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Non-Aqueous Phase Liquid
Mobility Limits in Soil
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SOIL & GROUNDWATER RESEARCH BULLETIN

NON-AQUEOUS PHASE LIQUID (NAPL) MOBILITY LIMITS IN SOIL

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ABSTRACT

Conservative screening concentrations for non-aqueous phase liquids (NAPL) that could be considered immobile in unsaturated zone soils are presented. Total concentrations measured at a crude oil or petroleum product release site (using total petroleum hydrocarbon [TPH] or a similar analysis method) can be compared to the screening concentrations to determine the potential for NAPL to migrate in soil. The screening values are based on an analysis of published data for a range of soil texture classifications and a range of NAPL density from 0.7 to 1.5 g/cm3.

The paper includes summary tables and histograms of residual NAPL void fraction, Sr, as a function of soil type. These provide a basis for selecting conservative values used in calculating screening concentrations for immobile NAPL. For example, in medium to coarse sands, with Sr = 0.06 cm3-oil/cm3-void, one would expect that NAPL would be immobile in 90% of samples with equivalent NAPL concentration levels for this soil type.

Measured concentrations of immobile NAPL reported in the literature vary considerably with soil type, chemical composition, and the measurement method. The proposed screening levels are conservative (lower range) estimates within the range of measured residual NAPL concentration values. Higher values could be applicable in many cases, both in unsaturated and saturated soil conditions.

This paper addresses immobile bulk NAPL in soils at concentrations up to the threshold of mobility. This document does not address the movement and flow of NAPL, the dissolution of NAPL chemical into soil pore water solution, nor NAPL volatilization into soil pore air. Transport by these mechanisms may be estimated using other published and accepted methods.

INTRODUCTION

Organic chemicals released to soil may migrate as vapors in soil gas, as dissolved constituents in soil pore water, or as a bulk phase liquid which is immiscible in water. Assessment of potential migration pathways for chemical releases into the environment are discussed in several related documents (USEPA 1996, 1991; ASTM E1739, PS104-98). These migration pathways are important in a general risk-based site assessment. This paper is confined to discussion of the mobility of non-aqueous phase liquids, either as pure chemicals or as chemical mixtures.

Many organic chemicals, including hydrocarbons, are nearly immiscible in water. Release of a non-aqueous phase liquid (NAPL) to near-surface unsaturated soil can result in downward gravity-driven migration of the NAPL towards the water table. At the water table, light nonaqueous phase liquids (LNAPL), including petroleum, which are less dense than water, will mound and spread horizontally. LNAPL may also move with the groundwater gradient. Dense nonaqueous phase liquids (DNAPL) will migrate downward, mound, and spread horizontally, until a path of least resistance further downward into the saturated region is found. This could be when the accumulation is great enough to exceed the capillary entry pressure into the saturated zone, or when the DNAPL mound reaches a region of high vertical permeability, or when it reaches a fracture.

The volume of mobile NAPL depletes as immobile residual chemical is left behind through the soil column in which the NAPL is descending. NAPL migration may be limited by this depletion, or by physical barriers, such as low permeability layers. Our intent in this paper is to determine conservative NAPL concentrations in unsaturated soil, below which the NAPL will be immobile. By "conservative" we mean under-predicting the concentration at which mobility would actually occur.

PRESENCE OF A NAPL IN SOIL

For a pure chemical, NAPL will not be present at concentrations below the soil saturation limit (USEPA, 1996; ASTM E1739, PS104-98), defined as:

$$C_{sat,soil,i} = S_i \cdot \left(\frac{\theta_w + K_{oc,i} \cdot f_{oc} \cdot \rho_s + H_i \cdot \theta_a}{\rho_s} \right) \quad [1]$$

with

$C_{sat,soil,i}$ soil saturation limit for chemical i (mg/kg)

S_i pure chemical aqueous solubility limit for chemical i (mg/L)

θ_w soil water content (cm3-water/cm3-soil)

$K_{oc,i}$ organic carbon/water partition coefficient for chemical i (L-water/kg-oc)

f_{oc} mass fraction of organic carbon in soil (g-oc/g-soil)

ρ_s dry soil bulk density (g/cm³)

H_i Henry's law coefficient for chemical i (cm³-water/cm³-air)

θ_a soil air content (cm³-air/cm³-soil)

For a pure chemical, $C_{sat,soil}$ is a value above which the chemical is present in soil pore water at its aqueous solubility limit, and is present in soil pore air at its saturated vapor concentration. Equilibrium partitioning of the chemical between soil (sorbed), pore water, and pore vapors at concentrations below $C_{sat,soil,i}$ is presumed.

For mixtures of miscible chemicals that are fractionally soluble in water, including petroleum, the concentration at which NAPL will be present is a function of the mixture composition. The soil saturation limit for the mixture, using methods presented in Johnson *et al.,* (1990), Mott (1995), and Mariner (1997), is:

$$\sum_{i=1}^{N} \left(\frac{C_{sat,soil,T} \cdot \chi_i \cdot \rho_s}{S_i \cdot (\theta_w + K_{oc,i} \cdot f_{oc} \cdot \rho_s + H_i \cdot \theta_a)} \right) = 1 \quad [2]$$

with

$C_{sat,soil,T}$ soil saturation limit for the NAPL mixture, total concentration (mg/kg)

χ_i mass fraction of each chemical i in the NAPL mixture (kg/kg)

N   the number of individual chemicals in the mixture

Note that Eq. [2] simplifies to Eq. [1] for a single chemical. The component concentration of a chemical i at the soil saturation limit in a mixture is ($C_{sat,soil,T} \cdot \chi_i$). The soil saturation limit calculated for a pure chemical, in every case, will be greater than the chemical component concentration ($C_{sat,soil,T} \cdot \chi_i$) calculated for a mixture, that is:

$$C_{sat\text{-}soil,i} \geq C_{sat,soil,T} \cdot \chi_i$$

Eq. [1] overstates $C_{sat\text{-}soil,i}$ for components in a mixture because it does not consider effective vapor pressure and solubility limits (Rault's law) for the mixture components (USEPA, 1996). The soil saturation limits for mixtures (and pure chemicals) tabulated in this paper were calculated with computer codes included with DeVaull *et. al.,* (1999). This method is consistent with the references cited above.

RESIDUAL NAPL CONCENTRATION

Our intent in this paper is to define a soil concentration, $C_{res,soil}$, below which the NAPL, if present, will not migrate due to convection or gravity. This refers to a pure chemical concentration or a total chemical mixture concentration, as applicable. This residual NAPL concentration in soil is specified as:

$$C_{res,soil} = \left(\frac{\theta_o \cdot \rho_o}{\rho_s} \right) \cdot 10^6 \; \frac{mg}{kg} \quad [3]$$

with

$$\theta_o = S_r \cdot \theta_T$$

and

$C_{res,soil}$ residual NAPL concentration in soil (mg-res/kg-soil)

θ_o residual non-aqueous phase volume fraction (cm³-res/cm³-soil)

ρ_o density of chemical residual non-aqueous phase liquid (g-res/cm³-res)

ρ_s dry soil bulk density (g-soil/cm³-soil)

θ_T soil porosity (cm³-void/cm³-soil)

S_r fraction of residual non-aqueous phase filled void (cm³-res/cm³-void)

Residual non-aqueous phase volume fraction (θ_o, or retention capacity) is similarly defined by Cohen and Mercer (1990) and Zytner *et. al.,* (1993), but in dimensional units of (cm³-res/L-soil). The value of $C_{res,soil}$ is generally much larger than the soil saturation limit, $C_{sat,soil}$. Eq. [3] includes only the residual NAPL volume. Additional chemical mass within the soil matrix is contained in soil pore water and soil pore air, and is sorbed onto soil. These volumes may be included in a slightly more complicated equation consistent with the assumptions in Eqs. [1] and [2]; these terms may generally be neglected. This leaves the residual NAPL concentration in soil, $C_{res,soil}$, directly related to the residual NAPL volume fraction in soil, θ_o, or the residual NAPL fraction in the voids, S_r.

Below the residual NAPL concentration in soil, $C_{res,soil}$, capillary retention forces are greater than the gravitational forces which tend to mobilize the NAPL. These capillary forces (in this context, including surface tension effects, van der Waals, and Coulombic forces), particularly at low residual non-aqueous phase levels, may exceed the gravitational force by several orders of magnitude. The residual NAPL concentration in soil, $C_{res,soil}$, may depend on NAPL properties including liquid density, surface tension, and viscosity. It also may depend on soil properties including porosity, organic carbon fraction, moisture content, relative permeability, moisture wetting history, and soil heterogeneity.

For concentrations greater than the threshold $C_{res,soil}$ level, capillary retention forces are less than the gravitational forces, and the NAPL is mobile. Movement of NAPL in soil is beyond the scope of this paper. It is covered in a number of references, however, including Charbeneau (1999), Huntley and Beckett (1999), USEPA (1991), Cohen and Mercer (1990), and Pfannkuch (1983).

This paper describes the determination of screening values for NAPL immobility in soil. Screening values are expressed as the residual NAPL concentration in soil, $C_{res-soil}$, the non-aqueous phase volume fraction in soil, θ_o, and the residual non-aqueous phase fraction in the soil voids. Our study included a review of existing measured data on residual NAPL concentration in soil, published empirical models, and methods of field measurement.

The calculated value, $C_{sat,soil}$, as previously defined in Eqs. [1] and [2] predicts the presence or absence of a residual NAPL. Since a NAPL must be present to be mobile, it also represents a conceivable screening concentration for NAPL mobility. However, observed residual NAPL concentrations based either on laboratory measurement or physical removal of NAPL from impacted sites are typically several *orders of magnitude* higher

Table 1. Residual NAPL Concentration in Soil Compared to Soil Saturation Limit.

Name	Ref	S_r residual NAPL in the void fraction (cm^3/cm^3)	$C_{res,soil}$ residual NAPL concentration in soil (mg/kg)	$C_{sat,soil}$ soil saturation limit (mg/kg)	ρ_o liquid chemical density (g/cm^3)	MW molecular weight (g/g-mol)	S aqueous solubility (mg/L)	P_{vap} vapor pressure (mm Hg)
trichloroethylene (TCE)	a	0.2	70,000	1,045	1.46	131	1,100	75
benzene	b	0.24	53,000	444	0.88	78	1,750	95
o-xylene	c	0.01	2,000	143	0.88	106	178	6.6
gasoline	d,e	0.02 to 0.6	3,400 to 80,000	106	0.78	99	164	102
diesel	d,f	0.04 to 0.2	7,700 to 34,000	18	0.94	207	3.9	0.79
fuel oil	d,f	0.08 to 0.2	17,000 to 50,000	18	0.94	207	3.9	0.79
mineral oil	g	0.1 to 0.5	20,000 to 150,000	3	0.81	244	0.36	0.035

Notes: Unsaturated zone fine to medium sand. Nominal values $\theta_w = 0.12$ cm^3/cm^3, $f_{oc} = 0.005$ g/g in $C_{sat,soil}$ calculation.
a = Lin et al. (1982); b = Lenham and Parker (1987); c = Boley and Overcamp (1998); d = Fussell et al. (1981); e = Hoag and Marley (1986); f = API (1980); g = Pfannkuch (1984).

than $C_{sat,soil}$. The value $C_{sat,soil}$ specifies the presence or absence of a residual phase; it does not address mobility. In this effort, we have used available data to define values for $C_{res,soil}$ which can be conservatively used to screen sites for NAPL mobility. A comparison of calculated $C_{sat,soil}$ values with measured values of $C_{res,soil}$ is shown in Table 1 for selected chemicals and hydrocarbon mixtures.

The trend of $C_{sat,soil}$ in Table 1 decreases with decreasing chemical (or mixture) solubility and vapor pressure. The measured values of residual NAPL concentration in soil and residual NAPL fraction in voids do not show a similar decreasing trend. Therefore, using a calculated $C_{sat,soil}$ value as a screening level for the mobility of a residual phase becomes increasingly and significantly more conservative for less soluble, less volatile chemicals and chemical mixtures.

Screening levels for NAPL mobility consistent with the definition of residual NAPL concentration n soil, $C_{res,soil}$, have already been implemented in a number of programs. The State of Ohio [OAC 3745-300-08 Generic Numerical Standards] has promulgated rules, including values of residual NAPL concentration in soil, for several combinations of specified soil types and petroleum composition ranges. The State of Washington [WAC 173-340-747 Part VII Cleanup Standards] has proposed values based on a similar methodology. CONCAWE (1979, 1981) provides residual NAPL concentration in soil values for a range of petroleum products and soil types.

EXISTING MODELS AND METHODS
Monographs are available which detail the movement of NAPL in soils (Charbeneau, 1999; Huntley and Beckett, 1999; USEPA, 1991; Cohen and Mercer, 1993; and Pfannkuch, 1983). Several investigators have specifically developed empirical models for predicting immobile NAPL, as a residual NAPL concentration in soil, $C_{res,soil}$, for a limited number of NAPL types in various soil matrices. Summaries of two published approaches follow.

Hoag and Marley (1986) proposed an empirical method to estimate residual NAPL saturation values for gasoline in dry sand and in sand matrices containing moisture at field capacity. Their equations, which relate measured gasoline retention at residual saturation with soil particle surface area, are:

$$C_{res,soil} = \left(1.154 \cdot 10^{-2} \cdot d_p + 0.652 \cdot 10^{-3}\right) \cdot \frac{6}{2.65 \cdot d_p \cdot \rho_w} \cdot 10^6 \frac{mg}{kg} \quad [4a]$$

zero soil moisture

$$C_{res,soil} = \left(1.136 \cdot 10^{-2} \cdot d_p + 0.131 \cdot 10^{-3}\right) \cdot \frac{6}{2.65 \cdot d_p \cdot \rho_w} \cdot 10^6 \frac{mg}{kg}$$

field capacity soil moisture [4b]

with

$C_{res,soil}$ residual NAPL concentration in soil (mg-res/kg-soil)

d_p average sand particle diameter (cm)

ρ_w density of water $(g/cm^3) = 1$

Eqs. [4a] and [4b] refer, respectively, to residual NAPL concentration in dry soil and soil initially at field moisture capacity. An assumption in these equations is that the soil particles and soil surface area can be defined by an average soil particle diameter (Sauter mean diameter). These authors found that changes in soil surface area adequately predicted changes in residual NAPL saturation. Smaller soil particles have greater available surface area in a given volume or weight of soil, and the associated narrower pores will result in greater capillary forces. Residual NAPL concentration in soil therefore decreases with increasing particle size. At field capacity moisture content, measured $C_{res,soil}$ was reduced. At field capacity moisture, many of the smaller pore spaces are saturated with water. This reduces the overall pore volume available for trapping NAPL.

Eqs. [4a] and [4b] were developed using Connecticut sands sieved into three classifications; fine ($d_p = 0.0225$ cm), medium ($d_p = 0.0890$ cm) and coarse ($d_p = 0.2189$ cm). A fourth set of experiments was conducted using mixed sands with the mixture being made from equal portions of each of the above three classifications. Effectively, Eqs. [4a] and [4b] have been developed for data in the range of:

$$0.02 \text{ cm} < d_p < 0.22 \text{cm}$$

Zytner *et. al.,* (1993) correlated measured soil retention capacity with soil porosity, soil bulk density, and NAPL density. Their experiments included several NAPL types in a variety of natural soils. The soils were air dried (less than 1.5% moisture), saturated with NAPL, and then allowed to drain. Their empirical equation, for dry soils is:

$$C_{res,soil} = \left(1.05 \cdot \theta_T \cdot \frac{\rho_o}{\rho_s} - 0.15\right) \cdot 10^6 \frac{mg}{kg} \quad [5]$$

with

$C_{res,soil}$ residual NAPL concentration in soil (mg-res/kg-soil)

θ_T soil porosity (cm³-void/cm³-soil)

ρ_o density of chemical residual NAPL (g-res/cm³-res)

ρ_s dry soil bulk density (g-soil/cm³-soil)

This study was limited to air dried soils and did not specifically include sand. It does, however, show a dependence of $C_{res,soil}$ on soil porosity, θ_T, and chemical density, ρ_o.

A wide range of natural soils was used in the development of Eq. [5], including sandy loam ($\theta_T = 0.45$), clay ($\theta_T = 0.466$), organic top soil ($\theta_T = 0.555$), two different peat mosses ($\theta_T \sim 0.8$), as well as mixtures of these soils. Three NAPL types were included in their work to assess the influence of NAPL density on retention capacity: tetrachloroethene ($\rho_o = 1.622$ g/cm³), trichloroethene ($\rho_o = 1.456$ g/cm³), and gasoline ($\rho_o = 0.75$ g/cm³). $C_{res,soil}$ values obtained in their study ranged from 414,000 to 6,894,000 mg/kg for PCE, 329,000 to 5,219,000 mg/kg for TCE, and 94,000 to 2,738,000 mg/kg for gasoline. Effectively, Eq. [5] has been developed for data in the range of:

$$0.23 < \left(\theta_T \cdot \frac{\rho_o}{\rho_s} \right) < 6.7 \qquad [6]$$

The broad range of values for $C_{res,soil}$ can be attributed to the range in soil densities, from 0.2 g/cm³ (peat moss) to 1.5 g/cm³ (sandy loam).

Although the $C_{res,soil}$ measurements used in developing Eqs. [4] and [5] were conducted by different researchers using different soils, a comparison of dry fine sand data (Hoag and Marley, 1986; $\theta_T = 0.4$, and $\rho_s = 1.6$ g/cm³) with dry sandy loam data (Zytner *et. al.,* 1993; $\theta_T = 0.45$, $\rho_s = 1.5$ g/cm³) show very good agreement of $C_{res,soil}$ of 104,000 and 115,000 mg/kg, respectively, for gasoline.

MEASURED DATA AND COMPARISON WITH MODELS

Cohen and Mercer (1990) compiled measured residual NAPL saturation data from several investigators, including residual NAPL fraction in the voids, S_r, or residual NAPL volume fraction, θ_o, for a number of organic liquids and soil types. These values represent the residual amount of hydrocarbon remaining in soil pore volume after the soil was saturated with hydrocarbon and then allowed to drain. Values from Cohen and Mercer, with additional tabulated data from other references, are included in Table 2 (see pages 5 and 6). This table also includes additional values derived from the experimental data, including the residual NAPL concentration in soil, $C_{res,soil}$.

The values in Table 2 vary considerably between experiments, soil types, and chemicals. While this may be due to differences in laboratory test methods, it may also indicate the reasonable range in measured residual NAPL concentration in soils encountered between different soil types, chemical types, and measurement observations.

Calculated values for the soil saturation limit, $C_{sat,soil}$, for the indicated chemicals or chemical mixtures, are included in Table 2. These values are plotted in Figure 1. In all cases, $C_{res,soil}$ is greater than $C_{sat,soil}$. As a measure of immobile NAPL, $C_{sat,soil}$
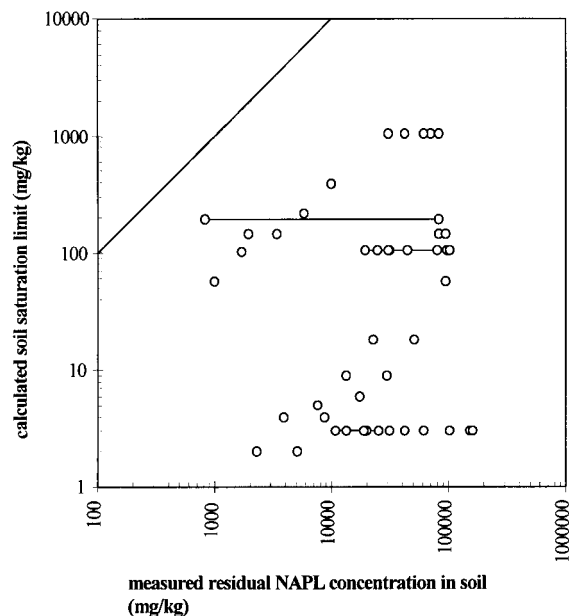

Figure 1. Comparison of data for residual NAPL concentration in soil, $C_{res,soil}$, to the calculated soil saturation limit, $C_{sat,soil}$. All plotted values are from Table 2. The solid diagonal line marks a direct correspondence between residual NAPL concentration in soil and soil saturation limit. For ranges of residual NAPL concentration in soil data in the same test series (Table 2), the upper and lower values are joined by a horizontal line. In all cases the calculated soil saturation limit is much less than the measured residual NAPL concentration in soil.
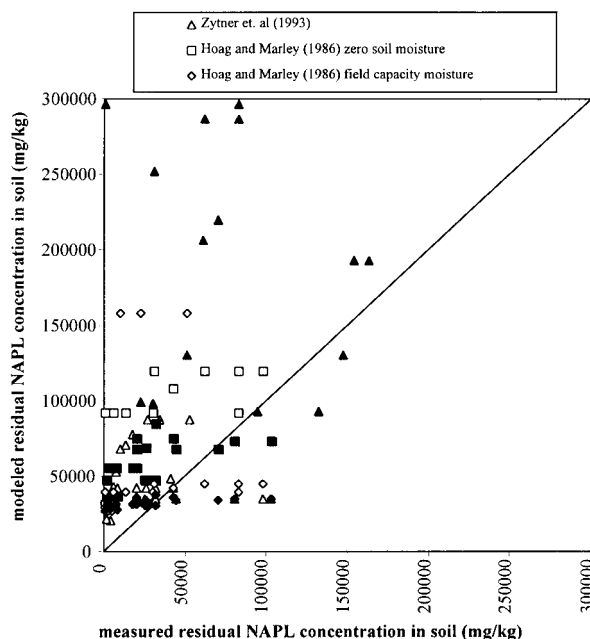

Figure 2. Comparison of data for residual NAPL concentration in soil, $C_{res,soil}$, from Table 2 to the models of Eq. [4a] Hoag and Marley (1986), zero soil moisture; Eq. [4b] Hoag and Marley (1986), field capacity soil moisture; and Eq. [5] Zytner et al., (1993). Filled points indicate the data value is within the intended range of model applicability. For ranges of residual NAPL concentration in soil data (Table 2), both the upper and lower values are shown as points. The solid diagonal line marks a direct correspondence between measured and modeled residual NAPL concentration in soil. The plot indicates that the empirical models generally predict higher residual NAPL concentration in soil than the measured values given in Table 2.

Table 2. Summary values of residual NAPL concentration in soil, $C_{res,soil}$, residual NAPL volume fraction, θ_o, and residual NAPL fraction in the voids, S_r. Calculated values for soil saturation limit, $C_{sat,soil}$, are also shown. Parameters for the calculations are shown in the second part of the table.

	NAPL	Soil Type	Ref	S_r (cm^3/cm^3)	$1000 \cdot \theta_o$ (cm^3/cm^3)	$C_{res,soil}$ (mg/kg)	$C_{sat,soil}$ (mg/kg)
					Measured		
1.	Gasoline	coarse gravel	1	0.01	2.5	1,000	57
2.	Gasoline	coarse sand and gravel	1	0.01	4	1,697	102
3.	Gasoline	medium to coarse	1	0.02	7.5	3,387	143
4.	Gasoline	fine to medium sand	1	0.03	12.5	5,833	215
5.	Gasoline	silt to fine sand	1	0.05	20	10,000	387
6.	Middle distillates	coarse gravel	1	0.02	5	2,286	2
7.	Middle distillates	coarse sand and gravel	1	0.02	8	3,879	4
8.	Middle distillates	medium to coarse	1	0.04	15	7,742	5
9.	Middle distillates	fine to medium sand	1	0.06	25	13,333	9
10.	Middle distillates	silt to fine sand	1	0.1	40	22,857	18
11.	Fuel oils	coarse gravel	1	0.04	10	5,143	2
12.	Fuel oils	coarse sand and gravel	1	0.05	16	8,727	4
13.	Fuel oils	medium to coarse	1	0.08	30	17,419	6
14.	Fuel oils	fine to medium sand	1	0.1	50	30,000	9
15.	Fuel oils	silt to fine sand	1	0.2	80	51,429	18
16.	Light oil & gasoline	soil	2	0.18	72	40,800	9 (a)
17.	Diesel & light fuel oil	Soil	2	0.15	60	34,000	NE (b)
18.	Lube & heavy fuel oil	Soil	2	0.2	80	53,067	NE
19.	Gasoline	coarse sand	3	0.15 to 0.19	61 to 77	24,954 to 31,609	106
20.	Gasoline	medium sand	3	0.12 to 0.27	48 to 109	19,767 to 44,476	106
21.	Gasoline	fine sand	3	0.19 to 0.6	76 to 240	31,065 to 98,100	106
22.	Gasoline	Graded fine-coarse	3	0.46 to 0.59	184 to 236	80,500 to 103,250	106
23.	Mineral oil	Ottawa sand	4	0.11	39	20,116	3
24.	Mineral oil	Ottawa sand	4	0.14	49	25,602	3
25.	Mineral oil	Ottawa sand	4	0.172	60	31,454	3
26.	Mineral oil	Ottawa sand	4	0.235	82	42,975	3
27.	Mineral oil	glacial till [NA]	4	0.15 to 0.28	30 to 56	13,500 to 25,200	3
28.	Mineral oil	glacial till	4	0.12 to 0.21	24 to 42	10,800 to 18,900	3
29.	Mineral oil	alluvium [NA]	4	0.19	95	61,071	3
30.	Mineral oil	Alluvium	4	0.19	95	61,071	3
31.	Mineral oil	loess [NA]	4	0.49 to 0.52	240	154,000 to 163,800	3
32.	Paraffin oil	coarse sand	5	0.12	48	27,000	
33.	Paraffin oil	fine sediments	5	0.52	229	147,086	
34.	Paraffin oil	Ottawa sand	5	0.11 to 0.23	39	20,382 to 42,618	
35.	Trichloroethene	medium sand	6	0.2	78	70,448	1045
36.	Trichloroethene	fine sand	6	0.15 to 0.2	65 to 86	62,344 to 83,125	1067
37.	Trichloroethene	loamy sand	7	0.08	33	30,713	1057
38.	Tetrachloroethene	Fine/med. beach sand	8	0.002 to 0.20	1 to 82	830 to 83,025	195
39.	O-Xylene	Coarse sand	9	0.01	3	1,936	143
40.	Gasoline	Sandy loam	10	0.42 to 0.59	189 to 266	94,500 to 132,750	
41.	Tertrachloroethene	Sandy loam	10	0.85	383	413,000	
42.	Trichloroethene	Sandy loam	10	0.75 to 0.92	338 to 412	328,000 to 401,208	

Notes: 1 = Fussell et al. (1981); 2 = API (1980); 3 = Hoag and Marley (1986); 4 = Pfannkuch (1984); 5 = Converly (1979); 6 = Lin et al. (1982); 7 = Cary et al. (1989); 8 = Poulsen and Kueper (1992); 9 = Boley and Overcamp, (1998); 10 = Zytner et al. (1993). (a) - Assumed 50:50 mixture diesel and gasoline to estimate $C_{sat,soil}$. (b) - NE = Not estimated, composition data not available. Between reported S_r or θ_o, the italicized values represent the calculated term. These values were converted to concentrations in soil using available values for NAPL density, soil bulk density and porosity, as shown in the table.

Table 2. (continued) Values for soil properties used in the calculations.

	Hydrocarbon NAPL	Soil Type	θ_T Soil Porosity (cm³/cm³)	θ_w Pore Water (cm³/cm³)	f_{oc} Fraction of Organic Carbon (f_{oc})	ρ_s Soil Bulk Density (g/cm³)	ρ_o Liquid Density (g/cm³)	d_p Soil Particle Size (mm)
1.	Gasoline	coarse gravel	0.28	0.02	0.001	1.75	0.7	2 to 4
2.	Gasoline	coarse sand and gravel	0.35	0.03	0.002	1.65	0.7	0.5 to 4
3.	Gasoline	medium to coarse sand	0.39	0.04	0.003	1.55	0.7	1 to 0.25
4.	Gasoline	fine to medium sand	0.41	0.043	0.005	1.5	0.7	0.5 to 0.1
5.	Gasoline	silt to fine sand	0.44	0.045	0.01	1.4	0.7	0.25 to 0.002
6.	Middle distillates	coarse gravel	0.28	0.02	0.001	1.75	0.8	2 to 4
7.	Middle distillates	coarse sand and gravel	0.35	0.03	0.002	1.65	0.8	0.5 to 4
8.	Middle distillates	medium to coarse sand	0.39	0.04	0.003	1.55	0.8	1 to 0.25
9.	Middle distillates	fine to medium sand	0.41	0.043	0.005	1.5	0.8	0.5 to 0.1
10.	Middle distillates	silt to fine sand	0.44	0.045	0.01	1.4	0.8	0.25 to 0.002
11.	Fuel oils	coarse gravel	0.28	0.02	0.001	1.75	0.9	2 to 4
12.	Fuel oils	coarse sand and gravel	0.35	0.03	0.002	1.65	0.9	0.5 to 4
13.	Fuel oils	medium to coarse sand	0.39	0.04	0.003	1.55	0.9	1 to 0.25
14.	Fuel oils	fine to medium sand	0.41	0.043	0.005	1.5	0.9	0.5 to 0.1
15.	Fuel oils	silt to fine sand	0.44	0.045	0.01	1.4	0.9	0.25 to 0.002
16.	Light oil and gasoline	soil	0.4	0.04	0.005	1.5	0.75	
17.	Diesel and light fuel oil	Soil	0.4			1.5	0.9	
18.	Lube and heavy fuel oil	Soil	0.4			1.5	0.9	
19.	Gasoline	Coarse sand	0.4	0.04	0.002	1.6	0.7	1 to 0.5
20.	Gasoline	Medium sand	0.4	0.04	0.002	1.6	0.7	0.5 to 0.25
21.	Gasoline	fine sand	0.4	0.04	0.002	1.6	0.7	0.25 to 0.1
22.	Gasoline	well graded fine-coarse sand	0.4	0.04	0.002	1.6	0.7	1 to 0.1
23.	Mineral oil	Ottawa sand [NA]	0.35	No water	0.002	1.7	0.9	0.5
24.	Mineral oil	Ottawa sand [NA]	0.35	No water	0.002	1.7	0.9	0.35
25.	Mineral oil	Ottawa sand [NA]	0.35	No water	0.002	1.7	0.9	0.25
26.	Mineral oil	Ottawa sand [NA]	0.35	No water	0.002	1.7	0.9	0.18
27.	Mineral oil	glacial till [NA]	0.2	No water	0.002	2	0.9	
28.	Mineral oil	glacial till	0.2	0.02	0.002	2	0.9	
29.	Mineral oil	alluvium [NA]	0.5	No water	0.002	1.4	0.9	
30.	Mineral oil	Alluvium	0.5	0.03	0.001	1.4	0.9	
31.	Mineral oil	loess [NA]	0.49	No water	0.002	1.4	0.9	
32.	Paraffin oil	coarse sand	0.4			1.6	0.9	1 to 0.5
33.	Paraffin oil	fine sediments	0.44			1.4	0.9	0.05 to 0.002
34.	Paraffin oil	Ottawa sand	0.35			1.7	0.9	0.5 to 0.18
35.	Trichloroethene	medium sand	0.39	0.04	0.003	1.6	1.46	0.5 to 0.25
36.	Trichloroethene	fine sand	0.43	0.04	0.005	1.5	1.46	0.25 to 0.1
37.	Trichloroethene	loamy sand	0.41	0.06	0.005	1.4	1.46	
38.	Tertrachloroethene	fine to medium beach sand	0.41	0.04	0.005	1.6	1.62	0.5 to 0.1
39.	O-Xylene	Coarse sand	0.33	0.04	0.003	1.6	0.88	1 to 0.5
40.	Gasoline	Sandy loam	0.45			1.5	0.75	
41.	Tertrachloroethene	Sandy loam	0.45			1.5	1.62	
42.	Trichloroethene	Sandy loam	0.45			1.5	1.46	

Notes: Porosity data and particle size information (ranges) estimated from USEPA (1991); pore water data adapted from Carsel and Parrish, (1988); f_{oc} data adapted from Wiedemeier et al., (1999).

underpredicts measured values of $C_{res,soil}$ by a factor ranging from 5 to over 50,000. As was noted in Table 1, the difference between $C_{sat,soil}$ and $C_{res,soil}$ increases with decreasing NAPL volatility and decreasing aqueous solubility.

A comparison of the data in Table 2 for residual NAPL concentration in soil, $C_{res,soil}$ to the models of Eq. [4a], [4b], and [5] is shown in Figure 2. Within the applicable range of values in the original references, both models predict values of $C_{res,soil}$ which are, on average, biased high relative to the comparable values listed in Table 2. In all cases, excepting point 38 (tetrachloroethene) in Table 2, for Eq. [4a], the model to data ratio ranges from 0.7 to 69; for Eq. [4b], the ratio ranges from 0.3 to 27; for Eq. [5], the model to data ratio ranges from 0.3 to 11. Point 38 has an exceptionally broad range of measured $C_{res,soil}$ values in the same soil.

Both the models of Zytner *et. al.,* (1993) and Hoag and Marley (1986) are correlations based on measured data. The indicated bias between the models and data of Table 2 could be due to differences in data measurements methods, or may indicate the reasonable range in variability for this type of measurement.

SCREENING VALUES FOR RESIDUAL NAPL CONCENTRATION

Based on the model to data comparisons of the last section, it is possible to specify conservative screening values for NAPL mobility based on a range of qualifying information. In many cases the screening levels will be very conservative estimates of mobility. In such cases, site-specific measurements may be used to refine the estimate, if necessary. Such measurements, for example, could include observation (or lack thereof) of floating and migrating hydrocarbon in shallow groundwater wells surrounding a known NAPL source area.
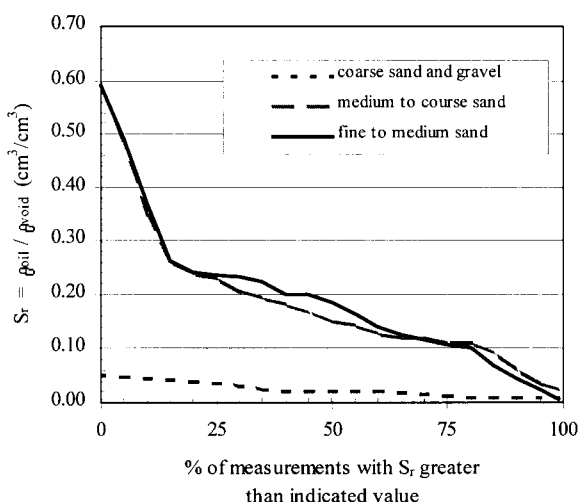

Figure 3. Cumulative distribution for measured residual NAPL void fraction, S_r, as a function of soil type. These cumulative histograms are based on the data in Table 2. Values for the "medium to course sand" and the "fine to medium sand" are very similar over the distribution. The "coarse sand and gravel" shows much lower values and narrower distribution of S_r over the range of different experiments. Tolerance limits for these distributions are given in Table 3.

Table 3. Screening values for residual phase void fraction as a function of soil type. The tabulated values are based on distributions of data from Table 2 for each soil type. The 95% statistical tolerance limit indicates that 5% of individual measurements showed lower values for S_r; the 50% tolerance limit is the median value for the soil type. The 90% tolerance limit is sufficiently conservative for most screening applications. The distribution of values is plotted in Figure 3.

Soil type	Indicated statistical tolerance limit		
	95%	90%	50%
	residual NAPL fraction in the voids, S_r, (cm³-res/cm³-void)		
coarse sand and gravel	0.01	0.01	0.02
medium to course sand	0.04	0.06	0.15
fine to medium sand	0.02	0.05	0.19

Table 4. Residual Saturation Screening Values. Values are tabulated for medium to coarse sand and represent lower limits from Table 2. If a tolerance limit is needed, or for chemicals not listed (but with densities in the range of 0.7 to 1.5 g/cm³, including petroleum products and crude oil), we suggest the use of the S_r parameters in Table 3 as screening values.

	Name	S_r residual NAPL fraction in the voids (cm³/cm³)	$C_{res,soil}$ residual NAPL concentration in soil (mg/kg)
(3.)	Gasoline	0.02	3,000
(8.)	Middle distillates	0.04	8,000
(13.)	Fuel oils	0.08	17,000
(39.)	O-xylene	0.01	2,000
(35.)	Trichloroethylene (TCE)	0.2	70,000

Note: Data row from Table 2 is indicated.

Several histograms of measured residual NAPL void fraction, S_r, as a function of soil type, are shown in Figure 3. These histograms are based on the relevant data in Table 2 and provide a basis for estimating conservative values of S_r within a specified statistical tolerance limit. Numerical values are given in Table 3. For example, with a medium to coarse sand, in specifying a screening level of $S_r = 0.06$, we would expect 90% of individual samples with equivalent NAPL concentrations below this level to be immobile in this soil type.

We expect that the tolerance limits in Table 3 and Figure 3 are biased conservatively, given that the Table 2 data showed lower residual NAPL concentration in soils than the empirical correlations of Eqs. [4] or [5]. The data in Table 2 is for NAPLs with densities ranging from about 0.7 to 1.5 g/cm³. The screening values for residual NAPL fraction in the voids, S_r, in Table 3, should be valid and reasonably conservative for this range in NAPL density.

Consolidated minimum values for S_r are shown in Table 4 for the various NAPL types in Table 2 listed as "medium sands". Again, these should be reasonably conservative screening values for NAPL mobility, for the indicated pure chemicals and hydrocarbon mixtures. No tolerance limits are specified for the Table 4 values, given the sparse data available when the screening values are qualified by both soil type and NAPL composition. If a tolerance limit is needed, or for chemicals not listed in Table 4 (with densities in the range of 0.7 to 1.5 g/cm³ including petroleum and crude oil), we suggest the use of the S_r parameters in Table 3 as screening values. A tolerance limit of 90% is reasonable in most cases.

These screening values are intended to be worst-case estimates for mobility. Higher values may be applicable on a site-specific basis. For example, with an adequate distance in unsaturated

soil between the lower depth of a mobile NAPL and groundwater, it may also be reasonable to account for potential NAPL redistribution in the unsaturated soil layer. This redistribution would decrease the concentrations of mobile NAPL to concentrations in soil equivalent. to S_r. After this redistribution, an acceptable distance between the deepest expected NAPL penetration and the historical top boundary of the water table capillary fringe must still remain.

These screening values, as already discussed, are intended for use in estimating conservative limits of NAPL mobility. The data of Table 2 may be used for other purposes, such as relating a known released volume of NAPL to an equivalent soil volume at the residual concentration level. While it is not the purpose of this paper to detail this type of calculation, the variability of an estimated residual concentration level, as illustrated in Figure 3, clearly needed to be considered.

SUMMARY AND CONCLUSIONS

Screening values describing residual saturation of NAPLs in unconsolidated vadose zone soils have been tabulated. These values are proposed for use in estimating concentrations of immobile NAPL in soil. The values, in Tables 3 and 4, are based on measured, published values for residual NAPL concentrations in soil, $C_{res,soil}$, in the unsaturated soil zone.

Another value, the soil saturation limit, $C_{sat,soil}$, has already found use as a screening level for NAPL mobility. $C_{sat,soil}$ is a calculated value estimating the presence of a residual NAPL. Data in this paper shows $C_{sat,soil}$, is a factor up to 50,000 times less than the residual NAPL concentration in soil, $C_{res,soil}$. For screening immobile NAPL concentrations the soil saturation limit is exceptionally conservative. We would instead recommend use of the values in Tables 3 and 4.

A complete site assessment, in addition, would also include evaluation of other potential transport mechanisms, including soluble dissolution into mobile soil pore water, and volatilization into soil pore air. These transport mechanisms, as noted previously, are discussed elsewhere.

Use of residual NAPL concentration in soil values for screening immobile NAPL presumes homogenous soils and soil properties. Consolidated soil matrices, macropores, and fractures will greatly affect the flow and movement of NAPL and must be recognized when these screening values are applied. Further, we note that the values have been developed using a limited data set, from multiple authors, and no attempt has been made to judge bias or error in the individual measurement techniques.

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