A Model for Determination of the Phase Distribution of Petroleum Hydrocarbons at Release Sites

by Henry V. Mott, Ph.D., P.E.

Abstract

A model and computer-based numeric approximation for computing the equilibrium distributions of contaminants at petroleum release sites is presented. A database of contaminant-specific parameters, including solubility and organic-carbon partitioning coefficient, is assembled. Applications and limitations of the model are discussed.

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Introduction

Determinations of the allowable residual soil concentrations of petroleum hydrocarbons are extremely important with regard to the cleanup of released petroleum products. These residual levels should be sufficiently low so as to preclude both contamination of ground water and danger to public health. A decision to halt cleanup of a release too soon could compromise both environmental protection and public health, while continuance beyond what is necessary to achieve the proper protection is wasteful. Given limited resources, great care must be exercised in choosing the proper end point for a cleanup effort. This discussion addresses a physical/chemical model that may be used with assays of soil samples obtained from release sites and component-specific parameters to estimate the distribution of the components of a petroleum release among the phases (soil, water, vapor, nonaqueous liquid) potentially present at such sites. Use of a model such as presented herein may greatly assist in decisions regarding closure of remediated release sites.

Petroleum hydrocarbons of concern are gasoline, diesel fuel, heating oil, and aviation fuels. The compositions of these fuels are highly variable with regard to the exact components contained and the proportions of these components. The properties of these components that control their respective mobilities in the environment are also highly variable. Moreover, the soil properties

(such as porosity, hydraulic conductivity, mineralogy, and organic carbon content) at various release sites can also be highly variable. This variability leads to the potential for great complexity if site-specific determinations are to be made. Fortunately, several key factors (the organic carbon content of the soil and the component-specific organic carbon partition coefficient, vapor pressure, and aqueous solubility) can be used in an approach that allows for an enhanced capability for interpretation of soil sample assay information. This approach has been developed into a model that employs component concentration measurements of contaminated soils currently required by many regulatory agencies. Information regarding the properties of a large number of petroleum components has been obtained from the literature and is included in the model. The approach suggested herein employs the assumption that the four-phase system of a subsurface contaminated soil can be described by equilibrium.

A Model for Interpreting Contaminated Soil Assay Information

Contaminants in the soil must reside in or with the vapor phase, water, nonaqueous phase liquid, or the solid phase. The system tends toward an equilibrium such that the chemical potential or fugacity of any given component is equal in all phases present. Shortly after any significant precipitation event, the vadose zone soil (above the local ground water table and associated capillary fringe) drains to field capacity, and the movement of water through the soil ceases. Once percolation of water through the soil ceases, the system can remain fairly stagnant for days or even weeks with the only transport activity within the system being the flow of air in response to thermal and pressure gradients or vapor phase diffusion of moisture and other components due to concentration gradients. Under this relatively stagnant condition, equilibrium can be quite closely approached. In areas where infiltration of precipitation occurs, during and after significant precipitation events, uncontaminated water from precipitation percolates through the contaminated soil, flushes the equilibrated water from the contaminated zones, contacts the phases that contain the contaminants, and disturbs the near equilibrium previously attained. Contaminants then tend to dissolve in the water, and a new equilibrium between the contaminated phase(s) and the water becomes the limiting case for the aqueous concentrations. Successive equilibrations of this nature will lead to progressively lower aqueous concentrations. When uncontaminated water percolates into a contaminated zone of the soil, previously established conditions are disturbed, and the concentrations of contaminants in the water must be less than those defined by the previously established conditions due to loss of mass from the system. These dynamic conditions may closely approach equilibrium if the rate of water flow is sufficiently low, but they will generally never achieve true equilibrium. Pavlostathis and Jagial (1991) found that trichloroethylene (TCE) sorbed to soil did not readily

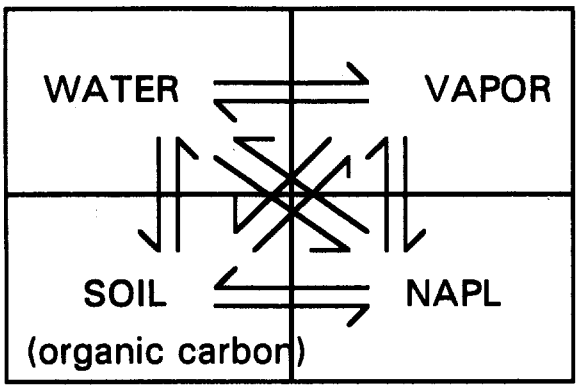

Figure 1. Schematic representation of the vadose zone system equilibria.

desorb and, in fact, that a significant fraction of the sorbed TCE was quite resistant to desorption. Pavlostathis and Mathavan (1992) subsequently found that the degree to which sorbed TCE resisted desorption was a function of the contact time between neat TCE and the soil sorbent. This resistance to desorption was attributed to both mass transfer and hysteretic limitations. Petroleum hydrocarbons sorbed to soils from neat NAPLs could, in a similar manner, also be quite resistant to desorption. This would, of course, reduce the degree to which water percolating through such contaminated zones would dissolve petroleum components as compared to that associated with a fully reversible sorption process. If allowable concentrations of petroleum hydrocarbons in the soil are based upon the true equilibrium distribution of contaminants among the transporting and stationary phases as thermodynamically driven by the sorption (as opposed to the desorption) process, the resulting limits will be inherently conservative. Unfortunately, uncertainties exist, as are discussed later, that cloud our ability to define this true equilibrium condition. Nonetheless, we must make decisions relative to remediation of releases; thus, an analytic tool allowing quantitative description of equilibrium conditions based on field-generated information would prove useful in the decision-making process.

The four phases of the soil mixture requiring consideration in the equilibrium calculations described herein are the soil, particularly the organic carbon fraction f^{oc}; the nonaqueous phase liquid NAPL; the vapor; and the water. The system is represented schematically in Figure 1.

The bi-directional arrows represent the various equilibria that are established across the respective phase boundaries. This representation assumes that each of the phases is in intimate contact with the other three. If a NAPL exists, the composition of the aqueous phase at equilibrium can be estimated directly from the composition of the nonaqueous phase. Banerjee (1984), working predominantly with halogenated benzenes, Cline et al. (1991), working predominantly with gasolines, and Lee et al. (1992), working with diesel fuels, all found that dissolution equilibria between aqueous solutions and multi-component NAPLs that form liquid mixtures could be satisfactorily described using a rela-

tionship analogous to Raoult's law:

$$C_i^w = S_i^w \; X_i^N \qquad (1)$$

where C_i^w is the solubility (ML^{-3}) of compound i in water at equilibrium with a multi-component NAPL; S_i^w (ML^{-3}) is the solubility of compound i in water at equilibrium with a NAPL consisting of pure component i; and X_i^N is the mole fraction concentration of compound i in the NAPL mixture. Equation 1 then may be used to estimate the corresponding aqueous concentration of each component of a multi-component NAPL that is in equilibrium with water, providing that the composition of the NAPL is known. The concentration of component i in the vapor phase, C_i^V, may also be related to the composition of the NAPL through Raoult's Law:

$$C_i^v = \frac{P_i^{vap} \; X_i^N}{RT} \qquad (2)$$

where p_i^{vap} is the pressure of component i; R is the gas constant; and T is the temperature in °K. The partitioning equilibria between the soil and the aqueous phase at low aqueous concentrations may be described as a number of parallel single-component sorption relationships using the linear sorption model experimentally verified by Karickhoff et al. (1979), Chiou et al. (1979), and Chiou (1983). The aqueous concentration of component i can in turn be related to the composition of the NAPL yielding:

$$q_i^s = F^{oc} \; K_i^{oc} \; C_i^w = F^{oc} \; K_i^{oc} \; S_i^w \; X_i^N \qquad (3)$$

where q_i^S is the adsorbed concentration of compound i ($M_i M_S^{-1}$); K_i^{oc} is the partition coefficient describing the equilibrium sorption relationship between compound i and organic carbon associated with the sorbent phase ($M_i M_S^{-1} M_i^{-1} L^3$); and F^{oc} is the fraction by mass of the solid phase that is organic carbon. Many solutes exhibit nonlinear sorption relationships with natural soils and sediments. In many cases, K_i^{oc} values have been derived from such nonlinear data. Use of nonlinear sorption relationships where applicable would improve accuracy at the expense of computational complexity. Users of this model must bear in mind that inaccuracies may result from use of partition coefficients rather than the true nonlinear sorption relationships for some systems. The largest errors would, of course, occur in systems with high aqueous concentrations. Of the petroleum hydrocarbons considered herein, benzene, toluene, and the xylenes are the most susceptible to these types of errors; pure component solubilities are in the range of hundreds of mg/L, and effective concentrations, in consideration of the potential for X_i^N to be near 0.10, could range between 10 and 200 mg/L. If the computed concentration of benzene, toluene, or any of the xylenes is significantly greater than 10 mg/L, the potential for error due to the linear approximation is greatest. The major advantage of using the linear sorption approximation is the ability to estimate sorption capacity parameters using the huge database of octanol-water partition coefficients.

The magnitude of F^{oc} must be determined experimentally. Methods vary widely with precision better than 10 percent relative standard deviation for aqueous samples containing particulate organic carbon (*Standard Methods* 1989). The precision for soil samples is likely somewhat lower, as digestion is often more difficult than for aqueous samples. Errors associated with the computation of the adsorbed fraction could then be quite significant. Mineral surfaces of swelling clays were suggested by Karickhoff (1984) to be important only for compounds that were somewhat polar and only if the ratio of the clay fraction to the organic fraction of the soil was above the range of 15:1 to 30:1. Specific information relative to the sorption capacity of mineral surfaces for the individual components of petroleum hydrocarbons is rather scarce in the literature. These surfaces are, for the most part, hydrophilic, rendering the potential for significant sorption interactions with nonpolar, hydrophobic contaminants to be rather small and important only in soils having organic carbon fractions below about 0.005 g^{oc}/g^{soil}. Users of the computational model described herein are cautioned about applications to systems wherein the soils have low organic carbon contents.

The components determined by the soil assay must reside with the whole soil, which consists of four phases: water, vapor, solid, and nonaqueous liquid (NAPL). The method of assay, which generally consists of solvent or thermal extraction of the contaminants from the soil and subsequent analysis using gas chromatography with flame ionization or mass specific detection, yields the total quantity of each component associated per unit mass of whole soil. The distributions of these total masses among the four phases present must then be computed to fully understand the system. The equilibria described above, coupled with application of mass conservation, yield a model capable of such computations. A solution of this model has been developed in the form of a FORTRAN code entitled SOILCALC, available from the author. For convenience, molar quantities and concentrations are used rather than mass quantities and concentrations. The following general equation results from application of mass conservation to an arbitrary component of the petroleum mixture residing within the soil: Total quantity of i = quantity in water + quantity in vapor + quantity on soil + quantity in NAPL, or:

$$Mol_i^T = \frac{M^w}{\rho^w} \; C_i^w + V^v \; C_i^v + M^s \; q_i^s + Mol^N \; X_i^N \qquad (4)$$

where Mol_i^T is the molar quantity of i associated with a given mass of soil on a dry basis; M^W is the mass of water associated with the soil; ρ^W is the density of water; V^V is the volume of vapor associated with the soil; M^S is the dry mass of soil; and Mol^N is the molar quantity

of NAPL associated with the given mass of soil. Substitution of Equations 1 through 3 into four yields:

$$Mol_i^T = \frac{M^w}{\rho^w} S_i^w X_i^N + V^v \frac{P_i^{vap} X_i^N}{RT} + M^s F^{oc} K_i^{oc} S_i^w X_i^N + Mol^N X_i^N \quad (5)$$

where the vapor volume can be determined based on the mass and density of the solid phase, the moisture content of the soil, the total porosity, and the assumption that the volume of the voids occupied by the NAPL is insignificant relative to the volumes of water and vapor. For systems that have free product or those at or near field capacity with regard to residual NAPL, this assumption may introduce unacceptable inaccuracy. For systems with total petroleum hydrocarbon (TPH) levels of 0 to 2000 ppm, this assumption is quite good. A similar analysis was presented by Feenstra et al. (1991); however, their approach was to assume either that the soil contained no NAPL or that NAPL was present and the composition could be assumed or otherwise was known. Presence of NAPL would then be indicated by computed aqueous concentrations above the solubility level of the component in question for the first case or equal to the effective solubility as computed from Equation 1 in the second case. SOILCALC makes neither of these assumptions in directly computing the presence or absence of NAPL as well as distributions of contaminants among the phases present.

Equation 5 may then be simplified by lumping terms and rearranging into the form:

$$X_i^N = Mol_i^T/(A_i + Mol^N) \quad (6)$$

where:

$$A_i = \frac{M^w}{\rho^w} S_i^w + V^v \frac{P_i^{vap}}{RT} + M^s F^{oc} K_i^{oc} S_i^w \quad (7)$$

Equation 6 may then be written for each component quantitated in an assay of a given contaminated soil given that the temperature, moisture content (M^W), porosity of the soil (ε), and organic carbon fraction of the soil (F^{OC}) are known. The assay of the soil is normalized to one kg of soil (M^S) for convenience in computations. Values of solubility (S_i^W), vapor pressure (P_i^{vap}), and soil organic carbon partition coefficient (K_i^{OC}) were obtained as measured values from the literature or were estimated using certain reliable methods as will be described later. The resulting system of equations may then be quite easily solved using a successive substitutions approach with the beginning value of Mol^N approximated as ΣMol_i^T. Each X_i^N is then computed using Equation 6, then each Mol_i^N ($= X_i^N Mol^N$), in turn computed as $Mol_i^T - A_i X_i^N$. A new approximation of $Mol^N = \Sigma Mol_i^N$ is computed. New vectors of X_i^N and Mol_i^N values are then computed with subsequent update of Mol^N. Convergence criteria center upon successive values of Mol^N and each of the X_i^N values with that conditions that $|(Mol_{k+1}^N - Mol_k^N)/Mol_k^N| < 10^{-8}$ and $|(X_{i,k+1}^N - X_{i,k}^N)/X_{i,k}^N| < 10^{-10}$ necessary for convergence of the solution. The additional constraint is imposed that $|\Sigma X_i^N - 1| < 10^{-8}$ in order for the solution to be considered valid. If this difference is larger than 10^{-8}, a three-phase solution (water, vapor, and soil) is likely quite appropriate. In this case, Equation 5 may be somewhat simplified and solved for C_i^W and, hence, the component phase distribution from:

$$C_i^w = \frac{Mol_i^T}{\frac{M^w}{\rho^w} + V^v \frac{P_i^{vap}}{S_i^w RT} + M^s F^{oc} K_i^{oc}} \quad (8)$$

where the term P_i^{vap}/S_i^W is the equivalent of the Henry's Law constant for distribution of components between the aqueous and vapor phases.

Evaluation of Model Parameters

Numerous correlations are available that relate K_i^{oc} to surrogate thermodynamic parameters of respective compounds such as the octanol-water partition coefficient K_i^{ow}, and aqueous solubility, S_i^W. A compilation of these correlations is given by Lymann (1982). Of these, the correlation that appears most appropriate for the components of petroleum hydrocarbons in the soil was developed by Karickhoff et al. (1979) for predominantly nonhalogenated aromatic hydrocarbons:

$$\log_{10} K_i^{oc} = \log_{10} K_i^{ow} - 0.21 \quad (9)$$

The search of the literature associated with this investigation did not yield a correlation specific to nonhalogenated aliphatic hydrocarbons. Correspondingly, Equation 9 was used to estimate the K_i^{oc} values from K_i^{ow} values for both the aromatic and aliphatic hydrocarbons considered herein. The true magnitude of K_i^{oc} can vary greatly depending upon the nature of the organic matter under consideration. Correlations such as Equation 9 are developed experimentally using reference solids. The actual correlations then can also be greatly affected by experimental procedures as well as by the reference solids used. Correspondingly, the magnitudes of K_i^{oc} obtained from such global correlations can vary from those for the specific sorbent by an order of magnitude or more (Lymann 1982). In the case that a user has more specific sorption capacity data available, such data can be inputted by the user into the file of component properties associated with SOILCALC.

Measured values of octanol-water partition coefficients for many components of fuels considered herein were obtained from the literature, and those not available were estimated using the fragment-factor method of Hansch and Leo (1979) as presented by Grain (1982a). The procedure involved beginning with the measured $\log_{10} K_i^{ow}$ of the base compound and adding or subtracting the appropriate fragments and factors based upon the specific functional groups associated with the compound under consideration. As with all estimation methods, some errors are associated with this approach. The factor-fragment method was tested

by Grain (1982a). Fragments and factors were summed for 39 compounds of widely varying structure to estimate the magnitudes of $\log_{10}K_i^{ow}$, and these estimates were compared with measured values. The average deviation of the estimated value from the measured value was 0.14 log unit. The approach used herein, using the measured value of a base compound and adjusting for functionality, is suggested by Grain (1982a) to provide significantly greater accuracy than the approach in which the K_i^{ow} values are determined solely by summing fragments and factors. A listing of petroleum components identified in various fuels and respective values of $\log_{10}K_i^{ow}$ is given in Table 1. This list includes a number of polycyclic aromatic hydrocarbons (PAH) found to be present in samples of diesel fuels and kerosenes (Obuchi et al. 1984; Williams et al. 1986; Davies et al. 1988a and 1988b; Barbella et al. 1989; State of California 1989; Nelson 1989).

Aqueous solubility values are available from the literature for a number of the compounds listed in Table 1. Solubility values for those components whose measured values were not available in the literature were estimated by log-log regression of the super-cooled liquid solubility against the octanol-water partition coefficient, with the super-cooled solubility computed as (Miller et al. 1985):

$$S_i^{w,liq} = S_i^{w,solid}/F \quad (10)$$

where $F = \exp[\Delta S(1-T_M/T)/R]$; ΔS is the entropy fusion ($\Delta S/R$ was taken as 6.8); T_M is the compound melting point in °K; and T is the system temperature. A plot of the values of $\log S_i^{w,liq}$ versus $\log K_i^{ow}$ is given in Figure 2. All three classes of compounds appear to lie along a common regression line; thus, a single correlation was obtained using all 33 measured solubility values. The resulting correlation was:

$$\log S_i^{w,liq} = 0.4692 - 1.0481 \log K_i^{ow}, \quad r^2 = 0.959 \quad (11)$$

This correlation was in turn used to estimate the liquid solubilities of the components whose solubilities could not be determined from the literature. A listing of aqueous solubilities (known and estimated and converted to equivalent liquid values) incorporated into the data file for this model is also given in Table 1. All liquid solubilities were corrected to a temperature of 25 °C. Since the petroleum hydrocarbons associated with releases are nearly always in liquid form, the liquid solubilities rather than solid solubilities are used in the solution model.

Vapor pressures of components were obtained from various sources. Values for certain components were listed in *Lange's Handbook* (Dean 1992); others were found in the *CRC Handbook* (Weast 1989); and others were estimated from boiling point information using Method 1 suggested by Grain (1982b). Certain boiling point information was not available in the literature and was therefore estimated using the Lydersen-Forman-Thodos Method (Rechsteiner 1982). Information from *Lange's Handbook* was in the form of the three coefficients of the Antoine Equation; whereas, vapor pressures given in the *CRC Handbook* and computed from

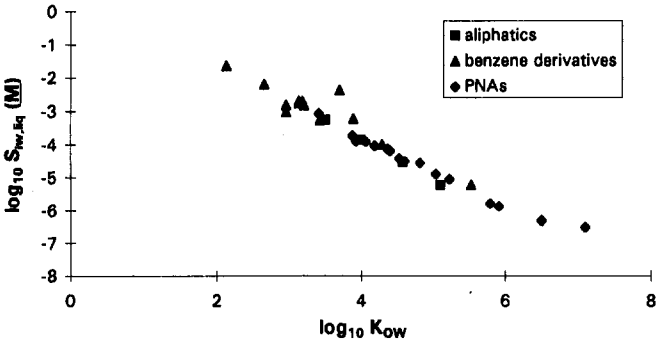

Figure 2. A plot of aqueous solubility vs. octanol-water partition coefficient. Solubility values of solids were converted as necessary to super-cooled liquid values at 25 °C.

boiling point information were discrete ordered pairs of vapor pressure and temperature. These ordered pairs were fit to the Antoine Equation to obtain the coefficients A, B, and C using the method suggested by Dean (1992). The component vapor pressure values used in the solution were then computed using the Antoine Equation from input in the form of A, B, and C coefficients. The vapor pressure coefficients and boiling point information as appropriate are listed in Table 1. The vapor pressure data used herein in all cases represent the components in the liquid state. Many of these compounds are, in fact, solids at the temperatures to be considered; thus, extrapolations of vapor pressure relationships below the ranges of the determinations were necessary. Reid et al. (1987) caution against extrapolations using the three-parameter Antoine Equation and suggest use of the four-parameter Wagner Equation for such extrapolations:

$$\ln P_i^{vap} = (a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6)/T_r \quad (12)$$

where $\tau = 1-T_r$, and T_r is the reduced temperature, $T/T_{critical}$. Much of the vapor pressure data in the literature is in the form of the coefficients for the Antoine Equation. Conversion of such data to the Wagner Equation could also result in significant error. Assembly of the experimental vapor pressure data for the components considered herein is well beyond the scope of this work. Extrapolations used herein are all to the lower temperature region. The Antoine Equation predicts monotonically lower vapor pressure with decreasing temperature. Many of the components for which these extrapolations are made have quite low vapor pressures in the temperature range considered and are unimportant vapor phase constituents. Although large errors relative to true vapor pressure values may, in fact, be associated with extrapolations using the Antoine Equation with this model, the errors contributed to the overall system solution are quite minor. Efforts associated with conversion of vapor pressure data to the four-parameter Wagner Equation appear to be unwarranted at this time.

Discussion

The SOILCALC model discussed herein begins with the assumption that all hydrocarbon components quan-

Table 1
Values of Selected Parameters Used in the Model SOILCALC

Component	$Log_{10}K^{ow}$	$Log_{10}K^{oc}$	S_i^W (M)	Antoine Eq. Coefficients A	B	C	T_b(°K)
n-pentane	3.50[1,2]	3.29	5.65E-04[1]	6.85296	1064.84	233.01[9]	
isopentane	3.27[2]	3.06	1.10E-03[8]	6.83315	1040.73	235.45[10]	
1-pentene	2.84[4]	2.63	3.11E-03[8]	6.84424	1044.01	233.50[10]	
3-methyl-1-butene	2.93[4]	2.72	2.50E-03[8]	6.82455	1012.37	236.65[9]	
2-methyl-1-butene	2.93[4]	2.72	2.50E-03[8]	6.84637	1039.69	236.65[9]	
2-methyl-1,3-butadiene	2.38[4]	2.17	9.43E-03[8]	7.01187	1126.159	238.88[9]	
trans-2-pentene	2.85[4]	2.64	3.03E-03[8]	6.89983	1080.76	232.57[9]	
2-methyl-2-butene	2.93[4]	2.72	2.50E-03[8]	6.96659	1124.33	236.63[9]	
3-methyl-1,2-butadiene	2.38[4]	2.17	9.43E-03[8]	7.15195	1194.537	239.47[9]	
cyclopentane	3.00[2]	2.79	2.11E-03[8]	6.88676	1124.162	231.36[9]	
cis-2-pentene	2.85[4]	2.64	3.03E-03[8]	6.84308	1052.44	228.69[9]	
n-hexane	3.99[4]	3.78	1.43E-04[1]	6.87601	1171.17	224.41[9]	
3,3-dimethyl-1-butene	3.40[4]	3.19	8.04E-04[8]	6.67751	1010.516	224.91[9]	
3-methyl-1-pentene	3.38[4]	3.17	8.43E-04[8]	6.75523	1086.316	226.20[9]	
2,3-dimethylbutane	3.85[2]	3.64	2.71E-04[8]	6.80983	1127.187	228.90[9]	
2-methylpentane	4.03[4]	3.82	1.76E-04[8]	6.83910	1135.410	226.57[10]	
3-methylpentane	4.03[4]	3.82	1.76E-04[8]	6.84887	1152.368	227.13[9]	
methylcyclopentane	3.53[4]	3.32	5.87E-04[8]	6.86283	1186.059	226.04[9]	
cyclohexane	3.44[2]	3.23	7.30E-04[8]	6.84130	1201.53	222.65[9]	
2-ethyl-1-butene	3.56[4]	3.35	5.46E-04[8]	6.99712	1218.352	231.30[9]	
n-heptane	4.57[4]	4.36	3.05E-05[1]	6.89677	1264.90	216.54[9]	
2,2-dimethylpentane	4.56[4]	4.35	4.89E-05[8]	6.81480	1190.033	233.30[9]	
2,3-dimethylpentane	4.56[4]	4.35	4.89E-05[8]	6.85382	1238.017	221.82[9]	
3-methylhexane	4.52[4]	4.31	5.38E-05[8]	6.86764	1240.196	219.22[9]	
methylcyclohexane	3.97[4]	3.76	2.03E-04[8]	6.82300	1270.763	221.42[9]	
3-ethylpentane	4.72[4]	4.51	3.32E-05[8]	6.87564	1251.827	219.89[9]	
1-methyl-1-cyclohexene	3.42[4]	3.21	7.66E-04[8]	6.795	1152.	226.[11]	341[13]
n-octane	5.10[1,4]	4.89	5.97E-06[1]	6.91868	1351.99	209.15[9]	
2,2,4-trimethylpentane	5.09[4]	4.88	1.36E-05[8]	6.81189	1257.84	220.74[9]	
2,2-dimethylhexane	5.05[4]	4.84	1.50E-05[8]	6.83715	1273.59	215.07[9]	
2,3,4-trimethylpentane	5.09[4]	4.88	1.36E-05[8]	6.85396	1315.08	217.53[10]	
2-methylheptane	5.10[4]	4.89	1.33E-05[8]	6.91735	1337.47	213.69[9]	
3-methylheptane	5.10[4]	4.89	1.33E-05[8]	6.89944	1331.53	212.41[9]	
cis 1,2-dimethylcyclohexane	4.50[4]	4.29	5.65E-05[8]	6.83746	1367.311	215.84[9]	
trans 1,2-dimethylcyclohexane	4.50[4]	4.29	5.65E-05[8]	6.83308	1353.811	219.13[9]	
n-nonane	5.63[4]	5.42	3.69E-06[8]	6.93893	1431.82	202.01[9]	
2,4,4-trimethylhexane	5.58[4]	5.37	4.17E-06[8]	6.93893	1431.82	202.01[12]	
2,2-dimethylheptane	5.72[4]	5.42	2.97E-06[8]	6.93893	1431.82	202.01[12]	
3,3,4-trimethylhexane	5.58[4]	5.37	4.17E-06[8]	6.93893	1431.82	202.01[12]	
2,4-dimethylheptane	5.63[4]	5.42	3.69E-06[8]	6.93893	1431.82	202.01[12]	
4,4-dimethyl-3-ethyl-2-pentene	5.26[4]	5.05	9.02E-06[8]	6.820	1344.	215.[11]	126[13]
4-methyloctane	5.63[4]	5.42	3.69E-06[8]	6.93893	1431.82	202.01[12]	
3,4-dimethylheptane	5.63[4]	5.42	3.69E-06[8]	6.93893	1431.82	202.01[12]	
n-decane	6.17[4]	5.96	1.00E-06[8]	6.94365	1495.17	193.86[9]	
2,2,4-trimethylheptane	6.16[4]	5.95	1.03E-06[8]	6.94365	1495.17	193.86[12]	
3,3,5-trimethylheptane	6.16[4]	5.95	1.03E-06[8]	6.94365	1495.17	193.86[12]	
2,3,4-trimethylheptane	6.16[4]	5.95	1.03E-06[8]	6.94365	1495.17	193.86[12]	
n-dodecane	7.18[4]	6.97	8.76E-08[8]	6.99795	1639.27	181.84[9]	
4-n-propylheptane	6.34[4]	6.13	6.66E-07[8]	6.97220	1569.57	187.70[12]	
2,6-dimethyloctane	6.15[4]	5.94	1.05E-06[8]	6.4075	1247.3	188.37[10]	
undecane	6.64[4]	6.43	3.23E-07[8]	6.97220	1569.57	187.70[9]	

Table 1 (Continued)
Values of Selected Parameters Used in the Model SOILCALC

Component	$Log_{10}K^{ow}$	$Log_{10}K^{oc}$	S_i^W (M)	Antoine Eq. Coefficients A	B	C	T_b(°K)
2,5-dimethylundecane	7.70[4]	7.49	2.50E-08[8]	7.00756	1690.67	174.22[12]	
n-tridecane	7.49[4]	7.28	4.15E-08[8]	7.00756	1690.67	174.22[9]	
n-tetradecane	8.01[4]	7.80	1.18E-08[8]	7.01300	1740.88	167.72[9]	
n-pentadecane	8.53[4]	8.32	3.37E-09[8]	7.02359	1789.95	161.38[9]	
n-hexadecane	9.05[4]	8.84	9.60E-10[8]	7.02867	1830.51	154.45[9]	
n-heptadecane	9.57[4]	9.36	2.74E-10[8]	7.0143	1865.1	149.20[9]	
n-octadecane	10.09[4]	9.88	7.80E-11[8]	7.0022	1894.3	143.30[9]	
2-methylheptadecane	10.09[4]	9.88	7.80E-11[8]	7.8471	2670.4	220.70[10]	
n-nonadecane	10.61[4]	10.40	2.22E-11[8]	7.0153	1932.8	137.6[9]	
2,6,10,14-tetramethylpentadecane	10.61[4]	10.40	2.22E-11[8]	7.0153	1932.8	137.6[3]	
n-eicosane	11.13[4]	10.92	6.34E-12[8]	7.1522	2032.7	132.1[9]	
n-heneicosane	11.65[4]	11.44	1.81E-12[8]	6.95	2151.	172.[11]	629[13]
benzene	2.13[1]	1.92	2.29E-02[1]	6.90565	1211.033	220.790[9]	
ethylbenzene	3.13[1]	2.92	1.76E-03[1]	6.95719	1424.255	213.21[9]	
n-propylbenzene	3.69[1]	3.48	4.34E-03[1]	6.95142	1491.297	207.14[9]	
1,2,3-trimethylbenzene	3.42[4]	3.21	5.45E-04[1]	7.04082	1593.958	207.08[9]	
1,2,4-trimethylbenzene	3.42[2]	3.21	7.66E-04[8]	7.04383	1573.267	208.56[9]	
1,3,5-trimethylbenzene	3.65[3]	3.44	4.40E-04[8]	7.07436	1569.622	209.58[9]	
diethylbenzene	4.48[4]	4.27	5.93E-05[8]	6.99658	1580.187	201.15[9]	
sec-butylbenzene	4.45[4]	4.24	6.37E-05[8]	6.94219	1533.95	204.39[10]	
ethylxylene	4.45[4]	4.24	6.53E-05[8]	7.5521	1979.3	237.38[10]	
1,2,3,4-tetramethylbenzene	4.00[4]	3.79	1.89E-04[8]	7.0594	1690.54	199.48[9]	
1,2,3,5-tetramethylbenzene	4.00[4]	3.79	1.89E-04[8]	7.0779	1675.43	201.14[9]	
1,2,4,5-tetramethylbenzene	4.00[2]	3.79	1.89E-04[8]	7.0800	1672.43	201.43[9]	
isopropylbenzene	3.66[2]	3.45	4.29E-04[8]	6.93666	1460.793	207.78[9]	
n-butylbenzene	4.28[1]	4.07	1.03E-04[1]	6.98317	1577.965	201.378[9]	
pentamethlylbenzene	4.53[4]	4.32	5.26E-05[8]	6.86	1702.	195.[11]	505[13]
1,2,4-trimethyl-5-ethylbenzene	4.69[4]	4.48	3.57E-05[8]	3.0293	116.4	–34.6[9]	
n-hexylbenzene	5.52[1]	5.31	6.27E-06[1]	6.86	1678.	196.5[11]	225[14]
dimethylisopropylbenzene	5.50[4]	5.29	5.06E-06[8]	6.85	1590.	201.[11]	472[13]
styrene	2.95[2]	2.74	1.54E-03[5]	7.14016	1574.51	224.09[9]	
ethylstyrene	4.30[4]	4.09	9.16E-05[8]	6.97550	1592.4	198.[9]	
indan	2.95[2]	2.74	9.33E-04[6]	6.88	1534.	205.[11]	451[13]
1,6-dimethylindan	4.39[4]	4.18	7.37E-05[8]	6.85	1590.	201.[11]	472[14]
o-xylene	3.13[1]	2.92	2.08E-03[1]	6.99891	1474.679	213.69[9]	
m-xylene	3.20[1]	2.99	1.51E-03[1]	7.00908	1462.266	215.11[9]	
p-xylene	3.18[1]	2.97	2.02E-03[1]	6.99052	1453.430	215.31[9]	
toluene	2.65[1]	2.44	6.28E-03[1]	6.95464	1344.800	219.48[9]	
2-ethyltoluene	3.88[4]	3.67	6.21E-04[1]	7.00314	1535.374	207.30[9]	
3-ethyltoluene	3.88[4]	3.67	2.52E-04[8]	7.01582	1529.184	208.51[9]	
4-ethyltoluene	3.88[4]	3.67	2.52E-04[8]	6.99802	1527.113	208.92[9]	
1,2-diaminobenzene	0.15[4]	–0.06	2.05E+00[8]	8.0219	2658.4	231.60[10]	
1,3-diaminobenzene	–0.01[4]	–0.22	3.02E+00[8]	8.0219	2658.4	231.60[10]	
1,4-diaminobenzene	–0.17[4]	–0.38	4.44E+00[8]	8.0219	2658.4	231.60[10]	
biphenyl	4.06[2]	3.85	4.57E-05[6]	7.24541	1998.725	202.733[9]	
methylbiphenyls	4.14[2]	3.93	1.35E-04[8]	7.4788	2244.1	224.06[10]	
naphthalene	3.41[2]	3.20	2.46E-04[6]	6.8181	1585.86	184.82[9]	
methylnaphthalene	3.87[2]	3.66	1.88E-04[6]	7.05252	1833.608	196.7[9]	
dimethylnaphthalenes	4.36[2]	4.15	2.86E-05[6]	7.1739	1967.	195.[9]	
ethylnaphthalene	4.39[1]	4.18	6.92E-05[6]	7.9442	2704.6	232.15[10]	
trimethylnaphthalenes	4.81[1,2]	4.60	1.20E-05[6]	6.88	1809.	189.[11]	537[13]

Table 1 (Continued)
Values of Selected Parameters Used in the Model SOILCALC

Component	$Log_{10}K^{ow}$	$Log_{10}K^{oc}$	S_i^W (M)	Antoine Eq. Coefficients A	B	C	T_b(°K)
propylnaphthalene	5.05[4]	4.84	1.50E-05[8]	7.5644	2336.6	232.90[10]	
acenaphthene	3.92[1]	3.71	2.57E-05[6]	7.72819	2534.234	245.576[9]	
fluorene	4.18[2]	3.97	1.20E-05[6]	7.7618	2637.1	243.2[9]	
methylfluorenes	4.84[4]	4.63	6.06E-06[8]	6.89	1948.	181.5[11]	577[14]
dimethylfluorenes	5.50[4]	5.29	5.06E-06[8]	6.90	1982.	179.6[11]	587[14]
phenanthrene	4.52[1,2]	4.25	7.08E-06[6]	7.26082	2379.14	203.76[9]	
methylphenanthrenes	5.12[4]	4.91	1.27E-05[8]	6.91	2106.	172.8[11]	623[14]
dimethylphenanthrenes	5.78[4]	5.57	2.57E-06[8]	6.91	2141.	170.8[11]	633[14]
anthracene	4.59[2,7]	4.44	4.17E-07[6]	7.67401	2819.63	247.02[9]	
fluoranthene	5.22[6]	5.01	1.30E-06[1]	6.373	1756.	118.[9]	
pyrene	5.03[1,2]	4.82	6.61E-07[6]	5.6184	1122.0	15.2[9]	
chrysene	5.79[1]	5.58	8.71E-09[6]	6.99	2472.	154.[11]	721[13]
3-methylchrysene	6.45[4]	6.24	5.10E-07[8]	6.95	2482.	152.[11]	731[14]
6-methylchrysene	6.45[4]	6.24	5.10E-07[8]	6.95	2482.	152.[11]	731[14]
benz(a)anthracene	5.91[6]	5.70	6.17E-08[6]	6.98	2423.	157.[11]	707[14]
benzo(a)pyrene	6.50[6]	6.29	4.52E-07[8]	7.01	2749.	139.[11]	800[14]
benzo(e)pyrene	6.50[4]	6.29	1.51E-08[6]	7.01	2749.	139.[11]	800[14]
perylene	6.50[1]	6.29	1.58E-09[6]	7.01	2749.	139.[11]	800[14]
benzo(g,h,i)perylene	7.10[6]	6.89	9.55E-10[6]	7.04	3071.	122.[11]	890[14]

[1] From Miller et al. (1985).
[2] From Hansch and Leo (1979).
[3] From Lymann (1982).
[4] Estimated by the fragment-factor method of Hansch and Leo (Grain 1982a) using a base component of known K^{ow}.
[5] From Banerjee et al. (1980).
[6] From Yalkowski and Valvani (1980).
[7] From Karickhoff et al. (1979).
[8] From C^{sl} versus K^{ow} relationships depicted in Figure 2.
[9] A, B, and C coefficients from Dean (1992).
[10] A, B, and C coefficients estimated using method of Dean (1992) and P^v values from Weast (1989).
[11] P^v values estimated from boiling point using method #1 given by Grain (1982b) and A, B, and C coefficients estimated using method of Dean (1992).
[12] Used value for n-aliphatic.
[13] From Weast (1989).
[14] Estimated using Lyderson-Forman-Thodos method (Rechsteiner 1982) using a base known value.

titated from a soil assay reside in the NAPL; through an iterative, successive substitution algorithm, steps toward the system solution in which the compositions of the NAPL, if present, and the other phases are computed based on the soil assay and properties specific to the individual components quantitated at the release site. SOILCALC then requires no assumptions relative to the composition of an existing NAPL phase in computing the distributions of components among all phases present. If the final solution for a system includes significant NAPL (> 0.5 mg NAPL/kg dry soil), SOILCALC converges quite rapidly to a solution. If the final solution is clearly a case in which NAPL is computed not to be present, SOILCALC again converges quite rapidly to a solution for which the sum of the mole fraction concentrations of the components of the NAPL do not sum to unity. The user would then opt for the no-NAPL solution interactively with SOILCALC. Conversely, systems closely approaching saturation of the aqueous, vapor, and solid phases with hydrocarbons will require a large number of iterations to arrive at a solution. These possibilities are illustrated using simplified systems considering C6 through C9 n-aliphatic hydrocarbons. Input data and computational results are summarized in Table 2. The first test clearly indicates the presence of a NAPL. This approximation converged in less than 500 iterations (several seconds of run time using a 386 DX-40 PC). The second test illustrates the results for a system that is clearly on the borderline with respect to saturation of the aqueous phase with the hydrocarbons. This solution converged in about 3500 iterations (≈2 minutes run time). In case such as this, the user must decide whether to accept the NAPL solution or not. Such a decision is made interactively with SOILCALC. The third test is the no-NAPL solution of the second case. Note that the distributions of components among the aqueous, vapor, and soil phases are identical to the number of significant figures presented in the model output for Tests 2 and 3. The sum of the NAPL mole fractions is near unity but well short of the 1.0000000 expected

Table 2

Illustrations of Component Distributions for Various Solution Approximations Using Program SOILCALC. F^{oc} = 0.01 kg/kg, M^{w} = 0.05 kg/kg, ϵ = 0.40, T = 20 °C

Comp.	M_i^T (mg/kg$_S$)	M_i^W (mg/kg$_S$)	M_i^V (mg/kg$_S$)	M_i^S (Mg/kg$_S$)	M_i^N (mg/kg$_S$)	X_i^N
A solution that clearly indicates presence of NAPL.						
C6	2.500E+02	1.493E−01	2.795E+01	1.800E+02	4.193E+01	0.2429
C7	2.500E+02	4.062E−02	1.040E+01	1.861E+02	5.347E+01	0.2663
C8	2.500E+02	1.104E−02	4.258E+00	1.715E+02	7.427E+01	0.3245
C9	2.500E+02	3.926E−03	7.244E−01	2.065E+02	4.272E+01	0.1663
					ΣX_i^N =	1.0000000
A NAPL solution of a borderline case: NAPL may or may not be present.						
C6	1.920E+02	1.378E−01	2.580E+01	1.661E+02	1.060E12	0.2241
C7	1.920E+02	3.968E−02	1.016E+01	1.818E+02	1.445E12	0.2602
C8	1.920E+02	1.207E−02	4.653E+00	1.873E+02	2.224E12	0.3546
C9	1.920E+02	3.637E−03	6.710E−01	1.913E+02	1.087E12	0.1540
					ΣX_i^N =	0.9929000
A noNAPL solution of a borderline case: NAPL may or may not be present.						
C6	1.920E+02	1.378E−01	2.580E+01	1.661E+02	0.000E+00	
C7	1.920E+02	3.968E−02	1.016E+01	1.818E+02	0.000E+00	
C8	1.920E+02	1.207E−02	4.653E+00	1.873E+02	0.000E+00	
C9	1.920E+02	3.637E−03	6.710E−01	1.913E+02	0.000E+00	
A noNAPL solution of a clearly noNAPL case.						
C6	1.000E+02	7.177E−02	1.344E+01	8.649E+01	0.000E+00	
C7	1.000E+02	2.067E−02	5.293E+00	9.469E+01	0.000E+00	
C8	1.000E+02	6.285E−03	2.423E+00	9.757E+01	0.000E+00	
C9	1.000E+02	1.894E−03	3.495E−01	9.965E+01	0.000E+00	
A NAPL solution of a clearly noNAPL case: sum of NAPL mole fractions is < unity.						
C6	1.000E+02	7.177E−02	1.344E+01	8.649E+01	6.720E−15	0.1167
C7	1.000E+02	2.067E−02	5.293E+00	9.469E+01	8.132E−15	0.1355
C8	1.000E+02	6.285E−03	2.423E+00	9.757E+01	1.346E−14	0.1847
C9	1.000E+02	1.894E−03	3.495E−01	9.965E+01	7.434E−15	0.0802
					ΣX_i^N =	0.5171354

by SOILCALC for a correct NAPL solution. Test 4 illustrates the solution for a clearly no-NAPL case, and Test 5 illustrates the solution that results from convergence of the NAPL solution for a clearly no-NAPL case. Note again that the aqueous, vapor, and soil concentrations are virtually identical for the two cases. The quantity of NAPL computed to be present is quite insignificant. The no-NAPL solution presents much clearer output. For these components and the soil properties given, the threshold soil TPH level for the presence of a NAPL is apparently around 780 mg/kg$_{soil}$.

SOILCALC computations from soil assays have been compared against ground water assays from several South Dakota release sites. Lindholm (1994) found good agreement between the aqueous TPH concentration (sum of aqueous mass concentrations of petroleum hydrocarbons) computed using SOILCALC with the assay of a ground water sample that was taken from the well six months later. Meyer (1993) compared computations completed using SOILCALC and based on assays of soil samples taken from three monitoring well installations with assays of ground water samples taken later from the wells. Agreements between the ground water assays and SOILCALC computations, based on TPH, were within 20 percent to 50 percent. To date, no other specific laboratory or field testing has been accomplished to verify the accuracy or utility of SOILCALC computations for systems containing aqueous liquid, NAPL, vapor, and solid. Such investigations were beyond the scope of this effort. The next phases in the development of SOILCALC (or any other similar model) should be comparisons of model output with the results of laboratory tests to verify the accuracy of the model. Further testing should then address comparisons of model output with field samples.

The parameter values for vapor pressure, solubility, and organic carbon partition coefficient were purposefully left in a data file that could be modified if desired at a later date as additional component information was needed or if the user obtained more specific information relative to a given case. The organic carbon partition coefficient varies significantly with the composition of

the organic matter (Garbarini and Lion 1986). Measured aqueous solubility values are quite sensitive in many cases to the method of measurement; thus, significant variation occurs among literature sources for many compounds. If a user has values believed to be more accurate than the values contained in the data file, use of user-supplied data is encouraged. Users may want to conduct sensitivity analyses or wish to obtain statistical confidence limits corresponding to the uncertainty associated with the use of specific parameter values. Virtually any parameter value can be modified to accommodate such analyses.

Component-specific assays that identify and quantitate virtually all anthropogenic organics contained in a soil sample are vital as input for SOILCALC. If contaminants are not completely recovered from samples, the resulting computations performed using SOILCALC will, of course, be negatively biased with regard to the quantity of NAPL present. If components are unidentified or identified incorrectly, computed mole fraction concentrations of NAPLs would be in error with propagation of these errors to the final output. Minnich (1993) performed a literature review relative to the performance of assays of soils for volatile organic contaminants (VOCs). Solvent extraction techniques using methanol and limited sample disruption techniques based on head space assays of field-prepared samples both provide for greater recoveries of VOCs from soils than conventional sampling and handling techniques. Great consideration must be given to the procedures used in obtaining soil samples. Conventional methods involve obtaining core samples using conventional drilling equipment and subsampling these cores to obtain samples of small size. These samples are packed into bottles or jars at the site and sent to the laboratory. Laboratory personnel then subsample from these samples. These conventional procedures require exposure of the sample to the atmosphere at least twice with associated large losses of VOCs from the samples (Minnich 1993). To avoid these losses of VOCs and the subsequent inaccuracies in interpretations of soil samples such as those that may be performed with SOILCALC, soil samples must be properly preserved in the field. Minnich (1993) discusses several options for obtaining and preserving these samples, and ASTM standard D 4547-91 gives three procedures for obtaining and preserving soil samples for VOC assays.

The user of SOILCALC must bear in mind that this model is merely a computational tool; results will only be as accurate as the input data. Many sources of error are inherent in this data. Assays of soil can be in error due to incomplete extraction of contaminants from the soil due to hysteretic behavior, failure to identify and quantitate all components eluded during gas chromatographic assay, imprecision or bias associated with the determination of the organic carbon fraction, and improper methods of obtaining or preserving soil samples for assay. The parameter values provided with this model for organic carbon partition coefficients can differ from site-specific values by an order of magnitude or more. Aqueous solubility values obtained from the literature vary significantly among investigators for identical compounds. Great care was exercised in selecting the values included with this model; however, many of the values could be significantly in error. Potential users are encouraged to check and double check the parameter values included with this model and adjust them if deemed appropriate based on site-specific or updated information. Users are also advised to perform sensitivity analyses for specific systems where the results of SOILCALC modeling may be critical to decisions to be rendered with regard to remediation of release sites.

The component listing for petroleum hydrocarbons is not complete. Five additional compounds, additives in gasolines, have been detected in soil samples from various release sites in South Dakota: ethanol, methyl-*tert*-butyl ether, *tert*-amyl-methyl ether, 1,2-dichloroethane, and 1,2-dibromoethane (Slenz 1994). Inclusion of these compounds in the database for SOILCALC would be appropriate; however, these cannot be considered as easily as the petroleum hydrocarbons. Ethanol and the ethers are polar and, thus, at low concentrations in a petroleum-based NAPL, would have activity coefficients much larger than unity. The halogenated compounds would also potentially have activity coefficients significantly removed from unity. Inclusion of these compounds would be facilitated by enhancement of the SOILCALC code to compute the activity coefficients of all or selected components in both the NAPL and aqueous phases at each iteration using a method such as UNIFAC. Should such an enhancement be completed, a solution technique such as that employed by SOILCALC could be used with some degree of confidence for interpretation of soil assay results from virtually any release site impacted by synthetic organic contaminants. The organic carbon partition coefficients, aqueous solubilities, and vapor pressures must be known, and the capability to compute activity coefficients in both NAPL and aqueous solutions as functions of solution composition must be available.

The SOILCALC code has been distributed to 50 environmental assessment, remediation, and testing firms in South Dakota, North Dakota, Minnesota, Nebraska, Iowa, Illinois, Colorado, and Wyoming. Additional comparisons of the nature described above, as well as improved interpretation of soil assay information relative to petroleum release sites, are anticipated. The development of program SOILCALC was funded by the South Dakota Groundwater Research and Public Education Program, and the model is essentially public domain software. The executable FORTRAN code and documentation can be obtained by contacting the author.

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References

American Society for Testing Materials. 1992. Standard practice for sampling waste and soils for volatile organics. In *1992 Annual Book of ASTM Standards,* Vol. 11.04, 108-111. Philadelphia: ASTM.

Banerjee, S. 1984. Solubility of organic mixtures in water. *Environmental Science Technology* 18, no. 4.

Banerjee, S., S. Yalkowsky, and S. Valvani. 1980. Water solubility and octanol/water partition coefficients: Limitations of the solubility-partition coefficient correlation. *Environmental Science Technology* 14, 1227.

Barbella, R., A. Ciajola, and A. D'Anna. 1989. The emission of heavy hydrocarbons from a diesel engine and a spray flame. *Fuel* 68, 690.

State of California. 1989. Guidelines for site assessment, cleanup, and UST closure. Leaking Underground Fuel Tank Task Force.

Chiou, C.T., L.J. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. *Science* 206.

Chiou, C.T., P.E. Porter, and D.W. Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environmental Science Technology* 17, no. 4.

Cline, P.V., J.J. Deflino, and P.S.C. Rao. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. *Environmental Science Technology* 60, no. 5: 914.

Crookson, D.J., C.J. Rix, I.M. Shaw, and B.E. Smith. 1984. High-performance liquid chromatographic procedure for direct determination of the compound class composition of diesel and kerosene fuels using refractive index detection. *Journal Chromatography* 312, 237.

Davies, I.L., K.D. Bartle, P.T. Williams, and G.E. Andrews. 1988a. On-line fractionation and identification of diesel fuel polycyclic aromatic compounds by two-dimensional microbore high-performance liquid chromatography/capillary gas chromatography. *Anal. Chem.* 60, 204.

Davies, I.L., K.D. Bartle, G.E. Andrews, and P.T. Williams. 1988b. Automated chemical class characterization of kerosene and diesel fuels by on-line coupled microbore HPLC/capillary GC. *Journal Chromatographic Science* 26, 125.

Dean, J. 1992. *Lange's handbook of chemistry.* New York: McGraw-Hill.

Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. A method for assessing residual NAPL based on organic chemical concentrations in soil samples. *Ground Water Monitoring Review* 11, no. 2: 128.

Hansch, C., and A. Leo. 1979. *Substituent constants for correlation analysis in chemistry and biology.* John Wiley and Sons.

Garbarini, D.R., and L.W. Lion. 1986. Influence of the nature of soil organics on the sorption of toluene and trichloroethylene. *Environmental Science Technology* 20, no. 12: 1263.

Grain, C.F. 1982a. Activity coefficient. In *Handbook of chemical property estimation methods,* ed. W.J. Lymann, W.F. Reehl, and D.H. Rosenblatt. New York: McGraw-Hill.

Grain, C.F. 1982b. Vapor pressure. In *Handbook of chemical property estimation methods,* ed. W.J. Lymann, W.F. Reehl, and D.H. Rosenblatt. New York: McGraw-Hill.

Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *ASCE Journal Hyd. Eng.* 110, no. 6.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research* 13.

Lee, S., M. Hagwall, J. Delfino, and P.S.C. Rao. 1992. Partitioning of polycyclic aromatic hydrocarbons from diesel fuel into water. *Environmental Science Technology* 26, no. 11: 2104.

Lindholm, B. 1994. South Dakota Department of Environment and Natural Resources, personal communication.

Lymann, W.J. 1982. Adsorption coefficients for soils and sediments. In *Handbook of chemical property estimation methods,* ed. W.J. Lymann, W.F. Reehl, and D.H. Rosenblatt. New York: McGraw-Hill.

Meyer, M. 1993. GeoTek Inc., Sioux Falls, South Dakota. Unpublished laboratory information.

Miller, M.M., S.P. Wasik, G. Huang, W. Shiu, and D. Mackay. 1985. Relationships between octanol-water partition coefficient and aqueous solubility. *Environmental Science Technology* 19, no. 6.

Minnich, M. 1993. Behavior and determination of volatile organic compounds in soil: A literature review. EPA 600 R 93/140. Washington, D.C.: U.S. EPA Office of Research and Development.

Nelson, P.F. 1989. Combustion-generated polycyclic aromatic hydrocarbon in diesel exhaust emission. *Fuel* 68, 283.

Obuchi, A., H. Aoyama, A. Ohi, and H. Ohuchi. 1984. Determination of polycyclic aromatic hydrocarbons in diesel exhaust particulate matter and diesel fuel. *Journal Chromatography* 312, 247.

Pavlostathis, S.G., and G.N. Mathavan. 1992. Desorption kinetics of selected volatile organic compounds from field contaminated soils. *Environmental Science Technology* 26, no. 3: 532.

Pavlostathis, S.G. and K. Jagial. 1991. Desorptive behavior of trichloroethylene in contaminated soil. *Environmental Science Technology* 25, no. 2: 274.

Rechsteiner, C.E., Jr. 1982. Boiling point. In *Handbook of chemical property estimation methods,* ed. W.J. Lymann, W.F. Reehl, and D.H. Rosenblatt. New York: McGraw-Hill.

Reid, R., J. Prausnitz, and B. Poling. 1987. *The properties of gases and liquids.* New York: McGraw-Hill.

Slenz, K. 1994. Energy Laboratories Inc., Rapid City, South Dakota. Unpublished laboratory data.

Standard methods for the examination of water and wastewater. 1989. Washington, D.C.: APHA, AWWA, and WEF.

Weast, R., ed. 1989. *CRC handbook of chemistry and physics.* Boca Raton: CRC Press.

Williams, P.T., K.D. Bartle, and G.E. Andrews. 1986. The relation between polycyclic aromatic compounds in diesel fuels and exhaust particulates. *Fuel* 65, 1150.

Yalkowski, S., and S. Valvani. 1980. Solubility and partitioning I: Solubility of non-electrolytes in water. *Journal of Pharmaceutical Science* 69. no. 8: 912.

Biographical Sketches

***Henry V. Mott** is an associate professor of civil and environmental engineering at the South Dakota School of Mines and Technology (501 E. St. Joseph St., Rapid City, SD 57701). He earned his bachelors degree in civil engineering from the South Dakota School of Mines and Technology in 1973, a masters degree in environmental engineering from Washington State University, Pullman, in 1984, and a Ph.D. in environmental engineering from the University of Michigan, Ann Arbor, in 1989. Dr. Mott has conducted research in the areas of organic contaminant migration through slurried earthen barriers, remediation of petroleum releases in unsaturated zone soils by soil venting, and fate and migration of petroleum contaminants in subsurface soils. His teaching specialties include environmental chemistry, contaminant fate and migration, and unit operations of environmental engineering.*