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An Algorithm for the Estimation of NAPL Saturation and Composition from Typical Soil Chemical Analyses

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A [illegible] composition of a single or multicomponent NAPL within a soil sample. These estimates are possible because, in addition to distributing the organic chemicals between aqueous, sorbed, air, and NAPL phases according to traditional partitioning equations, the algorithm incorporates equations [illegible] solution is obtained by solving the set of nonlinear equations implicitly. The algorithm is built into a code called NAPLANAL, which is tested and applied to actual core samples collected in the field.

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Introduction

It is an extraordinary feature of modern hydrogeological practice that estimating the mass or volume of nonaqueous phase liquid (NAPL) in a soil or rock is not deemed essential to the design of remediation systems. A brief inspection of past issues of this journal will show that NAPL volumes are seldom estimated from field data. Such a volume estimate permits the calculation of an approximate remediation period for the NAPL-contaminated soil or rock. An essential parameter for estimating NAPL volumes in a NAPL-contaminated soil or rock is the NAPL saturation of the porous medium. Mercer and Cohen (1990) have tabulated NAPL saturation data from the literature.

Paraphrasing Bear (1972), when the pore space of an aquifer sediment or fractured rock is contaminated with NAPL, the saturation (or degree of saturation) of NAPL at a particular point is defined as the fraction of pore space occupied by NAPL within a representative elementary volume (REV) around the considered point:

$$S_N = \frac{\text{volume of NAPL within REV}}{\text{total pore volume within REV}} \quad (1)$$

As pointed out by Corey (1994), "saturation can be conceptualized (but not measured) as a point property varying in space in a manner entirely analogous to porosity." The constraint of being unable to measure the saturation at a point arises from the size of the REV, which

Mayer and Miller (1992) found to vary directly with the nonuniformity of the porous medium such that "the upper range of these REV estimates (i.e., ~10-10^4 cm^3) exceeds the scale of . . . field samples typically taken to estimate NAPL residual saturation levels." It is for this reason of scale that Jin et al. (1995) have proposed using a partitioning interwell tracer test for measuring NAPL volume over a large interwell pore volume.

While soil cores cannot provide reliable NAPL saturations over large zones of the subsurface, they can provide information on the approximate volumes of NAPL present in the core samples. Furthermore, continuous coring can indicate the relative NAPL saturations with depth, which may allow an experienced observer to deduce whether pooling of NAPL may be occurring upon some capillary barrier, such as a clay lens. In addition, the analysis and interpretation of soil chemical data from cores indicate the nature of the chemical composition of the NAPL in the source zone. Finally, the chemical analysis of soil cores provides an approximate initial value of NAPL saturation which can be used in multiphase, multicomponent simulators such as UTCHEM for modeling surfactant-enhanced aquifer remediation (e.g., Brown et al. 1994) and the application of partitioning interwell tracer tests (e.g., Jin et al. 1995).

We are not aware of any published method for calculating NAPL saturation from a soil sample chemical analysis when more than one organic compound is identified in the analysis. Feenstra et al. (1991) showed how a measured organic concentration can be used to assess whether a single- or multicomponent NAPL is present in a soil sample, but not how NAPL saturation could be calculated. In addition, the method requires an a priori assumption of the NAPL chemical composition. Mott (1995) improved on the Feenstra et al. (1991) method by presenting a method that can be used to estimate multicomponent NAPL composition from a complete organic chemical soil sample analysis and to determine whether NAPL is present in the sample. The method, which is incorporated in a code called SOILCALC, distributes mass among all phases including the NAPL phase. However, because the method assumes that NAPL occupies no pore space, SOILCALC cannot be used to calculate NAPL saturation. Consequently, its calculations of NAPL composition and the concentrations of organic compounds in each phase are not accurate unless NAPL saturation is approximately two orders of magnitude lower than typical residual NAPL saturations. Typical residual NAPL saturations range from 10 percent to 20 percent in the vadose zone and from 15 percent to 50 percent in the saturated zone (Mercer and Cohen 1990).

In this paper, a model is presented for the implicit calculation of NAPL saturation, NAPL composition, and phase distribution of organic compounds in a core sample of soil or rock. This model was developed in 1993 as an extension of the model presented in Feenstra et al. (1991). In addition to the phase partitioning relationships, the model incorporates equations for the conservation of mass and volume. The algorithm distributes the organic chemicals among aqueous, air, sorbed, and NAPL phases so that both the NAPL saturation and the correct NAPL composition are determined regardless of the amount of NAPL in the sample.

Partitioning Theory

If NAPL exists in a core sample from the unsaturated zone, the NAPL components will be distributed among four physical phases: air, soil, water, and NAPL. Each NAPL component (i.e., each compound in the NAPL) is distributed among the phases according to thermodynamic equilibrium principles and mass transfer kinetic factors. The system reaches equilibrium when the chemical potential of any constituent is equal in all phases. Figure 1 shows a schematic representation of the equilibrium relationship.

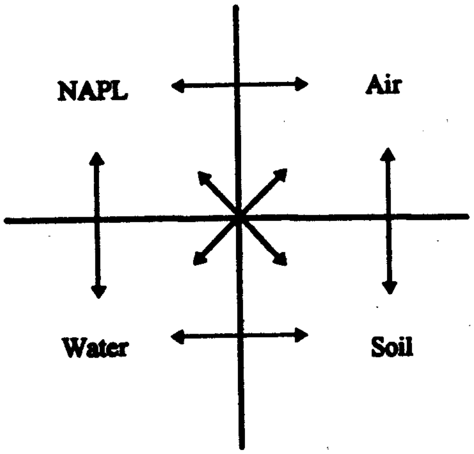

Figure 1. Schematic representation of phase equilibrium and partitioning.

To estimate the distribution of the total mass of a chemical among the phases at equilibrium, the chemical's phase partitioning behavior must be known. All nonaqueous concentrations are defined using traditional equilibrium equations that are functions of aqueous concentrations. These relationships are presented later. In each relationship, at least one chemical property of each organic compound (e.g., aqueous solubility, vapor pressure, and partition coefficient) must be known. In each case, the value of the chemical property is temperature dependent. Consequently, the values used in the model must be representative of the original soil or rock temperature. Values for these properties at specific temperatures can be found in the literature (e.g., Mercer et al. 1990) or estimated (e.g., Lyman et al. 1990; Drefahl and Reinhard 1995).

NAPL-Water Partitioning

NAPL-water partitioning depends on the aqueous solubilities of the NAPL components and the concentrations of the NAPL components in the NAPL. The relationship is analogous to Raoult's law for ideal gas mixtures. For an ideal NAPL in contact with water the aqueous phase concentration of a NAPL component is equal to the pure phase aqueous solubility of the component multiplied by the mole fraction of the component in the NAPL mixture. Mathematically, this relationship is written as:

$$C_w^i = x_i S_i \qquad (2)$$

where C_w^i is the aqueous phase concentration of component i (mass i in water per volume water); x_i is the mole fraction of the component in the NAPL mixture (mole i in NAPL per mole NAPL); and S_i is the aqueous solubility of pure component i (mass i in water per volume water). Feenstra et al. (1991) refers to C_w^i as the effective aqueous solubility of component i when the aqueous phase is at equilibrium with a NAPL. This general NAPL-water partitioning relationship has been confirmed by Banerjee (1984), Mackay et al. (1991), Cline et al. (1991), Lee et al. (1992a,b), and Broholm and Feenstra (1995) for NAPL mixtures of structurally similar compounds. This relationship is not highly dependent on temperature.

Air-Water Partitioning

The equilibrium concentration of component i in air is related to the aqueous concentration by Henry's law. Henry's law states that equilibrium water-air partitioning is described by a linear relationship. The relationship can be written as:

$$C_a^i = K_H^i C_w^i \qquad (3)$$

where C_a^i is the concentration of i in air (mass i in air per volume air), and K_H^i is the dimensionless Henry's constant. The Henry's constant is often reported in the literature in its dimensional form, $K_H^{i\prime}$ (e.g., atm-L/mol). The dimensional Henry's constant is calculated from the equation:

$$K_H^{i\prime} = \frac{P_{vap}^i}{S_i} MW_i \qquad (4)$$

where P_{vap}^i is the component's vapor pressure (e.g., atm), and MW_i is the component's molecular weight (mass i per mole i), which is needed to convert the previously defined mass-based aqueous solubility S_i to molar units. The two Henry's constants are related through the equation:

$$K_H^i = \frac{K_H^{i\prime}}{RT} \qquad (5)$$

where R is the universal gas constant (0.08206 atm-L/mol-K) and T is temperature in Kelvin. As the equation reveals, air-water partitioning is highly dependent on temperature.

Soil-Water Partitioning

Sorption to soil organic matter can also be described by a linear function of the aqueous organic compound concentration. The relationship can be written as:

$$C_s^i = K_{oc}^i f_{oc} C_w^i \qquad (6)$$

where C_s^i is the sorbed concentration of component i (mass i sorbed per mass soil); K_{oc}^i is the organic carbon to water partition coefficient of component i (mass i sorbed per mass organic carbon divided by mass i in water per volume water); and f_{oc} is the mass fraction of natural organic carbon within the soil matrix (mass natural organic carbon per mass soil).

The mass fraction of natural organic carbon has to be measured for the particular soil to be evaluated. Although the effect of temperature is small, the K_{oc}^i value can be highly sensitive to pH if the organic compound is ionizable (Drefahl and Reinhard 1995).

The linear isotherm model of Equation 6 has been experimentally verified for various organic compounds by Karickhoff et al. (1979), Chiou et al. (1979), Schwarzenbach and Westall (1981), and Chiou et al. (1983). It has been noted, however, that linear sorption is valid only for f_{oc} greater than about 0.001 (Schwarzenbach and Westall 1981) and greater than about 3 to 7 percent of the solid mass fraction of clay (Karickhoff 1984); otherwise, sorption of organic compounds on clays and mineral surfaces can be significant.

Conservation Equations and Relationships

Soil, water, air, and NAPL account for the total volume of a soil sample containing NAPL. The volume conservation equation is:

$$\phi_s + \phi_w + \phi_a + \phi_n = 1 \qquad (7)$$

where ϕ_s is the volumetric soil content (volume soil per total volume); ϕ_w is the volumetric water content (volume water per total volume); ϕ_a is the volumetric air content (volume air per total volume); and ϕ_n is the volumetric NAPL content (volume NAPL per total volume). The soil porosity ϕ (volume void per total volume) is equal to the sum of the volumetric air, water, and NAPL contents:

$$\phi = \phi_a + \phi_w + \phi_n \qquad (8)$$

Thus, the volumetric soil content ϕ_s equals $1 - \phi$.

Each NAPL component in a soil sample is distributed among the phases present. As a result, the total mass of component i in the sample equals the sum of the masses of component i in all phases. The mass conservation equation is:

$$\rho_t C_t^i = \phi_w C_w^i + \phi_a C_a^i + \phi_n C_n^i + \phi_s \rho_s C_s^i \qquad (9)$$

where ρ_t is the total density of the soil sample (mass of sample per volume of sample); C_t^i is the measured total concentration of i in the sample (mass i in sample per mass of sample); C_n^i is the concentration of i in the NAPL (mass i in NAPL per volume NAPL); and ρ_s is the density of the solid (approximately 2.65 kg/L for sand). The total density, ρ_t, is approximately equal to the weighted average of the densities of the four phases:

$$\rho_t = \phi_w\rho_w + \phi_a\rho_a + \phi_n\rho_n + \phi_s\rho_s \qquad (10)$$

where ρ_w is the density of water (approximately 1.0 kg/L); ρ_a is the density of air (approximately 0.0013 kg/L at 20°C); and ρ_n is the density of the NAPL mixture (mass NAPL per volume NAPL). ρ_n can be expressed as:

$$\rho_n = \Sigma C_n^i = \frac{\Sigma x_i MW_i}{\sum \frac{x_i MW_i}{\rho_i}} \qquad (11)$$

where ρ_i is the density of pure component i in liquid form (mass i per volume i). Some components, such as vinyl chloride or anthracene, may not occur as liquid in their pure form under environmental conditions. For these components, hypothetical pure phase liquid densities are computed by extrapolation.

The mole fraction of component i in the NAPL mixture is related to mass concentration by the equation:

$$x_i = \frac{C_n^i MW_n}{\rho_n MW_i} \qquad (12)$$

where MW_n is the equivalent molecular weight of the NAPL mixture (mass NAPL per mole NAPL). MW_n is approximately equal to the weighted average of the molecular weights of the NAPL components:

$$MW_n = \Sigma x_i MW_i \qquad (13)$$

Finally, the sum of the NAPL mole fractions is equal to 1:

$$\Sigma x_i = 1 \qquad (14)$$

Estimation of NAPL Saturation and Composition

A complete chemical analysis of a core sample provides the total mass of each component per unit mass of sample (i.e., the value of C_t^i for each component). To determine the saturation and composition of NAPL in the sample, the total mass of each component in each phase and the total volume of each phase must be determined. The partitioning theory and conservation relationships presented in the previous section can be used for this purpose. The solution allows calculation of the NAPL saturation from the equation:

$$S_N = \frac{\phi_n}{\phi} \qquad (15)$$

The method presented here is a numerical solution of the partitioning and conservation equations. PC software called NAPLANAL was developed to perform the numerical simulation. NAPLANAL can be used to estimate the following: (1) the NAPL saturation and composition in a soil sample containing NAPL; (2) the concentrations of organic compounds in each phase; and (3) the NAPL composition and NAPL volume in samples of NAPL-water emulsions (ϕ_s = 0). A copy of NAPLANAL is available from the INTERA web site (http://www.intera.com) for a small fee.

The algorithm is first demonstrated by considering a hypothetical soil sample from an unsaturated formation containing NAPL with N chemical components. Calculation of NAPL saturation and composition requires the following measurements or estimates as input: total concentrations of NAPL components in the soil sample (C_t^i), volumetric water content (ϕ_w), soil porosity (ϕ), volumetric soil content ($\phi_s = 1 - \phi$), soil organic carbon content (f_{oc}), organic carbon to water partition coefficients (K_{oc}^i), Henry's law constants in dimensionless form (K_H^i), molecular weight of each component (MW_i), and densities of water, air, soil, and each NAPL component (ρ_w, ρ_a, ρ_s, and ρ_i).

Equations 2, 3, 6, and 8 through 14 provide a total of 5N+5 independent equations that describe partitioning and conservation of organic compounds in a soil sample. Given the measurements and estimates listed in the previous paragraph, there are 5N+5 unknowns. These unknowns are as follows: NAPL component concentrations in water, air, soil, and NAPL (C_w^i, C_a^i, C_s^i, and C_n^i); component mole fractions in the NAPL mixture (x_i); volumetric contents of air and NAPL (ϕ_a and ϕ_n); density of sample (ρ_t); and the equivalent density and molecular weight of the NAPL (ρ_n and MW_n).

An equal number of unknowns and independent equations guarantees a unique solution. NAPLANAL solves the system of equations and unknowns using an algorithm that combines the rapid local convergence of the Newton-Raphson method for a system of nonlinear equations with a globally convergent strategy. For the sample problems tested so far, the computation time for reaching a solution is less than one minute using a 486 DX66 PC.

For core samples from the saturated zone, the air volumetric content (ϕ_a) and air phase concentrations (C_a^i) are equal to zero. Thus, the terms and equations involving the air phase are dropped from the system of equations. As a result, the number of equations reduces to 4N+5, while the number of unknowns reduces to 4N+4. Because there are fewer unknowns than equations, a measurement for either soil porosity (ϕ) or soil volumetric water content (ϕ_w) is sufficient for estimation purposes. Users of NAPLANAL have the choice of treating either ϕ or ϕ_w as an unknown parameter. A gas chromatography method is currently being developed to allow simultaneous measurement of ϕ_w and the concentrations of organic compounds in a soil sample.

The NAPLANAL code begins with the assumption that there is no NAPL present in the sample (i.e., ϕ_n = 0). The density of the sample can then be calculated from Equation 10 as:

$$\rho_t = \phi_w\rho_w + (\phi - \phi_w)\rho_a + (1 - \phi)\,\rho_s \qquad (16)$$

The first approximation of the aqueous concentration can be calculated from Equation 9 by:

$$C_w^i = \frac{C_t^i \rho_t}{\phi_w + K_H^i(\phi - \phi_w) + f_{oc}K_{oc}^i \rho_s (1 - \phi)} \qquad (17)$$

as shown by Feenstra et al. (1991). If NAPL exists in the sample, then this first approximation of C_w^i should exceed the effective aqueous solubility of component i. Equations 2 and 14 imply that C_w^i equals the effective aqueous solubility when:

$$\sum_i \frac{C_w^i}{S_i} = 1 \qquad (18)$$

Thus, a summation exceeding 1 when Equation 17 is used to estimate C_w^i implies that NAPL is present in the sample and that the NAPL saturation algorithm must be used instead to estimate C_w^i. A summation in Equation 18 equal to or less than one indicates there is no NAPL in the sample (i.e., S_N and ϕ_n equal zero). In this case, Equation 17 provides valid explicit estimates of aqueous concentrations. Air and sorbed concentrations are then calculated directly from Equations 3 and 6. When the summation in Equation 18 is less than 1, C_w^i is less than the effective aqueous solubility and calculation of x_i from Equation 2 is invalid.

Petroleum Hydrocarbon Example

In this example, the petroleum hydrocarbon data from Mott (1995) are used to compare the results of NAPLANAL and SOILCALC. The example problems consider hypothetical soil samples contaminated with C6 through C9 n-aliphatic hydrocarbons. For direct comparison of NAPLANAL and SOILCALC results, the input data are identical. The physical and chemical properties of the soil samples and the petroleum hydrocarbons used in the calculations are summarized in Table 1.

Table 1
Chemical Property Data Used in the Examples by Mott (1995)

Component i	K_{oc}^i (mL/g)	K_H^i	S_i (mg/L)	ρ_t (kg/L)	MW_i (g/mol)
Hexane	6025.60	46.49	12.31	0.66	86.07
Heptane	22908.68	63.59	3.06	0.68	100.20
Octane	77624.71	95.74	0.68	0.70	114.22
Nonane	263026.8	45.80	0.47	0.72	128.26

	f_{oc}	ϕ_w	ϕ
Soil Sample Data	0.01	0.08	0.4

The three soil samples differ only in the total hydrocarbon component concentration. These data are shown in Table 2. The first data set represents a soil sample containing 250 mg/kg of each component. The second data set, which is a borderline case (NAPL may or may not be present based on SOILCALC results), represents a soil sample containing 192 mg/kg each component. The third data set, which is a no NAPL case, represents a soil sample containing 100 mg/kg each component. Results from SOILCALC and NAPLANAL are summarized in Table 2. SOILCALC results are in parentheses.

SOILCALC assumes that NAPL occupies zero void space (i.e., the NAPL saturation is assumed insignificant relative to water and air content). Because of this assumption, SOILCALC does not have NAPL saturation estimation capability. In contrast, NAPLANAL implicitly calculates NAPL saturation. For the first two sets of data, the results indicate NAPL saturations of 0.15 percent and 0.02 percent, respectively. At such low NAPL saturations (i.e., approximately 1 percent or less of typical residual NAPL saturations [Mercer and Cohen 1990]), the pore space occupied by NAPL is indeed insignificant relative to pore space occupied by water and air. As a result, the two models give similar results, as shown in Table 2. However, there are still differences in the component mass distributions, especially for the mass of components in the NAPL phase. Because NAPLANAL calculates NAPL saturation, it should provide more accurate results than SOILCALC, especially at higher NAPL saturations.

Field DNAPL Examples

NAPLANAL was used to calculate the saturations and compositions of DNAPL and the phase distributions of DNAPL components in several core samples collected from a chemical plant on the Gulf Coast. DNAPL is NAPL that is denser than water. The plant has manufactured a variety of chlorinated ethanes and ethenes, such as 1,2-dichloroethane (EDC), trichloroethene (TCE), tetrachlorothene (PCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA),

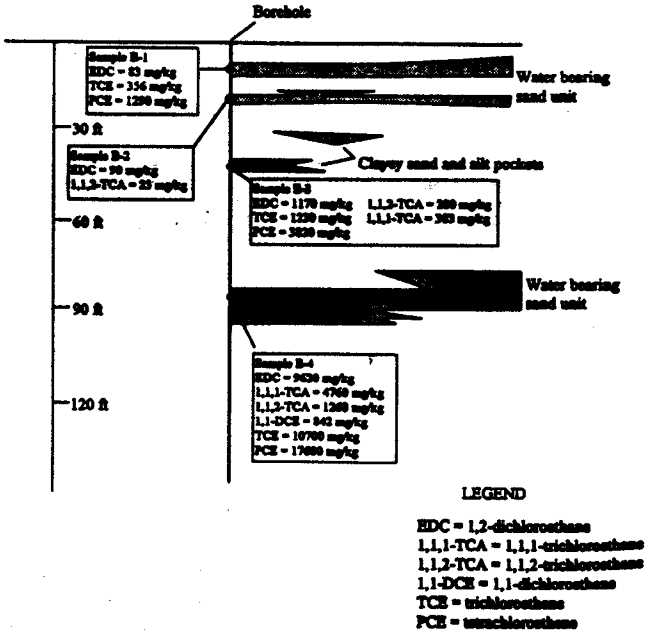

Figure 2. Cross-sectional view of soil sample location and total soil concentration.

Table 2

Comparison of NAPLANAL and SOILCALC Results

SOILCALC Results Are in Parentheses (Mott 1995). Concentrations Are Normalized by Total Sample Mass. For Comparison Purposes, Calculations Are Not Rounded to Reflect Significant Figures.

Component i	Measured Sample Conc. C_t^i (mg/kg)	Sample Conc. in Aq. Phase $C_w^i \phi_w \rho_t^{-1}$ (mg/kg)	Sample Conc. in Air Phase $C_a^i \phi_a \rho_t^{-1}$ (mg/kg)	Sample Conc. Sorbed $C_s^i \phi_s \rho_s \rho_t^{-1}$ (mg/kg)	Sample Conc. in NAPL $C_n^i \phi_n \rho_t^{-1}$ (mg/kg)	Mole Fraction in NAPL x_i
Data Set #1						
Hexane	250	1.467E-01 (1.493E-01)	2.680E+01 (2.795E+01)	1.735E+02 (1.800E+02)	4.953E+01 (4.193E+01)	0.2460 (0.2429)
Heptane	250	3.949E-02 (4.062E-02)	9.871E+00 (1.040E+01)	1.776E+02 (1.861E+02)	6.251E+01 (5.347E+01)	0.2667 (0.2663)
Octane	250	1.055E-02 (1.104E-02)	3.970E+00 (4.258E+00)	1.607E+02 (1.715E+02)	8.530E+01 (7.427E+01)	0.3193 (0.3245)
Nonane	250	3.852E-03 (3.926E-03)	6.936E-01 (6.710E-01)	1.989E+02 (2.065E+02)	5.040E+01 (4.272E+01)	0.1680 (0.1663)
NAPL saturation = 0.15%					$\sum x_i =$	1.0000 (1.0000)
Data Set #2						
Hexane	192	1.366E-01 (1.378E-01)	2.499E+01 (2.580E+01)	1.615E+02 (1.661E+02)	5.322E+00 (1.060E-02)	0.2290 (0.2241)
Heptane	192	3.894E-02 (3.968E-02)	9.749E+00 (1.016E+01)	1.751E+02 (1.818E+02)	7.114E+00 (1.445E-02)	0.2629 (0.2602)
Octane	192	1.160E-02 (1.207E-02)	4.374E+00 (4.653E+00)	1.768E+02 (1.873E+02)	1.083E+01 (2.224E-02)	0.3511 (0.3546)
Nonane	192	3.601E-03 (3.637E-03)	6.493E-01 (6.710E-01)	1.859E+02 (1.913E+02)	5.438E+00 (1.087E-02)	0.1570 (0.1540)
NAPL saturation = 0.02%					$\sum x_i =$	1.0000 (0.9929)
Data Set #3						
Hexane	100	7.316E-02 (7.177E-02)	1.339E+01 (1.344E+01)	8.654E+01 (8.648E+01)	(6.720E-15)	(0.1167)
Heptane	100	2.106E-02 (2.067E-02)	5.274E+00 (5.293E+00)	9.471E+01 (9.469E+01)	(8.132E-15)	(0.1355)
Octane	100	6.404E-03 (6.285E-03)	2.415E+00 (2.423E+00)	9.758E+01 (9.757E+01)	(1.364E-15)	(0.1847)
Nonane	100	1.930E-03 (1.894E-03)	3.481E-01 (3.495E-01)	9.965E+01 (9.965E+01)	(7.434E-15)	(0.0802)
No NAPL					$\sum x_i =$	(0.5171)

1,1-dichloroethane (1,1-DCA), and 1,1-dichloroethene (1,1-DCE). Spillage, waste-disposal operations, and pipeline leakage of these solvents have resulted in ground water contamination at the site. Previous investigations at the site have revealed silty water-bearing sand units separated by fractured clay units. In some areas, the clays are discontinuous and have allowed DNAPL to migrate to a sand unit 80 feet beneath the ground surface. Pumping tests have confirmed hydraulic communication between the sand units.

Table 3

Chemical Property Data Used in the Analysis of the Soil Samples

Component i	K_{oc}^i (mL/g)	K_H^i	S_i (mg/L)	ρ_i (kg/L)	MW_i (g/mol)
1,1-dichloroethene	65	0.87	400	1.22	97
1,2-dichloroethane	14	0.038	8690	1.26	99
1,1,1-trichloroethane	152	0.54	720	1.35	133.4
1,1,2-trichloroethane	56	0.031	4500	1.44	133.4
trichloroethene	126	0.3	1100	1.47	131.5
tetrachloroethene	364	0.54	200	1.63	165.8

Total soil chemical concentrations in four core samples from a single borehole were measured to evaluate the suitability of the site for a pilot-scale test of surfactant-enhanced aquifer remediation. The saturation and composition of the DNAPL mixture are important parameters in the decision-making process. The locations of the core samples and the analyzed soil chemical concentrations are shown in Figure 2. The samples are as follows: B-1, located in a sand unit at about 10 feet below ground surface (bgs); B-2, located in a sand unit at about 20 feet bgs; B-3, located in a unit of clayey sand with silt pockets at about 43 feet bgs; and B-4, located in a sand unit at about 80 feet bgs. The volumetric water contents of the core samples were not measured. The porosity and fraction organic carbon content of the sands were assumed

Table 4
NAPLANAL Calculations from Soil Sample Analyses
Concentrations Are Normalized by Total Sample Mass. Results Are Rounded to Two Significant Figures.

Component i	Measured Sample Conc. C_t^i (mg/kg)	Sample Conc. in Aq. Phase $C_w^i \phi_w \rho_t^{-1}$ (mg/kg)	Sample Conc. Sorbed $C_s^i \phi_s \rho_s \rho_t^{-1}$ (mg/kg)	Sample Conc. in NAPL $C_n^i \phi_n \rho_t^{-1}$ (mg/kg)	Mole Fraction in NAPL x_i
Sample B-1					
1,2-dichloroethane	83	50	0.74	32	0.032
trichloroethene	356	46	6.4	300	0.23
tetrachloroethene	1290	27	11	1300	0.74
NAPL saturation = 0.54%					
Sample B-2					
1,2-dichloroethane	90	89	1.7		
1,1,2-trichloroethane	23	22	1.4		
No NAPL					
Sample B-3					
1,2-dichloroethane	1170	300	4.8	860	0.19
1,1,1-trichloroethane	383	8.2	1.4	370	0.063
1,1,2-trichloroethane	200	24	1.5	170	0.029
trichloroethene	1230	40	5.7	1200	0.20
tetrachloroethene	3820	18	7.6	3800	0.51
NAPL saturation = 2.3%					
Sample B-4					
1,2-dichloroethane	9620	370	6.8	9200	0.28
1,1,1-trichloroethane	4760	12	2.3	4700	0.11
1,1,2-trichloroethane	1260	19	1.4	1200	0.028
1,1-dichloroethene	842	1.6	0.14	840	0.026
trichloroethene	10700	40	6.8	11000	0.24
tetrachloroethene	17600	9.6	4.6	18000	0.32
NAPL saturation = 17%					

to be 0.375 and 0.0015, respectively. These values are equivalent to average values measured by Liljestrand and Charbeneau (1987) in similar shallow sands in the area. Table 3 lists the physical properties attributed to the chlorinated solvents in the core samples.

According to the results of the NAPLANAL calculations, presented in Table 4, only a small amount of DNAPL is present in sample B-1. The ground water in B-2 appears to contain no DNAPL. Samples B-3 and B-4 have calculated NAPL saturations of about 2.3 percent and 17 percent, respectively. The computed NAPL composition in each of these core samples is different. Although PCE appears to be the predominant NAPL component in all samples containing NAPL, the mole fraction of PCE decreases with depth while the TCE and EDC mole fractions increase. This trend suggests historical variations in the composition of infiltrating DNAPL and/or different locations of DNAPL releases having different DNAPL compositions.

In the aforementioned calculations, soil porosity was estimated. Neither porosities nor water contents had been measured for these samples. A graph relating the porosity to the calculated NAPL saturation and composition for samples B-3 and B-4 is shown in Figure 3. Samples B-3 and B-4 represent soil samples having relatively low and high NAPL saturations, respectively. The graph shows that the uncertainty of the porosity value on the calculations of NAPL saturation and composition is small considering the relatively small possible range of soil porosity in sandy sediments.

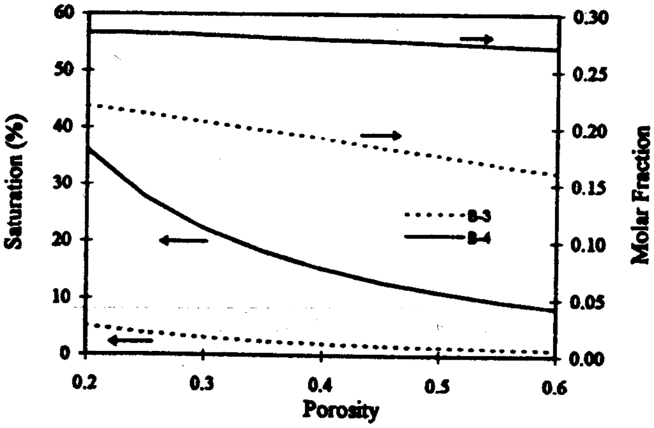

Figure 3. Effect of porosity on NAPL saturation and composition estimation results.

Conclusions

The NAPL saturation algorithm presented in this paper provides a useful tool to investigators involved in site characterization studies at NAPL-contaminated sites. This algorithm allows the quantification of NAPL saturation and NAPL composition in a soil sample from a typical soil chemical analysis. This information is useful in modeling and designing site-specific surfactant-enhanced aquifer remediation strategies (e.g., Brown et al. 1994) and partitioning interwell tracer tests (e.g., Jin et al. 1995). The calculations require only the soil information typically gathered in ground water contamination studies, specifically total chemical concentrations, water moisture content, porosity, natural organic content, and specific physical and chemical properties of the contaminants. A PC software program, NAPLANAL, was developed to perform these calculations.

The accuracy of the calculations depends on the accuracy of the input data. A sample's chemical analysis can be compromised by improper sampling and preservation, failure to identify and quantify all organic contaminants, and incomplete extraction of contaminants. In addition, the values of the physical properties of the soil sample and the chemical properties of the NAPL components affect the results. Thus, sensitivity analyses, such as the example shown for porosity, are strongly encouraged. Such sensitivity analyses can be performed easily using NAPLANAL.

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