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A Method for Assessing Leaching Potential for Petroleum Hydrocarbons Release Sites: Multiphase and Multisubstance Equilibrium Partitioning

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This article presents the rationale for the mathematical fate and transport model, which has been provided in the accompanying spreadsheet (GWProt). This spreadsheet model may be used as a simple and scientifically defensible regulatory tool for determining the risk-based soil clean up level of petroleum release sites to protect groundwater quality. The model incorporates either a three- or four-phase partitioning equilibrium mechanism, depending on the detection of Non-Aqueous Phase Liquid phase presence mathematically, as well as Raoult's Law convention and default dilution and attenuation factors. A database of contaminant-specific parameters, including solubility and organic-carbon partition-coefficient, molecular weight, and Henry's Law constant, is assembled for benzene, toluene, ethylbenzene, xylenes, and 12 other TPH equivalent carbon fractions. In addition to distributing organic chemicals among aqueous, sorbed solid, air, and NAPL phases, according to traditional partitioning equations, the algorithm incorporates equations for the conservation of mass and volume. A unique solution is obtained by solving a series of mass balance equations simultaneously using the iterative spreadsheet routine built in MICROSOFT EXCEL™ Solver — with the restrictions that the volume is conserved and the sum of the mole fractions is equal to one. Sample calculations are presented for a range of parameter values to illustrate the use of the model and the relative leachability of a wide range of representative fuels. Sensitivity analysis was also performed to quantify the effects of uncertainty in the estimates of the key model parameters on model results. Model predictions were compared with the results from a water-fuel experiment. The noncarcinogenic Hazard Index (HI) for groundwater through direct ingestion was calculated using predetermined oral reference dose ($\mathbf{R}_{\mathbf{fd}}$) values. Applications and limitations of the model are also discussed.

KEY WORDS*: soil leaching potential, equilibrium partitioning, petroleum hydrocarbons, spreadsheet model.*

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INTRODUCION

Over the last decade, the State of Washington has relied on soil clean up levels from look-up tables for petroleum release sites. Soil clean up levels for ground water protection may also be derived by multiplying the target ground water clean up level by a factor of 100. Although convenient, this methodology is neither scientifically defensible nor site-specific. The properties of petroleum hydrocarbon components, and the soil properties that control their respective mobilities in the soil environment are extremely variable. This variability leads to the potential for great complexity if a site-specific determination is to be made. This article expands on the previous work of the Total Petroleum Hydrocarbon Criteria Working Group (Gustafson *et al*., 1997), ASTM RBCA E1739-95 (1995), Feenstra *et al*. (1991), Mott (1995), and Mariner *et al*. (1997). A review of previous work has resulted in the development of a multiphase and multisubstance equilibrium partitioning model that has been incorporated into a spreadsheet-type computer algorithm (MS EXCEL^{TM}). This computer model may be used to derive site-specific petroleum soil clean up levels that are protective of groundwater. The model employs component concentration measurements of contaminated soils and simple soil assay information that is easily available.

Complex mixtures such as petroleum hydrocarbons, contain components with properties, including vapor pressure, water solubility, and partition coefficient that range across several orders of magnitude. Individual Total Petroleum Hydrocarbons (TPH) constituents were grouped into fractions in accordance with Equivalent Carbon (EC) number, with each fraction having no greater than an order of magnitude difference in the environmental behavior of the constituents. The EC number is related to the boiling point of individual constituents and is equivalent to the retention time of the compounds in a boiling point gas chromatography column, normalized to the n-alkanes. The relationship between EC number and boiling point was empirically determined. Separating TPH constituents into these fate and transport fractions simplifies environmental modeling conducted in support of human health risk assessment at petroleum-contaminated sites. The detailed derivation of the fate and transport fractions and their EC numbers is found in TPH Criteria Working Group Volume 3 (Gustafson *et al*., 1997). The spreadsheet incorporates either three- or four-phases partitioning, depending on the detection of Non-Aqueous Phase Liquid (NAPL) phase presence mathematically, as well as Raoult's Law convention and the concept of US EPA dilution factor.

The objectives of this article are to (1) present the rationale for the mathematical fate and transport model, as provided in the accompanying spreadsheet, for implementing a simple and scientifically defensible regulatory tool for determining the risk-based soil cleanup level of petroleum release sites that is protective of groundwater; (2) evaluate the range of the relative leachability and Noncarcinogenic Hazard Index of the six representative fuels; (3) conduct a sensitivity analysis to quantify the effects of a key model parameter; and (4) assess the extent of agreement between results of a fuel-water experiment and the prediction made by the model.

THEORY

Step 1. Estimation of Soil Pore Water Concentration at the Source of Contamination

The chemical analysis of a soil sample for organic compounds generally provides a measure of the total amount of the chemical of interest in the sample, expressed typically as mass of chemical per unit dry weight of the soil sample. This analysis quantifies the total amount of chemical that has dissolved in the pore water of the sample, sorbed on the soil solids, present in NAPL, and present in the soil gas. However, the chemical analysis cannot indicate directly how the chemical of interest is distributed between these phases and whether NAPL is present. If NAPL is present in the soil, it will be distributed among the phases according to thermodynamic equilibrium principles and mass transfer kinetics. The system reaches equilibrium when the chemical potential of any constituents is equal in all phases. The model calculations are based on the assumptions of homogeneity of the sample, equilibrium partitioning of chemicals between phases, and the conservation of mass and volume. The following abbreviations are used in the calculations:

Four phases of NAPL, pore water, pore air, soil sorbed and total are represented by the subscripts *NAPL*, *w*, *a*, *s*, and *t*, respectively;

- M^i is the mass of component *i* in each of the four phases and total;
- C^i is the concentration of component *i* in each of the four phases and total;
- K^i_{oc} is the soil organic carbon to water partition coefficient of component *i;*
- f_{oc} is the mass fraction of natural soil organic carbon within the soil matrix;
- H_i is the dimensionless Henry's Law constant of component *i;*
- S_i is the pure aqueous solubility of component *i*;
- x_i is the mole fraction of component *i* in the NAPL mixture;
- n is the total soil porosity;
- θ_w is the volumetric water content in soil;
- θ_a is the volumetric air content in soil;
- θ_{NAPL} is the volumetric NAPL content;
- MW_i is the molecular weight of component *i;*

- $\boldsymbol{MW_{NAPL}}$ is the weighted average (or equivalent) of molecular weight of NAPL mixture;
- $\boldsymbol{\rho_b}$ is the dry soil bulk density;
- $\boldsymbol{\rho_i}$ is the density of component *i* in liquid form;
- $\boldsymbol{\rho_{NAPL}}$ is the density of the NAPL mixture.

The equilibrium concentration of components *i* in air phase 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:

$$C_a^i = H_i C_w^i \tag{1}$$

Sorption to soil organic matter can also be described by a linear function of the aqueous concentration:

$$C_s^i = K_{oc}^i f_{oc} C_w^i \tag{2}$$

Even though the linear isotherm relationship of Eq. 2 has been experimentally verified for various organic compounds (Karickhoff *et al*., 1979; Chiou *et al*., 1983), linear sorption is valid only for f_{oc} values greater than about 0.001 (Schwarzenbach *et al*., 1981). For an ideal NAPL mixture in contact with water, the aqueous phase concentration of a NAPL component is equal to the pure aqueous solubility of component multiplied by the mole fraction of the component in the NAPL mixture. Mathematically, this relationship is written as

$$C_w^i = x_i S_i \tag{3}$$

Feenstra *et al*. (1991) refers to C^i_w as the effective aqueous solubility of component *i* when the aqueous phase is at equilibrium with a NAPL mixture. The total mass of component *i* in the soil sample equals the sum of the masses of component *i* in all phases. The mass conservation equation is

$$M_t^i = M_{NAPL}^i + M_w^i + M_a^i + M_s^i \tag{4}$$

The total porosity (n) and the volumetric water content of soil (θ_w) are assumed to be fixed values. For a unit volume of soil, the following relationships apply:

$$M_t^i = C_t^i \rho_b \tag{5}$$

$$M_a^i = C_a^i \theta_a = H_i C_w^i \theta_a \tag{6}$$

$$M_s^i = C_s^i \rho_b = K_{oc}^i f_{oc} C_w^i \rho_b \tag{7}$$

$$M_w^i = C_w^i \theta_w \tag{8}$$

$$M_{NAPL}^i = C_{NAPL}^i \theta_{NAPL} \tag{9}$$

With the assumption that there is no NAPL present in the soil sample (i.e., $M^i_{NAPL} = 0$), by substitution of Eq. 5 into Eq. 4 and rearrangement:

$$C_t^i = \frac{M_w^i + M_a^i + M_s^i}{\rho_b} \tag{10}$$

By substitution of Eqs. 6, 7, and 8 into Eq. 10 and by rearrangement, the pore water concentration can be expressed in terms of the total soil concentration for a three-phase soil system as:

$$C_w^i = \frac{C_t^i \rho_b}{\theta_w + K_{oc}^i f_{oc} \rho_b + H_i \theta_a} \tag{11}$$

where a NAPL phase exists, the mole fraction of component *i* in the NAPL mixture is related to mass concentration by the equation (Mariner *et al.*, 1997):

$$x_i = \frac{C_{NAPL}^i MW_{NAPL}}{\rho_{NAPL} MW_i} \tag{12}$$

where MW_{NAPL} is the equivalent molecular weight of the NAPL mixture after the phase equilibration and ρ_{NAPL} is the hypothetical pure phase liquid density computed by extrapolation, and can be expressed, respectively, as:

$$MW_{NAPL} = \sum x_i MW_i \tag{13}$$

$$\rho_{NAPL} = \sum C_{NAPL}^i = \frac{\sum x_i MW_i}{\sum \left(x_i MW_i \big/ \rho_i \right)} \tag{14}$$

The final NAPL mixture molecular weight after phase equilibration is expected to be different from that before equilibration, particularly when a small amount of highly soluble NAPL mixture is present in a soil sample (e.g., in the TPH range of 100 mg/kg with gasoline contaminated soil). By substitution of Eqs. 13 and 14 into Eq. 12 and subsequently into Eq. 9 and rearrangement of Eq. 9, the mass of component *i* in the NAPL phase can be expressed as:

$$M_{NAPL}^i = \frac{x_i MW_i \theta_{NAPL} \rho_{NAPL}}{MW_{NAPL}} = \frac{x_i MW_i \theta_{NAPL}}{\sum \left(x_i MW_i \big/ \rho_i \right)} \tag{15}$$

By substitution of Eq. 5 through 8 and Eq. 15 into Eq. 4:

$$C_t^i = C_w^i H_i \theta_a + C_w^i K_{oc}^i f_{oc} \rho_b + C_w^i \theta_w + \frac{x_i MW_i \theta_{NAPL}}{\sum \left(x_i MW_i \big/ \rho_i \right)} \tag{16}$$

By rearranging terms in Eq. 16 with Eq. 3, the resulting equation for a four-phase soil system takes the form:

$$C_t^i = \frac{x_i S_i}{\rho_b} \left(H_i \theta_a + K_{oc}^i f_{oc} \rho_b + \theta_w + \frac{MW_i \theta_{NAPL}}{S_i \sum \left(x_i MW_i \big/ \rho_i \right)} \right) \tag{17}$$

The sum of NAPL mole fractions is equal to “one”:

$$\sum x_i = 1 \tag{18}$$

The volume conservation equation is written as:

$$n = \theta_w + \theta_a + \theta_{NAPL} \tag{19}$$

The method presented here is a numerical solution of the partitioning and conservation equations presented above. PC software (called “GWProt”) based on the iterative spreadsheet routine built in Microsoft EXCEL™ Solver was developed to perform the numerical simulation to estimate the following: (1) the concentration of component *i* in each phase; (2) the NAPL saturation, volume, and composition in a soil sample containing NAPL. With “N” components, Eqs. 17 through 19 provide a total of “N + 2” independent equations that describe partitioning and conservation in a soil sample. Given the measurements and estimates listed in Table 1, there are “N + 2” unknowns. These unknowns are “N” number of mole fractions (x_i) in the NAPL mixture for each component and volumetric contents of air (θ_a) and NAPL (θ_{NAPL}). An equal number of unknowns and independent equations guarantee a unique solution. A unique set of solutions for x_i is obtained by solving a series of mass balance equations simultaneously with a certain controlled initial trial value of volumetric NAPL content, θ_{NAPL}. For the sample problems tested, the computation time for reaching a solution was usually less than 4 s using a 586 Pentium 233 MHZ PC (64 MB RAM). The code begins with the assumption that there is no NAPL present in a soil sample. As shown by Feenstra *et al*. (1991), if NAPL exists in the sample, then the first approximation (assuming three phases) of soil pore water concentration from Eq. 11 should exceed the effective aqueous solubility of component *i*, Eqs. 3 and 18 imply that C^i_w equals the effective aqueous solubility when:

$$\sum \frac{C_w^i}{S_i} = 1 \tag{20}$$

TABLE 1
Fate and Transport Characteristics and Associated Properties of Fuel Components

	MW	S	H	K_{oc}	Liquid Density	R_{fd}[a]
	mg/mol	mg/L	unitless	L/kg	mg/L	mg/kg-day
Aliphatics						
EC >5-6	8.10E+04	2.80E+01	3.40E+01	7.94E+02	6.79E+05	5.7
EC >6-8	1.00E+05	4.20E+00	5.10E+01	3.98E+03	7.26E+05	5.7
EC >8-10	1.30E+05	3.30E-01	8.20E+01	3.16E+04	7.33E+05	0.03
EC >10-12	1.60E+05	2.60E-02	1.30E+02	2.51E+05	7.60E+05	0.03
EC >12-16	2.00E+05	5.90E-04	5.40E+02	5.01E+06	7.66E+05	0.03
EC >16-21	2.70E+05	1.00E-06	6.40E+03	1.00E+09	7.80E+05	2
EC >21-34	3.25E+05	1.00E-06	6.40E+03	1.00E+09	7.80E+05	2
Aromatics						
Benzene	7.80E+04	1.78E+03	2.30E-01	7.94E+01	8.77E+05	0.003
Toluene	9.20E+04	5.20E+02	2.70E-01	2.51E+02	8.67E+05	0.2
Ethylbenzene	1.06E+05	1.52E+02	3.58E-01	5.37E+02	8.67E+05	0.1
Xylenes	1.06E+05	1.98E+02	2.52E-01	5.86E+02	8.75E+05	2.0
EC >8-10	1.20E+05	6.50E+01	4.90E-01	1.58E+03	8.71E+05	0.05
EC >10-12	1.30E+05	2.50E+01	1.40E-01	2.51E+03	9.04E+05	0.05
EC >12-16	1.50E+05	5.80E+00	5.40E-02	5.01E+03	1.02E+06	0.05
EC >16-21	1.90E+05	5.10E-01	1.30E-02	1.58E+04	1.23E+06	0.03
EC >21-35	2.40E+05	6.60E-03	6.80E-04	1.26E+05	1.28E+06	0.03

Note: Table extracted in part from Gustafson *et al*., 1997, Table 8.

[a] R_{fd} values are supplied by the Washington Department of Ecology.

Thus, a summation exceeding "one" implies that NAPL is present in the sample and that the NAPL saturation algorithm must be used instead to estimate C^i_w. A summation in Eq. 20 equal to or less than "one" indicates there is no NAPL in the sample, then C^i_w is less than the effective aqueous solubility and calculation of x_i from Eq. 3 is invalid. When a NAPL phase is present, Eqs. 17 through 19 are satisfied and the calculated volumetric NAPL content (θ_{NAPL}) is always positive and Eq. 20 should be greater than "one". Once x_i is computed with the iteration technique, the soil pore water concentration (C^i_w) at a source could be estimated with Eq. 3.

In order to run the model, estimates or values of the following input parameters are needed: total soil concentration of component i in the soil sample (C^i_t); porosity (n); volumetric water content (θ_w); dry soil bulk density (ρ_b); mass fraction of natural organic carbon (f_{oc}); organic carbon to water partition coefficient of component i (K^i_{oc}); dimensionless Henry's Law constant of component i (H_i); pure aqueous solubility of component i (S_i); molecular weight of component i (MW_i); density of component i in a liquid form (ρ_i). A database (Table 1) of contaminant-specific parameters was assembled for BTEX (benzene, toluene, ethylbenzene, xylenes) and 12 different EC groups as proposed by the TPH Criteria Working Group (Gustafson *et al*., 1997). Comparisons were conducted for a wide range of TPH concentrations of six representative fuels (Table 2): fresh and weathered gasoline, fresh and weathered diesel, mineral oil, and Bunker C oil (personal communication with the Washington Department of Ecology, 1998). The default hydro-geological input parameters used for calculations in this study were 0.003 for soil organic fraction; 1.85 g/cm^3 for dry soil bulk density; 0.421 for total soil porosity; 0.321 for volumetric water content. It should also be noted that the model conservatively assumes that there is no chemical or biological degradation; no volatilization; no diffusion-dispersive transport mechanisms; and that equilibrium soil/water partitioning is instantaneous, reversible, and linear in the unsaturated source zone.

Step 2. Determination of Default Dilution Factor and Calculation of Hazard Index

As leachate moves through soil and groundwater, contaminant concentrations are attenuated by adsorption and degradation. Once the leachate enters groundwater, it is diluted further by clean groundwater, which further reduces concentrations

TABLE 2
Default Petroleum Product Weight Fraction

	Fresh Gasoline	Weathered Gasoline	Fresh Diesel	Weathered Diesel	Mineral Oil	Bunker C Oil
Aliphatics						
EC >5-6	0.2300	0.0920	0.0000	0.0010	0.0000	0.0000
EC >6-8	0.2200	0.2750	0.0000	0.0010	0.0000	0.0000
EC >8-10	0.0900	0.1200	0.0200	0.0110	0.0010	0.0000
EC >10-12	0.0300	0.0130	0.0700	0.0600	0.0030	0.0000
EC >12-16	0.0000	0.0000	0.3500	0.3000	0.1600	0.0950
EC >16-21	0.0000	0.0000	0.3400	0.3700	0.7000	0.0790
EC >21-34	0.0000	0.0000	0.0000	0.0000	0.000	0.1160
Aromatics						
Benzene	0.0250	0.0080	0.0000	0.0000	0.0000	0.0000
Toluene	0.1200	0.0980	0.0000	0.0000	0.0000	0.0000
Ethylbenzene	0.0200	0.0300	0.0000	0.0000	0.0000	0.0000
Xylenes	0.1100	0.1300	0.0000	0.0000	0.0000	0.0000
EC >8-10	0.1300	0.2200	0.0100	0.0010	0.0010	0.0000
EC >10-12	0.0250	0.0140	0.0100	0.0060	0.0010	0.0000
EC >12-16	0.0000	0.0000	0.0800	0.0320	0.0070	0.1450
EC >16-21	0.0000	0.0000	0.1200	0.1880	0.0800	0.3610
EC >21-35	0.0000	0.0000	0.0000	0.0320	0.0460	0.2040

Note: Default Petroleum Product Weight Fractions are supplied by the Washington Department of Ecology. Unit of the data set above is dimensionless.

before contaminants reach receptor points (i.e., drinking water wells). This reduction in concentration can be expressed by a dilution attenuation factor, defined as the ratio of soil pore water concentration to receptor point groundwater concentration. A methodology chosen by U.S. EPA addresses only one of these dilution-attenuation processes: contaminant dilution in groundwater, which is referred to as a Dilution Factor (DF). A default DF of 20 has been selected as protective for contaminated soil sources up to half-acre in size (U.S. EPA, 1996) using a “weight of evidence” approach. If adsorption or degradation processes are expected to significantly attenuate contaminant concentration, then one should reexamine the appropriate DF on a site-specific basis. All of the model-predicted groundwater concentrations **at well** presented in this article are based on the default DF of 20.

The Hazard Index (HI) calculation is used to assess the potential impacts to human-health (direct ingestion of petroleum-contaminated groundwater). Calculation of a HI of the non-carcinogenic TPH contaminant should take the form with the adjustment for additive risk of TPH, as described by the Washington Department of Ecology (1991):

$$HI = \left[\frac{(DWIR)}{(DF)(ABW)}\right]\sum\left(\frac{C_w^i INH_i}{R_{fdi}}\right) \tag{21}$$

where $DWIR$ is the drinking water ingestion rate (1.0 L/day); ABW is the average body weight during the period of exposure (16 kg); INH_i is the inhalation correction factor (two for volatile substances, one for all other substances); R_{fdi} is the oral reference dose of component i, which are supplied by the Washington Department of Ecology.

With GWProt, one could compute the approximate soil clean up levels based on the assumption that the fuel composition ratio in the soil sample is always constant. Under the target groundwater TPH clean up level or HI values specified, GWprot is capable of performing the backward calculation to derive site-specific soil clean up levels in terms of TPH by reversing all calculation procedure. An executable copy of “GWProt” can be obtained by contacting the author.

MATERIALS AND METHODS

Batch Fuel-Water Equilibration Experiments and Analytical Methods

A limited batch equilibrium experiment with fuel-water mixtures was conducted to test the hypothesis stated in this study. The laboratory fuel-water mixing study was conducted using commercial-grade fuels (two gasoline brands and one diesel brand) that were collected from service stations within the immediate vicinity of Seattle, Washington. The following fuel to water ratios were used in the experiment: 2 mL:100 mL and 0.04 mL:100 mL for gasoline; 200 mL:2000 mL and 5 mL:2000 mL for diesel fuel, respectively. To mix the fuel with water, an aliquot of fuel was introduced to the surface of distilled, deionized, organic-free water. Glass-stoppered Pyrex reagent bottles with Teflon-plugged stopcocks positioned approximately 5 cm from the base were used to equilibrate the fuel-water mixture. The equilibration vessels were then placed in a Magni-Whirl shaker and agitated at room temperature for 24 h. A 30-min settling period was allowed, followed by withdrawal of the aqueous phase from the bottom of the equilibration vessel with minimal disturbance. Water samples were stored in amber glass bottles with Teflon-lined screw caps until analysis.

Both the neat fuel and the water extract were analyzed for EC fractions and individual water soluble fraction components. BTEX, Volatile Petroleum Hydrocarbons (VPH), and Extractable Petroleum Hydrocarbons (EPH) were selected as target components to analyze in accordance with the Washington State's "Analytical Methods for Petroleum Hydrocarbons" (1997). VPH were analyzed using the purge-and-trap technique. Detection is achieved by Photo Ionization Detector (PID) and Flame Ionization Detector (FID) in series. Quantitation was based on comparing PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram was used to determine the individual concentrations of targeted analytes (BTEX) and the collective concentration of aromatic hydrocarbons within the C8 through C10, C10 through C12, and C12 through C13 ranges. The FID chromatogram was used to determine the collective concentration of aliphatic hydrocarbons within the C5 through C6, C6 through C8, C8 through C10, and C10 through C12 ranges. To avoid double counting of the aromatic contribution to the aliphatic ranges, the PID concentrations were subtracted from the FID concentrations to yield the aliphatic ranges values. A sample submitted for EPH analysis was extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated. Sample clean up and separation into aliphatic and aromatic fractions was conducted using a modification of EPA method 3630 (silica gel clean up). The two extracts produced were then concentrated to final volumes of 10 mL each (i.e., an aliphatic extract and an aromatic extract) and were then separately analyzed by a gas chromatograph equipped with a capillary column and a FID. The resultant chromatogram of aliphatic compounds was collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34 aliphatic hydrocarbon ranges. The resultant chromatogram of aromatic compounds was collectively integrated within the C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21, and >C21 through C34 ranges.

RESULTS AND DISCUSSION

Model Application

With Eq. 13, the computed average molecular weight of fuels before equilibration with other phases was found to be 100, 105, 203, and 211 g/mol for fresh and

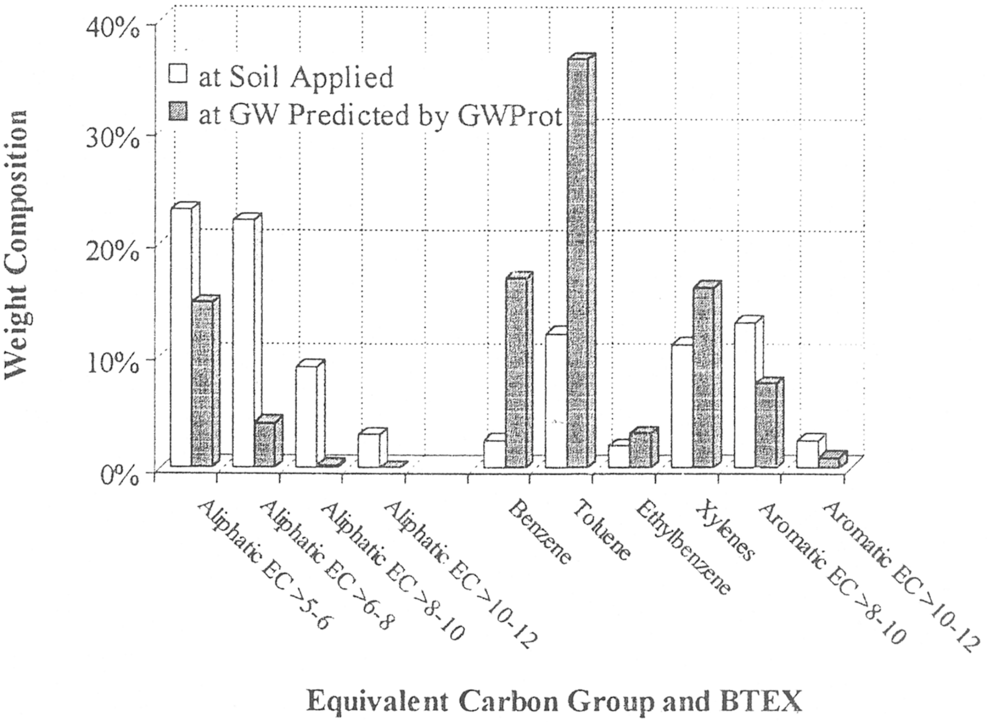

FIGURE 1

Relative distribution of Equivalent Carbon group in different media with fresh gasoline-contaminated soil at TPH of 100 mg/kg.

weathered gasoline, fresh and weathered diesel, respectively. These molecular weights were found to be within acceptable ranges based on the study done by Cline *et al*. (1991) and Lee *et al*. (1992). As shown in Figure 1, the mass distribution patterns between total soil applied and aqueous phase predicted by GWProt are not identical. The majority of the total dissolved concentration for fresh gasoline is comprised of BTEX (73% @100 mg/kg of Soil TPH to 89% @5000 mg/kg of Soil TPH), with the other two significant dissolved components coming from the aromatic EC >8-10 and aliphatic EC 5-6 groups.

Raoult's Law describes the behavior of solutes in an ideal two-phase mixture at equilibrium. At equilibrium, the chemical potential of each solute is uniform among all phases. By using Raoult's Law and assuming ideal behavior, predictions can be made for a maximum concentration of components that may be present in the aqueous leachate leaving a hydrocarbon contaminated subsurface soil. However, Raoult's Law assumes that the mole fractions of the components in the NAPL phase are the same as those of the total soil sample. Yet, Raoult's Law cannot take into account the differences between the mole fractions in the total soil sample and those in the NAPL phase in equilibrium with the other three phases. As demonstrated by Cline *et al.* (1991) and Lee *et al*. (1992), Raoult's Law approach for gasoline and diesel fuels may be acceptable for most field-scale applications involving a high level of hydrocarbon contamination at spill sites. As Figure 2 illustrates, the dissolved equilibrium TPH concentration is proportional to the residual level in the soil at lower residual TPH levels (a three-phase) where components are sorbed to the soil, dissolved in the soil moisture, and present in the soil vapor space. As NAPL phase starts to form, the dissolved equilibrium TPH concentration becomes gradually less dependent on the residual level and more dependent on the composition of residual fuel. The dissolved equilibrium TPH concentration is independent of the residual level, but a function of composition for "very high" residual levels where significant amount of free-phase liquid is trapped in the soil interstices. The transition between three- and four-phase systems is dependent on both the residual level in soil and the composition of the fuel that has been released. GWProt automatically detects a soil that has a NAPL phase by mathematically using the three-phase partitioning model solution with Eqs. 11 and 20. The three-phase model solution is used where the four-phase solution is not appropriate for any given soil. These phase-transition trends for the other fuels are similar to the trend noted for fresh gasoline. The model implicitly could calculate NAPL saturation (Figure 3). Under the hydro-geologic conditions described in the section of THEORY, the transition between three- and four-phase occurs at 92, 92, 6.2, 5.6, 3.7, 5.6 mg/kg of soil TPH for fresh and weathered gasoline, fresh and weathered diesel, mineral oil, and Bunker C fuel oil, respectively. Heavier fuels

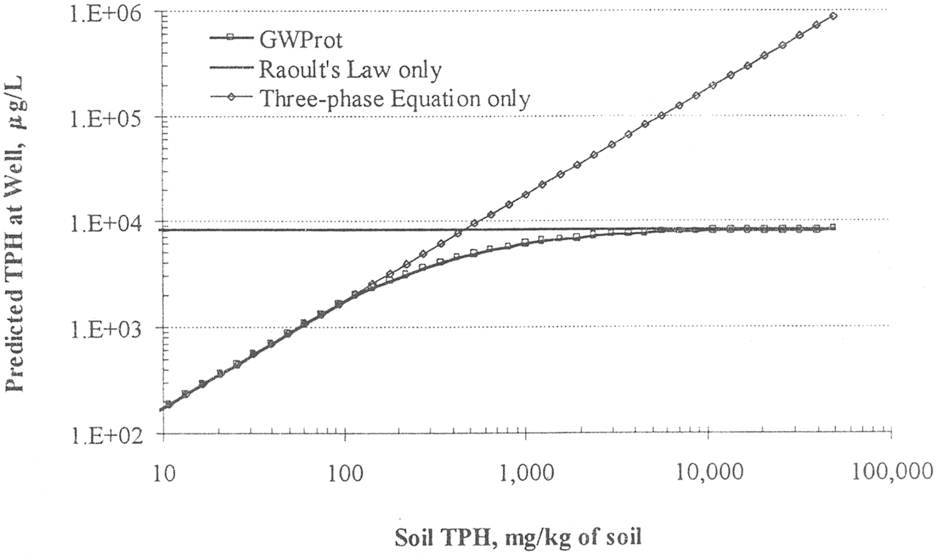

FIGURE 2

Comparisons of TPH at well with different models with fresh gasoline-contaminated soil.

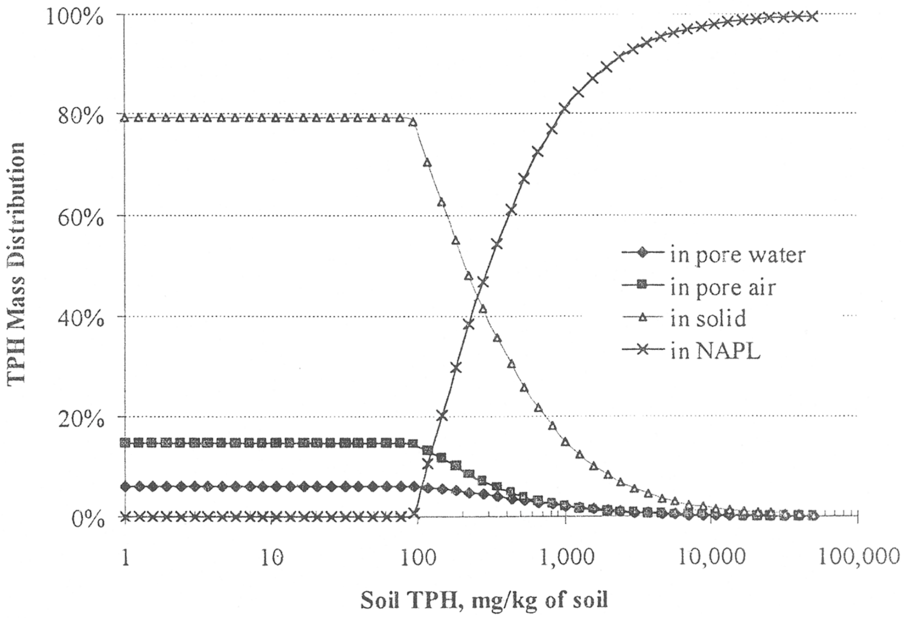

FIGURE 3

TPH mass distribution predicted by GWProt with fresh gasoline-contaminated soil.

(diesel, mineral oil, and Bunker C) will normally be present in soil as a NAPL at much lower residual concentrations than gasoline.

When the total soil TPH is increased, the dissolved concentration of relatively lower EC groups increases continuously, whereas the dissolved concentration of relatively higher EC groups (aliphatic EC groups of >6-8, >8-10, and >10-12 and aromatic EC >10-12) tends to increase until it results in the formation of NAPL phase, then gradually decreases afterward (Figure 4). The ratio between the concentration predicted by GWProt and by Raoult's Law was also computed (Figure 5). For all ratios greater than 1.0, Raoult's Law underpredicts the dissolved concentration that would be found in the water phase. For fresh and weathered gasoline, the dissolved concentration is higher than those predicted by Raoult's Law for the aliphatic EC groups of >6-8, >8-10, and >10-12 and at some soil concentrations for aromatic EC >10-12 and aliphatic EC >5-6.

In the case of diesel, Raoult's Law underpredicts concentrations in water for aliphatic EC group >12-16 and >16-21, aromatic EC group >21-35, and aromatic EC group >16-21 for some soil concentrations. Raoult's Law also underpredicts the dissolved concentration at some soil concentrations of aromatic EC group >21-35 for mineral oil and aromatic EC group >21-35 and aliphatic EC group >21-34 for Bunker C fuel. Due to the significantly different affinities (water-dissolvable, adsorptive, and volatile capacities) of the different EC groups, Raoult's Law generally overpredicts the concentrations in water for the relatively lower EC

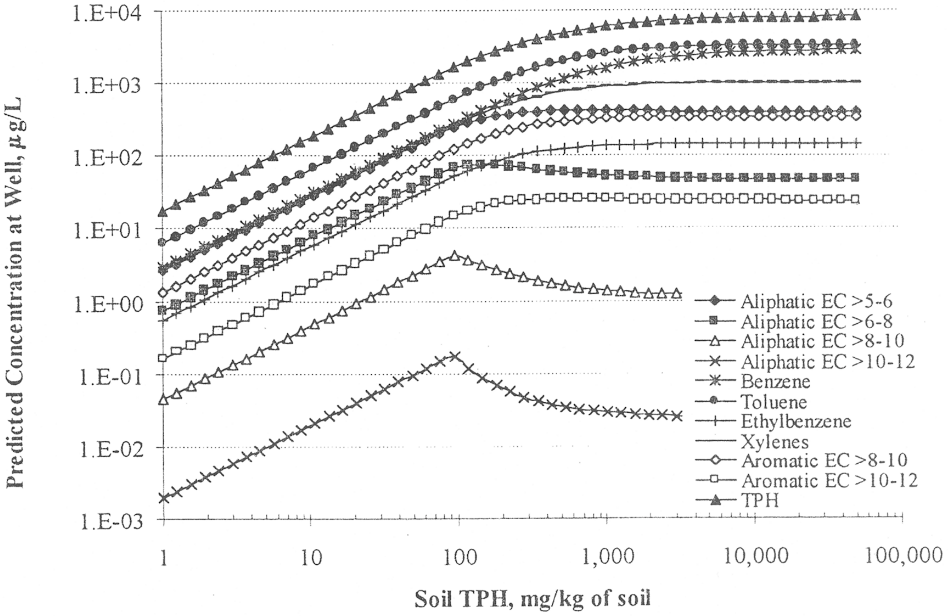

FIGURE 4

Predicted concentration of Equivalent Carbon group and BTEX at well with fresh gasoline-contaminated soil.

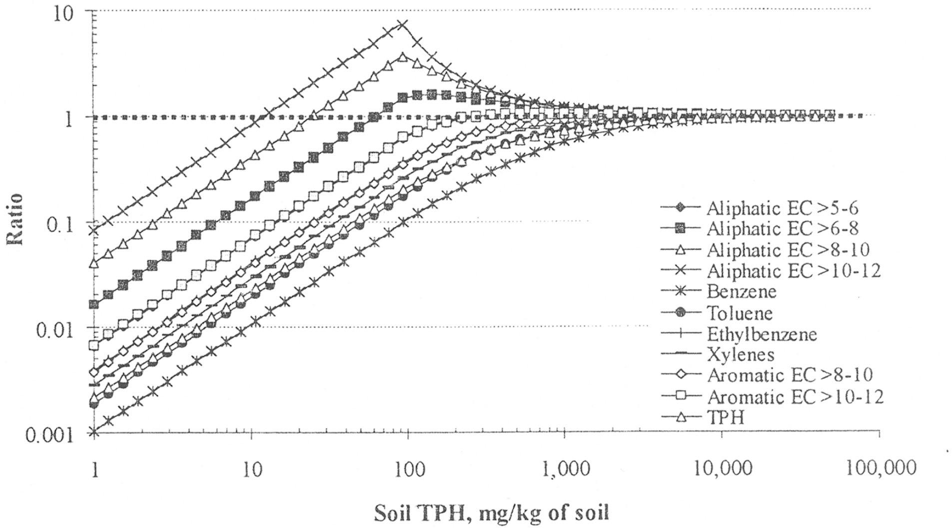

FIGURE 5

Ratio between the concentration at well predicted by GWProt and Raoult's Law with fresh gasoline-contaminated soil groups present and underpredicts for the relatively higher EC groups that are present in the soil system. This occurs because as the NAPL phase fuel equilibrates with the other phases, the lighter EC groups preferentially leave the NAPL phase for the air and water phases. Light aromatics are particularly soluble and light aliphatics particularly volatile. The removal of the lighter components due to preferential partitioning to water and air phases enriches the residual NAPL in the higher EC groups. These combined processes enrich the mole fractions of the higher EC groups in the equilibrated NAPL compared with the mole fractions in the total soil sample, leading to the underprediction of their dissolved concentrations compared with the Raoult's Law prediction. However, GWProt takes into account the effect of multiphase partitioning on the composition of the NAPL for a more accurate estimation of the equilibrium concentration. At relatively high total soil concentrations, Raoult's Law and GWProt predict very similar concentrations because as the total concentration of NAPL in the soil increases, the mole fractions in the residual NAPL phase become more similar to the mole fractions of the total soil sample.

For gasoline, when the soil TPH concentration exceeds 57 to 68 mg/kg, the predicted groundwater concentration becomes greater than 1000 μg/L, whereas the predicted groundwater concentration for heavier oils is always less than 100 μg/L for most soil concentration (Figure 6). For fresh and weathered gasoline, HI at the predicted groundwater is over 1.0 for almost all soil concentrations (Figure 7). Ninety-seven percent of the HI at the predicted groundwater is comprised of BTEX (@ soil contaminated with fresh gasoline at TPH of 100 mg/kg). For heavier oils, the HI at the predicted groundwater is never higher than one. With the hydrogeologic conditions described in the Theory asection nd the properties and weight fraction of fuel components shown in Tables 1 and 2, the highest HI value for predicted groundwater concentrations is 121, 44, 0.23, 0.074, 0.032, and 0.093 for fresh and weathered gasoline, fresh and weathered diesel, mineral oil, and Bunker C fuel oil, respectively. GWProt predicts that the soil TPH range resulting in 10 and 90% of the maximum equilibrium concentration possible in aqueous phase computed by Raoult's Law is found to be 46 and 3440 mg/kg; 43 and 2750 mg/kg; 22 and 2860 mg/kg; 12 and 1870 mg/kg; 14 and 3120 mg/kg; 7 and 650 mg/kg for fresh and weathered gasoline, fresh and weathered diesel, mineral oil, and Bunker C fuel oil, respectively (Figure 8).

Sensitivity Analyses

A sensitivity analysis of model input parameters found that the soil organic carbon fraction, f_{oc}, had the most impact on model results. To analyze the sensitivity on the effect of f_{oc} change on equilibrium concentration, the range of the total concentration in the soil was varied from 1.0 mg/kg to 50,000 mg/kg for fresh gasoline. The f_{oc} was then varied from 0.001 to 0.1, while all other variables were held constant.

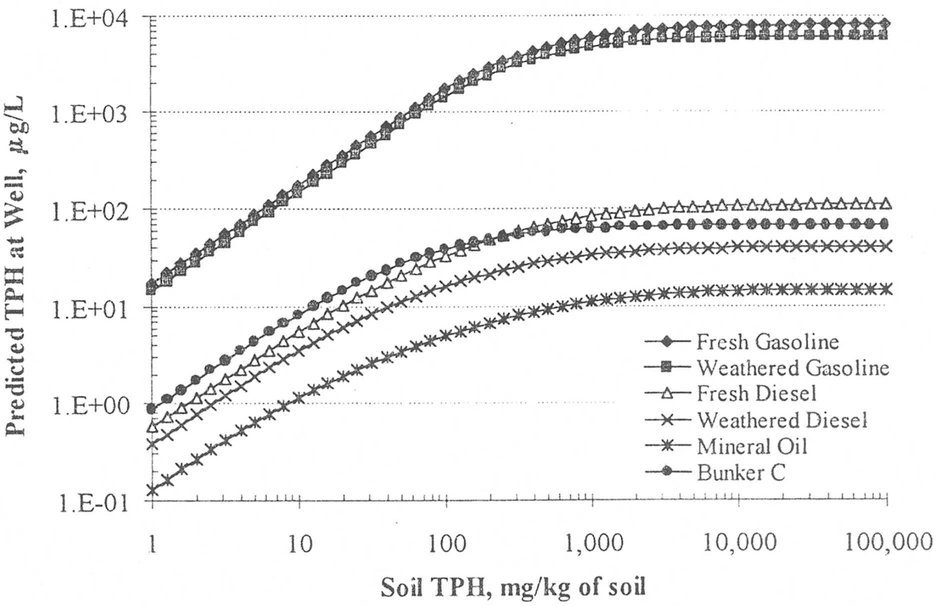

FIGURE 6

TPH predicted at well vs. soil TPH applied.

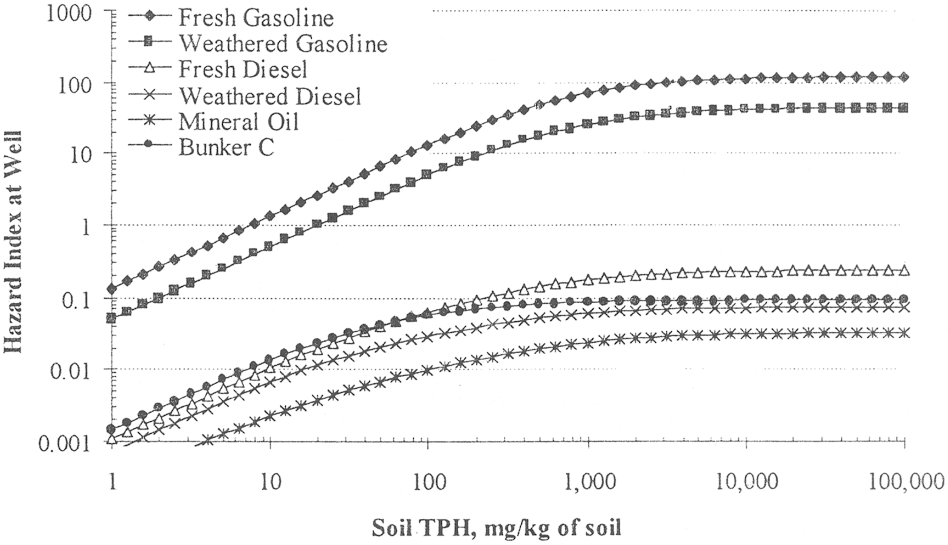

FIGURE 7

Predicted Hazardous Index at well vs. soil TPH applied.

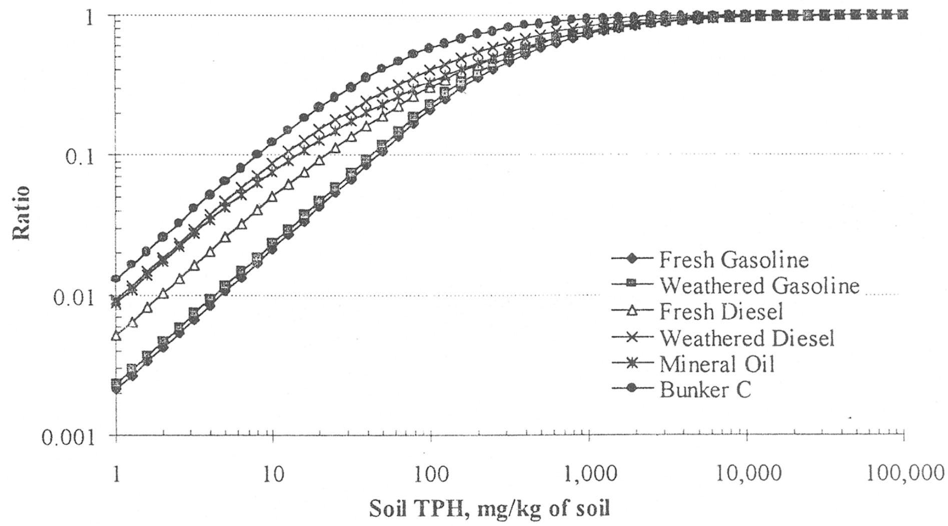

FIGURE 8

Ratio between TPH predicted at well by GWProt and Raoult's Law.

For TPH soil gasoline concentrations of 100 mg/kg and 1000 mg/kg, there were 98 and 89% decrease in the total concentration in water phase, respectively, when the f_{oc} increased from 0.001 to 0.1 (Figures 9 and 10). The HI decreased 97 and 92% over that same range. The effect of variation in f_{oc} on the dissolved concentrations from the other heavier fuels was almost identical to those found in gasoline. It was also found that at lower total soil residual levels, the amount of soil organic carbon had more of an impact on the equilibrium groundwater concentration. The decreases in the predicted dissolved concentrations and the HI are caused by the increased sorption of the NAPL constituents to the soil solid that decreases the amount of NAPL available to dissolve in the water.

Results of Fuel-Water Partitioning Experiment

The concentration range of components identified in the aqueous extracts, its corresponding predicted values by the model, and the range in weight percent in the neat fuels are summarized in Tables 3 and 4. As expected, the hydrocarbons that partition into the aqueous phase were predominantly aromatic compounds, including BTEX for gasoline. For all data obtained, the measured BTEX and TPH values were within a factor of two of predicted values by the study model, whereas the concentration of the individual heavier EC groups appeared to vary over as much as "three" orders of magnitude. Compared with gasoline, diesel fuel is compositionally more complex, thus greater deviations from ideal behavior might be expected. For gasoline, the large difference in values predicted by Raoult's Law

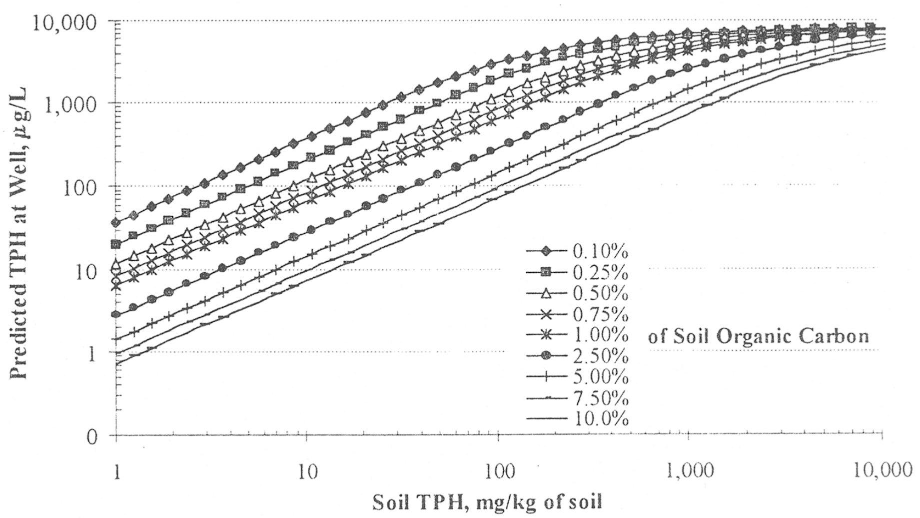

FIGURE 9

Sensitivity analysis with different soil organic carbon fraction with fresh gasoline-contaminated soil.

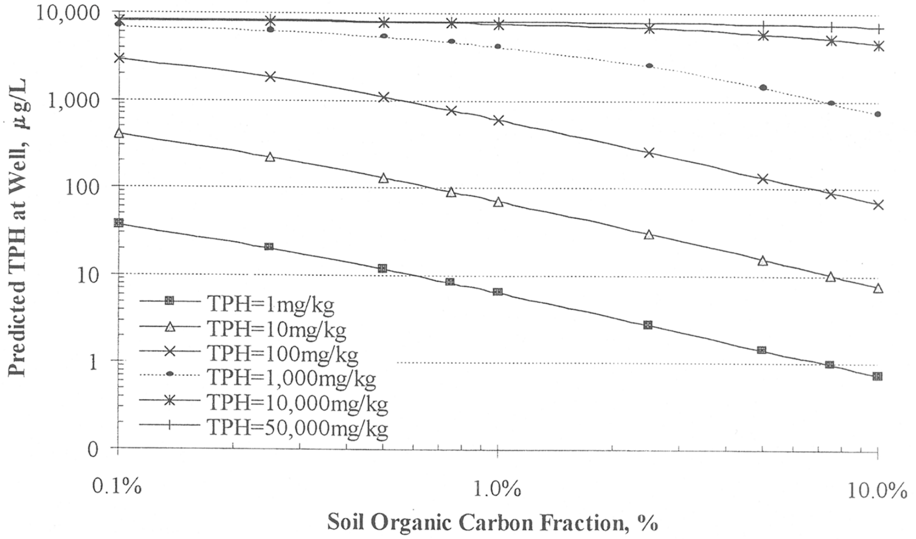

FIGURE 10

Soil organic carbon fraction versus TPH predicted at well with different soil TPH ranges applied (with fresh gasoline-contaminated soil).

TABLE 3
Water-Gasoline Fuel Experiment Results

	Neat Fuel	Aqueous Phase Concentration, μg/L					
			Predicted by			Predicted by	
Components	Measured, % Weight Composition	Measured	GWProt	Raoult's Law	Measured	GWProt	Raoult's Law
Gasoline #1		2mL : 100mL			0.04mL : 100mL		
Aliphatic EC >5-6	28.48	17400-19600	9941	9966	3540-3820	6009	9966
Aliphatic EC >6-8	17.18	0.5-5310	742	730	1970-2250	1011	730
Aliphatic EC >8-10	4.59	0.5	12	12	1170-1810	22	12
Aliphatic EC >10-12	5.52	0.5	1	1	2100-3140	2	1
Aliphatic EC >12-16	0.00	0	0	0	0	0	0
Aliphatic EC >16-21	0.00	0	0	0	0	0	0
Aliphatic EC >21-34	0.00	0	0	0	0	0	0
Benzene	2.91	56500-56700	58398	67147	4650-4950	7563	67147
Toluene	7.69	46000-48900	43018	44013	11100-11500	16853	44013
Ethylbenzene	1.70	3140-3270	2488	2467	1710-1840	2322	2467
Xylenes	8.93	17100-19000	16962	16874	9690-10300	13945	16874
Aromatic EC >8-10	5.52	1130-2460	3072	3027	100-1460	4128	3027
Aromatic EC >10-12	10.86	6740-8100	2153	2115	4920-6980	3575	2115
Aromatic EC >12-16	6.62	4730-12800	264	259	3410-3530	483	259
Aromatic EC >16-21	0.00	0	0	0	0	0	0
Aromatic EC >21-35	0.00	0	0	0	0	0	0
TPH	100.0	162940-165940	137050	146610	45340-50600	55913	146610
Gasoline #2		2mL : 100mL					
Aliphatic EC >5-6	29.92	19200-20200	10025	10005			
Aliphatic EC >6-8	15.31	0.5	634	622			
Aliphatic EC >8-10	3.77	0.5	9	9			
Aliphatic EC >10-12	2.56	0.5	0	0			
Aliphatic EC >12-16	0.00	0	0	0			
Aliphatic EC >16-21	0.00	0	0	0			
Aliphatic EC >21-34	0.00	0	0	0			
Benzene	3.67	60100-62300	71222	81104			
Toluene	14.66	72800-77300	78503	79894			
Ethylbenzene	2.72	3900-4060	3823	3776			
Xylenes	13.44	20300-21200	24515	24286			
Aromatic EC >8-10	4.14	0.5	2214	2173			
Aromatic EC >10-12	7.90	0.5	1502	1470			
Aromatic EC >12-16	1.90	0.5	73	71			
Aromatic EC >16-21	0.00	0	0	0			
Aromatic EC >21-35	0.00	0	0	0			
TPH	100.0	16100-176800	192521	203412			

vs. measured concentrations at the fuel to water ratio of 0.04 mL:100 mL (Gasoline #1 loading of TPH 300 mg/kg) suggests that Raoult's Law could overpredict the equilibrium water concentration at a relatively low range of soil concentrations. The measured aqueous-phase equilibrium concentrations for BTEX and EC groups for gasoline and diesel were plotted against the predicted aqueous-phase concentrations by GWProt. A regression analysis was conducted with a best-fitting linear equation with the intercept "zero value" enforced. The correlation was good for gasoline but not for diesel fuel. The null hypothesis was tested with t-distribution statistics to see if the slope was different from "unity". The p-value for the t-test result was >0.4, <0.0005, and 0.25 for gasoline, diesel, and both combined data set,

TABLE 4
Water-Diesel Fuel Experiment Results

Components	Neat Fuel Measured, % Weight Composition	Aqueous Phase Concentration, µg/L Measured	Predicted by GWProt	Predicted by Raoult's Law	Measured	Predicted by GWProt	Predicted by Raoult's Law
Diesel		**200mL : 2000mL**			**5mL : 2000 mL**		
Aliphatic EC >5-6	0.06	45-46	40.8	41.1	46-151	29.7	41.1
Aliphatic EC >6-8	0.31	24-35	26.9	27.0	10.0-27.0	25.3	27.0
Aliphatic EC >8-10	1.02	67-99	5.4	5.4	106-163	5.4	5.4
Aliphatic EC >10-12	4.18	204-276	1.4	1.4	227-287	1.4	1.4
Aliphatic EC >12-16	30.0	739-1890	0.2	0.2	828-847	0.2	0.2
Aliphatic EC >16-21	39.34	1570-3710	0.0	0.0	1210-1430	0.0	0.0
Aliphatic EC >21-34	3.25	129-578	0.0	0.0	200-1940	0.0	0.0
Benzene	0.007	152-156	326.2	344.1	40-298	105.7	344.1
Toluene	0.035	268-274	398.4	403.9	151-786	258.5	403.9
Ethylbenzene	0.035	65-70	101.9	102.3	52-103	89.5	102.3
Xylenes	0.21	319-340	823.0	826.6	259-520	699.4	826.6
Aromatic EC >8-10	0.63	9.0-14.0	708.8	709.7	0.5-31	673.6	709.7
Aromatic EC >10-12	3.64	878-880	1446.5	1447.0	499-591	1426.7	1447.0
Aromatic EC >12-16	9.67	1100-1820	772.6	772.6	780-918	773.1	772.6
Aromatic EC >16-21	7.61	324-731	42.2	42.2	239-246	42.3	42.2
Aromatic EC >21-35	0.00	112-225	0.0	0.0	10.0-64	0.0	0.0
TPH	100.0	6039-11109	4694.3	4723.3	6490-6556	4130.9	4723.3

respectively. Several factors other than nonideal behavior could have contributed to the observed deviations, including analytical problems; the presence of microemulsions during the withdrawal of the water after shaking; the possible presence of surfactants; the possible volatilization losses during the experiments. Certain fuel components may be co-solvents. A change in the activity coefficients in the NAPL phase might also cause the deviation. If components are unidentified or identified incorrectly, the computed mole fraction concentration of NAPL would be in error with propagation of these errors to the final output. Finally, and probably more importantly, the physico-chemical parameters assigned to each EC group could be significantly different from what those would be in a particular situation.

CONCLUSIONS

The GWProt model presented in this article provides a useful theoretical tool for calculating soil clean up levels that are protective of groundwater at complex NAPL-contaminated sites (e.g., Petroleum hydrocarbon). GWProt also allows the quantification of NAPL saturation and NAPL composition in a soil sample from the typical soil chemical analysis. This type of information is useful in designing site-specific remediation strategies and determining soil leaching potential. Sensitivity analysis with the soil organic carbon fraction is strongly encouraged. An attempt to group the components based on EC groups was not generally successful for heavier oils. The conclusions concerning the dissolved equilibrium concentration for each scenario are strongly dependent on the initial fuel compositions as well as total residual soil concentration in the soil. Differences were not found to be significant in leaching potential between the weathered and unweathered fuel. The fact that very few of the EC groups present contribute to the noncarcinogenic risk to groundwater suggests that a simpler analytical scheme (e.g., BTEX only for gasoline) may be sufficient to evaluate this aspect of the risk in many cases.

The current default soil clean up level of 200 mg/kg for diesel oil is found to be overly protective of the groundwater quality under the default hydro-geologic conditions conservatively chosen and representative diesel fuel compositions given. The user of GWProt must keep in mind that a model is merely a computational tool, and results will only be as accurate as the input data and the baseline assumptions. Numerical outcomes shown in this article rely on a number of limiting assumptions that should be kept in mind in their interpretation and application.

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REFERENCES

ASTM 1995. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. E1739-95, American Society for Testing and Materials.

Chiou, C. T., Porter, P. E., and Schmedding, D. W. 1983. Partition Equilibra of Nonionic Organic Compounds between soil organic matter and water. *Environ. Sci. Technol*. **17**, 227–231.

Cline, P. V., Delfino, J. J., and Rao P. S. C. 1991. Partitioning of aromatic constituents into water from gasoline, and other complex solvent mixtures. *Environ. Sci. Technol*. **25**, 914–920.

Feenstra, S., Mackay, D. M., and Cherry J. A. 1991. A method for Assessing residual NAPL based on organic chemical concentrations in soil samples. *Ground Water Monitor. Review*. **11**, 128–136.

Gustafson, J. B., Tell, J. G., and Orem D. 1997. Selection of Representative TPH Fractions based on Fate and Transport Considerations. TPH National Criteria Working Group. Volume 3, Amherst Scientific Publisher.

Karichhoff, S. W. and Brown D. S. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res*. 13, 241-248.

Lee, L. S., Hagwall, M., Delfino, J. J., and Rao, P. S. C. 1992. Partitioning of polycyclic aromatic hydrocarbons from diesel fuel into water. *Environ. Sci. Technol*. **26**, 2104–2110.

Mariner, P. E., Minquan, J., and Jackson. R. E. 1997. An algorithm for the estimation of NAPL saturation and composition from typical soil chemical analyses*. Ground Water Monitor Remediation* **17**, 122–129.

Mott, H.V. 1995. A model for determination of the phase distribution of petroleum hydrocarbons at release sites. *Ground Water Monitoring and Remediation*. **15**, 157–167.

Schwarzenbach, R. P. and Westall. J. 1981. Transport of nonpolar organic compounds from surface water to groundwater: laboratory sorption studies. *Environ. Sci. Technol*. **15**, 1360–1366.

U.S. Environmental Protection Agency 1996. Soil Screening Guidance: Technical Background Document. Office of Solid Waste and Emergency Response, Washington, D.C. EPA/540/R-95/128.

Washington Department of Ecology 1991. The Model Toxics Control Act cleanup legislation, Chapter 173–430 WAC.

Washington Department of Ecology 1997. Analytical Methods for Petroleum Hydrocarbons, Ecology Publication No. ECY97–602.