

Appendix 4M

Phase partitioning relationships

Soil consists of matter in several phases, exhibiting complex equilibrium relationships. For simplicity in modelling the distribution of contaminants between the various phases, it has been assumed that soil is in a steady-state equilibrium condition. In practice, phase composition and properties are constantly changing in response to changes in pressure, temperature, water content and other factors. In hydrocarbon impacted soils, depending on the type of soil, the moisture content, and the composition and quantity of the hydrocarbons, hydrocarbons may be present in following phases:

- adsorbed
- dissolved in soil moisture
- vapour
- separate phase hydrocarbon liquids.

The general arrangement of the various phases in which hydrocarbons may be present in the soil environment is presented in Figure 4M1. Where the concentration of hydrocarbons is relatively low, hydrocarbons may be present in the following phases: adsorbed, dissolved and vapour. As the concentration of hydrocarbons increases, a separate phase hydrocarbon liquid may form. Due to the relative surface tensions of the soil moisture and the liquid hydrocarbons, the hydrocarbon layer will tend to form between the water and air layers, as shown in Figure 4M1. As the hydrocarbon concentration increases the hydrocarbon layer will tend to displace the water phase from the matrix, followed by the air phase.

An equilibrium exists between the hydrocarbons in the adsorbed, dissolved, vapour and separate liquid phases in the soil. These equilibrium relationships may be represented, as shown in Figure 4M2, as graphs of the relationships between the hydrocarbon concentrations in each of these phases.

At relatively low hydrocarbon concentrations, the concentration in each phase is linearly related to the concentration in other phases, e.g. as the concentration in the adsorbed phase increases, the dissolved phase concentration increases proportionally. Similarly, as the dissolved phase concentration increases, the soil-air or vapour phase concentration increases linearly (Henry's Law). This relationship holds until the dissolved phase concentration reaches its solubility limit, at which point separate phase hydrocarbon liquids will begin to occur.

Once the solubility of the hydrocarbons in the soil moisture has been exceeded and separate phase hydrocarbon liquids have begun to form, the vapour phase concentration will remain constant for any increase in bulk concentration i.e. the vapour phase concentration is limited to that in equilibrium with the separate phase hydrocarbon mixture. It should be noted that the solubility of a compound which is part of a hydrocarbon mixture, is in water phase less than that of the pure compound by a ratio equal to the mole fraction of the compound in the mixture.

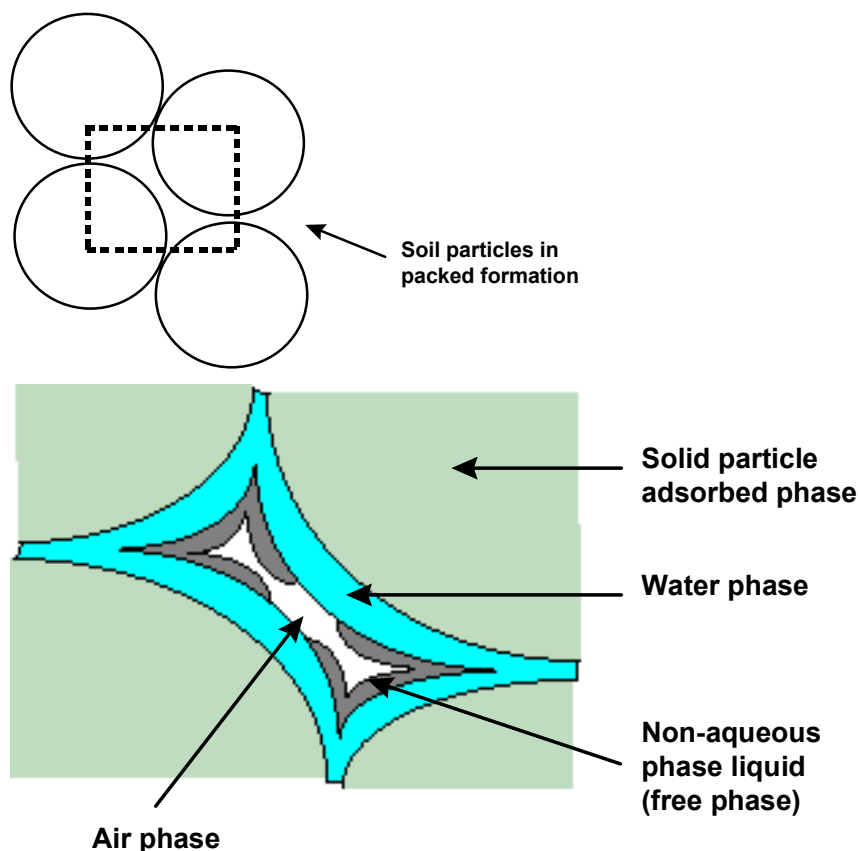


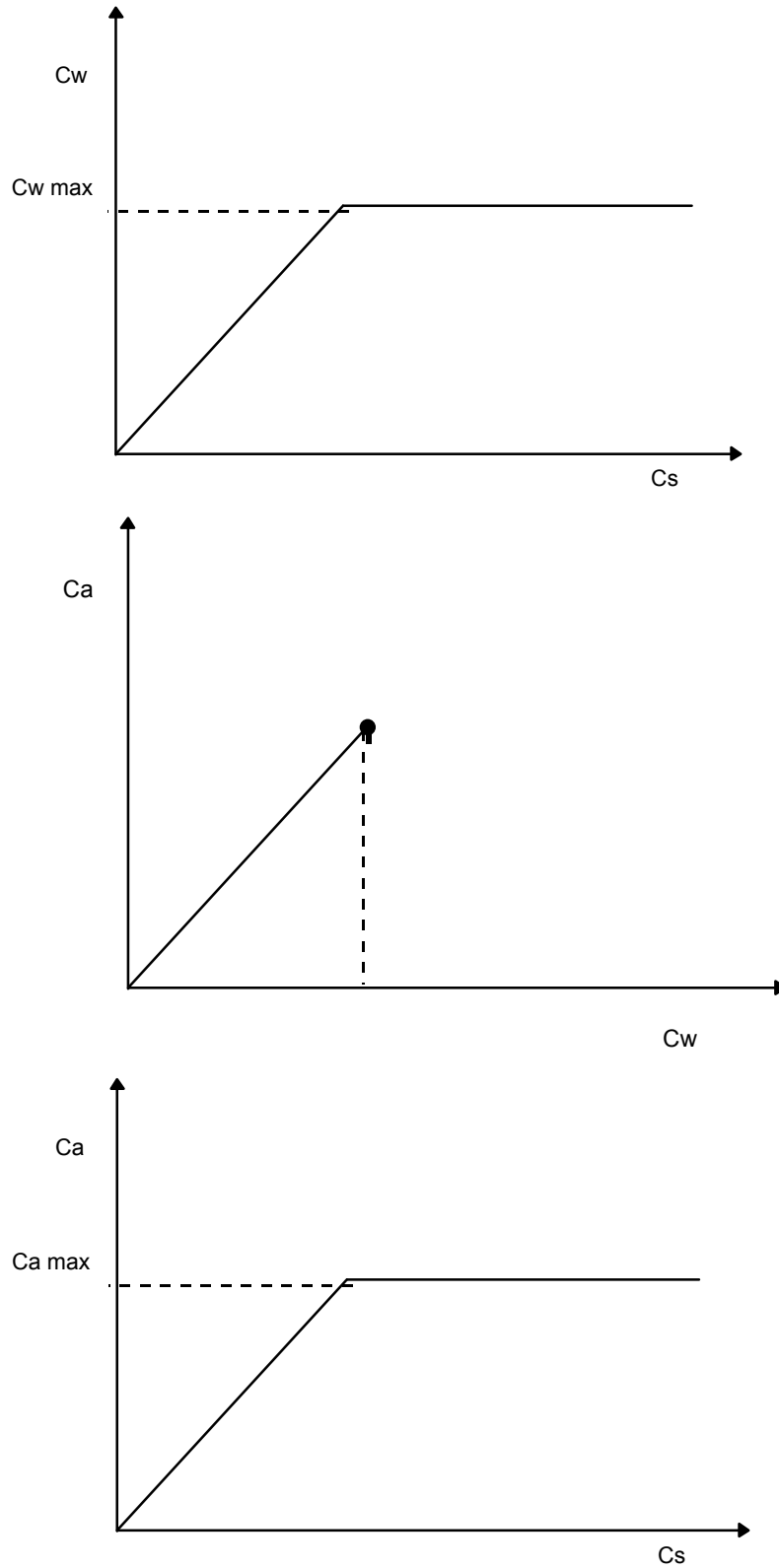
Figure 4M1 Hydrocarbon phase distribution in soils

The volatilisation model used to derive Tier 1 acceptance criteria does not account for the upper limit on the vapour phase concentration in the soil. Most volatilisation models incorporate a linear relationship between the soil, water and air phases, typical of that prior to the occurrence of separate phase hydrocarbon liquids. Hence if the soil concentration exceeds the threshold for the onset of separate phase hydrocarbon liquids, the vapour phase concentration, and hence the risk, will be overestimated.

The Tier 1 acceptance criteria tables (Tables 4.10 - 4.12 of Module 4) include criteria that are presented in brackets. These criteria exceed the threshold at which separate phase hydrocarbons may be expected to occur, and hence, are likely to overestimate the risk to human health. Similarly, for groundwater (Tables 5.9 - 5.10 of Module 5), calculated Tier 1 acceptance criteria which exceed the maximum solubility limit for a pure compound are indicated by an "S". Tier 1 acceptance criteria which are greater than the solubility of a compound in water when part of a petrol mixture are indicated with brackets. The solubility of individual components in petrol mixtures are variable as the solubility is dependent upon composition of the mixture and may be influenced by fuel type and weathering.

Table 4M1 presents typical contaminant concentrations in soil at which separate phase is likely to begin to form in the soil matrix.

Figure 4M2 Equilibrium phase relationships



Where:

- C_a = Soil-air contaminant concentration
- C_w = Water phase contaminant concentration
- C_s = Adsorbed phase contaminant concentration
- $C_w \text{ max}$ = Maximum solubility limit for contaminant (part of mixture) in water
- $C_a \text{ max}$ = Maximum soil-air concentration corresponding to maximum solubility limit

Table 4M1 Estimates of Total Concentration in Soil Corresponding to the Onset of Separate Phase^{1,2,3,4,}

Chemical	Soil concentration (mg/kg)					
	Sand	Silt	Silty Clay	Clay	Pumice	Peats
C ₇ -C ₉	150	140	110	100	210	450
C ₁₀ -C ₁₄	16	16	16	16	27	65
C ₁₅ -C ₃₆	35	35	35	35	58	140
Benzene	9.6	12	14	15	18	33
Toluene	31	33	36	37	54	120
Ethylbenzene	8.2	8.4	8.6	8.6	14	32
Xylenes	8.2	8.9	9.7	9.9	14	31
Naphthalene	120	120	130	130	210	480
Pyrene	15	15	15	15	25	60
Benzo(a)pyrene	1.4	1.4	1.4	1.4	2.3	5.6

Notes:

1. Composition based on API Document - for regular unleaded fuel.
2. Estimates directly proportional to composition mole fraction and hence values may change depending on fuel composition.
3. Refer to Table 4.7 of Module 4 for soil properties.
4. Where soil concentrations exceed values presented above then residual separate phase hydrocarbons may form within the soil matrix