phases, which is assumed to be negligible here. Two dimensionless quantities are developed from the balance of the forces: (1) the capillary number (N_{Ca}), which is defined in terms of the aqueous flow component in the direction of the pore. N_{Ca} relates viscous to capillary forces; and (2) the bond number (N_B), which represents the ratio of the buoyancy to capillary forces. The total trapping number, N_T, is calculated from Capillary Number, N_{Ca}, and Bond Number, $N_{B,}$ as follows,

$$N_{Ca} = \frac{q_w \mu_w}{\sigma_{ow}}$$

$$N_B = \frac{\Delta \rho g k k_{rw}}{\sigma_{ow}}$$

$$N_T = \sqrt{N_{Ca}{}^2 + 2N_{Ca}N_B \sin\alpha + N_B{}^2}$$

q_w = Darcian velocity (cm/s);

μ_w = volume averaged fluid viscosity, dyn s/cm;

σ_{ow} = the interfacial tension between the NAPL and fluid, dyn/cm;

$\Delta\rho$ = density difference between the fluid and PCE, g/cm^3;

g = gravity, 980.6 cm/s^2;

k = intrinsic permeability, cm^2;

k_{rw} = relative permeability, unitless, assumed to be 1; and

α = the angle of the flow makes with the horizontal direction to the right (counter clockwise).

In the case of vertical upward flow, sin α = 1, and the relationship between N_T and N_{Ca}, N_B simplifies to:

$$N_T = |N_{Ca} + N_B|.$$

For horizontal flow, sinα = 0, and

$$N_T = \sqrt{N_{Ca}{}^2 + N_B{}^2}$$

Pennell et al. (1996) also pointed out that the critical value of N_T required to initiate residual PCE DNAPL mobilization was within the range of 2×10^{-5} to 5×10^{-5}. However, onset of mobilization with much lower critical N_T (10^{-7}~10^{-6}) values have been observed with soil containing a moderate amount of clay (Padgett and Hayden, 1999; Zhai et al., 2005). To be safe, it is necessary to run lab-scale mobilization experiment with column packed with soil sampled from the target site.

For vertical penetration of DNAPL to occur, the DNAPL displacement pressure of the finer impeding layer must be lowered to a value less than the pressure exerted by the DNAPL pool. Therefore, the onset of vertical mobilization can be predicted by the relative magnitude of these two quantities, i.e. the actual thickness of the DNAPL pool, and the DNAPL displacement pressure of the underlying finer layer. Miller et al. (2004) proposed that the maximum DNAPL pool equilibrium thickness (approximately the actual thickness of the DNAPL pool if it was not newly formed) on a horizontal capillary barrier surrounded by otherwise homogeneous porous media is determined by the hysteresis between the DNAPL initial wetting curve (imbibition) and the initial drainage curve of the porous media. The leading edge of the DNAPL pool follows the imbibition curve and the other part of the pool follows the drainage curve. Therefore the maximum equilibrium thickness, T_e, in this case can be calculated as:

$$T_e = \frac{P_{d,c}^{wN} - P_{i,c}^{wN}}{\Delta \rho g}$$

where P_d^{wN} and P_i^{wN} are the drainage and imbibition water-NAPL entry pressure, and the 'c' subscript refers to the coarse media.

On the other hand the maximum thickness, T_m, of the DNAPL pool that can be supported by a fine stratified layer is determined by the difference of the capillary pressure at the base of the pool, *P''*, and that at the top of the pool, *P'*:

$$T_m = \frac{P'' - P'}{\Delta \rho g}$$

Usually P" is set equal to the entry pressure of the fine layer upon which the pool is perched, and P' is set equal to the entry pressure of the coarse material where the pool resides (Miller et al. 2004). Assuming the entry pressure is positively proportional to the interfacial tension, and given the air-water displacement pressure obtained through lab test for fine and coarse media, the maximum thickness of DNAPL pool with injected fluid, T_m^{cs} can be estimated as:

$$T_m^{cs} = \frac{\rho_w (h_f^{aw} - h_c^{aw})}{\Delta \rho g} \bullet \frac{\gamma^{cs/dnapl}}{\gamma^{a/w}}$$

where h_f^{aw} and h_c^{aw} are the air-water displacement pressure for the fine material and coarse material respectively, $\gamma^{cs/dnapl}$ is the interfacial tension between the injected cosolvent/surfactant fluid and DNAPL, and $\gamma^{a/w}$ is the interfacial tension between air and water. If $T_m^{cs} > T_e$, vertical mobilization is not likely to occur; if $T_m^{cs} < T_e$, it indicates the fine layer can't support such a thick DANPL pool and vertical penetration will occur (Roy and Smith 2004). It can be seen that the prediction of vertical mobilization requires careful laboratory bench-scale characterization of both the aquifer material and surfactant/cosolvent solution.

Water-miscible Cosolvents versus Surfactants: Advantages/disadvantages

The commonly used cosolvents in environmental applications are alcohols with densities typically around 0.8 g/cm^3. When used at volume fractions higher than 20%, the cosolvent/water solution will have a density significantly lower that of water, which will cause the cosolvent/water solution to flow preferentially to the upper portion of the aquifer, referred to as density-induced fluid override. Jawitz et al (1998a) observed this phenomenon when they used 20% ethanol to flush an unconfined aquifer created in a 2-dimensional flow chamber. The fluid override can reduce the sweep efficiency of a cosolvent if flushing is to be performed under the water table. Because of the low CMC values (thus relatively low surfactant concentrations needed) for most of the surfactants used widely for environmental application (Table 2), fluid override problems are not likely to be associated with surfactant flushing.

Although surfactant flushing technology has shown significant potential for use in NAPL remediation practices, one of the major problems associated with surfactant flushing is the potential formation of thermodynamically unstable emulsions. The unstable emulsion undergoes phase separation and may cause reduction of permeability due to clogging of soil pores (Ouyang et al., 2002). The other problem associated with using surfactants is their toxicity, which can be overcome by employing biodegradable surfactants.

On the other hand, most alcohols at cosolvent volume fractions amenable for *in-situ* cosolvent flushing are not as effective at dissolving DNAPL as many available surfactants. Therefore, alcohol flushing requires many more pore volumes of flushing solution than a well-designed surfactant flushing scheme to achieve the desired performance objectives. Furthermore, for DNAPLs exhibiting higher molecular weight, viscosity, and compositional complexity, the low molecular weight alcohols are less effective at DNAPL dissolution, while the higher weight or more complex alcohols are immiscible and much less soluble in water. Therefore, the range of DNAPL types that can be flushed with alcohols alone is relatively limited and mostly restricted to the lighter chlorinated ethanes and ethenes (ITRC, 2003). Cosolvent flushing is also affected more by field heterogeneity resulting in preferential flow. In the case of surfactant flushing, a more uniform sweep may be induced by mobility control using either polymer, which increases the viscosity of the injected solutions, or surfactant foam addition, which involves the in-situ generation of foam in high permeability zones to divert flow into low-permeability zones (ITRC, 2003).

Disposal of Flushing Wastes

Extraction fluids must be recovered from the underlying aquifer to prevent uncontrolled transport of contaminants and to optimize recycling of the flushing solution. The recovered solution may contain a very high volume fraction of surfactant and/or cosolvent relative to contaminant concentrations, which will vary with the quantity of NAPL contamination in the treatment zone and performance of the flushing system. The presence of alcohols frequently used as cosolvents increases the BOD/COD of the wastewater, and surfactants in the wastewater can cause the formation of foam upon contact with air. The extracted groundwater can be classified as a RCRA hazardous waste, because of high alcohol or surfactant content and/or elevated concentrations of NAPL contaminants. High operating cost inhibits the off-site management of a large quantity of hazardous waste. On-site treatment of recovered groundwater may reduce the cost significantly by eliminating transport costs and providing the potential of recycling injected chemicals.

The design of the wastewater treatment system depends on site-specific conditions. Federal, state, and local regulations need to be considered for the discharge standards of the treatment system. A wastewater treatment system designed to recycle injected chemicals must be able to reduce the contaminant concentrations enough to allow regulatory approval for re-injecting the extracted water while retaining as much surfactant and/or cosolvent as possible. Numerical simulations can be performed in the design phase to estimate the concentrations of flushing agents and contaminants in the extracted groundwater.

There are three primary principles to separate chemicals from extracted water: physical separation, phase separation, and degradation. Physical separation can be achieved by gravitational settling and size exclusion Gravity-based separations include decanting, flocculation, and sedimentation. A typical application based on size exclusion-based separation is membrane filtration. Phase partitioning removes the species of interest from the extracted groundwater by transferring it into a different phase, which can be a solid, liquid, or gas. The transfer mechanism is mainly volatility and sorption. Typical applications using volatility based separations are air stripping and steam stripping. The tendency of a contaminant to partition from the water phase into air is measured by the Henry's law constant (high Henry's constant indicates a strong tendency to partition to the air phase). Surfactants or cosolvents tend to hold contaminants in solution, which reduces the Henry's law constant. Typical applications involving sorption-based separations, which is inversely proportional to solubility, are carbon adsorption and solvent extraction. The octanol-water partition coefficient, K_{ow}, is a common measure of the relative affinity of a compound for the solid or organic liquid phase and water (a high K_{ow} indicates a high preference for the nonpolar material).

Degradation is the destruction of dissolved chemicals of concern through chemical, photochemical, biological, or thermal processes. Due to the high concentrations of organic chemicals present in the extracted groundwater, degradation processes are usually either not feasible or not economical, unless pretreatment processes such as physical separation or phase partitioning is first employed to reduce contaminant concentrations to tens of ppm levels. Biological degradation applications uses microbes to consume organic chemicals as an energy and/or carbon source. It is usually the most cost effective treatment method for a waste stream containing readily biodegradable surfactants. Mineralization, the complete degradation of the contaminants to carbon dioxide and water is the ideal endpoint for biodegradation processes. However, biodegradation of organic contaminants can generate by-products with simpler structures than the parent compound, but still toxic. By-products may require further treatment or disposal considerations (e.g., vinyl chloride production from chlorinated solvent degradation or sludge disposal from biological operations). Although chemical oxidation and chemical reduction reactions can be effective for treating dissolved-phase PCE and TCE in groundwater (Glaze and Kang, 1988; Hirvonen et al., 1996; Huang et al., 2001; Schnarr et al., 1998; Yan and Schwartz, 1999; Yan and Schwartz, 2000), the recovered wastewater can be several orders of higher in organic compound concentrations. Oxidizing agents are not selective and will react with any organic material including soil or dissolved organic matter and surfactant or cosolvent, thus consuming large quantities of oxidant to sufficiently reduce the COD loading. Photochemical degradation processes are more selective but are considerably more expensive. Additionally, ultraviolet lamps are susceptible to fouling by the precipitation of divalent cations. Thermal processes are impractical for degrading organic compounds within large volumes of wastewater. Detailed descriptions of each treatment method can be found in various references (AATDF, 1997; NFESC, 2002).

Technology Limitations

The following factors may limit the applicability and effectiveness of the in-situ soil flushing process:

- The flushing solution must be compatible with the *in-situ* environment.
- Subsurface heterogeneity can interfere with uniform distribution of flushing solutions.
- Low-permeability soils are difficult to treat.
- Surfactants can adhere to soil and reduce effective soil porosity.
- The flushing solution injection and collection systems must be designed and operated to limit the spread of contaminants to clean areas.
- The flushing solution must be recovered and treated.
- Complex waste mixtures (e.g., multiple contaminant classes) increase the difficulty of formulating a flushing solution.

Contaminant properties

Subsurface contaminants can be grouped into various classes, including synthetic organic compounds, naturally occurring organic compounds, inorganics (cations, anions, and radionuclides). Synthetic organic compounds are the focus of soil flushing because they tend to be removed through surfactant/cosolvent flushing. Most synthetic organic compounds encountered at contaminated sites are only sparingly soluble in water. As a result, they can exist in the subsurface as a NAPL. Many of NAPLs are highly persistent in the subsurface environment and cannot be removed from the subsurface within a reasonable time period by pump-and-treat. This persistence may be caused by slow dissolution kinetics of the compounds from NAPLs, slow diffusion of the contaminants from low permeability zones (which have accumulated pollutants over decades) or resistant desorption of the contaminants by the aquifer material (Teutsch et al., 2001). Several types of NAPLs commonly encountered at fields sites are discussed in detail below. Table 3 lists the contaminants considered for treatment by *in-situ* soil flushing.

Table 3. Contaminants considered for treatment by *in-situ* soil flushing (USEPA 1996a)

Contaminants	Industries Where Used
Halogenated solvents	Drycleanig, Electronic Assembly
Gasoline and fuel oils	Petroleum, Automobile
PCBs and Chlorinated phenol	Lubricant, Transformer

Chlorinated Solvents

One of the major components of DNAPLs in interest is chlorinated solvents, especially perchloroethylene (PCE), and trichloroethylene (TCE), which are used for dry cleaning and metal cleaning. Due to poor handling and disposal practices, solvents such as PCE and TCE enter the soil-water environment through leaks and improper disposal. It is estimated that there are more than 400,000 sites in US where soil and groundwater are contaminated by chlorinated solvents.

The chemical properties of chlorinated solvents and its metabolites are listed in Table 4. The high density of the chlorinated solvents (1.2 to 1.7 g/cm^3) relative to that of water (1 g/cm^3) and the low absolute solubilities of chlorinated solvents (typically on the order of hundreds of mg/L) mean that when a significant quantity of such a compound is spilled on the ground surface, liquid solvent will be able to migrate as a DNAPL phase into the subsurface, potentially accumulating as one or more pools on the top of low permeability layers. Also, chlorinated solvents have relatively low viscosities and this allow rapid downward movement in the subsurface. Chlorinated solvent mobility in the subsurface increases with increasing density/viscosity ratios (Cohen and Mercer 1993). The half-life of PCE in groundwater is estimated to be between 1 to 2 years assuming aqueous aerobic conditions, but may be considerably longer under certain conditions. There is scientific evidence that PCE may cause cancer from prolonged exposure even at levels below MCL. The US EPA classifies PCE as a probable human carcinogen. The EPA maximum contaminant level for PCE in drinking water is 0.005 mg/L.

Table 4. Chemical properties for chlorinated solvents and its metabolites

Compound	Vapor pressure (mm Hg at 20°C)	Solubility (mg/L)	Density (g/cm^3)	log K_{oc} (at 20-25°C)
Tetrachloroethylene (PCE)	14	143	1.62	2.43
Trichloroethylene (TCE)	58	1,000	1.46	1.26
cis-Dichloroethylene (*cis*-DCE)	160	3,500	1.28	-
Chloroethene (Vinyl Chloride)	195	1.1	0.91	-

In-situ soil flushing of chlorinated solvents has been well studied and some successful remediation cases have been reported (Brooks et al., 2004; Imhoff et al., 1995; Jawitz et al., 2000; Reitsma and Kueper, 1998a; Reitsma and Kueper, 1998b). PCE and TCE can also be biologically degraded through anaerobic reductive dehalogenation which involves electron transfer from of an electron donor (substrate) to an electron acceptor (chlorinated solvent). This enables the residual flushing solution be left on site after the soil flushing process to serve as an electron donor allowing sequential displacement of chlorine atoms by hydrogen. However, reductive dechlorination of PCE and/or TCE using native microorganisms often stalls at dichloroethene (DCE) or vinyl chloride because of a slow reaction rate and/or the lack of appropriate dechlorinating bacteria. Figure 11 shows the PCE degradation pathway through reductive dechlorination. *Cis*-DCE and vinyl chloride are even more toxic and recalcitrant in the environment so the accumulation of these metabolites is undesirable. Therefore, research related to microbial reductive dehalogenation of PCE is focusing on complete dechlorination of PCE to ethene.

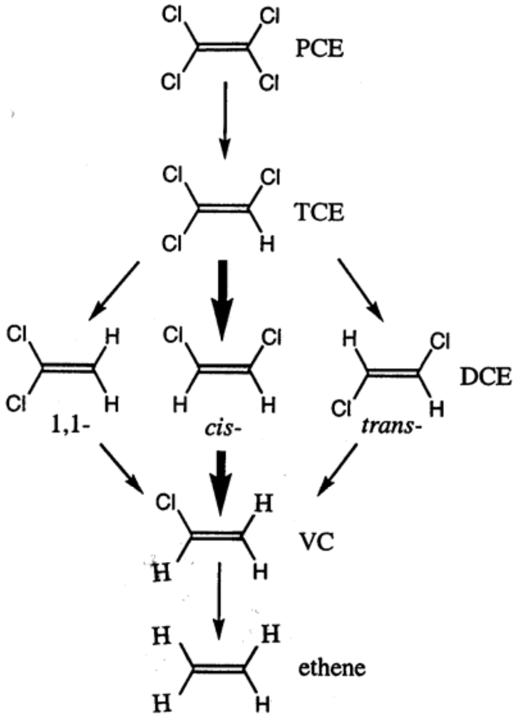

Figure 11. Microbial Dechlorination Pathway of PCE to Ethene (Middeldorp et al., 1999)

PCBs (Polychlorinated Biphenyls)

Polychlorinated biphenyls are mixture of up to 209 individual chlorinated compounds (known as congeners) in which 2-10 chlorine atoms are attached to the biphenyl molecule (Figure 12).

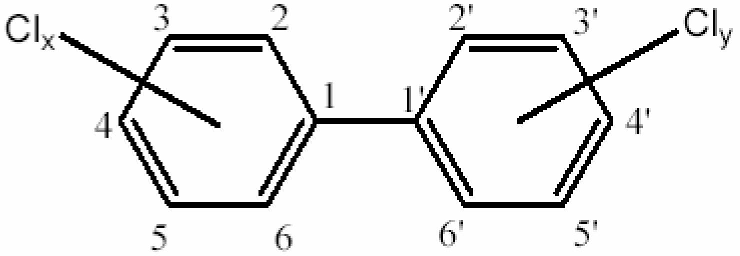

Figure 12. The general structure of polychlorinated biphenyls (PCBs)

PCBs have been used as coolant and lubricants in transformers and other electrical equipment because they don't burn easily and are good insulators. The trade name of PCBs is Aroclor. The manufacture of PCBs was stopped in the U.S. in 1977, because of evidence that they build up in the environment and can cause harmful health effects (ASTDR, 2000). PCBs have been recognized as priority soil/sediment contaminants at many sites. PCBs have limited solubility in water and have very low vapor pressure at soil ambient temperature, chemical, and bioremediation technologies may also not be very efficient under ambient conditions (Di et al., 2002), thus amenable for solvent extraction technology consideration. Technologies that have been applied, tested, or are under development include thermal sorption, solidification/stabilization, solvent extraction and slurry-phase bioremediation.

Gasoline and diesel fuel

Gasoline contains over 500 hydrocarbons that may have between 3 to 12 carbons. The main sources of soil and groundwater contamination by gasoline originate from underground storage tank spills in gas station. For example, in Indiana more than 7,700 regulated underground storage tank leaks have been reported since 1986. According to the Indiana Department of Environmental Management's annual state of the environment report at the end of 2002, nearly 51% of these tanks had been approved cleanup and closure. Approximately six percent of all active release sites are considered significant threats to humans or the environment and are undergoing cleanup. Figure 13 shows the leaking underground storage tank releases through 1993 and 2002.

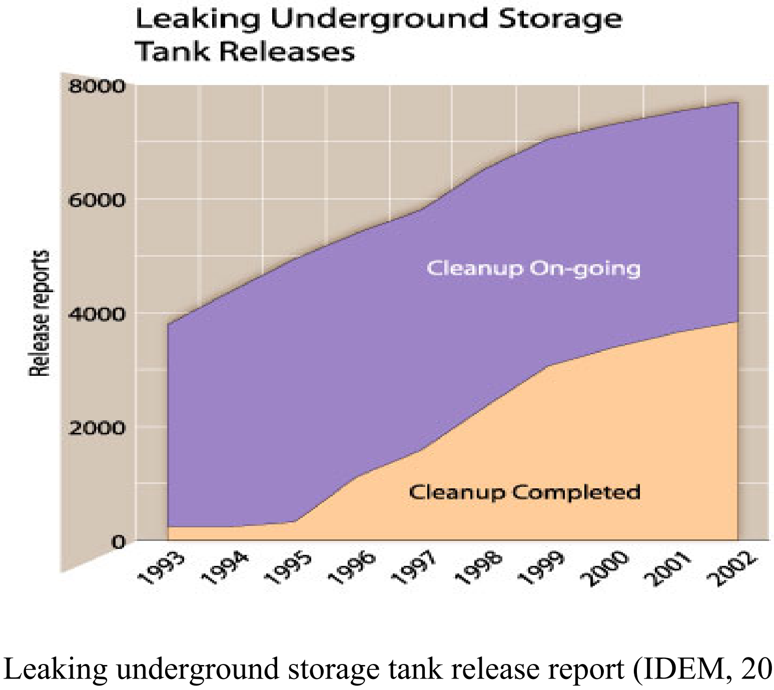

Figure 13. Leaking underground storage tank release report (IDEM, 2003)

The gasoline pool underground will be above or slightly under the water table and will serve as continuous release of a high concentration of aromatic hydrocarbons, such as BTEX (benzene, toluene, ethylbenzene, xylene) into groundwater. One gallon of gasoline containing one percent benzene can contaminate about two-million gallons of groundwater. The difference between diesel and gasoline is that gasoline contains more aromatic hydrocarbons and shorted aliphatics whereas diesel fuel is primarily straight and branched alkanes. Although diesel fuel and fuel oil are denser than gasoline and move more slowly through the soil, they will eventually reach groundwater (Herbel et al. 1998), and release high concentrations of BTEX into groundwater continuously.

The most recent problem associated with gasoline contamination is MTBE (methyl tertiary-butyl ether), which is added as an oxygenate to perform more complete combustion of gasoline and reduce carbon monoxide and N-oxide emissions. However, MTBE in drinking water causes taste and odor problem and MTBE is classified as a possible human carcinogen by the EPA as a result of inhalation cancer tests (Zogorski, 2001). MTBE's physical and chemical properties have given the environmental industry cause for concern. It has relatively high water solubility (approximately 50,000 mg/l), so it can achieve higher dissolved concentrations in groundwater than other gasoline components. It has a lower affinity for sorption than other gasoline components (Table 5), and therefore, moves with a velocity close to that of groundwater. Its low Henry's constant leads to its partitioning to the water phase rather than air. MTBE also has a much lower biodegradation rate than other gasoline components of concern, such as benzene, toluene, ethyl benzene and xylene, and has the potential to travel considerable distances from the release site. As a result, MTBE's fate and transport in the environment has been an area of active research in recent years. Current and emerging technologies for the remediation of gasoline components, including residual and dissolved MTBE are: soil vapor extraction; bioventing; air sparging; *in-situ* ground water bioremediation; ex situ groundwater bioremediation; pump and treat; *in-situ* chemical oxidation; and monitored natural attenuation. Many states have or will opt out of using MTBE and seek other alternatives for fuel efficiency.

Table 5. Chemical Properties of Selected Hydrocarbons (Modified from Fiorenza et al., 2002)

Compound	Vapor pressure (mm Hg, 20°C)	Solubility (mg/L)	Henry's law constant (dimensionless)	log K_{oc} (at 20-25°C)
Aromatic gasoline hydrocarbons				
Benzene	95.2	1,750	0.22	1.58
Toluene	30.0	515	0.26	2.13
Ethylbenzene	10.0	152	0.32	1.98
m, p, o-xylene mixture	7.0	198	0.29	2.38
Oxygenates				
Methyl tertiary butyl ether (MTBE)	240	48,000	0.022 to 0.12	0.55 to 0.91

Biofriendly solvents

Several compounds, including ethanol and ethyl lactate, are being investigated for their efficiency as cosolvents to remove of chlorinated ethenes (Imhoff et al., 1995; Jawitz et al., 2000; Ridgway, 2001). Once soil flushing has removed the contaminant source material, recovery of the cosolvent is needed and is known to be more expensive than the cost of the co-solvent itself (Ridgway, 2001), thus reuse of solvent is essential for cost-effective application (Gannon et al., 1989).

Biofriendly solvents have been a topic for research on in-situ cosolvent flushing. They are biodegradable products and generally nontoxic to microorganisms, therefore a residual amount of solvent may be allowed to remain in the subsurface after soil flushing. There is an economic benefit when there is no need to recover used solvent. There would be an additional benefit if biofriendly solvent could also be used as a substrate by the indigenous microorganisms to induce anaerobic conditions and enhance *in-situ* reductive dehalogenation (Ridgway, 2001). Reductive dehalogenation is the removal of halogen from halogenated compounds. Newell et al. (Newell et al,. 2001) reported this approach may have the potential to increase the naturally-occurring rate of DNAPL mass destruction at many sites without any long-term operating costs except monitoring.

Ethyl lactate

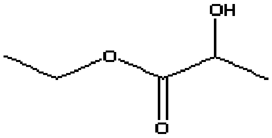

Figure 14. Molecular structure of Ethyl lactate

One of biofriendly compound that has recently been studied is ethyl lactate. Ethyl lactate (NTEC Versol^{TM}, Versol Inc., Mt. Prospect, IL) is an organic solvent made from corn or other renewable carbohydrates. It is the ethyl ester of natural L (+) lactic acid, produced by fermentation from sugar. It is a clear and colorless liquid of low volatility and is completely miscible with water and most organic solvents. It is nontoxic, hydrolyzes to known biodegradable intermediates and is currently being used as a replacement for a chlorinated solvents used in degreasing metal parts during manufacturing (Trychta et al., 1999). It is also used as a synthetic flavoring for cheese, animal feed, and beer in addition to a solvent degreaser for machine parts. Until recently, ethyl lactate was too costly to use as a routine solvent; however, an improved purification process developed by Argonne National Labs has made it more economical (Biocycle, 1999 June, page 21). The water soluble ethyl lactate hydrolyzes when water reacts with the ester group; however, this hydrolysis step is generally slow. For example, it takes about 5 days before any drop in pH due or production of lactic acid is noticeable in a 50/50 ethyl lactate/water solution at room temperature. The rate of hydrolysis accelerates with increasing temperature and at pH values below 5 and above 8 (NTEC Versol).

Ethyl lactate is nontoxic and hydrolyzes to known biodegradable nontoxic intermediates, so a residual amount may be allowed at the site after a soil flushing. An additional benefit would be obtained if the residual ethyl lactate could be used by the indigenous microorganisms as a substrate to induce anaerobic conditions and enhance *in-situ* bioremediation (Ridgway 2001). Ethyl lactate has not been used as a cosolvent for field scale NAPL removal. Lab experiments have shown that it has a strong solubilization power for PCE and toluene (Lee et al., 2006), and that it promoted microbial dechlorination of PCE (Jayaraj et al., 2004). Ethyl lactate hydrolyzes to lactic acid and alcohol resulting in the potential to invoke a pH drop in the system. Reductive dechlorination prefers near neutral pH and greatly affected by pH drop. More research is needed to obtain information about its fate in the subsurface and its effect on dechlorinating microorganisms following *in-situ* flushing.

Ethanol

Ethanol is an important component of liquor, and should also be considered to be a biofriendly solvent. It was used on a pilot-scale field test for enhanced remediation of a DNAPL source zone of a former dry cleaning operation in Jacksonville, FL by Sillan (1998) and Jawitz et al. (2000). The 95/5 ethanol/water solution was used with an estimated mass reduction of 62% without inducing mobilization of PCE. After the alcohol flushing, Mravik et al. (2003) evaluated the effect of solvent extraction residuals on PCE dehalogenation in the field. They flushed the site with 34kL of 95% ethanol with 2.72kL of ethanol left in the subsurface to serve as an electron donor for PCE dehalogenation for which enhanced biotransformation of PCE to ethene was observed after 3 years. This result shows the biofriendly cosolvent flushing systems can be designed and utilized to aid in the enhancement of biodegradation processes at DNAPL sites after flushing.

Time and Cost Estimates of Soil Flushing

Soil flushing is expected to achieve clean up in an operation and maintenance duration of 4 to 9 months, depending on the following conditions:

- Cleanup goals
- The volume of *in-situ* media requiring treatment
- Contaminant concentrations and distribution
- *In-situ* characteristics including permeability and anisotropy
- Flushing solution delivery capacity.

The range of estimated costs that have been documented are presented in Figure 15. Costs can be reported per unit volume of porous medium treated, per unit volume of NAPL recovered, and per unit area of site. According to Lowe et al. (1999), it should be noted that different methods were used to prepare these cost estimates, so they may not be directly comparable and it should also be noted that all of the estimates were prepared for sites with contamination less than 15 meters (49 feet) below ground surface. Some of the capital cost components will be independent of system size. For larger sites, the costs of chemicals and residual disposal are significant, making up over 60% of the total cost and for smaller sites, the produced fluids treatment system may also be a significant cost component.

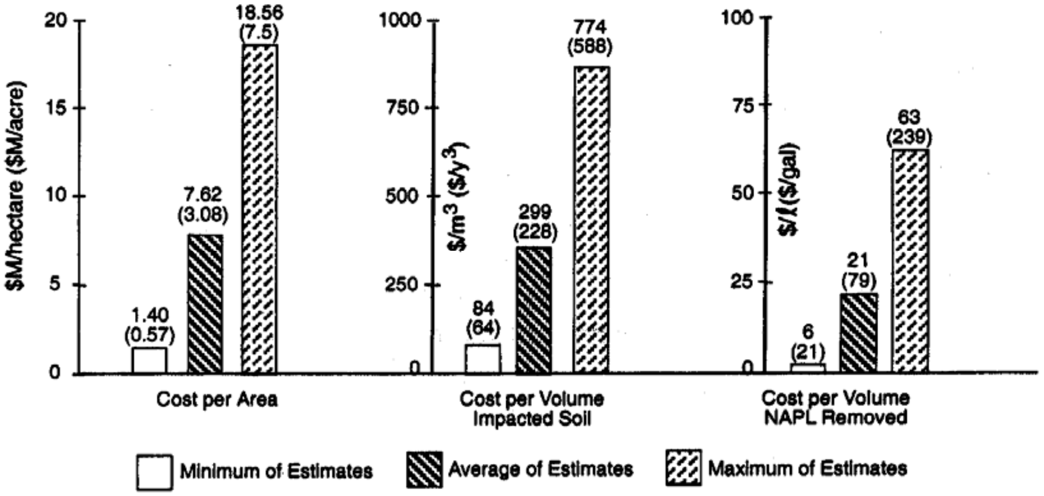

Figure 15. Average and the range of cost estimates (Lowe et al. 1999).

The major cost items included in the cost estimate range for soil flushing are summarized n Table 6. Indirect costs such as project management, design and engineering, vendor selection, home office support, permit preparation and fees, regulatory interaction, site characterization, treatability testing, performance bond, and contingencies can be further included in the estimated cost range. Costs can also be estimated from some case summary reports (ITRC, 2003) with cost information for sites with similar conditions (size, hydrologic condition, and contaminant type and amount).

Table 6. Items for estimation of Cost for Soil flushing (NAVFAC)

Fixed Cost Items
Injection and recovery well and pump installation
Sampling wells installation
Flushing solution preparation system installation
Flushing solution treatment system installation
Variable Cost Items
Operating and maintenance labor
Utilities
Chemicals
Site supervision
Site quality assurance and health and safety support
Sampling and analysis for process control
Residuals Management Activities
Off-site disposal of sludge residual from flushing solution treatment

Permits and Regulatory Approval

Even if sites have no specific permitting authority, the regulators of the site (federal, state, and possibly local/regional) typically need to accept the concepts and objectives of the field demonstration. To include the regulators as part of the team early in the development of the process is one way to considerably facilitate regulatory acceptance. Two EPA publications (USEPA, 1995; USEPA, 1996b) provide excellent reviews of the regulatory requirements for obtaining state approval. EPA (1995a) summarized the concerns of states identified in the survey as follows:

> “The survey identified state concerns about the toxicity of the surfactant, masking effects (on analytical tests), transfer of contaminants from soil to groundwater, satisfactory hydrologic control, and adequate monitoring to ensure that processes taking place in the subsurface are understood. In particular, state regulators need to be convinced that use of surfactants will not make the situation worse, that NAPLs are not

mobilized without being recovered, and that the surfactant itself can be recovered or remediated."

Both CERCLA sites and non-CERCLA sites (RCRA sites, private sites, state Superfund sites, federal facilities, etc.) may have potentially applicable regulation at state and federal levels. In particular, they both are regulated by the Underground Injection Control (UIC) program, under which injection of any fluid into a well is prohibited unless authorized by permit or rule. USEPA groups underground injection into five classes based on the well functions, construction, and operating features, so that technical requirements can be applied consistently to the classes. Injection wells for aquifer remediation and experimental technologies are designated as Class V. Class V injection wells covered by federal UIC program are authorized by rule and do not require a separate UIC permit. But a Class V injection well under state UIC program may require a permit depending on state-specific regulation (USEPA, 1996b).

One of regulatory barriers to the implementation of in-situ soil flushing is to obtain injection approval for the surfactant and/or cosolvent. This is especially obvious if the flushing agents selected are listed as subsurface contaminants and considered for remediation. Toxicity should be one of the criteria used in selection of chemical for flushing in the screening stage of the design. Some researchers have focused on use of food-grade surfactants or cosolvents, the so-called "environmental-friendly" chemicals, for soil flushing to increase likelihood of getting regulatory approval. Such "environmental-friendly" chemicals include the above mentioned ethyl lactate and ethanol.

The extracted or treated groundwater may need to be discharged to a municipal waste water treatment plant (WWTP), which is also referred to as publicly owned treatment works (POTW) for which a National Pollutant Discharge Elimination System (NPDES) permit is required. Other wastes generated, including waste water treatment sludge and residual solids, spent carbon and ion exchange resin, must be managed and properly disposed of to avoid cross-media contamination. If the treated cosolvent/surfactant solution is to be re-injected for recycle, it is necessary to make sure the contaminant level is low enough to meet the UIC requirements. Depending on the treatment method used, some additional permit may be required, such as an air discharge permit if air or stream stripping is used to separate chlorinated solvents from cosolvent or surfactant solutions (AATDF, 1997).

Worker safety issues such as drilling wells, installing and operating aboveground treatment units, piping, and handling of chemicals must be addressed. Most surfactants and cosolvents contain alcohols, which when used at high concentrations can be flammable and explosive. Proper personal protection equipment are required as defined by OSHA, 29 CFR 1910.120. Appropriate Material Safety Data Sheets (MSDAs) for all chemical involved should be included in the Site Safety Plan (ITRC, 2003).

Evaluation of the Applicability of surfactant/cosolvent flushing

The use of surfactant and cosolvent flushing is increasing, although technology development is still emerging. Key screening issues for application of soil flushing have been well defined by Lowe et al. (1999) and are summarized in Table 7. Full scale remediation case studies using in-situ flushing technology completed by 2001 reported in the Abstracts of Remediation Case studies (Roundtable 2003) are summarized in Table 8. Numerical simulation is a very useful tool to evaluate the performance of in-situ soil flushing. Various simulation tools are readily available (AATDF, 1997). The mostly commonly used model is UTCHEM, which when verified with some lab and field data, is comprehensive and a good predictor (NFESC 2002; Ouyang et al. 2002). A detail description of UTCHEM can be found at NFESC report (2002). It is strongly recommended that numerical simulation, lab test and pilot scale test be performed before a full-scale application. Step-wise implementation procedures are given in detail in AATDF report (1997).

Performance Metrics

The performance of an in-situ soil flushing system can be assessed by several metrics. Traditionally the mass removed is an important criteria. Mass-based metrics include the final average NAPL saturation and the percentage of the contaminant mass removed. These metrics required the initial and final NAPL mass to be known, which can estimated from soil coring data, or more precisely, through partitioning inter well tracer tests (PITT) (Brooks et al., 2002). However, the uncertainties associated with either soil coring or PITT can make mass–based metrics quite complicate. Some lab tests indicate that the residual amount surfactant or cosolvent left by in-situ flushing can lead to the underestimate or over estimate of NAPL saturation through PITT (Cho et al., 2004; Cho et al., 2003). A more comprehensive performance metric is the risk associated with any NAPL remaining after treatment, as well as the risk reduction accomplished with the NAPL-removal action. The percentage of a NAPL recovered as a performance metric overlooks the risk of un-removed NAPL. To evaluate the effectiveness of NAPL removal, the final NAPL saturation should be considered rather than the percentage of mass removal (ITRC 2003). Another criterion to evaluate a flushing system may be based on the percentage of the injected chemicals recovered, which is also a measure of the efficiency of hydraulic control (ITRC, 2003). High NAPL recovery usually is associated with of high recovery efficiency of injected chemicals; however, high recovery of injected chemical does not indicate high NAPL recovery, as poor sweep efficiency may occur even if injected fluids are effectively captured. If the NAPL recovery is low, the recovery of injected chemicals may shed light on why this occurred (ITRC 2003).

Recently, the source strength or mass flux of contaminants emanating from the source has been introduced as a new site remediation performance metric for consideration (ITRC, 2004). Contaminant mass flux is defined as “rate per unit area at which solute mass in the groundwater crosses a spatial plane oriented at a right angle to the direction of groundwater flow” (Rao, 2003) (Figure 16). It is argued that the natural attenuation capacity of a plume can be estimated from the contaminant flux at two or more parallel control planes. If the contaminant flux exiting from a source zone is below the natural attenuation capacity, the plume is under control, and it will shrink and disappear (ITRC, 2004). Source strength is not only a function of NAPL mass, but also depends on NAPL distribution and hydrodynamic characteristics of the source zone. Therefore, decreases in NAPL mass does not necessarily lead to correspondingly large decreases in mass flux. From a risk perspective, flux provides more accurate information on risk reduction due to source depletion (ITRC, 2004). Flux can be measured through several ways, including continuous pumping from an extraction well, multilevel sampling along a transect of wells, and integrated pump test, and passive borehole flux meter (ITRC, 2004). A more innovative flux measurement is passive borehole flux meter, which is non-destructive, and can provide higher vertical resolution (Hatfield et al., 2004). Flux meters contain sorbent material preloaded with tracers. After being deployed to monitoring wells, the tracers will leach due to groundwater flux, providing cumulative or time-average groundwater velocity. Meanwhile contaminants will be captured by the sorbent, allowing calculation of cumulative or time-averaged contaminant flux. After a predetermined period of time, flux meters are retrieved and analyzed for amount of tracer left and contaminant captured. The combination of these two gives contaminant flux at different depth intervals.

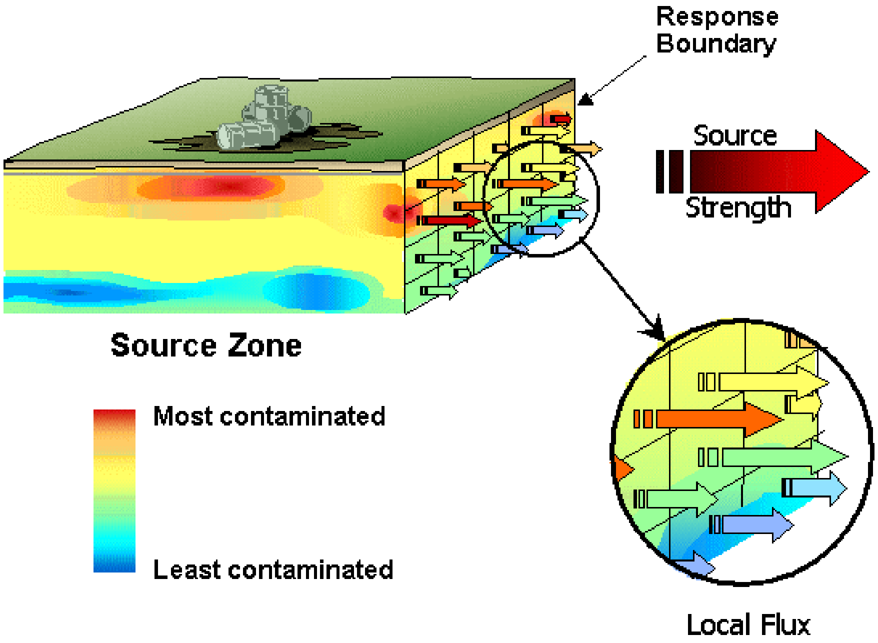

Figure 16. Concept of Mass Flux/Discharge and Source Strength (ITRC, 2004)

When flux is to be used to performance metrics, it should be noted that, unless most of the NAPL mass is removed, the concentration of contaminant is likely to increase due for a short period until surfactant or cosolvent residuals dissipate, especially if substantial amounts of flushing solution is left behind. Therefore, the flux determined immediately after flushing may be higher than before pre-treatment for a short duration.

Table 7. Surfactant/Cosolvent Flushing Screening Issues (Modified from Lowe et al., 1999)

Screening Issue	**Comments**
Are NAPL present?	Because surfactant/cosolvent flushing is primarily a NAPL remediation technology, the presence or absence of NAPL is a key screening consideration. Initially, this can be evaluated through development of a site conceptual model.
Are the soils sufficiently permeable to transmit a chemical system?	One of the technology limitation is, low-permeability soils are difficult to treat, factors controlling flushing rates should be identified.
Do chemical systems exist that can remove the target compound at the site of concern?	Preliminary selection of a chemical system can be accomplished through consideration of contaminant type, hydrogeologic setting, and previous experience. This is an important step in developing a preliminary cost estimate.
Once above ground, is there a cost-effective means to treat the produced fluids?	Fundamental to the feasibility of surfactant/cosolvent flushing are cost-effective methods to manage the produced fluids.
Can a surfactant/cosolvent system achieve the remedial objectives?	In terms of remedial objectives, surfactant/cosolvent flushing by itself has the potential to remove substantial amounts of mass from a targeted interval, but likely will not restore water in the targeted interval to typical drinking water standards
From a regulatory perspective, is it feasible to deliver a chemical system to the target?	Obtaining regulatory acceptance for delivery of chemicals to the subsurface can be a significant challenge because of concerns regarding potential adverse effects of the chemicals.
Is surfactant/cosolvent flushing economically feasible?	Surfactant/cosolvent flushing may be a relatively expensive technology. Economic analyses should be conducted on both a net present worth and an annual cost basis when comparing technologies.
Within the constraints of current or planned land use, is it feasible to implement a surfactant/cosolvent remedy?	Fluid injection, recovery, and treatment systems may involve an extensive network of piping and process equipment. Such systems may not be compatible with some land uses (e.g., process areas in petroleum refineries).
Are there any significant adverse risks associated with implementing surfactant/cosolvent flushing at the site of interest?	Adverse vertical migration of DNAPLs, loss of target zone permeability, and production of difficult to manage residual fluids and/or solids are all potential issues to be addressed.

Table 8. Summary of remediation case studies (full-scale) conducted before 2001 using *in-situ* soil flushing (Federal Remediation Technologies Roundtable, 2003)

Site Name, Location	**Technology**	**Media**	**Contaminants**	**Year Begin**	**Year Published**
Camp Lejeune Marine Corps Base, Bldg 25, Camp Lejeune, NC	In-situ flushing	Groundwater; DNAPLs	PCE ; TCE ; DCE ; Volatiles-Halogenated ; BTEX ; Volatiles-Nonhalogenated	Not provided	2001
Fernald Environmental Management Project, OH	In-situ flushing	Groundwater	Heavy Metals	1998	2001
Former Sages Dry Cleaners, Jacksonville, FL	In-situ flushing (Ethanol Cosolvent)	Groundwater; DNAPLs	PCE; TCE; DCE; Volatiles-Halogenated	Not provided	2001
Multiple Dry Cleaner Sites	In-situ flushing; Thermal Treatment; In-Well Air Stripping	Groundwater; DNAPLs	PCE; TCE; Volatile-Halogenated	Not provided	2001
RMI Titanium Plant, Ashtabula Environmental Management Project, OH	In-situ flushing	Groundwater; Soil	TCE; Volatiles-Halogenated; Radioactive Metals	1999	2001
Site 88, Building 25, Marine Corps Base Camp Lejeune, NC	In-situ flushing	Groundwater; DNAPLs; LNAPLs	Petroleum Hydrocarbons; Volatiles-Nonhalogenated; PCE; Volatiles-Halogenated	1999	2001

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