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GROUNDWATER CONTAMINATION BY CREOSOTE

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ABSTRACT

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Creosote has been used as a wood preserving chemical in North America for approximately a hundred years. Releases of creosote at many past and present site of wood preserving operations have resulted in the accumulation of significant quantities of creosote liquids in the subsurface underlying the sites. Creosote, like chemicals such as chlorinated solvents, halogenated benzenes and polychlorinated biphenyls (PCBs) belongs to a group of chemicals which are referred to as dense non-aqueous phase liquid (DNAPL) chemicals. These chemicals are immiscible in water like petroleum hydrocarbons, but unlike petroleum hydrocarbons, they are more dense than water. Because creosote is immiscible and is more dense than water, creosote can penetrate downward into the subsurface will depend on the quantity released and nature of the release, and the residual capacity of the soil. Because DNAPL is more dense than water it can penetrate significantly below the water table and form zones of residual contamination or form a layers or pools on barriers of lower permeability soil or rock. DNAPL can migrate considerable distances through the subsurface. Because DNAPL can penetrate below the water table it can create a significant source of groundwater contamination.

Groundwater which comes in contact with creosote liquids in the subsurface will dissolve small, but potentially significant, quantities of chemicals from the creosote. Creosote is a complex mixture of PAH (polycyclic aromatic hydrocarbons) compounds such as phenanthrene, naphthalene, acenaphthene, fluorene, fluoranthene, anthracene and pyrene; phenolic compounds and aromatics such as benzene, toluene, ethylbenzene and xylenes (BTEX). PAH compounds are generally regarded as having low water solubilities, however, PAH solubilities can be thousands of times greater than drinking water standards for compounds such as benzo(a)pyrene. The magnitude of the dissolved-phase concentrations in groundwater will depend on the concentration of the constituent compounds in the creosote and the solubilities of the constituent compounds. PAH compounds such as naphthalene, acenaphthylene, acenaphthene, and fluorene having the highest solubilities would be expected to exhibit the highest dissolved concentrations in groundwater. Less soluble compounds such as benzo(a)pyrene, benzo(ghi)perylene and dibenzo(a,h)anthracene would be expected to occur at much lower concentrations. In most geologic media, PAH compounds will migrate at the rates much slower than the rate of groundwater movement because PAH compounds are sorbed significantly by geologic materials. The water solubility of PAH compounds is inversely related to the degree to which the compounds will be sorbed onto geologic materials. The most soluble compounds such as naphthalene, acenaphthylene, acenaphthene, fluorene and anthracene will be less strongly sorbed than fluoranthene, chrysene, benzo(a)pyrene and benzo(ghi)perylene. In general, because of the low mobility, PAH compounds would not be expected to be significant groundwater contaminants compared to phenolics and BTEX components of the creosote which should be much more soluble and correspondingly much more mobile in groundwater.

Except when complete excavation is possible, the complete clean-up of creosote, like other DNAPLs, from below the water table has not been demonstrated to be feasible with available technologies. Currently, physical or hydraulic containment are the only options available to control further groundwater containing to the enhanced recovery of creosote from the subsurface.



1. Introduction

Creosote is a complex mixture of polycyclic aromatic hydrocarbons (PAH), nitrogen and sulfurcontaining heterocyclic aromatic hydrocarbons, phenolics, and sometimes aromatics such as benzene, toluene, ethyl benzene and xylenes (BTEX). Creosote is typically distilled from coal tar. Creosote, in its pure form or mixed with petroleum hydrocarbons (such as fuel oil), has been used as a wood preserving chemical in North America for approximately one hundred years. Releases of creosote at many past and present sites of wood preserving operations have resulted in the accumulation of significant quantities of creosote liquids in the subsurface underlying these sites. Creosote, like industrial chemicals such as chlorinated solvents, halogenated benzenes and polychlorinated biphenyls (PCBs) belongs to a group of chemicals which are referred to as dense non-aqueous phase liquids (DNAPLs). These chemicals are immiscible in water like petroleum hydrocarbons, but unlike petroleum hydrocarbons, they are more dense than water. For the purpose of this paper, pure creosote liquid which is more dense than water (DNAPL) will be referred to simply as creosote.

The potential for groundwater contamination by creosote is high because its high density enables creosote released into the subsurface to penetrate downward through the unsaturated zone above the water table (vadose zone) and the saturated zone below the water table (groundwater zone) as a separate non-aqueous phase. The tendency for DNAPL creosote to sink through the saturated zone differs from that of petroleum hydrocarbons which will float on the groundwater due to their lower densities. In the subsurface, small but significant quantities of chemicals can be dissolved by groundwater in contact with the creosote and can result in groundwater contamination.

The potential for groundwater contamination by creosote is high because very large quantities of these chemicals have been and are still used at wood preserving facilities throughout North America. At such sites, subsurface contamination can result from leaking underground or aboveground storage tanks, pressure treating vessels and drip sumps. Groundwater contamination resulting from creosote sources in the subsurface can be serious because drinking water standards for PAH, phenolic and BTEX compounds are low. Dissolved concentrations of micrograms per litre or less in groundwater used for water supply can cause taste and odour problems and are considered to represent potential health risks. Although DNAPL creosote is immiscible in water, the effective solubilities of its components are often many orders of magnitude higher than their respective drinking water standards. Table 1 shows the pure-phase liquid solubility of creosote components compared to the New York State Guidelines or Criteria for Potable Groundwater. New York State standards are shown here because Canada has few guidelines or standards for organic chemicals in groundwater and New York has designated guidelines or criteria for more organic chemicals than most other jurisdictions.

2. DNAPL Migration

2.1 Porous Media

Based on recent laboratory studies, modeling studies and field experiments together with observations at many chemical spill and waste disposal facilities in North America, several general conceptual models can be described for the development of groundwater contamination from DNAPL such as creosote. In these conceptual models, a quantity of DNAPL is introduced into the subsurface such as might occur at a wood preserving facility. In such situations, creosote may penetrate downward through the vadose zone and the groundwater zone.

The migration of creosote through the subsurface can be described using the same general principles of multi-phase flow applicable to petroleum hydrocarbons. Consideration of creosote

migration must account for the interactions between the creosote, water and air phases in the vadose zone, and the creosote and water phases in the groundwater zone. For the purpose of this discussion, it is convenient to consider two different but related aspects of DNAPL migration through geologic media: conditions for DNAPL entry, and conditions for DNAPL flow.

The entry of DNAPL into geologic media is controlled primarily by capillary phenomena arising from the fact that there exists a finite interfacial tension between two or more mutually immiscible fluids. In addition, the wettability of the water-DNAPL-geologic solid system will dictate largely under which conditions DNAPL will enter a porous or fractured medium. Below the water table where DNAPL is typically non-wetting with respect to water, DNAPL entry will occur more readily in higher permeability media, under conditions of higher driving pressures, for DNAPL with higher densities and for DNAPL with lower interfacial tension. This implies that for water-saturated conditions in the subsurface, finer-grained strata such as silts and clays or rocks having small aperture fractures may exclude entry of DNAPL and represent barriers to DNAPL migration. Above the water table in regions of low water content, DNAPL may act as a wetting fluid with respect to air. There is also evidence (Villaume, 1983) that coal tar / creosote may be the wetting-phase below the water table in some circumstances. In such cases DNAPL entry may occur more readily into finer-grained media and smaller fractures.

The flow of DNAPL through geologic media will depend on DNAPL properties such as density and viscosity; the pressure driving the DNAPL migration; the intrinsic permeability of the geologic medium; and the degree of DNAPL saturation of the pore space in the medium. Higher rates of DNAPL flow will occur in more permeable media, for higher DNAPL saturations, and for DNAPL having higher density and lower viscosity. Creosote generally has a density slightly greater (1.01 g/cm³ to 1.04 g/cm³) than water and viscosities much higher than water so that in a given geologic medium with conditions of high DNAPL saturation, DNAPL migration may occur at rates significantly slower than those for groundwater.

Conceptual models of DNAPL migration and the development of groundwater contamination from DNAPL sources in granular media are illustrated by Figures 1A, 1B and 1C, and conceptual models for fissured or fractured media are shown in Figure 2. These models are described in the following section. These conceptual models are derived primarily from research on other DNAPL chemicals such as chlorinated solvents, however, these models are also valid for creosote.

Figure 1A represents the case of a relatively small spill or release in which all of the DNAPL has penetrated into the vadose zone and forms a zone of residual DNAPL contamination because the volume released did not exceed the retention capacity of the vadose zone. Within this residual zone, the DNAPL is present as immobile, unconnected and partially connected blobs and filaments. In this case the DNAPL did not reach the water table. For a given volume of DNAPL released in a given geologic medium, the depth of penetration will be influenced by the area over which the release occurs and the rate of release. Two experimental field releases of DNAPL tetrachloroethylene (PCE) into the vadose zone of a stratified sand aquifer were performed by Poulsen and Kueper (In preparation). One release of 6 L simulated an instantaneous spill over an area of 0.1 m^2 on the ground surface. The PCE from this spill penetrated to a depth of 2.15 m. A second release of 6 L simulated a slow leak with an area of 1 cm² over a time of 100 minutes. For this spill the PCE penetrated 3.3 m to the water table. For the same volume of release, DNAPL solvent penetration was greater for the slow release spill. For both spills, DNAPL migration was strongly influenced by the stratification of the sand. DNAPL migrated preferentially along coarser-grained layers, and did not enter the finer-grained layers. The influence of stratification on DNAPL migration appeared greater for the slow release spill compared to the instantaneous release. The behaviour of creosote would be expected to be analogous although creosote would migrate at a slower rate than PCE because it is less dense and more viscous than PCE.



From laboratory column experiments using homogeneous sand materials, residual contents of DNAPL chemicals in unsaturated soils were found to range from 3 to 30 L/m³ or 1 to 10% of the pore space (Schwille, 1988). For the stratified sands in the field experiments conducted by Poulsen and Kueper (In preparation), residual DNAPL contents of the layers containing DNAPL were measured to range from of 2% to 18% of the pore space. The residual contents are comparable to those measured for petroleum hydrocarbons (Wilson and Conrad, 1984). Predictions of the depth of penetration based on the volume of the release and estimates of the residual content would be useful in the assessment of DNAPL spills. However, because of the influence of heterogeneity of the geologic medium on the migration of DNAPL and thus the distribution of residual, such predictions of the depth of penetrations of the depth of penetrations of the depth of penetrations are useful in the depth of penetration based on the work because of the influence of heterogeneity of the geologic medium on the migration of DNAPL and thus the distribution of residual, such predictions of the depth of penetrations are useful be subject to a high degree of uncertainty.

BTEX compounds have high vapor pressures and in situations where creosote containing such compounds exists in the vadose zone, a plume of vapors will develop in the soil air surrounding the DNAPL source. Theoretical and modeling studies of vapor transport performed by Mendoza and McAlary (1990) and Mendoza and Frind (1990a, 1990b) indicated that the diffusion of vapors outward from DNAPL sources can result in the formation of vapor plumes in the vadose zone which may extend tens of metres from the source and which develop in period of weeks to months. For high vapor pressure compounds with relative vapor densities significantly greater than air, advective sinking of dense vapors through the vadose zone to the water table may occur in high permeability media. Confirmation of the findings of these theoretical and modeling studies is provided by field experiments of trichloroethylene (TCE) vapor transport in the vadose zone of a sand aquifer performed by Hughes et al. (1990). However, comparable studies for the development of vapor plumes from creosote sources have not been reported.

For the conceptual model shown in Figure 1A, groundwater contamination develops when water that infiltrates through the zone of residual DNAPL and the vapor plume carries dissolved contaminants to the water table. As infiltration of precipitation occurs from time to time, a plume of dissolved contaminants develops in the groundwater zone.

In Figure 1B, the volume of DNAPL released is sufficiently large for DNAPL to move into the groundwater zone but not large enough for DNAPL to reach the bottom of the aquifer. Lateral groundwater flow patterns may not effect the movement of DNAPL through the groundwater zone. In laboratory experiments by Schwille (1988) the downward penetration of TCE and PCE in coarse and medium sand was not noticeably affected by horizontal groundwater flow velocities as high as 14 m/day. Creosote has a much lower density than TCE or PCE (1.01 to 1.05 g/cm³ compared to 1.47 to 1.63 g/cm³). Consequently, the gravitational force which causes creosote to sink will be less and lateral groundwater flow may have a greater influence on creosote migration. As in the vadose zone, the migration of DNAPL in the groundwater zone will be strongly influenced by heterogeneity of the geologic media. Finer-grained layers will restrict downward migration of DNAPL and may result in the formation of DNAPL layers and pools or deflect DNAPL migration laterally. Lateral migration of DNAPL may occur independent of the direction and magnitude of groundwater flow. The effect of heterogeneity on DNAPL migration has been clearly illustrated by laboratory experiments and modeling studies performed by Kueper et al. (1989) and Kueper and Frind (1990a and 1990b).

The few data available on residual contents of DNAPL chemicals in saturated soils indicate values ranging from 5 to 50 L/m^3 or 2 to 15% of the pore space in sandy soils which are higher than for unsaturated soils (Schwille, 1988). Residual contents are higher in the finer-grained soils. In general, the degree of residual saturation formed at the trailing edge of a migrating DNAPL body will be function of the maximum DNAPL saturation previously attained in that region of the medium. Regions invaded by large amounts of DNAPL will be characterized by higher residual contents. The presence of DNAPL in the pore space in the residual zones reduces, but does not

prevent, groundwater flow through the residual zones (Anderson *et al.*, 1987). Groundwater that flows through these residual zones dissolves a portion of the DNAPL and results in dissolvedphase contaminants in the groundwater. Within the DNAPL layers or pool, DNAPL may occupy from 40% to 70% of the pore space. At these DNAPL saturation values, the permeability of the geologic medium to groundwater flow will be substantially reduced. In these zones, the rate of dissolution of the DNAPL will be lower than for residual zones because dissolution can only occur readily along the margins of the layers or pools.

Dissolved contaminants derived from the DNAPL in the groundwater zone will cause a contaminant plume to develop in the groundwater. In small-scale laboratory experiments, groundwater in contact with DNAPL, quickly (in minutes to hours) acquires dissolved concentrations approaching the solubility of the DNAPL (Pfannkuch, 1984; Anderson *et al.*,1987; Schwille, 1988; Imhoff *et al.* 1989). In the field, saturated dissolved concentrations are rarely observed in groundwater except in the immediate vicinity of large DNAPL sources. This has commonly been interpreted to mean that DNAPL is not present. However, other types of evidence indicate that such interpretations are often incorrect. Less-than-saturated dissolved concentrations may be a result of factors such as: dilution of the compounds of interest by other compounds in the DNAPL; the heterogeneous distribution of DNAPL as residual zones and layers or pools; dilution in monitoring wells having long intakes lengths; and, dispersion in the aquifer (Feenstra, 1990).

If the volume of spilled DNAPL is larger than the retention capacity of the vadose and groundwater zones, a portion of the DNAPL will settle out as a pool of free liquid on the bottom of the aquifer as shown in Figure 1C, or it will settle out on low permeability beds in the aquifer. DNAPL may form puddles or pools in depressions on such confining strata. In situations where the confining stratum is sloped, DNAPL can continue to move downslope and its movement need not be controlled by the direction of groundwater flow. Depending on the volume of the spill and the configuration of confining strata, DNAPL may move substantial distances laterally away from the area in which it was released. After release of DNAPL to the subsurface ceases, the DNAPL movement will slow and eventually cease as the force driving DNAPL movement diminishes. For high density and low viscosity DNAPLs such as chlorinated solvents, the cessation of DNAPL flow may occur relatively quickly, in weeks or months. For creosote with a lower density and higher viscosity, cessation of DNAPL flow may take longer.

Because of the tendency for DNAPL to sink, discontinuities in confining strata such as fissures, root holes, erosional opening and even unsealed boreholes can provide potential pathways for DNAPL migration deeper into the subsurface. The presence of discontinuities in confining strata and their potential importance must be considered for both surficial and subsurface aquitard layers. Depending on the geologic origin and history of the confining strata, weathering, erosion or vegetation may have created these types of discontinuities and they may be preserved even in deep strata. At a wood preserving site in St. Louis Park, Minnesota, creosote contamination has been reported at depths as great as 100 m, largely as a result of creosote migration downward along unsealed abandoned water wells (Hult and Schoenberg, 1981; Hult and Stark, 1985).

2.2 Fractured Media

DNAPL can penetrate into fractured media such as fissured clays and fractured rock formations. The entry of DNAPL into water-filled fissures or fractures will depend on the pressure driving the DNAPL migration, the DNAPL-water interfacial tension and the aperture of the fissure. The pattern of DNAPL movement will be controlled primarily by the orientation and interconnection of fractures (see Figures 2A and 2B). There will be little DNAPL retained on fracture surfaces as residual either above or below the water table. There have been no measurements of the DNAPL residual retained in natural media in the field or in the laboratory. Currently our only estimate of potential residual contents in fractures is derived from laboratory experiments conducted by Schwille (1998) using simulated planar fractures consisting of roughed parallel glass plates. For an aperture of 200 μ m between the glass plates, Schwille estimated the residual retention to be less than 0.05 L/m², or approximately 25% of the void space in the fracture. For natural fractures in rock, residual contents may be higher due to varying aperture sizes and trapping around closure points in the fractures. However, if we assume for the purposes of illustration a residual content of 0.05 L/m² for Schwille, a weakly fractured rock of moderate hydraulic conductivity with a fracture frequency of 5 fractures per metre, would have a bulk residual capacity of approximately 0.25 L/m³, substantially less than the residual contents for soils. A given volume of DNAPL introduced into the subsurface can spread to a much greater extent areally and to a greater depth than in porous media.

3. Release of Contaminants from Creosote Sources

The dissolution of creosote compounds into groundwater will depend on the solubility of the constituent compounds in water and the chemical composition of the creosote. The water solubility values of selected PAH and BTEX compounds are shown in Table 2. The water solubility of PAH compounds is inversely related to the degree to which the compounds will be sorbed onto geologic materials. Compounds which are weakly sorbed will be more soluble in water and compounds which are strongly sorbed will be less soluble in water. Pure PAH compounds are solids and the water solubility values typically reported in the literature are solid-phase solubilities. For situations where PAH compounds comprise creosote or petroleum liquids, liquid-phase solubility values should be used (Shiu et al., 1988). Liquid-phase solubility values are approximately three times higher than solid-phase values for low melting point compounds such as naphthalene, and are approximately two hundred times higher for high melting point compounds such as dibenzo(a,h)anthracene.

Creosote is a complex mixture of PAH compounds, phenolic compounds and sometimes BTEX compounds. A typical analysis of creosote is shown in Table 3. PAH compounds comprise approximately 60% of the creosote, with phenanthrene, naphthalene, acenaphthene, fluorene, fluoranthene, anthracene and pyrene being the principal constituents. The proportions of these PAH compounds in creosote varies with the source of the coal used, and the manufacturing and refining processes used to produce the creosote. However, the PAH compounds shown to be the principal compounds in Table 3 would be expected to be the principal constituents of most creosote. The dissolved concentration of individual compounds in equilibrium with creosote can be estimated by:

$C_W = X S_L$

where X is the mole fraction of the compound in the creosote and S_{L} is the liquid-phase solubility (Shiu *et al.*, 1988). The mole fraction of a compound is a measure of its molecular concentration based on its measured concentration normally expressed as a weight per unit weight of sample and the molecular weight of the compound. The calculated dissolved concentrations are also shown in Table 3 and range from approximately 13,000 $\mu g/L$ (ppb) for naphthalene to 1 $\mu g/L$ (ppb) for chrysene. The most soluble PAH compounds such as naphthalene and acenaphthene exhibit the highest dissolved concentrations in the water despite the fact that less soluble compounds such as anthracene, phenanthrene, pyrene and fluoranthene are present in the creosote at comparable or higher concentrations. For the dissolution of creosote, the PAH compounds having the highest dissolved concentrations in groundwater would be expected to be the most soluble compounds: naphthalene, acenaphthylene, acenaphthene, and fluorene. Less soluble compounds such as benzo(a)pyrene, benzo(ghi)perylene and dibenzo(a,h)anthracene would be expected to occur at much lower concentrations. If BTEX compounds are present in the creosote at even low

concentrations, their concentrations in the groundwater could be expected to be high compared to the PAH compounds because of their much higher solubility.

The dissolution of phenolic compounds from creosote is difficult to assess quantitatively because the solubility of the phenolic compounds will vary with the pH of the groundwater. However, they will generally have solubilities much higher than PAH compounds and therefore, like the BTEX compounds, dissolved phenolic concentrations in groundwater should be relatively high if phenolics are present in the creosote.

Creosote will not be rapidly dissolved by flowing groundwater. Consider, for example, a volume of sandy soil measuring 3 m by 3 m in area by 3 m in depth which contains residual DNAPL creosote. The residual content of DNAPL varies within the residual zone from 0 to 15% of the pore space but the bulk residual content is 10 L/m³. This quantity would represent approximately 270 L or 1.5 barrels of creosote. Groundwater flows through this zone at a linear velocity of 11 m/year reflecting rates common for a sandy aquifer (hydraulic conductivity of 10-3 cm/s. a hydraulic gradient of 0.01 and a porosity of 0.3). If we assume that the creosote is virtually all PAH compounds, the groundwater exiting such a residual zone would likely have PAH concentrations ranging from very low levels up to solubility levels depending on the distribution of the creosote. Even if the average PAH concentration in groundwater exiting this residual zone remained at its initial solubility (approximately 16,000 µg/L from Table 3), at least 700 years would be required to remove all of the residual creosote from the aquifer. Based on laboratory experiments (Schwille, 1988, Imhoff et al., 1989), the actual time required for complete dissolution of the DNAPL would be considerably longer because the dissolved concentrations resulting from dissolution, and thus the rate of dissolution, will decline with time as the DNAPL mass is depleted. The dissolution of DNAPL layers or pools will likely require even longer periods of time. Calculations such as this are consistent with the observation that groundwater contamination from creosote sources is continuing at sites at which chemical releases or disposal occurred many decades ago. It is possible that over a period of years those more soluble compounds, such as BTEX and phenolics which occur at initially low concentrations in the creosote, may be dissolved to the extent that they are virtually eliminated from the creosote.

4. Dissolved-Phase Migration

A variety of physical and chemical processes will act to control the rate of migration of contaminants such as PAH, phenolic and BTEX compounds as they move through the subsurface environment dissolved in the groundwater. These processes can be categorized as transport processes, or those which will act to move contaminants through the subsurface, and attenuation processes, or those that will act to reduce chemical concentrations in the groundwater and slow the rate of contaminant migration.

4.1 Advection

Advection is the transport of contaminants due to the movement of groundwater and is the dominant transport process in most geologic media. In low permeability clays and rocks, advection may be very slow and molecular diffusion will be the dominant transport process. For chemical contaminants such as chloride which are not affected significantly by attenuation processes, contaminant migration will occur at the rate of groundwater flow. The rate of groundwater movement is expressed as the linear groundwater velocity:

$$V = \frac{K i}{n}$$

where K is the hydraulic conductivity of the geologic medium, i is the hydraulic gradient and n is the porosity of the geologic medium. Hydraulic conductivity is a measure of the ability of a geologic medium to transmit water. Hydraulic gradient is a measure of the pressure difference in the groundwater between two locations which induces the movement of groundwater. The hydraulic gradient is typically expressed as the difference in groundwater level elevation over a specified distance. For example, a hydraulic gradient of 0.01 would represent a difference in groundwater level elevation of 1 m over a distance of 100 m.

For a medium-grained sand aquifer having a hydraulic conductivity of $1 \ge 10^{-2}$ cm/sec and a porosity of 0.3, if the hydraulic gradient were 0.01, the calculated linear groundwater velocity would be approximately 30 cm/day or 100 m/year.

4.2 Sorption

In most geologic media, creosote-derived compounds such as PAH, phenolics and BTEX will migrate at rates slower than the rate of groundwater movement because these compounds are sorbed by geologic materials. It is considered generally that sorption of organic chemicals occurs principally due to partitioning of the chemicals into the natural organic carbon material occurring in the geologic deposits. The degree of sorption of organic chemicals on geologic media is expressed as a distribution coefficient:

$$K_d = \frac{Concentration on solids}{Concentration in water} = K_{oc} f_{oc}$$

where K_{OC} is the organic carbon-water partition coefficient for the chemical and f_{OC} is the fraction organic carbon of the geologic medium. The higher the K_d, the greater the degree of sorption. The K_d for a chemical on a particular geologic medium can be determined by means of laboratory tests but is frequently estimated using K_{OC} values reported in the scientific literature for various chemicals and measured or estimated values of f_{OC} . Values of K_{OC} for selected PAH and BTEX compounds are shown in Table 2. The log K_{OC} values range from 1.92 for benzene to 6.98 for dibenzo(a,h)anthracene. BTEX compounds are much less strongly sorbed than PAH compounds. Among the PAH compounds, naphthalene, acenaphthylene, acenaphthene, fluorene and anthracene are less strongly sorbed than fluoranthene, chrysene, benzo(a)pyrene and benzo(ghi)perylene. As with the assessment of dissolution of phenolics from creosote, it is difficult to assess quantitatively the sorption of phenolic compounds because K_{OC} values will depend on the pH of the groundwater. However, in general, phenolic compounds will be less strongly sorbed than most PAH compounds.

The effect of sorption of the rate of contaminant migration is expressed as the retardation factor.

$$R = \frac{Velocity of groundwater}{Velocity of contaminant} = 1 + \frac{Pb}{n} K_d$$

where ρ_b is the dry bulk density of the geologic medium. For a retardation factor of 2, the contaminant moves at half of the groundwater velocity. For a retardation factor of 100, the contaminant moves at a hundredth of the groundwater velocity. Calculations of the retardation factors of the selected PAH and BTEX compounds have been made using published literature values for the K_{OC} and a range of estimated values for the f_{OC} typical for sandy aquifers and are shown in Table 4. The calculations illustrate that BTEX compounds will be relatively unretarded and there is expected to be a significant degree of retardation of all PAH compounds even for low values of f_{OC}. Phenolic compounds would also be expected to relatively unretarded. The calculations also indicate that the various PAH compounds will migrate at the different rate.



<u>Compounds such as naphthalene, acenaphthylene, acenaphthene and fluorene move tens to hundreds of times more rapidly than chrysene, benzo(a)anthracene, benzo(a)pyrene and benzo(ghi)perylene. In almost all hydrogeologic settings, strongly sorbed PAH compounds such as chrysene, benzo(a)anthracene, benzo(a)pyrene and benzo(ghi)perylene will be virtually immobile.</u>

4.3 Biodegradation

In laboratory and field studies it has be demonstrated that BTEX and PAH compounds can be degraded under aerobic (containing oxygen) conditions by bacterial populations which occur naturally in shallow soils (Kobayashi and Rittmann, 1982). <u>BTEX compounds are more rapidly degraded than PAH compounds</u>. In general) lower molecular weight PAH compounds such as naphthalene, acenaphthylene, acenaphthene and fluorene are more readily degraded than higher molecular weight PAH compounds. It is not known whether conditions would be suitable in deeper groundwater environments for BTEX and PAH biodegradation, or whether the rate of degradation would be sufficient to cause significant attenuation of BTEX and PAH migration. If this were to occur, the migration of compounds such as naphthalene, acenaphthylene, acenaphthene and fluorene would likely be attenuated to a greater degree than less readily degradable PAH compounds.

In field studies at wood preserving sites in Minnesota and Florida (Ehrlick *et al.*, 1982; Goerlitz *et al.*, 1985) have also indicated that phenolic compounds can be degraded under anaerobic conditions by bacterial populations in groundwater. At these sites, biodegradation has resulted in significant attenuation of the phenolics.

5. Cases of Groundwater Contamination by Creosote

The preceding sections have described the principal processes which will control contaminant migration in groundwater. At most sites there are insufficient data available on the groundwater velocities, sorption characteristics of the soils, composition, nature or history of the contamination sources to permit precise quantitative predictions of contaminant concentrations at a particular location or point in time. However, the effect of processes such as dissolution of creosote, sorption, or the migration DNAPL can be evaluated qualitatively by examination of the contaminant patterns. In the evaluation of contaminant migration in groundwater at a field site, the pattern of the compounds present in the groundwater should be consistent with the processes interpreted to be controlling contaminant migration.

For example, the most soluble compounds such as BTEX, phenolics and PAH compounds including naphthalene, acenaphthylene, acenaphthene and fluorene are expected to be the dominant compounds present in groundwater contaminated by such sources. Less soluble PAH compounds such as benzo(a)pyrene and benzo(ghi)perylene would be expected to occur at much lower concentrations in the groundwater (see Table 4). A similar preferential partitioning of the more soluble compounds into the groundwater will continue as the dissolved compounds migrate through the geologic medium and as less soluble compounds (particularly PAHs) are more strongly sorbed on the geologic materials.

This general scenario for preferential release of the most soluble compounds (such as BTEX, phenolics and naphthalene) from the creosote source and preferential attenuation of the less soluble PAH compounds was observed by Hult and Schoenberg (1981) in studies of groundwater contamination from a wood preserving plant in St. Louis Park, Minnesota. Similar findings were reported by Quinn *et al.* (1985) and Villaume *et al.* (1983) in studies of groundwater contamination from coal tar residues at coal gasification plants in Connecticut and Pennsylvania respectively.



5. Remedial Measures

At some wood preserving sites, remedial measures may be necessary to control groundwater contamination from creosote in the subsurface. The presence of creosote in the subsurface has critical implications with regard to remedial measures. <u>Creosote can potentially penetrate</u> downward into the subsurface to beyond the depth of feasible removal by excavation. Similarly, creosote can also migrate into areas which are otherwise inaccessible such as beneath buildings or process areas.

Zones of residual creosote and creosote pools in the subsurface can comprise very significant sources of long-term groundwater contamination unless they are removed, but complete removal has not been demonstrated to be possible with existing remedial technologies.

5.1 Groundwater Purge and Treat

To correct groundwater contamination problems, remedial measures involving purging by means of wells and treatment of contaminated groundwater have been implemented at many chemical spill and waste disposal sites and industrial facilities during the last decade. When designed, many of these systems were expected to achieve clean-up of the groundwater contamination but experience has found that such systems are seldom effective. The presence of DNAPL in the subsurface acting as an continuing source of dissolved contaminants has now been acknowledged by US EPA as a key factor contributing to the inability of purge and treat systems to effect aquifer clean up (Keely, 1989). However, purge and treat systems can be essential for control of off-site migration of the dissolved contaminant plumes emanating from DNAPL sources.

Purging and treatment contaminated groundwater from the dissolved plumes derived from DNAPL sources is generally not effective in removing the contaminant source because of the low solubility of the DNAPL chemicals and because the residual zones and pools can represent a very large mass of chemical. Consider, for example, a purge well system which recovers groundwater contaminated by creosote with an average PAH concentration of 1,000 μ g/L and at a rate of 450 L/min. Dissolved PAH concentrations as high as this are encountered at some sites but concentrations at many sites are much lower. Although seemingly low, such concentrations are many times higher than drinking water standards. Pumping rates of the order of 450 L/min. would be common in many purge well systems. For the system described above, the total amount of creosote recovered would be only 230 L per year or just over one barrel per year of creosote. If concentrations in the purged groundwater were lower, the amount of creosote recovered would also be lower. This quantity of chemical is small in comparison to the expected size of many DNAPL sources in the subsurface.

Theoretically, the rate of DNAPL dissolution in the subsurface could be accelerated by increasing the rate of groundwater flow through the DNAPL zones. Laboratory studies of dissolution of TCE pools by Schwille (1988) suggest that the rate of chemical mass transfer to the groundwater should increase almost in proportion in increases in groundwater velocity. Laboratory studies of dissolution of DNAPL residual by Anderson et al. (1988), Imhoff et al. (1989), and Geller and Hunt (1989) also suggest that the rate of chemical mass transfer to the groundwater should increase with increasing groundwater velocity except at very high velocities where mass transfer becomes rate limited. Because DNAPL sources may continue to persist in the subsurface for centuries, a useful increase in the rate of groundwater flow, and therefore the rate of DNAPL dissolution, would have to be a factor of at least 5 to 10 times. In high permeability media, hydraulic gradients 10 times higher than natural gradients will only exist close to pumping or injection wells. In low permeability, higher hydraulic gradients may be achievable but the radius of influence around such wells will be small. Consequently, in the subsurface it will be difficult to



usefully increase the rate of groundwater flow through DNAPL zones unless the the pumping or injection wells are situated directly within the DNAPL zones and the operation of wells is undesirable because of the potential for remobilization of the DNAPL. This potential effect will be discussed in following sections.

It must also be remembered that the processes influencing dissolution of DNAPL in the subsurface are not yet clearly understood. At some sites with groundwater purge and treat systems, that the rate of chemical mass removal from the system (chemical mass per time) actually decreases when the groundwater pumping rates are increased. Increased pumping rates may result in capture of larger volumes of uncontaminated groundwater and thereby reduce the dissolved concentrations in the system effluent, but dilution alone would be in proportion to the increased pumping rate and it should not reduce the mass removal rate. Decreased mass removal rates with increased pumping suggests transfer from the DNAPL to the groundwater becomes limited in some way.

It can be concluded that the benefit of purging and treating large volumes of contaminated groundwater versus its cost may be small with respect to the removal of chemical mass and the depletion of the contamination source. The long-term solution of the groundwater contamination from DNAPL sources in the subsurface must be directed to the permanent elimination or containment of the source from above and below the water table.

5.2 Excavation

Excavation is a remedial measure frequently recommended at waste disposal and chemical spill sites because it is conceptually direct, and potentially capable of complete removal of contamination sources above the water table. Excavation has been a preferred method of remediation by regulatory agencies. However, because the behavior of DNAPL chemicals and their potential to penetrate below the water table, excavation is seldom effective for DNAPL sources. Successful remediation of DNAPL sources by excavation can only be achieved when the DNAPL source can be located and this is frequently not possible. The DNAPL must also be accessible using available excavation techniques and equipment. This generally would require that the DNAPL be confined to the vadose zone at a depth of 5 to 10 m or less. At most sites, DNAPL has penetrated to a greater depth or has penetrated into otherwise inaccessible areas such as beneath buildings and into bedrock formations where excavation of DNAPL sources is not feasible. Because of recent legislation in many jurisdictions restricting land disposal of many chemicals, even when excavation might be appropriate for a DNAPL source, few if any disposal facilities are available for waste materials generated from the cleanup of such sites. In addition, at sites where the DNAPL chemicals are volatile or the method of excavation could release contaminated particulate material, the emission of contaminants into the air may be of sufficient environmental concern to prohibit excavation.

5.3 Potential In Situ Remedial Technologies

The following paragraphs introduce the various technologies which may have potential for the elimination of DNAPL such as creosote from the subsurface. Some of these technologies come from the petroleum industry where they are used for enhanced oil recovery (EOR) from petroleum reservoirs. It must be remembered that the standard by which EOR methods are judged to be effective for oil recovery is far different than the standard by which DNAPL clean-up technologies must be judged. For example, conventional oil recovery typically removes approximately 30% of the oil resident in a reservoir formation. EOR operations would be deemed highly successful if they resulted in the recovery of an additional 20% to 30%, still leaving 40% of the oil in place. In contrast, in order to eliminate DNAPL as a source of continuing groundwater contamination, it is likely that recovery of virtually all of the DNAPL would be required.



5.3.1 Elimination of Creosote from the Subsurface

Potential technologies for the elimination of DNAPL from the groundwater zone can be grouped according to whether they alter the hydrodynamic conditions under which the DNAPL exists in the subsurface to enhance recovery, alter the physical-chemical properties of the DNAPL to enhance recovery, or whether they degrade the chemicals in situ. Hydrodynamic techniques include:

- Recovery of DNAPL by pumping DNAPL only
- Recovery of DNAPL by pumping groundwater
- Water flooding

When DNAPL is found in boreholes and monitoring wells, recovery of the DNAPL by pumping the DNAPL alone, or in combination with the groundwater pumping, is frequently proposed as a remedial measure but there have been few accounts of their success at field sites. DNAPL and groundwater pumping tests conducted by Ferry et al. (1988) in a fractured sandstone formation indicate that DNAPL recovery is slow and cannot be sustained. Water flooding is based on techniques used in the petroleum industry for enhanced oil recovery from petroleum reservoirs. Water flooding relies on the displacement of DNAPL by water injected under pressure.

(Technologies which rely on altering the physical-chemical properties of the DNAPL include:

- Surfactant mobilization of DNAPL
- Chemically-enhanced solubilization using surfactants or co-solvents
- Steam injection to reduce DNAPL viscosity
- Radio Frequency (RF) heating to reduce DNAPL viscosity

These technologies rely on the injection of a chemical agent (surfactant or co-solvent) or heat to alter the physical-chemical properties of the DNAPL. Surfactant mobilization involves reducing interfacial tension to increase the mobility of DNAPL residual or pools so that DNAPL could be recovered using collector trenches or wells. Surfactant mobilization is based on techniques used in the petroleum industry for enhanced oil recovery from petroleum reservoirs. Chemicallyenhanced solubilization involves increasing the solubility of the components of the DNAPL to increase removal by water flow through the DNAPL zones. Chemically-enhanced solubilization has been studied only in the laboratory and at a pilot field scale. Steam injection and RF heating can be used to reduced DNAPL viscosity and enhance recovery by pumping or water flooding.

Microbial degradation technologies have be suggested for in situ treatment or destruction of DNAPL. There is certainly potential for this technology to effectively remove creosote because it is known that PAH, BTEX and phenolic compounds can all be degraded by naturally-occurring microorganisms in groundwater and soil. However, the rate of degradation of these compounds, even if enhanced, may be slow relative to the large mass of chemical represented by DNAPL creosote sources. In addition, in the immediate zone of a DNAPL creosote source the concentrations of organic compounds and metals may be high and these may be toxic to many microorganisms.

5.3.2 Elimination of Creosote from the Vadose Zone

<u>Vapor extraction technology has been applied to the removal of DNAPL chemicals such as</u> chlorinated solvents and other petroleum fuels from the vadose zone, but it is not applicable to creosote because it is comprised mainly of semi-volatile and non-volatile compounds (PAH). Some of the technologies described for the groundwater zone such as surfactant mobilization, chemically-enhanced solubilization, steam injection, RF heating and microbial degradation may also be applicable to the removal of creosote from the vadose zone.



5.3.3 Containment

Containment is suggested frequently for the control of DNAPL source areas when it is not possible to reliably remove the source by other means. In broad terms, containment could include:

- Physical containment by the construction of low permeability barriers such as grout walls, slurry trenches and steel sheet piling walls.
- Hydraulic containment by means of the pumping or injection of water via trenches or wells
- In situ stabilization or solidification of the DNAPL chemicals.

5.3.4 General Limitations

There are significant limitations on the applicability of all of the potential in situ remedial technologies introduced above. None have been demonstrated to be effective in the elimination of DNAPL from the subsurface. DNAPL or groundwater pumping have the potential to remove some portion of the DNAPL present in the subsurface but a significant residual DNAPL will always remain. The removal of the pumpable DNAPL from the subsurface will probably not result in any measurable improvement in the groundwater contamination emanating from the source area. Indeed, it can be envisioned that prior to removal of the pumpable DNAPL, the permeability of the formation to water was lower and the amount of chemical mass transfer to the groundwater controlled by the amount of groundwater flow through the DNAPL zone. With the removal of the pumpable DNAPL, groundwater flow through the DNAPL zone may increase and result in an increase in the amount of chemical mass transfer to the groundwater contamination resulting from the DNAPL zone worse.

<u>Geologic heterogeneity is probably the key factor which will reduce the effectiveness of most of</u> these technologies because their success depends on the delivery of some external agent (surfactant, steam, solubilizing agent, chemical reactant or microbial nutrients) and a transport medium (water or air) into the subsurface to contact the DNAPL. <u>Geologic heterogeneities will</u> result in a complex distribution of DNAPL in residuals zones, lenses and pools and a correspondingly complex groundwater flow pattern due to the reduction in permeability of the geologic medium by the presence of DNAPL. External agents and transport media injected into the subsurface will follow the zones of highest permeability and these zones are probably not where the bulk of the DNAPL resides.

A limitation common to those methods which rely on changing the hydrodynamics of the groundwater system or the physical-chemical properties of the DNAPL is the potential for remobilization and further spreading of DNAPL residual or pools downward into the subsurface. Groundwater pumping from within the DNAPL zone will change capillary pressure relationships between the DNAPL and the groundwater and DNAPL formerly held in place by capillary forces may be remobilized. Chemically-enhanced displacement relies on surfactants to greatly reduce the interfacial tension between the DNAPL and water. This reduction in interfacial tension will make the DNAPL much more mobile enabling it to penetrate into finer-grained strata or smaller aperture fractures. Steam displacement will result in similar increases in the mobility of the DNAPL as a result of lower interfacial tensions and DNAPL viscosity at higher temperatures. Chemically-enhanced solubilization relies on surfactants or co-solvents to increase the solubility of the DNAPL. However, the increase in solubility also results in a reduction of interfacial tension and increase in DNAPL mobility. Unless the downward or lateral movement of the remobilized DNAPL can be strictly contained by natural low permeability strata, engineered

barriers or hydraulic gradient control, it is possible that the application of such technologies may actually worsen the groundwater contamination problem.

6. Conclusions

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Releases of creosote at many past and present sites of wood preserving operations have resulted in the accumulation of significant quantities of creosote in the subsurface underlying these sites. Groundwater which comes in contact with can dissolve small, but potentially significant, quantities of chemicals from the creosote. BTEX, phenolics and PAH compounds such as naphthalene are the most soluble components of creosote and are expected to have the highest dissolved concentrations in groundwater. PAH compounds such as benzo(a)pyrene are expected to have very low dissolved concentrations in groundwater and are expected to be virtually immobile in most hydrogeologic settings.

At some wood preserving sites, remedial measures may be necessary to control groundwater contamination from creosote in the subsurface. Purging and treatment of contaminated groundwater may be effective in controlling or preventing) migration of dissolved contaminants in the groundwater, however, it will not result in significant removal of creosote from the subsurface. Excavation of creosote sources can only be effective if the sources are locatable, accessible, and the removed material can be treated or disposed of suitably. In many cases, excavation is either impossible or very costly.

At the present time, complete removal of creosote from the subsurface has not been demonstrated to be possible with existing in situ remedial technologies. The different existing technologies have different limitations and advantages under differing hydrogeologic settings. It is likely that successful clean-up of creosote sources in the future will require an integration of different existing or new technologies. The following is an example of how different technologies might it integrated for a site clean-up plan. Water flooding of the creosote zone (target zone) could be applied initially to remove most of the mobile creosote. Surfactants could then be injected or steam or RF heating applied to enhance creosote mobility and recovery of more creosote. Surfactants could also be used to enhance the solubilization of the components of the creosote. These steps would remove more creosote but would likely still leave a substantial residual. At this stage, however, the mass of creosote may have been reduced sufficiently to make microbial degradation more effective. All these steps might be applied in conjunction with containment measures to prevent escape of mobilized creosote or allow better control of hydraulic and geochemical conditions in the target zone. Any of these technologies applied individually would not be effective. Water flooding would leave behind a large residual. The application of surfactants, steam or RF heating may result in mobilization and downward or lateral escape of creosote unless the mass is initially reduced by water flooding or contained by other measures. Similarly, microbial degradation would not be effective unless the creosote mass is initially reduced by other techniques.

Future efforts in the clean-up of creosote in the subsurface should be directed toward testing and demonstration of existing technologies, development and testing of new technologies, and also importantly, toward attempts to integrate various technologies into overall site clean-up plans.

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Compound	NYSDEC GUIDELINE	HWC GUIDELINE	S(L)
	(μg/L)	(µg/L)	(µg/L)
Naphthalene	10	-	102,000
Fluorene	. 50		11,600
Anthracene	50	-	7,090
Phenanthrene	50	-	4,490
Pyrene	0.2*	-	2,670
Fluoranthene	0.2*	•	1,850
Chrysene	0.2*	-	379
Benzo(a)anthracene	0.2*	-	304
Benzo(a)pyrene	0.2*	0.01	116
Benzene	1.5	5	1,788,000
Toluene	50	24	578,000
Ethyl benzene	50	2.4	187,000
Xvlenes	50	300	200,000

TABLE 1. COMPARISON OF DRINKING WATER STANDARDS TO SOLUBILITY OF SELECTED PAH AND BTEX COMPOUNDS.

NYSDEC GUIDELINE - New York State Dept. of Environmental Conservation Guideline for Potable Groundwater 1984.

HWC GUIDELINE- Health and Welfare Canada Guideline for Drinking Water 1987

* Sum of these PAH compounds must not exceed 0.2 µg/L.

S(L) - Solubility of pure compound in liquid-phase in water from Miller et al. (1985).

Compound	log K(ow)	log K(oc)	S(s) (μg/L)	S(L) (μg/L)	
Naphthalene	3.35	3.14	30,600	102,000	
Acenaphthene	3.92	3.71	3,930	21,600	
Fluorene	4.18	3.97	1,840	11,600	
Anthracene	4.54	4.33	731	7,090	
Phenanthrene	4.57	4.36	1,180	4,490	
Pyrene	5.18	4.97	135	2,670	
Fluoranthene	5.22	5.01	263	1,850	
Chrysene	5.79	5.58	2	379	
Benzo(a)anthracene	5.91	5.70	14	304	
Benzo(a)pyrene	5.98	5.77	3.78	116	
Benzo(g,h,i)perylene	7.10	6.89	0.26	84	
Dibenzo(a,h)anthracene	7.19	6.98	0.50	124	
Benzene	2.13	1.92		1,788,000 ·	
Toluene	2.65	2.44	578,000		
Ethyl benzene	3.13	2.92		187,000	
Xvienes	3.14	2.93		200.000	

TABLE 2. CHEMICAL DATA FOR SELECTED PAH AND BTEX COMPOUNDS.

K(ow) - Octanol-water partition coefficient from Miller et al. (1985).

K(oc) - Organic carbon-water partition coefficient calculated from Karickhoff et al. (1979). log K(oc)= log K(ow) - 0.21 Data for xylenes is average of ortho, meta and para isomers.

S(s) - Solubility of pure solid-phase compound in water from Miller et al. (1985).

S(L) - Solubility of pure compound in liquid-phase in water from Miller et al. (1985).

			CREOSOTE			Dissolved	
Compound	MV .	(Wt. %)	(mol/kg)	Estimated Mole Fraction	S(L) (μg/L)	Concentration (µg/L)	
Naphthalene	128.20	9.64	0.752	0.12	102,000	12,730	
Acenaphthene	154.21	7.68	0.498	0.08	21,600	1,785	
Fluorene	166.21	7.61	0.458	0.08	11,600	881	
Anthracene	178.20	5.14	0.288	0.05	7,090	339	
Phenanthrene	178.20	14.30	0.802	0.13	4,490	598	
Pyrene	202.30	4.97	0.246	0.04	2,670	109	
Fluoranthene	202.30	6.12	0.303	0.05	1,850	93	
Chrysene	228.30	0.33	0.014	0.00	379	1	
Benzo(a)anthracene	228.30	1.52	0.067	0.01	. 304	3	
Benzo(a)pyrene	252.32	<0.1			116	×0.08	
Benzo(g,h,i)perylene	276.34	<0.1			84	<0.05	
				0.00			
Benzene	78.11	0.1	0.013	0.00	1,788,000	3,799	
Toluene	92.13	0.1	0.011	0.00	578,000	1,041	
Ethyl benzene	106.20	0.1	0.009	0.00	187,000	292	
Xylenes	106.20	0.1	0.009	0.00	200,000	313	
L	SUM	57.71	3.47	0.58			

TABLE 3. CALCULATED DISSOLVED CONCENTRATIONS IN GROUNDWATER IN EQUILIBRIUM WITH CREOSOTE.

Wt.% - Weight percent from typical analysis of creosote.

BTEX compounds were not detected but assumed to be 0.1% for these calculations.

MW - Molecular weight.

S(L) - Solubility of pure compound in liquid-phase in water from Miller et al. (1985).

Compound	log K(oc)	RETARDATION FACTOR			
		foc	foc	foc	
		0.0001	0.0003	0.001	
Naphthalene	3.14	2	4	10	
Acenaphthene	3.71	4	11	33	
Fluorene	3.97	7	18	59	
Anthracene	4.33	14	41	134	
Phenanthrene	4.36	15	44	143	
Pyrene	4.97	59	175	580	
Fluoranthene	5.01	64	191	635	
Chrysene	5.58	237	708	2,358	
Benzo(a)anthracene	5.70	312	933	3,108	
Benzo(a)pyrene	5.77	366	1,096	3,652	
Benzo(g,h,i)perylene	6.89	4,814	14,439	48,128	
Dibenzo(a,h)anthracene	6.98	5,922	17,764	59,211	
Benzene	1.92	1	1	2	
Toluene	2.44	1	2	3	
Ethyl benzene	2.92	2	3	6	
Xylenes	2.93	2	3	6	

TABLE 4. CALCULATED RETARDATION FACTORS FOR SELECTED PAH AND BTEX COMPOUNDS.

foc - Fraction organic carbon

Range in foc determined from:

Jackson et al. (1985) - Range of 0.0015 to 0.0131 for a regressional marine sand and gravel in Ottawa, Ontario. Jackson et al. (1985) - Range of 0.0001 to 0.0035 for a glacial outwash sand and gravel in Ottawa, Ontario. Schwarzenbach and Westall (1981) - Range of 0.0004 to 0.0073 for a glaciofluvial sand and gravel in Switzerland. Mackay et al. (1986) - Range of 0.0001 to 0.0009 for lacustrine sand in CFB Borden, Ontario. Figure 1. Conceptual models for DNAPL in porous media.



Figure 2. Conceptual models for DNAPL in fractured rock formations.

