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# PREDICTING THE EFFECT OF HYDROCARBON AND HYDROCARBON-IMPACTED SOIL ON GROUNDWATER

KIRK T. O'REILLY<sup>1</sup>, RENAE I. MAGAW<sup>1</sup>, AND WILLIAM G. RIXEY<sup>2</sup>

<sup>1</sup>CHEVRON RESEARCH AND TECHNOLOGY CO.

<sup>2</sup>DEPT OF CIVIL AND ENVIRONMENTAL ENGINEERING, UNIVERSITY OF HOUSTON

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*A SUMMARY OF RESEARCH RESULTS FROM API'S SOIL & GROUNDWATER TECHNICAL TASK FORCE*

## Introduction

Managing chemicals that have been released to the environment requires detailed knowledge about how they move once released and how they interact with the different media (i.e., soil, water, air, and biota) that they contact. Site managers charged with managing these chemicals need this information in order to estimate how much of these chemicals people and/or ecological receptors might be exposed to and the corresponding potential health risks associated with this exposure. This is generally accomplished through a risk assessment process, the results of which are then used to decide on an appropriate risk management strategy.

Movement of chemicals through the different media depends on the unique physical and chemical properties of the chemicals themselves and of the media with which they come into contact. In risk assessment, this movement through the environment is typically modeled with a variety of fate and transport (FT) models. The concept of partitioning between phases, which is how a chemical will distribute itself in the various phases (soil solids, vapor, and water), is an integral part of these models. Partitioning describes the relative concentration of a chemical in two or more phases in contact with each other at equilibrium.

Fate and transport equations were initially developed for evaluating one chemical at a time. In these early models, the partitioning between water, soil vapor, and soil organic matter is calculated individually for each chemical. This presents a problem for petroleum hydrocarbons, which are not present in the environment as individual chemicals, but rather as complex mixtures of organic compounds.

The accurate prediction of the concentration of an organic chemical contained in a mixture of many organic chemicals is essential to the assessment of potential risks. Accordingly, fate and transport equations used to examine petroleum hydrocarbons should include this "mixture effect." Some models commonly used and approved by regulatory agencies already include the partitioning concepts necessary for modeling the mixture effect. In some cases, however, the equations require minor modification. Some models do not consider the impact of petroleum mixtures. This can result in unrealistic predictions about the potential environmental impacts of petroleum. The goals of this bulletin are:

- (1) to describe the concepts of partitioning and how Raoult's Law can be used to describe the effect,
- (2) to describe the potential implications of including Raoult's Law in FT modeling of petroleum hydrocarbons,
- (3) to use the concepts presented and the available hydrocarbon data to demonstrate that most compounds in crude oil are not a risk to impact groundwater,
- (4) to present a method for screening oil impacted soils and calculate maximum dissolved hydrocarbon concentrations in leachate to assess their potential for impacting groundwater, and,
- (5) to review how Raoult's Law is used in some common transport models.

## Partitioning & Raoult's Law

Every chemical has a specific affinity for organic, water, and vapor phases. A chemical with a higher affinity for water will have a higher solubility than a chemical with a lesser affinity for the water phase. Similarly, volatile compounds have a high affinity for the vapor phase. The following discussion will focus on the partitioning between the organic and water phases. When exposed to both phases, a chemical will partition between the phases based on the relative affinity for each. The following figure demonstrates the equilibrium concentration of a chemical that has 100 times the affinity for the organic phase than for the water phase.

Concentration in Organic Phase	Concentration in Water Phase
100 mg/kg	1 mg/L

Doubling the mass of the chemical in the system will double the concentration in each phase.

Concentration in Organic Phase	Concentration in Water Phase
200 mg/kg	2 mg/L

The ratio between the equilibrium concentrations is independent of the total mass of the chemical.

Concentration in Organic Phase	Concentration in Water Phase
100,000 mg/kg	1,000 mg/L

This ratio of the concentration of a chemical in each of the organic and water phases is known as the partitioning coefficient  $K$ :

$$K = C_o / C_w \quad \text{Equation 1}$$

where:

$C_o$  = concentration in the organic phase (mg/kg)

$C_w$  = concentration in the water phase (mg/L)

Rearranging Equation 1 indicates that if  $K$  and the concentration in the organic phase are known, the dissolved concentration of a chemical can be predicted. Fate and transport models typically predict the dissolved concentration of a chemical in this manner.

$$C_w = C_o / K \quad \text{Equation 2}$$

$K$  depends both on the chemical being considered and the nature of the organic phase. Data on the partitioning coefficient,  $K_{ow}$ , where octanol is the organic phase, are available for many chemicals.  $K_{oc}$ , where the organic phase corresponds to soil organic carbon, is commonly used in FT equations. There are published  $K_{oc}$  values for many compounds of environmental interest.

The solubility and partitioning behaviors of organic compounds are inversely related. Solubility is the dissolved concentration of an organic compound in equilibrium with itself.

Percentage of Hydrocarbon Mixture Made up of Chemical	Hypothetical Concentration in Water Phase
100%	10,000 mg/L

For a compound present in an organic mixture, the dissolved concentration decreases as the concentration in the mixture decreases.

Percentage of Hydrocarbon Mixture Made up of Chemical	Hypothetical Concentration in Water Phase
50%	5,000 mg/L
Percentage of Hydrocarbon Mixture Made up of Chemical	Hypothetical Concentration in Water Phase
1%	100 mg/L

The maximum dissolved concentration, or effective solubility, of a chemical in an organic mixture is a function of its pure compound solubility and the mole fraction of the chemical in the organic phase. Published solubility values (S in equation 3, below) are available for many compounds of concern.

$$C_w = x * S \quad \text{Equation 3}$$

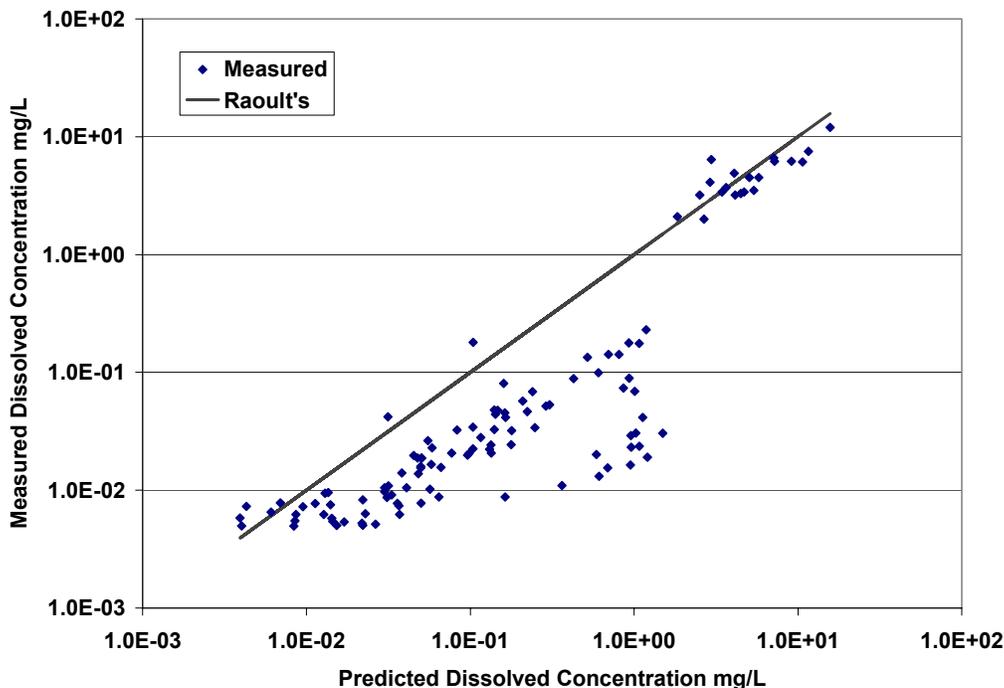
where:

- $C_w$  = concentration of chemical in water (mg/L)
- $x$  = mole fraction of chemical in organic phase (mole chemical/mole oil)
- $S$  = solubility of pure chemical in water (mg/L)

Equation 3 is known as Raoult's Law [for Francois-Marie Raoult (1830-1901)] and it is commonly used to predict the dissolved concentration of a chemical in water exposed to a hydrocarbon mixture. For example, benzene with a pure compound solubility of 1,800 mg/L and a mole fraction of 0.001 in crude oil would have a dissolved concentration of 1.8 mg/L. Raoult's law is valid for compounds that are liquids at room temperature. For solid compounds, such as the larger polycyclic aromatic hydrocarbons (PAHs), the "subcooled liquid solubility" is used in place of the pure chemical solubility (S) in equation 3. These values are also available in chemical reference books.

Mole Fraction of Benzene in Crude Oil	Dissolved Concentration of Benzene in Water
0.001	1.8 mg/L

To confirm that Raoult's law is appropriate for predicting the effective solubility of a chemical present in oil and put into contact with water, 15 crude oils from a variety of sources were analyzed for 43 aromatic compounds ranging from benzene through 5- and 6-ringed PAHs [1]. The oil was then placed in contact with water, and compounds present in the oil were allowed to partition into the water. The concentrations of the aromatic compounds in both the oil and water phases were determined. Figure 1 presents the data for all analytes in which the dissolved concentrations were above the laboratory analytical reporting limit of 5 ppb. Most of the results were at or below the dissolved concentration predicted by the application of Raoult's law. This is evidence that Raoult's law gives a conservative estimate of the effective solubility.



**Figure 1. Measured dissolved concentrations of analytes are generally less than those predicted by Raoult's Law.**

***Key Point- The maximum dissolved concentration of a compound in water exposed to petroleum can be predicted if its concentration in the petroleum is known.***

Equations 2 and 3 demonstrate that the effective solubility of a compound in water can be predicted if the relative affinity of the compound for the water phase, as measured by K or S, and the concentration of compound in the organic phase, as measured by C<sub>o</sub> or x, are known. Equations 2 and 3 are interchangeable if the units are converted correctly and the appropriate K for the organic phase is known.

$$C_w = x * S = C_o / K \tag{Equation 4}$$

Equation 5 can be used to convert between the two equations. Since x is a mole fraction, an estimate of the average molecular weight of the organic phase is required.

$$K_{oil} = (MW_i * 10^6) / (S_i * MW_o) \tag{Equation 5}$$

where:

- K<sub>oil</sub> = oil/water partitioning coefficient
- MW<sub>i</sub> = molecular weight of the compound (g/mole)
- MW<sub>o</sub> = average molecular weight of the organic phase (g/mole)
- S<sub>i</sub> = solubility of the compound of interest (mg/L)

Based on the distribution of compounds in the following hydrocarbons products, typical values for MW<sub>o</sub> in g/mole are:

Gasoline	100
Condensate	150
Diesel/Distillate	180
Crude	200-250
Gas oil	300

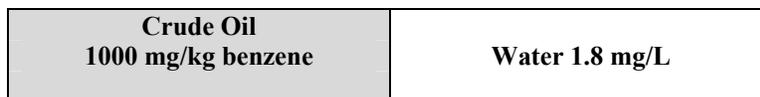
In practice, the results of Equation 2 are typically more conservative than those of Equation 3. The similarity between the organic compound of interest and the organic phase influences partitioning.  $S$  is based on the interaction of a dissolved compound and its pure phase, while a published  $K_{ow}$  is based on partitioning between a compound and octanol as the organic phase. Since a petroleum mixture is more like a hydrocarbon compound of concern than octanol, but less like a pure phase of the compound, Equation 2 may slightly overestimate measured concentrations, while Equation 3 can underestimate the dissolved concentration. Lee *et al* [2] and Ortiz *et al* [3] have shown that  $K_{ow}$  is a conservative estimate of  $K_{oil}$ . While in Rixey [4], the measured concentration of naphthalene was about 3x higher than predicted by Equation 3. Rixey recommends the use an activity coefficient factor in Equation 3 to improve the accuracy of the result and presents a method for estimating the coefficient.

Predictions based on published  $S$  or  $K$  are only as good as the data available. A review of the literature finds multiple values for these factors that may range over an order of magnitude. Predicted maximum dissolved concentration have similar accuracy. In the following sections predicted maximum dissolved concentrations are compared to regulatory or risk-based dissolved concentration levels. If the predicted and target concentrations are similar, additional evaluation of the material is appropriate. If the predicted concentrations are an order of magnitude or more lower than the target level, the petroleum source or hydrocarbon impacted material should not be a risk to groundwater.

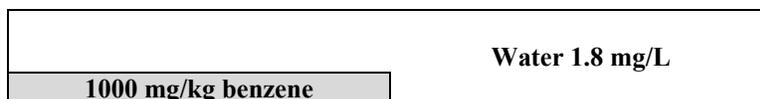
### Implication of Raoult’s Law on Groundwater Impacts of Petroleum Hydrocarbons

As described above, when petroleum hydrocarbons (for example, crude oil) are in contact with groundwater, the dissolved concentrations of the individual chemicals are generally not affected by the amount of oil in contact with the water. Only when the mass of the crude oil is very low does the amount of the crude oil present affect the effective solubility of individual compounds. At low oil concentrations, lower final concentrations in both phases can be expected due to partitioning into the soil organic matter.

Mass of crude oil = mass of water:



Mass of crude oil < mass of water:



Mass of crude oil > mass of water:



***Key Point- The dissolved concentration of petroleum hydrocarbons is not controlled by the amount of oil in contact with water, but by the concentration of the specific constituents in the oil.***

Since the effective solubility of any individual chemical depends on its concentration in the oil, but not on the amount of oil present (Equation 3), compositional information for an oil can be used to determine if a given compound in oil, or the oil itself, could present a risk to groundwater. Raoult’s law can be used to predict the effective solubilities (i.e., the maximum dissolved concentrations) of compounds of interest. The predicted concentrations can then be compared to groundwater protection goals, and if the predicted values are less than the protection goals, then the oil cannot present a risk to groundwater.

In Table 1, Equation 4 and data from Kerr *et al* [5] were used to calculate maximum dissolved concentrations of aromatic compounds in water exposed to a crude oil. These values were then compared to United States groundwater protection regulations, in the form of United States Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs)[6] or Water Health Based Limits (HBLs) for drinking water [7]. Kerr *et al.* [5] analyzed 69 oils for several aromatic compounds. The highest concentration of each of four representative compounds was used in this example and the molecular weight of the oil was assumed to be 200 g/mole. Since the highest concentration of each compound in any oil was used, this is a worst case evaluation.

	<b>C<sub>o</sub> max mg/kg</b>	<b>X max</b>	<b>S* mg/L</b>	<b>C<sub>w</sub> max mg/L</b>	<b>MCL mg/L</b>	<b>&gt;MCL</b>
Benzene	5900	1.51E-02	1.80E+03	2.72E+01	<b>5.00E-03</b>	<b>Yes</b>
Naphthalene	3700	5.69E-03	1.03E+02	5.77E-01	1.00E+00	No
Chrysene	120	1.05E-04	1.65E-01	1.74E-05	1.00E-02	No
Benzo(a)pyrene	8	6.11E-06	5.40E-02	3.30E-07	2.00E-04	No

\* subcooled liquid solubility if solid at 25 °C. From EPA Soil Screening Levels, Appendix C [8]

**Table 1. Calculated maximum dissolved concentrations of 4 aromatic compounds in crude oil.**

If any of the 69 crude oils were to be in direct contact with groundwater, benzene would be the only compound that could possibly have a dissolved concentration that would exceed its respective MCL (Table 2). This same analysis was extended to 13 PAH compounds that also have HBLs. Even at maximum concentrations in the 69 oils analyzed, the maximum dissolved concentrations of all PAHs are below HBL.

<b>PAH</b>	<b>C<sub>o</sub> max mg/kg</b>	<b>S* mg/L</b>	<b>C<sub>w</sub> max mg/L</b>	<b>HBL mg/L</b>	<b>&gt; HBL</b>
Naphthalene	3700	1.03E+02	5.8E-01	1.0E+00	No
Acenaphthene	58	2.12E+01	2.6E-04	2.0E+00	No
Anthracene	17	4.42E+00	1.5E-06	1.0E+01	No
Fluorene	380	1.24E+01	9.6E-04	1.0E+00	No
Benzo[a]anthracene	16	2.35E-01	4.3E-06	1.0E-04	No
Fluoranthene	15	1.08E+00	2.2E-07	1.0E+00	No
Chrysene	120	1.65E-01	2.5E-07	1.0E-02	No
Pyrene	9.2	1.04E+00	1.3E-06	1.0E+00	No
Dibenz[a,h]anthracene	8	6.23E-01	2.3E-08	1.0E-05	No
Benzo[a]pyrene	8	5.40E-02	7.3E-09	2.0E-04	No
Benzo[b]fluoranthene	14	3.85E-02	6.1E-09	1.0E-04	No
Benzo[k]fluoranthene	1.3	6.15E-01	5.2E-10	1.0E-03	No
Indeno[1,2,3-cd]pyrene	1.7	5.50E-04	3.5E-10	1.0E-04	No

\* subcooled liquid solubility if solid at 25 °C. From EPA Soil Screening Levels, Appendix C [8].

**Table 2. Calculated maximum dissolved concentrations of PAHs in crude oils.**

## Implications of TPH Impacts on Groundwater

Total Petroleum Hydrocarbon (TPH) fractionation schemes are beginning to be used by regulatory agencies in the United States to assess the potential migration and risks associated with petroleum hydrocarbons [9,10,11,12,13]. Raoult's law can be used to evaluate the potential impacts of TPH on groundwater in the same way that it can be used to evaluate the potential impacts of benzene and PAHs. A similar exercise to that presented above for benzene and PAHs can be performed for TPH fractions. However, because there are no U.S. EPA MCLs for TPH or TPH fractions, the groundwater Protective Concentration Limits (PCLs) set by the Texas Natural Resource Conservation Commission (TNRCC) as groundwater protection goals are used for comparison [11]. In the TNRCC program, screening level (Tier 1) health-risk based PCLs are available for 12 TPH fractions for the ingestion of groundwater (<sup>GW</sup>GW<sub>ing</sub>) exposure pathway.

By rearranging Equation 3, and substituting  $^{GW}GW_{Ing}$  (multiplied by a dilution factor [11]) for  $C_w$ , we can calculate the maximum concentration in the oil phase for each TPH fraction that would prevent TPH levels in groundwater concentrations from exceeding protective levels.

$$x = \frac{^{GW}GW_{Ing} * LDF}{S} \tag{Equation 6}$$

where:

- $^{GW}GW_{Ing}$  = PCL for ingestion of groundwater (mg/L). See Table 3 of [11].
- LDF = lateral dilution factor for roundwater (dimensionless) From Figure: 30 of [11].

In Equation 6, the quantity  $^{GW}GW_{Ing} * LDF$  is equal to  $C_w$  in Equation 3 and represents the water concentration in direct contact with soil and residual oil. The symbols  $^{GW}GW_{Ing}$  and LDF are used here to be consistent with notation used in the TNRCC rules.

Table 3 presents groundwater protection levels for various aromatic and aliphatic fractions, their respective pure solubilities, and the calculated maximum acceptable oil mole fractions for these fractions. These data indicate that the levels for the various aromatic fractions in crude oil can be greater than 25 mole percent. Note that for all aliphatic fractions and for aromatic fractions with carbon numbers greater than 10, even if these fractions existed as a pure liquid in soil, they could not present a risk to groundwater under a commercial/industrial land use scenario.

	$^{GW}GW_{Ing}^{(1)}$ (mg/L)	S <sup>(2)</sup> (mg/L)	$\chi$ Calculated Maximum Acceptable Mole Fraction in TPH
>7-8 C Aromatics (TPH)	7.3	530	0.26
>8-10 C Aromatics (TPH)	2.9	65	0.89
>10-12 C Aromatics (TPH)	2.9	25	1
>12-16 C Aromatics (TPH)	2.9	5.8	1
>16-21 C Aromatics (TPH)	2.2	0.65	1
>21-44 C Aromatics (TPH) <sup>(3)</sup>	2.2	0.0066	1
6 C Aliphatics (TPH)	4.4	36	1
>6-8 C Aliphatics (TPH)	4.4	5.4	1
>8-10 C Aliphatics (TPH)	7.3	0.43	1
>10-12 C Aliphatics (TPH)	7.3	0.034	1
>12-16 C Aliphatics (TPH)	7.3	0.00076	1
>16-44 C Aliphatics (TPH) <sup>(3)</sup>	150	2.5E-06	1
>44 C (TPH)	3.1 <sup>(4)</sup>	1.0E-04 <sup>(4)</sup>	1

Notes:

- (1) From Table 3 of TRRP Rules [11]. Corresponding to commercial/industrial use scenario. LDF = 20.
- (2) From Figure: 30 TAC §350.73 (e) of [11].
- (3) Extended for the C35 to C44 equivalent alkane number range for crude oils. Values listed are from [11] for up to C35.
- (4) From Ref. [14]

**Table 3. Calculated mole fractions in oil for various TPH fractions.**

**Key Point- Groundwater exposure to any petroleum or petroleum impacted soil will not result in dissolved TPH concentrations that exceed health-based dissolved limits if the >7-8 C Aromatic fraction is less than 26% and the >8-10 C Aromatic fraction is less than 89% of the oil.**

Another interpretation of the data in Table 3 is that if the concentrations of these fractions in a crude oil (or petroleum hydrocarbon mixtures in general) are below those shown in the  $^{GW}GW_{Ing}$  column of Table 3, then no amount of TPH in the soil could produce groundwater concentrations that would exceed protective levels. In this

case, acceptable TPH levels in soil would be limited by other exposure pathways, rather than by groundwater ingestion. In general, this technique could be used as a screening method for evaluating the potential of any given oil to produce groundwater TPH levels that would exceed groundwater protective levels.

### Implications of Raoult’s Law on Soil Impacts by Petroleum Hydrocarbons

When two organic phases and the water phase are in contact, a chemical will partition between the three phases. The equilibrium concentration in each phase will depend on the relative affinity of the chemical for the phases. In the following example, the affinity of the chemical is 100 times greater for phase 1 than water, and 75 times greater for phase 2 than water. This is similar to the relative affinity of petroleum hydrocarbons for oil and soil organic matter. At equilibrium, the ratio of the concentration of a compound in the three phases remains constant at 100:75:1.

<b>Organic Phase 1</b> 100 mg/kg	<b>Water</b>  1 mg/L
<b>Organic Phase 2</b> 75 mg/kg	

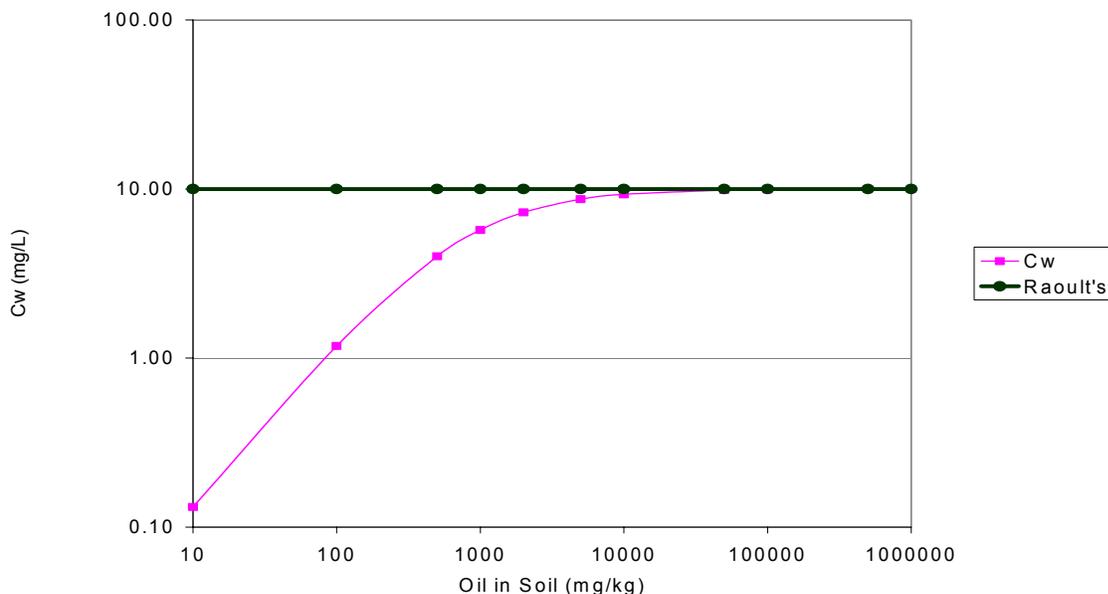
In unimpacted soil, both the soil organic content (SOC) and water are free of petroleum hydrocarbons. When oil is added to soil, an individual chemical contained in the oil will partition between the oil, SOC, and water. At low oil levels, the concentration of the chemical in the oil phase decreases due to loss to the SOC and water. This results in a lower dissolved concentration than would be expected for oil:water partitioning alone. As the mass of oil increases relative to the SOC, the final organic phase concentration remains closer to the initial oil concentration. The dissolved concentration gets closer to, but cannot exceed, the concentration predicted by Raoult’s law.

The partitioning between oil, SOC, and water is demonstrated in the following example. The concentration of the chemical of interest is initially 1000 mg/kg in the oil phase. Raoult’s law predicts a maximum dissolved concentration of 10 mg/L. The amount of oil ranges from 100 to 10,000 mg/kg soil. The SOC is 1000 mg/kg soil.  $C_{of}$  is the final concentration of the compound in the oil phase.  $C_s$  is the concentration in the SOC phase and  $C_w$  is the dissolved phase. The dissolved concentration never exceeds the 10 mg/L predicted by Raoult’s law.

Amount of Oil mg/kg	Amount of SOC mg/kg	Final Conc. In Oil Phase ( $C_{of}$ – mg/kg)	Conc. Of Chemical in SOC Phase ( $C_s$ – mg/kg)	Conc. Of Chemical in Dissolved Phase ( $C_w$ – mg/L)
100	1000	118	88	1.18
1000	1000	571	429	5.71
10000	1000	930	698	9.30

**Table 4. Partitioning behavior of a chemical between oil, SOC, and water.**

Figure 2 shows the same effect over a wider range of concentrations. The dissolved concentration of the compound increases with TPH concentrations at low levels, but the maximum dissolved concentration remains limited to the value predicted by Raoult’s law.



**Figure 2. The partitioning behavior of a chemical between dissolved and soil phases.**

**Key Point- At low oil concentrations in soil, SOC reduces the predicted dissolved concentrations, while at higher oil concentrations the maximum dissolved concentration is limited by Raoult's law.**

The partitioning of organic compounds between the SOC and water is the basis for setting soil screening levels that are protective of groundwater. The EPA Soil Screening Guidance presents the following equation for relating soil concentrations to dissolved concentrations [7]:

$$C_s = C_w * (K_d + ((\Theta_w + \Theta_a H') / \rho_b)) \tag{Equation 7}$$

where:

- $C_s$  = soil screening level (mg/kg)
- $C_w$  = dissolved groundwater protection goal (mg/L)
- $K_d$  = soil/water partitioning coefficient
- $\Theta_w$  = water filled porosity
- $\Theta_a$  = air filled porosity
- $H'$  = Henry's Constant
- $\rho_b$  = soil particle density

The component of the equation ' $(\Theta_w + \Theta_a H') / \rho_b$ ' takes into account the fraction of the compounds of concern in the water and vapor phase. Since  $(\Theta_w + \Theta_a H') / \rho_b$  is typically much smaller than  $K_d$ , Equation 7 can be simplified for this discussion to:

$$C_s = C_w * K_d \tag{Equation 8}$$

This is consistent with partitioning Equations 1 and 2 discussed earlier.

The soil/water partitioning coefficient  $K_d$  is a function of the amount of organic phase associated with the soil, and the  $K$  for that organic phase. For a soil in the absence of a non-aqueous phase liquid (NAPL) or oil phase [15]:

$$K_d = K_{oc} * f_{oc} \tag{Equation 9}$$

where:

- $K_{oc}$  = SOC/water partition coefficient
- $f_{oc}$  = the fraction of organic carbon in the soil (g/g)

If two organic phases are associated with the soil, Equation 9 can be expanded to [15]:

$$K_d = (K_{oc}^1 * foc^1) + (K_{oc}^2 * foc^2) \tag{Equation 10}$$

An oil impacted soil has two organic phases, the SOC and the oil. By replacing  $K_{oc}^2$  with  $K_{oil}$ , and  $foc^2$  with the oil concentration in the soil,  $K_d$  from Equation 10 can be inserted into Equation 8:

$$C_s = C_w * ((K_{oc} * foc) + (K_{oil} * f_{oil})) \tag{Equation 11}$$

As shown in Equation 5,  $K_{oil}$  can be calculated using Raoult's Law.

The importance of considering the partitioning of constituents between both the soil and oil phases is shown in the following example. In order to determine whether a soil TPH limit of 10,000 mg/kg would be protective of groundwater, an example is provided below using naphthalene as the chemical of concern. Table 5 shows the predicted dissolved naphthalene concentration for water in contact with soil impacted with a crude oil containing naphthalene at a concentration of 3,700 mg/kg oil. As seen in Table 2, this is equivalent to the highest naphthalene concentration measured in crude oil [5]. Using the approaches recommended in the EPA Soil Screening Guidance, one would predict that dissolved concentrations of naphthalene could exceed the 1.0 mg/L level at TPH concentrations above 1,600 mg/kg. In this example, the maximum amount of naphthalene that can be dissolved in water is limited by Raoult's law to 0.58 mg/L. Since the dissolved concentration cannot exceed the groundwater goal at any TPH concentration, the proposed 10,000 mg/kg TPH limit is protective of groundwater.

TPH mg/kg (soil)	Naphthalene mg/kg (soil)	Soil Partitioning Only- Dissolved Naphthalene (mg/L)	Soil and Oil Partitioning- Dissolved Naphthalene (mg/L)
100	0.37	0.06	0.06
1,000	3.7	0.62	0.30
1,600	5.9	1.0	0.37
2,500	9.3	1.5	0.42
5,000	18.5	3.1	0.49
10,000	37	6	0.54
25,000	92.5	15	0.56
50,000	185	31	0.58

**Table 5. Predicted dissolved naphthalene concentrations.**

### A Screening Method to Assess the Risk of Petroleum Impacted Soil

Calculating the maximum dissolved concentration of water in contact with oil-impacted soil depends on knowledge of the concentration of the compounds of concern in the oil phase. This can be directly measured if a sample of the source oil is available. It can also be determined from analysis of soil samples if the concentration of the oil phase in the soil is measured.

$$C_o = (C_{soil} / TPH) * 10^{-6} \tag{Equation 12}$$

or

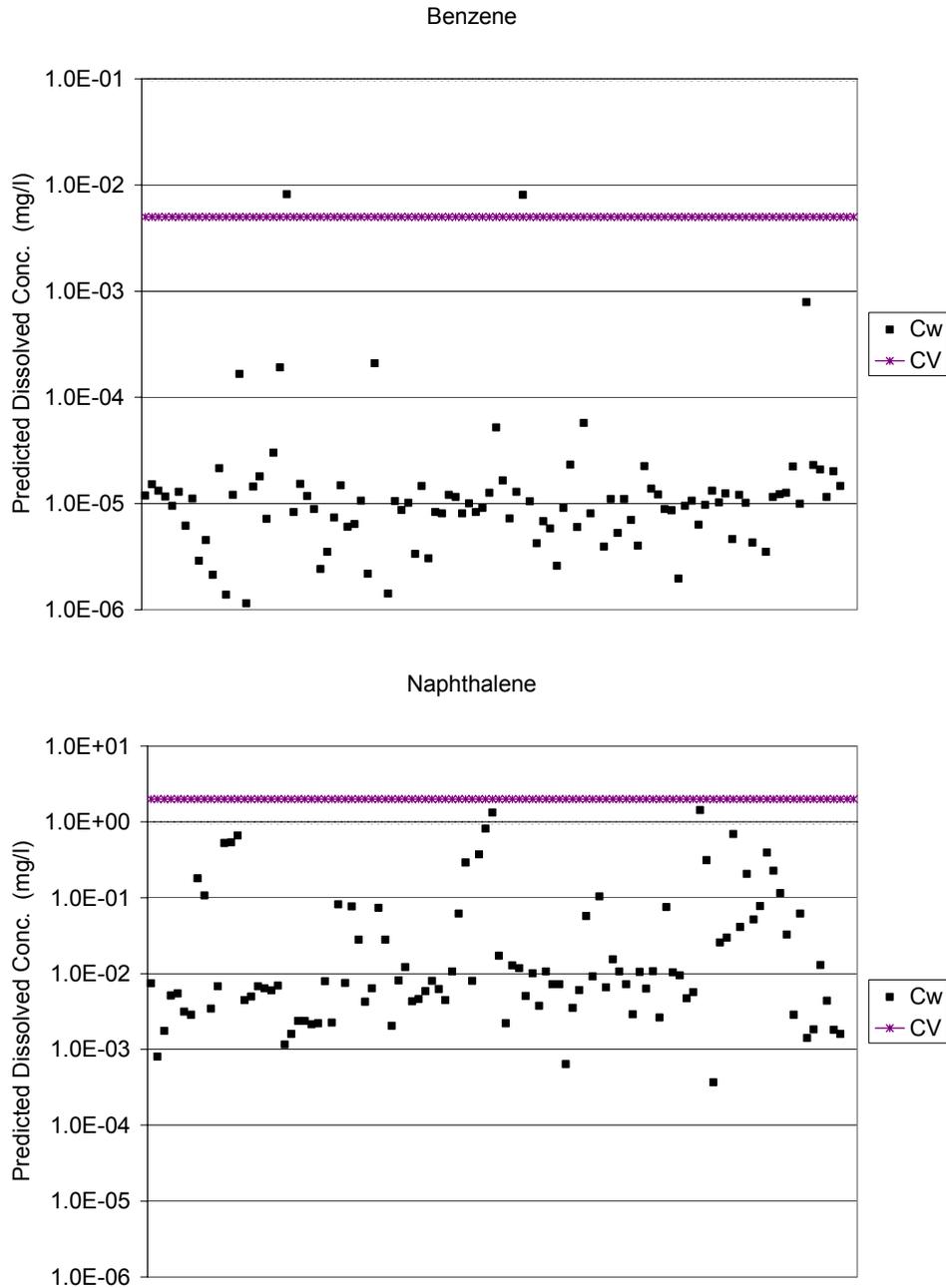
$$x = (C_{soil} / TPH) * (MW_o / MW_i) \tag{Equation 13}$$

where:

- $C_{soil}$  = concentration of the compound in the soil (mg/kg)
- TPH = concentration of the oil phase in the soil (mg/kg)
- $MW_i$  = molecular weight of the compound (g/mole)
- $MW_o$  = average molecular weight of the organic phase (g/mole)

Equations 2 and 12 or Equations 3 and 13 can be used to screen field data to determine whether oily soil at a site is a potential risk to groundwater. Given the weathered nature of petroleum in soil, the more soluble components are often depleted. These methods were used to screen the potential risk to groundwater of impacted soil at a petroleum refinery. In this example, groundwater protection "Critical Values" (CV) were negotiated with state regulators. Soils

were analyzed for BTEX, PAH, and TPH concentrations during site assessment activities. Phase Separated Hydrocarbons (PSH) collected from within wells were also analyzed. A spreadsheet was developed to calculate  $C_w$  for 100 field samples using Equations 2 and 12. Except for benzene in two samples, the predicted maximum  $C_w$  for all the COCs were below the CVs. The  $C_w$  for benzene in those two samples were 8 ppb, compared to a CV of 5 ppb. This indicates that neither impacted soil nor the PSH poses a risk via the groundwater ingestion pathway.



**Figure 3. Predicted Dissolved Concentrations ( $C_w$ ) of Benzene and Naphthalene in 100 samples based on Equation 12 and the measured  $C_{soil}$  for each sample.**

The previous evaluation suggested that hydrocarbon impacted soil at refineries may not be a risk to groundwater if it was exposed to a single spill event. To evaluate the impact of multiple hydrocarbon additions, 20 soil samples from a refinery landfarm were analyzed for TPH, BTEX, and PAHs. The soil had been exposed to numerous applications of oily material when the landfarm was in operation. The TPH ranged from about 2,000 to 100,000 mg/kg. BTEX was not detected in the samples. Although 15 of the 16 EPA priority pollutant PAHs were detected, benzo[a]anthracene was the only compound in which the calculated  $C_w$  exceeded the MCL. The  $C_w$  exceeded MCL

by less than 2.5x. If one includes a conservative Dilution Attenuation Factor of 10, none of the aromatic compounds of concern would be expected to impact groundwater above the MCL

### **The Use of Raoult's Law in Commonly Used Fate and Transport Models**

A number of models and equations that are used in state and federal regulatory programs for determining acceptable levels of contaminants in soils based on leaching to groundwater were evaluated to determine how partitioning between soil and water is treated and whether Raoult's law is incorporated. For those models that do incorporate Raoult's law, it was also determined whether Raoult's law is used correctly. The models that were evaluated included SESOIL [16,17], VADSAT [18], an ASTM-based RBCA toolkit [19], the Texas Risk Reduction Program Rules Guidance Document [11,12], the EPA Soil Screening Guidance (SSG) [7], and a proprietary spreadsheet prepared by the Petroleum Environmental Research Forum (PERF) [unpublished]. Each of these models/risk-based frameworks was evaluated. The results of the model evaluations are summarized in Table 6.

Three of the models, VADSAT, the RBCA toolkit, and the PERF Spreadsheet correctly use Raoult's law for predicting the leachate concentrations of BTEX and PAHs. VADSAT and the ASTM RBCA toolkit use the pure compound solubility for PAHs instead of the more accurate hypothetical subcooled liquid solubility. This should be corrected prior to use. The PERF spreadsheet and the Texas Risk Reduction Program Guidance Document correctly use Raoult's law for predicting dissolved TPH concentrations. As published, SESOIL and EPA SSG model only the partitioning between soil organic matter and pore water. The impact of the oil phase is ignored, thereby giving results that may be far too conservative, as illustrated in the previous example for naphthalene.

The Washington State Department of Ecology (DOE) is developing a multiphase model that uses Raoult's law to predict dissolved, NAPL, sorbed, and vapor phase concentrations associated with hydrocarbon impacted soils [20]. Constituents modeled include BTEX, TPH fractions, and seven PAHs. The DOE's goal is to develop a simple and scientifically defensible regulatory tool for determining risk-based soil limits that are protective of groundwater. The model was not publicly available when this document was prepared, and so we did not include it in our review.

## Summary

Protecting groundwater is a critical component of environmental management at sites impacted with petroleum hydrocarbons. The potential for chemicals of concern to leach from oil or petroleum impacted soil must be understood in order to assess the risk to groundwater. In this paper, the technical basis for calculating maximum dissolved hydrocarbon concentrations in leachate was presented. If the concentration of a constituent in either the oil or soil phase is known, the maximum dissolved concentration can be calculated. The dissolved concentration is limited by equilibrium partitioning between the oil and water phases. Partitioning between soil organic matter and these phases can further reduce the dissolved hydrocarbon leachate concentration.

Using data from the analysis of 69 crude oils, the maximum leachate concentrations for selected aromatic and polynuclear aromatic compounds were calculated. Except for benzene, the dissolved concentrations of these compounds are expected to be below conservative MCL or HBLs. Benzene appears to be the only organic compound present in crude oil that is a potential risk to human health based on groundwater ingestion.

These methods were also used to predict the potential from risk of TPH to groundwater based on the Texas Risk Reduction Rules. Other states have similar TPH approaches. The >7-8 C and >8-10 C aromatic fractions are the only fractions with a potential to impact groundwater. These two aromatic fractions would have to be greater than 26 and 89 mole percent of an oil to be a potential threat to groundwater.

Evaluation of soils collected at oil refineries suggests that the predicted concentration of hydrocarbon constituents in leachate would be insufficient to result in groundwater concentrations greater than regulatory limits.

<b>Model</b>	<b>Type</b>	<b>Uses Raoult's Law?</b>	<b>Calculates Raoult's law Correctly for BTEX?</b>	<b>Calculates Raoult's law Correctly for PAHs?</b>	<b>Calculates Raoult's law Correctly for TPH Fractions?</b>
<b>ASTM RBCA Toolkit</b>	Partitioning /Exposure Assessment Model	Yes	Yes	No; Need to input correct hypothetical solubilities	Not applicable
<b>PERF Spreadsheet</b>	Partitioning/Risk Assessment Model	Yes	Yes	Yes	Yes
<b>VADSAT</b>	Partitioning/Fate and Transport Model	Yes	Yes	No; Need to input correct hypothetical solubilities	Not applicable
<b>TRRP – TPH Guidance Document</b>	Partitioning/Risk Assessment Model	For TPH fractions only	No; Raoult's Law not used for BTEX	No; Raoult's Law not used for PAHs	Yes
<b>SESOIL Version 1995</b>	Partitioning/Fate and Transport Model	No	Not applicable	Not applicable	Not applicable
<b>EPA Soil Screening Guidance</b>	Partitioning /Risk Assessment Model	No	Not applicable	Not applicable	Not applicable

**Table 6: Summary of use of Raoult's Law in Six Fate and Transport Models**

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