Review of the Fate and Transport of Selected Contaminants in the Soil Environment

Draft Technical Report P5- 079/TR1

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Science at the Environment Agency

Science underpins the work of the Environment Agency, by providing an up to date understanding of the world about us, and helping us to develop monitoring tools and techniques to manage our environment as efficiently as possible.

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- **Providing advice**: To ensure that the knowledge, tools and techniques generated by the science programme are taken up by relevant decision-makers, policy makers and operational staff.

Professor Mike Depledge Head of Science

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EXECUTIVE SUMMARY

A specific element of the Environment Agency's R&D Programme focuses on the development of generic assessment criteria for assessing the risks to human health from chronic exposure to soil contaminants, known as Soil Guideline Values (SGVs). These are derived using the Contaminated Land Exposure Assessment (CLEA) model.

This Review of Environmental Behaviour of Selected Contaminants, R&D Technical Report P5-079/01, provides a critical review of the available data on the fate and transport behaviour of a number of contaminants for which SGVs will be derived and will enable substance-specific issues for modelling exposure to soil contamination to be identified. This report recommends physico-chemical data for use in modelling human exposure to each soil contaminant reviewed and provides comment on whether existing algorithms within the CLEA model continue to be appropriate for modelling the behaviour of the individual substances. However, the Environment Agency has not quality assured these values and recommend that prior to use these values should be quality assured. The values are recommended values at their specific experimental temperatures, however for Soil Guideline Value development these values where appropriate, have been normalised to approximate soil temperature.

A number of organic substances have been selected by the Environment Agency for review within this report. These have been selected on the basis of their toxicity to humans and occurrence on sites with land contamination. This report discusses these substances or group of substances in separate chapters. The contaminants considered are:

- Polycyclic aromatic hydrocarbons (PAHs);
- Chlorinated solvents, specifically vinyl chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, tetrachloroethane, carbon tetrachloride;
- Benzene, toluene, ethyl benzene and xylenes (BTEX); and
- Monohydric phenol (phenol).

Individual substances possess different physico-chemical properties distinguishing their differing physical form and behaviour in different media (soil, water, air). The physico-chemical properties are used to predict their fate and transport in the environment and hence are required for modelling.

For some properties, such as molecular weight, there is little variation in measurements reported in the literature. However other properties, such as log K_{ow}, may be subject to considerable variation due to differences in experimental technique, experimental conditions, or because of uncertainties introduced by estimating them from the structure by using numerical calculations. This variability may ultimately have a significant effect on the estimation of human exposure when using modelling techniques. It is therefore

important to select authoritative values. Where there is significant variation in value, the following hierarchy devised by the Environment Agency has been adhered to:

1. Authoritative values routinely used by leading researchers within the field, especially where these have already been used in other reports for the Environment Agency;
2. Values used by the European Union for their Risk Assessment Reports for existing substances;
3. Values used within the Environmental Health Criteria series of Monographs published by the World Health Organisation (WHO);
4. Values used by the United States Environmental Protection Agency (USEPA) in their derivation of Soil Screening Levels;
5. Values from authoritative peer reviewed databases, used by the above sources in the derivation of their values.

Justification for the choice of individual values is presented on a chapter by chapter basis for each contaminant or contaminant group.

The following physico-chemical parameters have been considered within this report:

- Molecular weight
- Aqueous solubility
- Vapour pressure
- Henry's Law Constant
- Octanol-water partition coefficient (K_{ow})
- Organic-carbon partition coefficient (K_{oc})
- Coefficients of diffusion in air and water
- Enthalpy of vaporisation
- Boiling Point
- Critical temperature

A table is compiled at the end of each chapter providing, where appropriate the minimum, maximum and recommended value for each of the parameters. Each chapter discusses the sources and behaviour of the substances in the soil environment. The behaviour of the substances in the soil environment addresses issues such as sorption, degradation and other chemical processes that may take place for a specific substance. This is used to inform a discussion of the implications for modelling human health pathways, including plant uptake, dermal exposure, and vapour inhalation.

1. INTRODUCTION

1.1 Technical Background

A specific element of the Environment Agency's Research and Development (R&D) Programme focuses on the development of generic assessment criteria for assessing the risks to human health from chronic exposure to soil contaminants, known as Soil Guideline Values (SGVs). These are derived using the Contaminated Land Exposure Assessment (CLEA) model described in CLR10 (Defra and Environment Agency 2002d)

The main purpose of assessing risk in situations of potential land contamination is to establish, using appropriate levels of information, whether a site poses actual or potential risks to human health or the environment which are considered unacceptable in the context within which the site is being assessed. The risk assessment procedure set out in current UK guidance (DETR, Environment Agency et al. 2002) is constructed around a tiered approach that incorporates the following steps:

- direct comparison between observed concentrations of contaminants and generic assessment criteria, which have been developed using generic assumptions about source, pathway and receptor characteristics; and

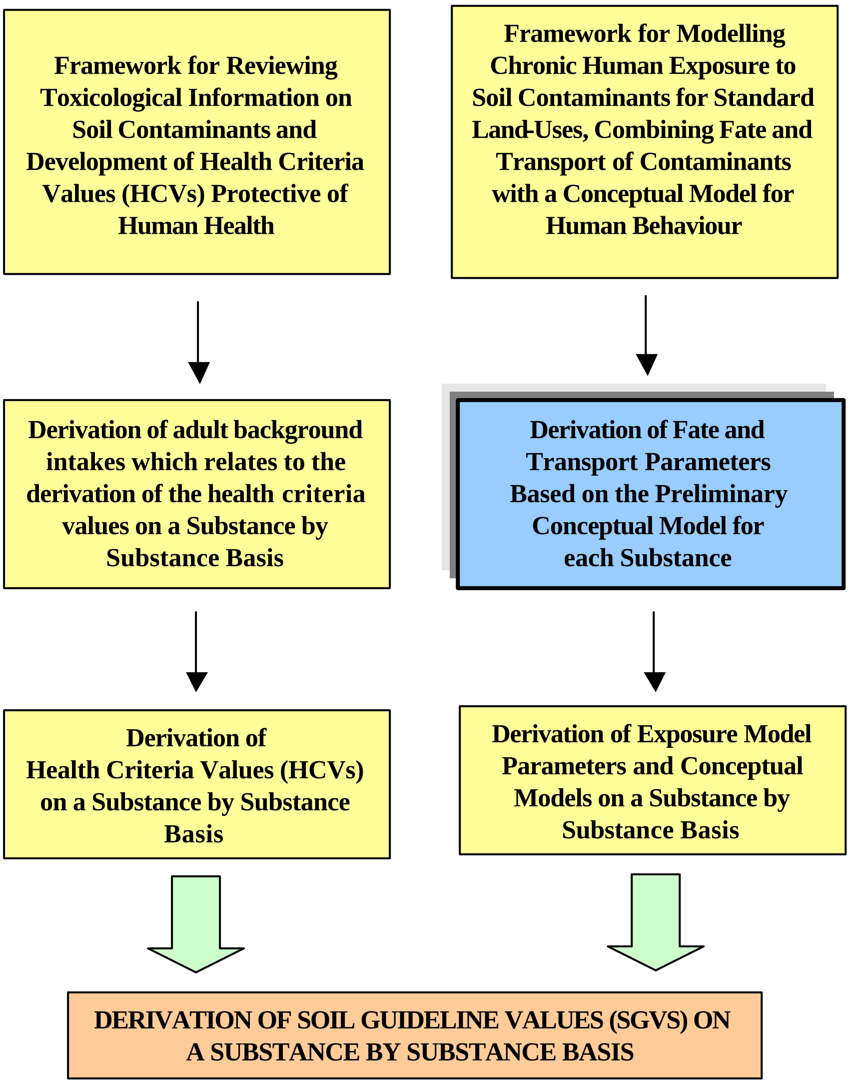
- use of modelling techniques that allow site-specific source, pathway and receptor characteristics to be taken into account in deriving risk estimates.

The generic assessment criteria to be used in the first step need to incorporate assumptions that ensure the values are protective under a wide range of anticipated conditions. Subject to the applicability of the selected values and the sufficiency of the base data, generic assessment criteria can therefore be used as "screening" values.

The research programme of the Environment Agency and Defra that supports the development of CLEA SGVs consists of five elements:

1. Setting the overall approach to establishing Index Doses and Tolerable Daily Soil Intakes (human health criteria values) for intake of contaminants derived from soil sources;
2. Setting the overall approach to estimating human exposure to soil contaminants for standard land-uses employing the CLEA model;
3. Deriving, for each individual substance or group of substances, the human health criteria values that are employed to derive SGVs for soil contaminants;
4. Deriving, for each individual substance or group of substances, the specific exposure parameters that are employed to derive SGVs for soil contaminants; and
5. Publish SGVs for each individual substance or group of substances that describe specific aspects of toxicology and exposure assessment relevant to understanding the development and use of the guideline values.

The link between the five elements in the research programme is illustrated in Figure 1.1.



Soil Guideline Value(SGV) is the Soil Concentration Where Predicted Exposure for Each Standard Land-Use is Less than or Equals the Health Criteria Value

Figure 1.1 Illustration of the link between the development of health criteria values and the human exposure model for soil contamination to derive Soil Guideline Values (SGVs).

(The blue box highlights where the work conducted in this review fits in the overall framework for the derivation of SGVs.)

1.2 Purpose of the Report

When developing SGVs, the fate and transport data of each substance, or group of substances, is reviewed to identify specific issues for modelling human exposure to soil contamination. The aim of this report is to:

- collate and critically review data on the fate and transport behaviour of a number of contaminants for which SGVs will be derived;
- recommend the physico-chemical parameters to be used for contaminants within the CLEA model fate and transport algorithms; and
- provide comment on whether existing algorithms within the CLR10 framework continue to be appropriate for modelling the behaviour of the individual substances.

The primary purpose of this report is to inform decisions made by technical specialists in the Environment Agency during preparation of SGVs using the CLEA model and to contribute to the SGV reports. The report also provides general information relevant to issues of exposure modelling not related to the CLEA model. However, it is not designed to be a step-by-step guide to carrying out detailed quantitative risk assessments (the Environment Agency is producing general guidance on conducting detailed quantitative risk assessments). This report has built on, and is consistent with, the principles of estimating exposure set out in R&D Publications CLR 7-10 developed by the Agency and Defra (Defra and Environment Agency 2002a-d).

The intended target audience is risk specialists in the public and private sectors but specifically developers, site assessors, regulators and the R&D community. It will support those assessors deriving site-specific assessment criteria for the identified substances and will assist their interpretation of the R&D Publications in the SGV series.

This report recommends physico-chemical data for use in modelling human exposure to each soil contaminant reviewed, however the Environment Agency has not quality assured these values and recommend that prior to use these value are quality assured. The values are recommended values at their specific experimental temperatures, however for Soil Guideline Value development these values where appropriate, are normalised to approximate soil temperature.

Although the primary purpose of the report is to provide information for the derivation of generic assessment criteria using the CLEA model, significant pathways which are not described in CLR10 are also included within the critical review. Examples include consumption of produce other than garden vegetables, for instance consideration of accumulation of contaminants within dairy produce and meat and fish, and volatilisation from groundwater. However, such pathways have been considered in less detail than those specifically addressed within CLR10. Similarly, processes not included when deriving SGVs using the CLEA model, such as losses to the environment (and specifically degradation), have been critically reviewed within the report but, for instance, without making recommendations for dissipation half-lives. This is because the report is intended to provide general information relevant to issues of exposure modelling not related to the CLEA model but is not designed to be a step-by-step guide to carrying out detailed quantitative risk assessments (DQRA). The individual chapters of the report have been subjected to external peer review to ensure that the most recent available information is included. It should, however, be recognised that the information contained within this report may be subject to revision based on advances in scientific understanding.

1.3 Selected Substances

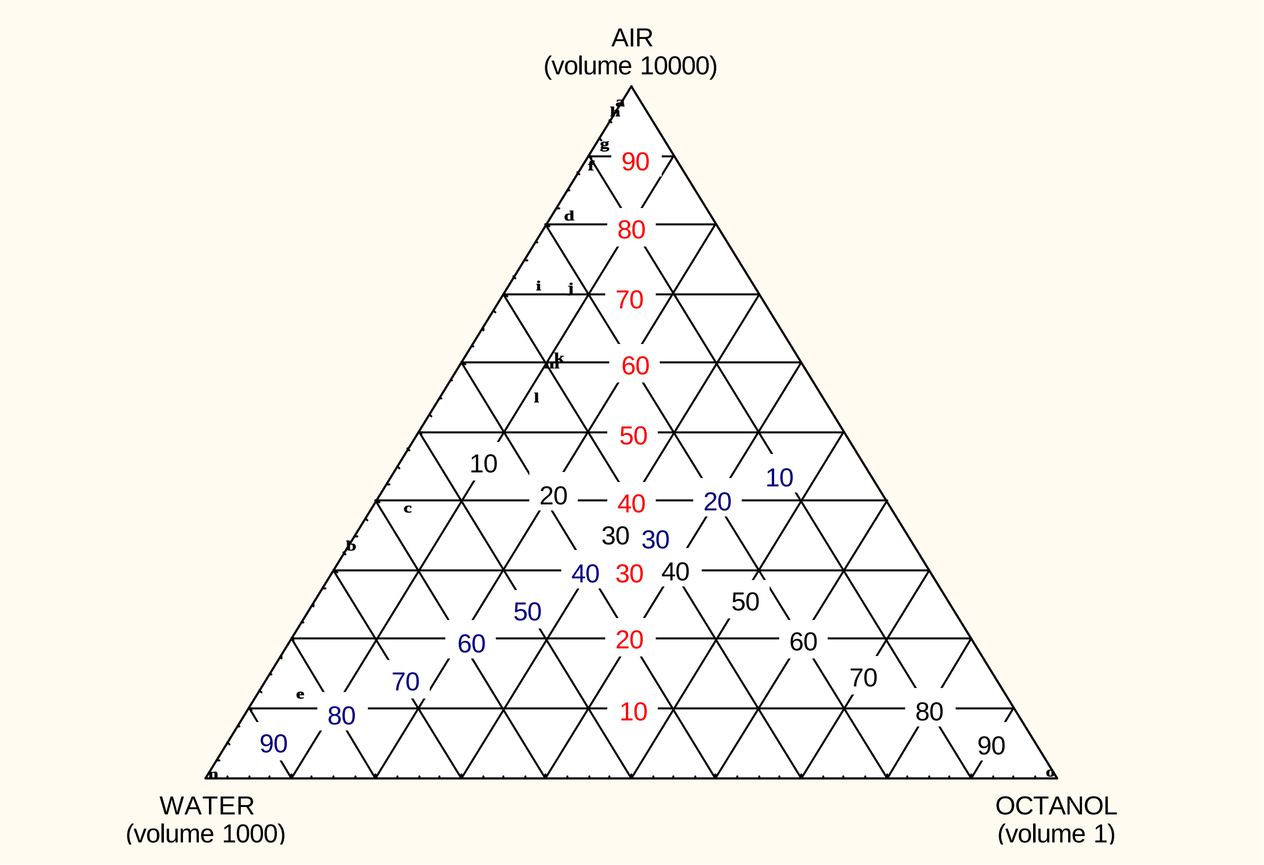
The following substances have been selected by the Environment Agency for review within this report:

- Polycyclic aromatic hydrocarbons (PAHs);
- Chlorinated solvents, specifically vinyl chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, tetrachloroethane, carbon tetrachloride;
- Benzene, toluene, ethyl benzene and xylenes (BTEX); and
- Monohydric phenol (Phenol).

These substances are amongst those identified within CLR8 (DEFRA and Environment Agency 2002b) as priority contaminants or families of contaminants “that are likely to be present on many current or former sites affected by industrial or waste management activity in the United Kingdom in sufficient concentrations to cause harm;” and that they pose a potential risk to human health. They have been prioritised on the basis that they are key organic contaminants. Similar data for other substances will be issued in future publications.

1.4 Physicochemical Properties

Physicochemical properties are particular to individual substances and describe their physical form and their behaviour in different media. They can therefore be used to predict their fate and transport in the environment. The evaluative triangle shown in Figure 1.2 (Collins C, pers. comm.) provides an example of how the relative partitioning of substances between the air, water and octanol (used to represent organic carbon, and especially lipid) can be used to predict the behaviour of a number of the contaminants considered in this review.



a = vinyl chloride,
b = 1,2-dichloroethane
c = 1,1,1-trichloroethane
d = trichloroethene
e = 1,1,2,2-tetrachloroethane
f = tetrachloroethene
g = carbon tetrachloride
h = benzene
i = toluene
j = ethyl benzene
k = m-xylene
l = o-xylene
m = p-xylene
n = phenol
o = 2,3,7,8-tetrachlorodibenzodioxin (TCDD)[1]

Figure 1.2 Evaluative Triangle, illustrated with chlorinated solvents, BTEX and phenol.

Interpretation of diagram – the scale (in %) should be read such that:

- numbers in black show increasing allocation of the compound to octanol
- numbers in red show increasing allocation of the compound to the air compartment
- numbers in blue show increasing allocation of the compound to water.

It can therefore be seen that with these compartmental volumes TCDD[1], a very hydrophobic compound, is almost totally in the octanol compartment, phenol totally in the water compartment and vinyl chloride in the air compartment. The other compounds of interest generally partition to air and water with little allocation to octanol. It can be proposed therefore that they would only weakly partition to soil.

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[1] This contaminant has not been discussed within the report and used for comparison purposes only

For some properties, such as molecular weight, there will be very little variation in measurements reported in the literature. However other properties, such as K_{ow}, may be subject to considerable variation due to differences in experimental technique, experimental conditions, or because of uncertainties introduced by estimating them from the structure. This variability may have a significant effect on the estimation of human exposure when using modelling techniques – see Sensitivity Analysis for the CLEA model (Environment Agency 2002b). It is therefore important to select authoritative values. Where there is significant variation in value, the following hierarchy has been broadly followed:

1. Authoritative values routinely used by leading researchers within the field, especially where these have already been used in other reports for the Environment Agency;

2. Values used by the European Union for their Risk Assessment Reports for existing substances;

3. Values used within the Environmental Health Criteria series of Monographs published by the World Health Organisation (WHO);

4. Values used by the United States Environmental Protection Agency (USEPA) in their derivation of Soil Screening Levels; and

5. Values from authoritative peer reviewed databases, used by the above sources in the derivation of their values.

Justification for the choice of individual values is presented on a chapter by chapter basis for each contaminant or contaminant group. The following physicochemical parameters have been considered:

- Molecular weight
- Aqueous solubility
- Vapour pressure
- Henry's Law Constant
- Octanol-water partition coefficient (K_{ow})
- Organic-carbon partition coefficient (K_{oc})
- Coefficients of diffusion in air and water.
- Enthalpy of vapourisation
- Boiling Point
- Critical temperature

The following section provides a brief explanation of each parameter, including a description of how it can be derived, its use in the CLEA model and its use in exposure modelling in general.

1.4.1 Molecular Weight

The molecular weight (MW) is usually quoted in g mol^{-1} of a substance. The term is often used interchangeably in the literature with relative molecular mass (RMM or Mr). It is calculated from the relative atomic masses of the individual elements involved and therefore any apparent variation is usually at the second or third decimal place and insignificant in exposure modelling terms. Molecular weight is sometimes used in exposure modelling to predict movement of substances through a membrane. For instance the work of Topp, Scheunert *et al*. (1986) relates uptake of organic chemicals into plants to molecular weight, and it can be used in algorithms for predicting the dermal absorption of chemicals from water (USEPA 2001c). MW is used within the current version of the CLEA model (Defra and Environment Agency 2002d) to predict dermal absorption of chemicals from soil, after an approach devised by USEPA (1992). It is also used, together with vapour pressure and solubility, to estimate Henry's Law Constant when there is no experimentally derived value.

1.4.2 Boiling Point

The boiling point is the temperature at which the saturated vapour pressure of a liquid is equal to the external atmospheric pressure and is dependent on atmospheric pressure. An increase in pressure has the effect of significantly raising the boiling temperature. Boiling point, within the CLEA model, is given in units of degrees Kelvin and is used in the calculation of the enthalpy of vapourisation as outlined in section 1.4.9.

Literature values are most commonly quoted in degrees centigrade (°C) therefore requiring a conversion whereby a temperature in K equals that in °C plus 273.15.

1.4.3 Aqueous Solubility

The aqueous solubility expresses the mass of a substance that will dissolve completely in a given volume of water. It is temperature dependent. It is important to note that laboratory solubility is measured in distilled water and that this may differ from aqueous solubility in natural waters (Fetter 1993). This is because solubility in natural waters (for instance soil pore water) may be influenced by the presence of other substances.

Generally substances with a high aqueous solubility, such as phenol, will tend to partition to the water compartment, and have lower octanol-water and air water (Henry's Law) partition coefficients, as shown in the evaluative diagram in Figure 1.2. In contrast substances such as TCDD partition almost totally to the octanol compartment and have little appreciable aqueous solubility.

Aqueous solubility is currently used within the CLEA model to estimate the Henry's Law Constant, where measured values are not available.

Aqueous solubility is usually given in units of mg l^{-1} (equivalent to gcm^{-3}). Within the CLEA model the units of mg l^{-1} are required and have been used throughout this report. Solubility is usually given in the literature at temperatures of between 20 and 25°C, and this is the temperature range for which solubility has been reported within this document.

1.4.4 Vapour Pressure

Vapour pressure is defined as “a measure of the tendency of a substance to pass from a solid or a liquid to a vapour state. It is the pressure of the gas in equilibrium with the liquid or the solid at a given temperature. The greater the vapour pressure, the more volatile the substance” (Fetter 1993).

The vapour pressure is used within the CLEA model, together with the aqueous solubility, to estimate the Henry’s Law Constant where measured values are not available. It may also be used within risk assessment tools to estimate the point at which saturation of the porewater with an organic substance is likely to occur.

There are a number of different units of vapour pressure. The SI units are Pascal (Pa) but atmosphere (atm) or Torr/mm mercury (mm Hg) are all also found within the literature.

The conversion between these units is shown below:

1 mmHg (1 Torr) is 133.3 Pa

1 atm is 101325 Pa

However, it should be noted that some literature sources use a conversion of 101300 (sometimes presented as 101.3 kPa), and that this value, combined with the rounding involved in presenting Pa as kPa, may create an artificial variation of approximately 5% in reported vapour pressures.

The unit required for vapour pressure within the CLEA model is Pa. In each chapter of this report the vapour pressure is therefore presented in the original reported units and in Pa.

1.4.5 Henry’s Law Constant

Henry’s law states “there is a linear relationship between the partial pressure of a gas above a liquid and the mole fraction of the gas dissolved in the liquid” (Fetter 1993). The law is obeyed provided that there is no chemical reaction between the gas and the liquid.

Understanding the partitioning between the water and air compartments is key to an understanding of the fate and transport behaviour of compounds, because it relates to subsurface behaviour (volatilisation from groundwater and soil pore water into soil air) as well as behaviour at the surface (volatilisation into air in the boundary layer). For instance (Bromilow and Chamberlain 1995) consider that the Henry’s Law constant is an indication of the route by which plant uptake of contaminants will occur. They state that chemicals with low Henry’s Law Constants will be taken up by the routes from the aqueous phase, those with high Henry’s Law Constants will be taken up predominantly from the vapour phase and those with constants of intermediate value will be taken up by both routes. Henry's Law Constant is generally used to model volatilisation from soil pore water and groundwater into outdoor and indoor air and bathroom air while showering. It may also be used in plant uptake modelling (e.g. Trapp and Matthies 1995). Henry's Law Constants are currently used within the CLEA model in the approach to outdoor and indoor vapour modelling (Defra and Environment Agency 2002d).

The Henry's Law Constant can either be expressed as the proportionality constant between the two properties (expressed in units of pressure / (mol m^{-3} of water)) or an air-water partition coefficient. The latter is the ratio of the aqueous solubility of a substance (mass per volume of water at a given temperature), to the saturated vapour concentration of the pure phase of the substance, and is expressed in volume per volume (cm^3/cm^3 i.e. dimensionless). A rise in temperature favours the gaseous state.

The proportionality constant is often quoted in units of atm-m^3 mol^{-1}. The units required for the CLEA model are Pa-m^3 mol^{-1}. 1 atm is 101325 Pa (see note under vapour pressure above on the effect of rounding).

Henry's Law Constant may either be determined experimentally or calculated from the solubility and vapour pressure. The approach of estimating Henry's Law Constant from solubility and vapour pressure is used in the Dutch Intervention Values (RIVM, Rikken et al. 2001c). However, others such as the EUSES methodology (EU 1996) and USEPA use experimental data where available. Ryan *et al.* (1988) state that they consider experimentally derived values for Henry's Law Constant to be more reliable than calculated values. In this report, the hierarchy of data described in section 1.4 is followed, and whether the Henry's Law Constant is experimental or calculated will depend on the data source. However, where there is no single authoritative data source, the preference has been to use experimentally derived values.

The exact method of calculating Henry's Law Constant from vapour pressure and solubility depends on the stage at which the temperature dependence is taken into account and the units used for solubility. For clarity, because calculated Henry's Law Constants are taken from different sources, the methods and units used by both USEPA (1996a) and RIVM, Rikken *et al.* (2001c) are shown.

USEPA (1996a) use the following calculation:

$$HLC = \frac{VP \cdot MW}{S}$$

Where:

HLC is Henry's Law Constant (atm-m^3 mol^{-1})
VP is vapour pressure (atm)
MW is molecular weight (g mol^{-1})
S is solubility (mg l^{-1}) at a given temperature.

The dimensionless form of the Henry's Law Constant (cm^3/cm^3) is obtained by multiplying a value in units of atm-m^3 mol^{-1} by 41 (USEPA 1996a). Thus to convert a value in units of Pa-m^3 mol^{-1} into the dimensionless form requires a division by 101325, followed by multiplication by 41.

Strictly speaking, Henry's Law Constants should be adjusted according to the temperature of the soil/groundwater system. The dimensionless form of the Henry's Law Constant at the temperature of the system may be estimated using the Clapeyron equation (USEPA 2000), according to the equation below: (the multiplication by 41 employed within USEPA (1996a) is a simplification of this equation for room temperature).

$$H_{TS} = \frac{\exp\left[-\frac{\Delta H_{v,ts}}{R_C}\left(\frac{1}{T_s}-\frac{1}{T_R}\right)\right]H_R}{RT_s}$$

Where:

H'$_{TS}$ is the Henry's Law Constant at the system temperature, dimensionless
ÄH$_{v,ts}$ is the enthalpy of vapourisation at the system temperature, cal mol^{-1}
T$_S$ is the system temperature, K
T$_R$ is the Henry's Law Constant reference temperature, K
H$_R$ is the Henry's Law Constant at the reference temperature atm-m^3 mol^{-1}
R$_C$ is the Gas constant (1.9872 cal/mol- K)
R is the Gas constant (8.205x10^{-5} atm-m^3/mol- K)

The calculation of the enthalpy of vapourisation at the system temperature is discussed below.

The EU Technical Guidance Document for risk assessment uses experimental values where available (usually taken from the Syracuse database) (EU 1996).

The dimensionless form of the Henry's Law Constant is related to the dimensioned form by the following equation:

$$H' = \frac{H}{RT}$$

Where:

H' is dimensionless Henry's Constant
H is Henry's Law Constant (Pa-m^3 mol^{-1})
R is gas constant (8.3144 Pa-m^3 mol^{-1} K^{-1})
T is Environmental temperature (K)

EU (1996) states that where no experimental values are available Henry's Law Constants should be calculated from solubility and vapour pressure.

RIVM, Rikken *et al.* (2001c) provide the following relationship for this calculation.

$$H = \frac{Vp}{S \cdot R \cdot T}$$

Where:

H is Henry's Law Constant (dimensionless)
Vp is vapour pressure (Pa)
S is water solubility (mol-m^{-3})
R is gas constant (8.3144 $\text{Pa-m}^3.\text{mol}^{-1}.\text{K}^{-1}$)
T is soil temperature (K).

Ryan *et al.* (1988) cite the volatilisation categories of Jury, Farmer *et al.* (1984) according to dimensionless Henry's Law Constants. These are:

- $2.5\text{x}10^{-3}$ (6.2 $\text{Pa-m}^3.\text{mol}^{-1}$) and above – likely to volatilise easily from soil solution;
- $2.5\text{x}10^{-5}$ ($6.2\text{x}10^{-2}$ $\text{Pa-m}^3.\text{mol}^{-1}$) and above – moderate tendency to volatilise from soil solution; and
- $2.5\text{x}10^{-7}$ ($6.2\text{x}10^{-4}$ $\text{Pa-m}^3.\text{mol}^{-1}$) and above – unlikely to volatilise from soil solution.

1.4.6 Octanol-water Partition Coefficient (K_{ow})

The octanol-water partition coefficient (K_{ow}) has been defined as "a measure of the degree to which an organic substance will preferentially dissolve in water or an organic solvent" (Fetter 1993). It may be experimentally derived for a substance by mixing it with equal amounts of water and octanol (an eight carbon chain alcohol), treated as a surrogate for organic solvents and other organic material, including tissues and lipids. It is therefore frequently used to provide an indication of tendency to bioaccumulate. The coefficient is the ratio of the substance in octanol to the ratio of the substance in water, once equilibrium has been reached. Thus, the higher the value, the greater the tendency of the substance to dissolve in octanol rather than in water. The K_{ow} is usually presented as a logarithm (i.e. log K_{ow}).

The log K_{ow} has been extensively used within environmental modelling as a surrogate for organic content within plants (e.g. Briggs, Bromilow *et al.* 1982, Briggs, Bromilow *et al.* 1983 and Travis and Arms 1988), and lipid content within dairy products (e.g. Travis and Arms 1988), animal fat (e.g. Travis and Arms 1988) and human skin (e.g. McKone and Howd 1992). Indeed some of the more simple empirical relationships for plant uptake are based on log K_{ow} (e.g. Travis and Arms 1988, Briggs, Bromilow *et al.* 1982, Briggs, Bromilow *et al.* 1983). This is because lipophilicity determines how easily substances move across plant membranes, and to what extent they will partition onto plant solids, limiting long-distance transport (Bromilow and Chamberlain 1995). For instance Briggs, Bromilow *et al.* (1983) considered that concentrations of contaminants in above ground plants would increase with increasing log K_{ow} up to a certain point because of the increasing absorption by the stem tissues and then decrease because of the decrease in transfer from the roots. Ryan *et al.* (1988) adjusted the optimum log K_{ow} downwards for uptake of contaminants from soil.

Currently log K_{ow} is used within the CLEA model to predict exposure from the following pathways, as described within CLR10 (Defra and Environment Agency 2002d) and USEPA (1992):

- Plant uptake of organic contaminants using the Briggs and Ryan empirical relationship; and
- Dermal uptake from soil.

However both these approaches are currently subject to review and may change in the near future.

Log K_{ow} is also used to estimate the partition coefficient for organic carbon (K_{oc}) in the absence of experimental data (see section 1.4.7).

Low log K_{ow} tends to indicate high polarity and aqueous solubility, whereas high log K_{ow} is an indication of highly lipophilic substances, usually with low aqueous solubility, as demonstrated in the evaluative triangle in Figure 1.2. Bromilow and Chamberlain (1995) consider that a log K_{ow} of 1 to 3 indicates "intermediate lipophilicity" and that a log K_{ow} of above 4 is "very lipophilic" (although in another part of the same chapter they define log K_{ow} of 2 to 4 as moderately lipophilic). In the context of this report substances of log K_{ow} of <2 (such as phenol and 1,2-dichloroethane) are considered to have low to moderate lipophilicity, those with log K_{ow} of 2-4 (such as carbon tetrachloride, BTEX compounds and naphthalene) are considered to be moderately lipophilic to lipophilic and those with a log K_{ow} above 4 (for instance most of the PAHs) are considered to be highly lipophilic.

The experimental methods that are traditionally used are either simple shake-flask methods or high pressure liquid chromatography (HPLC) on silica columns coated with octanol. For compounds with a log K_{ow} above 4, difficulties presented by these methods mean that alternative indirect methods, such as reverse phase HPLC on octadecylsilica columns, may be used (Bromilow and Chamberlain 1995). Where the log K_{ow} has not been experimentally derived for a given substance, it may be estimated using QSPR (quantitative structure property relationships) techniques. For instance, RIVM, Rikken *et al.* (2001c) recommends using specialist software to calculate log K_{ow} values for which experimental data are not available. Bromilow and Chamberlain (1995) state that for estimates conducted in this way to be accurate, there should be measured baseline data for one compound of that particular structural type.

There is often significant variation in literature values for K_{ow} for a particular compound. Karickhoff, Brown *et al.* (1979) state that this may be over several orders of magnitude, especially for K_{ow}s of 10^4 or greater (log K_{ow} of 4 or greater). They consider the variation to be largely due to the experimental process and attribute it to the following sources:

- Presence of impurities, especially those more water soluble than the parent compound (which may reduce the K_{ow});
- Compound loss from the water phase during phase separation and analysis, especially for hydrophobic organics; and
- Contamination of water-phase sample with octanol in excess of the equilibrium value.

In addition they noted that smaller changes in K_{ow} could occur as a result of compound concentration, especially near to saturation.

1.4.7 Organic-Carbon-Water Partition Coefficient (K_{oc})

The organic carbon partition coefficient (K_{oc}) expresses the tendency of a compound to be adsorbed onto the organic carbon within the soil i.e. the partitioning of the solute between soil water (l) and organic carbon (kg). It may be measured as the ratio of the mass of chemical sorbed per unit mass of soil to the mass of chemical in the soil water. This ratio is then divided by the mass of organic carbon per unit mass of soil, and is usually given in units of l water per kg organic carbon ($l.kg^{-1}$, or $cm^3.g^{-1}$). K_{oc} values may be presented as a logarithm. Both forms are shown in this review.

K_{oc} is widely used in exposure modelling to predict sorption to soil and plant material and the consequent likelihood of substances being available to volatilise or pass through the skin. It is currently used within the CLEA model within the algorithms for dermal uptake, plant uptake, and inhalation for outdoor and indoor vapour.

Gustafson *et al.* (1997) cite Lyman, Reidy *et al.* (1992) in that the range of K_{oc} values varies from 1 to 10,000,000. Of the substances considered in this review, some of the chlorinated solvents have the lowest K_{oc} values (less than 100, i.e. log K_{oc} of 2), some of the PAHs have a K_{oc} of over 1,000,000 (i.e. log K_{oc} of 6) and some of the dioxins and PCBs have K_{oc} values at the very maximum of the range quoted by Lyman.

K_{oc} may be measured in the field or laboratory, or calculated from measured K_{ow} values. Considerable variation for measured values of K_{oc} is noted in the literature for individual compounds, even once normalisation for soil organic carbon has been performed. Gustafson *et al.* (1997) note that this may be due to a number of factors, including:

- Errors in the analytical method;
- Uncertainty in input data;
- Variability in soil and sediment conditions, such as pH, temperature and ionic concentration; and
- Extrapolations which assume a linear isotherm and reversible adsorption (neither of which is necessarily true).

They observed that method errors are usually less than an order of magnitude but occasionally may be as high as two orders of magnitude.

Calculation of K_{oc} from K_{ow} has the advantage that there is consistency, in that both values are from a single source and methodology. However, individual soil properties are not taken into account. RIVM, Rikken *et al.* (2001c) recommends the use of measured values, although calculated values were used for the derivation of the current set of Dutch Soil Intervention Values. The Technical Guidance Document for conducting EU risk assessments (EU 1996) also recommends the use K_{oc} values estimated from K_{ow}.

Currently, CLR10 recommends the use of experimental values, in the absence of such values assessors are advised to use empirical relationships such as that of Karickhoff (1984).

The relationship used within the Dutch Intervention Values is that of Karickhoff (1981):

$$K_{oc} = 0.411 \cdot K_{ow} \text{ (RIVM 2001).}$$

USEPA (1996a) used the relationship of Di Toro (1985) for the derivation of log K_{oc} from log K_{ow} for most semi-volatile non-ionising organic compounds because it considers particle interactions. The relationship is shown below:

$$\text{Log } K_{oc} = 0.00028 + (0.983 \cdot \log K_{ow}).$$

USEPA (1996a) found that for volatile contaminants, the usual relationships between log K_{ow} and log K_{oc} did not hold for their experimental data from soils and sediments. They therefore derived a new relationship for volatile contaminants which fitted their data:

$$\log K_{oc} = 0.0784 + (0.7919 \cdot \log K_{ow}).$$

Ryan, Bell *et al.* (1988) cite a number of other relationships, including the relationship of Karickhoff (1981) and those of Schwarzenbach and Westall (1981) and Rao, Davidson *et al.* (1982) but conclude, “these relationships are surprisingly similar to one another considering they cover over 100 chemicals, as well as a large number of soils and sediments”.

Gustafson *et al.* (1997) use the mean of a range of relationships presented in Lyman, Reehl *et al.* (1982 and 1990) and Olsen and Davis (1990) for their prediction of K_{oc} for total petroleum hydrocarbons.

The EU risk assessment reports derive K_{oc} from K_{ow} according to a range of relationships, varying according to class of compound as recommended in the Technical Guidance Document (EU 1996). These relationships are taken from an overview prepared by Sabljic and Gusten (1995) for an EU funded project. The relationships for the classes of compound considered in this report are reproduced below:

- Predominantly hydrophobics $\log K_{oc} = 0.81 \log K_{ow} + 0.10$
- Nonhydrophobics $\log K_{oc} = 0.52 \log K_{ow} + 1.02$
- Phenols $\log K_{oc} = 0.57 \log K_{ow} + 1.08$

Where physicochemical properties have been taken from European risk assessment reports, these relationships will have been used to calculate log K_{oc}.

The recommendation of this report is that, where possible, SGVs are derived using a K_{oc} derived directly from the K_{ow}. This is because values of K_{oc} taken from the experimental literature will vary according to soil properties and SGVs may be developed for different soil types and conditions. The relationship used will depend on the data source which has been selected for each contaminant. The preference has been not to use calculated K_{oc} from USEPA because it is considered that the wide range of sediments and soils considered may differ from those in the UK. Calculated values from other sources, or experimentally derived values for appropriate soils, have been given preference within this report. By contrast, where possible, it is recommended that site-specific log K_{oc} values are measured for use in Detailed Quantitative Risk Assessment (DQRA).

1.4.8 Coefficients of Diffusion in Air and Water

The coefficient of diffusion in air (sometimes referred to as the diffusivity in air) has been defined as "a measure of the diffusion of a molecule in a gas medium as a result of intermolecular collisions. It is not a measure of turbulence or bulk transport (apparent diffusion)." Gustafson *et al.* (1997) also cited Lyman, Reehl *et al*. (1982 and 1990) in that molecular diffusion could become significant at air-water interfaces.

The coefficient of diffusion in water will therefore be a measure of the diffusion of a molecule in an aqueous medium. Gustafson *et al.* (1997) state that it is a function of the solute size, temperature and solution viscosity and is not a sensitive parameter.

The coefficients of diffusion are used in exposure modelling to calculate the effective diffusion coefficient through the soil. They are currently used within the CLEA model to calculate exposure via the dermal and inhalation pathways (Defra and Environment Agency 2002d).

Coefficients of diffusion are usually given in units of area/units of time. Units of $cm^2\ sec^{-1}$, $m^2\ sec^{-1}$ or $m^2\ hr^{-1}$ are found within the literature. The CLEA model requires units of $m^2\ sec^{-1}$.

Coefficients of diffusion in air for common soil contaminants usually appear to fall between 1 and $9x10^{-6}\ m^2\ sec^{-1}$. Within this review, however, vinyl chloride and 1,2-dichloroethane have extremely high values of approximately $1x10^{-5}\ m^2\ sec^{-1}$. The lowest coefficients of diffusion are exhibited by some of the PAHs, e.g. dibenz(a,h)anthracene, benzo(b)fluoranthene and benzo(k)fluoranthene have diffusion coefficients of $2x10^{-6}\ m^2\ sec^{-1}$.

Coefficients of diffusion in water are usually between 1x10^{-10} and 1x10^{-9} m^2 sec^{-1}. Within the substances considered within this review, a very high value is exhibited by *o* xylene (approximately 1x10^{-9} m^2 sec^{-1}), while, perhaps surprisingly, a very low value (approximately 1x10^{-10} m^2 sec^{-1}) is exhibited by vinyl chloride.

Coefficients of diffusion may be measured or estimated. Where it has not been possible to retrieve literature values, the methods used within Lyman *et al.* (1990) have been followed. These have been used to derive coefficients of diffusion within a previous report providing physicochemical properties for explosive substances Environment Agency (2000a) and are therefore considered appropriate for use here.

For air:

$$D_A = \frac{10^{-3} \cdot T^{1.75} \cdot \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2}$$

Where :

D_A is the coefficient of diffusion in air (cm^2 sec^{-1})
T is temperature (K)
M_r is $(M_A + M_B)/ M_A M_B$
M_A, V_A is the molecular weight and molar volume of air
M_B, V_B is the molecular weight and molar volume of the chemical of interest
P = Pressure (atm)

For water:

$$D_L = \frac{13.26 \text{ x } 10^{-5}}{n_w^{1.14}\, V'^{\,0.589}_B}$$

Where:

D_L is the coefficient of diffusion in water (cm^2 sec^{-1})
n_w is the viscosity of water
V'_B is the molar volume using the LeBas method.

1.4.9 Enthalpy of vapourisation

The enthalpy of vapourisation is also referred to as the latent heat of vapourisation and is the energy required to convert 1 mole of a liquid into 1 mole of a gas at a certain temperature and pressure. It is given in units of either kJ.mol^{-1}or cal.mol^{-1}.

$$\triangle H_{v,TS} = \triangle H_{v,b} \left(\frac{1- T_S/T_C}{1- T_B/T_C} \right)^n$$

Where:

Ä$H_{v,TS}$ is the enthalpy of vapourisation at the system temperature (cal.mol^{-1})
Ä$H_{v,b}$ is the enthalpy of vapourisation at the normal boiling point (cal.mol^{-1})

T_S is the system temperature (K)
T_C is the critical temperature (K)
T_B is the normal boiling point (K)
'n' is a constant (dimensionless).

Values of exponent 'n' as a function of T_B/T_C are after USEPA (2000):

- If $T_B/T_C < 0.57$, n= 0.30
- If $T_B/T_C = 0.57\text{-}0.71$, $n=0.74 (T_B/T_C) - 0.116$
- If $T_B/T_C = >0.71$, n = 0.41.

1 calorie = 4.184 J. Calories can be converted to kJ by multiplying by 4.184 and dividing by 1000.

The enthalpy of vapourisation is used to calculate the dimensionless Henry's Law Constant at the temperature of the soil/groundwater system.

1.4.10 Literature minima and maxima

For each parameter for each chemical, a minimum and maximum value is given in the main table in each chapter. It should be noted that these values have not been obtained from the same source or same experimental protocol. They have been presented to provide an indication of the range of values that have been reported.

2. POLYCYCLIC AROMATIC HYDROCARBONS

2.1 Introduction

The polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of two or more fused benzene ring structures in various arrangements (WHO 1998a, USEPA 1999a). The majority of PAHs in the environment are present as a consequence of their release as by-products from incomplete combustion processes (natural and anthropogenic).

The assessment of human health risks from PAHs is frequently undertaken using the most toxic components, typically benzo(a)pyrene, as marker compounds. Where concentrations of these more toxic compounds are within acceptable levels (CoT 2001) this will be protective of exposure to all PAHs. However, it is now realised that there may not be a direct relationship between exposure to benzo(a)pyrene and exposure to other compounds (e.g. Hietaniemi 1996). Further, there may be occasions where there may not be significant exposure to benzo(a)pyrene, but there may be significant exposure to other compounds which are, for instance, more soluble and/or more volatile. Consequently, the range of toxicity and physicochemical properties across PAH compounds means that it is appropriate to provide separate human health criteria values and Soil Guideline Values (SGVs) for individual PAHs.

The Environment Agency has selected 17 PAHs for consideration in this review (presented in order of increasing molecular weight, after Mackay, Shiu *et al*. (1991):

- naphthalene
- acenaphthylene
- acenaphthene
- fluorene
- phenanthrene
- anthracene
- fluoranthene
- pyrene
- chrysene
- benzo(a)anthracene
- benzo(b)fluoranthene
- benzo(k)fluoranthene
- benzo(a)pyrene
- indeno(1,2,3-c,d) pyrene
- benzo(g,h,i)perylene
- dibenzo(a,h)anthracene
- coronene

This list includes the “USEPA 16” and the PAHs for which Dutch Intervention Values are provided. Coronene has also been selected for inclusion by the Agency as a representative of the larger molecular weight PAHs (molecular formula $C_{12}H_{24}$), which are likely to be persistent in the soil (WHO 1998a). The PAHs considered in this review were chosen due to their toxicity and to ensure representation across a range of physicochemical characteristics.

2.1.1. Major Sources of PAHs to the Environment

The major source of PAHs in the environment is the incomplete combustion of organic materials (WHO 1998a). Therefore the occurrence of these compounds in the environment is the result of both natural events, such as forest fires, volcanoes and coal fires, and anthropogenic activities, such as waste incineration and vehicle emissions.

Some PAHs are manufactured for use in specific products, and emissions to the environment may also occur from these manufacturing processes. For example, anthracene is used as an intermediate in dye production, in the manufacture of synthetic fibres and as a diluent for wood preservatives; acenaphthene is used as a dye intermediate in the manufacture of pharmaceuticals and plastics, and as an insecticide and fungicide; fluorene is used as a chemical intermediate in many chemical processes and in the manufacture of dyestuffs; phenanthrene is used in the manufacture of dyestuffs and explosives and in biological research, and fluoranthene is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (ATSDR 1995).

With respect to emissions from natural sources, it has been reported that 2000 tonnes of total PAHs present in the atmosphere are attributable to natural forest fires (Environment Canada 1994). Global emissions of benzo(a)pyrene from volcanoes have been estimated as 1.2-14 tonnes year^{-1} (WHO 1998a).

However, although measurable emissions of PAHs from natural sources have been reported, the majority of the PAHs released to the environment arise from anthropogenic sources (Wild and Jones 1995). PAHs can therefore be considered as xenobiotic pollutants, i.e. they are released to the environment from anthropogenic activities at concentrations that are higher than those occurring naturally (Leisinger 1983).

Significant anthropogenic sources to the environment include (WHO 1998a; BRE 2001):

- Combustion of fossil fuels for space heating in residences and cooking. The main PAHs released are phenanthrene, fluoranthene, pyrene and chrysene. The type of fuel is significant in terms of PAH emissions. For example, emissions of PAHs from wood burning are 25-1000 times higher compared to charcoal burning (WHO 1998a). Emissions from these sources may be expected to be higher in the winter. Ninety-five percent of PAH emissions to the UK atmosphere is reported to be from domestic coal combustion (Wild and Jones 1995);
- Processing of coal, crude oil, and natural gas, including coal coking, coal conversion, petroleum refining, and production of carbon blacks, creosote, coal-tar, and bitumen (WHO 1998a; MacLeod, Morriss *et al.* 2001). Emissions of PAHs

from these sources are predominantly two (naphthalene) and three (phenanthrene, anthracene) ring compounds. However, due to technical improvements in the facilities involved in these processes, the closure of older industrial plants and a reduction in coke production, environmental emissions from these sources have reduced significantly during the 1990s (WHO 1998a). Although this statement was made from data obtained from studies in Germany, the results are likely to be applicable to other countries in Western Europe, the USA and Japan (WHO 1998a);

- Aluminium, iron and steel production in plants and foundries. Although little actual data are available on emissions from these facilities, their high energy demands mean that significant emissions of PAHs may be expected from associated burning of coal or oil; (BRE 2001)
- Combustion of refuse (WHO 1998a);
- Motor vehicle traffic. The PAHs emitted depend on the type of fuel used. Petrol-fuelled vehicles emit predominantly fluoranthene and pyrene whereas diesel-fuelled vehicles emit naphthalene and acenaphthene. The level of emission is dependent on the type of vehicle, the conditions of the engine and the environment in which it is being used (WHO 1998a);
- The use of creosote. Described as having the potential to release considerable quantities of PAHs to the UK environment (Wild and Jones 1995); and
- Tobacco smoke.

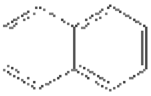
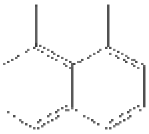
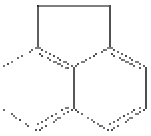
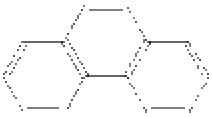
Emissions of PAHs to the environment during their manufacture are considered to be negligible relative to combustion sources.

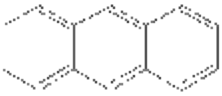
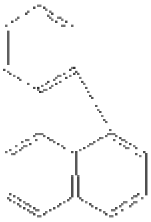
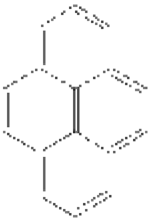
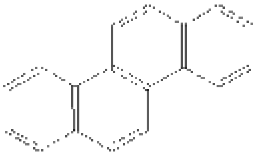
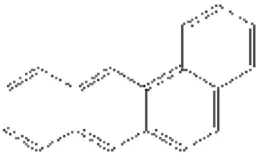
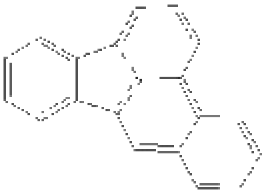
It was reported that concentrations of total PAHs and fluxes to the terrestrial environment in 1995 were at their lowest than at any time in the preceding 95 years, probably as a result of a reduction in the burning of coal for domestic heating (Wild and Jones 1995). There is however a significant degree of variation in levels and trends of individual PAH compounds (Wild and Jones 1995). Concentrations of phenanthrene in soils have declined since the 1960s, whereas levels of benzo(a)pyrene (and other heavy molecular weight PAHs) have increased (Wild and Jones 1995). The differences in levels of individual PAH congeners may be due to differences in the physicochemical characteristics of the compounds. Increases in levels of the higher molecular weight PAHs such as benzo(a)pyrene may be due to their greater sorption of soil organic matter and consequently greater retention in the soil (Wild and Jones 1995). The volatilisation of the lower molecular weight PAHs such as phenanthrene from soils may lead to lower levels in the soils, but a higher atmospheric burden (Wild and Jones 1995).

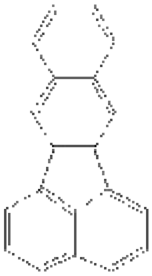
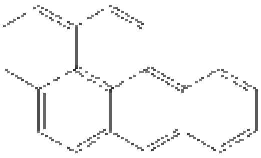
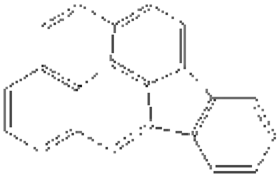
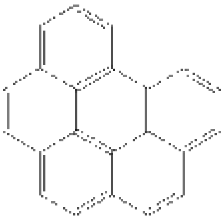
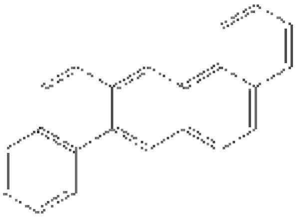
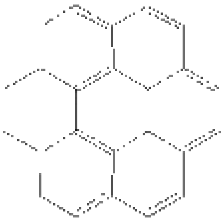
2.2 Identity

The structures of the PAHs to be addressed in this report are presented in Table 2.1. The most carcinogenic of the PAHs is currently considered to be benzo(a)pyrene (WHO 1998a).

Table 2.1 Nomenclature, structure, CAS number and IUPAC name of PAH compounds

PAH (IUPAC name if different)	Structure	CAS number	Common name(s)
Naphthalene		91-20-3	Naphthene Tar camphor Moth balls
Acenaphthylene		208-96-8	
Acenaphthene (1,8-hydroacenaphthylene)		83-32-9	1,8-hydroacenaphthylene Ethylenenaphthalene Periethylenenaphthalene
Fluorene (diphenylenemethane)		86-73-7	2,3-benzindene Diphenylenemethane
Phenanthrene		85-01-8	*o*-diphenyleneethylene phenanthren

PAH **(IUPAC name if different)**	**Structure**	**CAS number**	**Common name(s)**
Anthracene		120-12-7	Paranaphthalene Green oil Tetra olive NZG
Fluoranthene (1,2-benzacenaphthene)		206-44-0	Idryl 1,2-benzacenaphthene benzo(j,k)fluorene benz(a)acenaphthylene fluoranthrene
Pyrene		129-00-0	Benzo(def)phenanthrene
Chrysene		218-01-9	1,2-benzophenanthrene benzo(a)phenanthrene 1,2,5,6-dibenzonaphthalene
Benzo(a)anthracene (1,2-benzanthracene)		56-55-3	1,2-benzanthracene 2,3-benzophenanthrene naphthanthracene BaA B(a)A Tetraphene
Benzo(b)fluoranthene (2,3-benzofluoranthene)		205-99-2	2,3-benzofluoranthene 3,4-benzofluoranthene benz(e)acephenanthrylene B(b)F

PAH (IUPAC name if different)	**Structure**	**CAS number**	**Common name(s)**
Benzo(k)fluoranthene (8,9-benzofluoranthene)		207-08-09	8,9-benzofluoranthene 11,12-benzofluoranthene B(k)F
Benzo(a)pyrene		50-32-8	BaP B(a)P 3,4-benzopyrene
Indeno(1,2,3-c,d)pyrene		193-39-5	1,10-(1,2-Phenylene)pyrene; 2,3-o-phenylenepyrene; o-phenylenepyrene; Indeno[1,2,3-cd]pyrene; Indeno[1,2,3-cd]pyrene
Benzo(g,h,i)perylene		191-24-2	1,12-benzoperylene; Benzo[g,h,i]perylene; Benzo[g,h,i]perylene
Dibenzo(a,h)anthracene (1,2:5,6-dibenzanthracene)		53-70-3	1,2:5,6-dibenzanthracene DB(a,h)A 1,2,5,6-dibenzanthracene
Coronene		191-07-1	

2.2.1. Occurrence in Soil

The occurrence of PAHs in soil on a national basis is a consequence of atmospheric deposition, releases from sewage sludge spread on agricultural land and miscellaneous burning activities (i.e. heather burning and, historically, stubble burning[2]) (WHO 1998a). Over 53,000 tonnes of PAHs (combined levels of 12 individual compounds) are estimated to reside in the contemporary UK environment, with soil being the major repository (Wild and Jones 1995).

Although atmospheric transport and subsequent deposition has resulted in widespread contamination of the environment with these compounds, levels of PAHs in soil are higher in urban areas or near industrial sources (as a consequence of higher traffic densities, more incinerators or heating systems) and in areas of previous (historical) industrial activity such as coal gasification plants; than in rural areas (WHO 1998a). Levels of individual PAHs of up to 1 g kg^{-1} have been found in soils near industrial sources (WHO 1998a) although this concentration is particularly high, even for industrial locations (Halsall, 2003 pers. Comm.), Levels in rural areas are in the region of 5-100 µg kg^{-1} (WHO 1998a). Typical rural UK total PAH concentrations of individual PAHs in soil as a consequence of vehicle emissions range from 2-5 mg kg^{-1} (Wild and Jones 1995, WHO 1998a).

The degree of transfer of PAHs to the soil environment depends on the environmental characteristics (e.g. precipitation rates) and the physicochemical characteristics of the individual compounds, especially molecular weight, octanol-air partition coefficient (K_{oa}), aqueous solubility, octanol-water partition coefficient (K_{ow}), Henry's law constant and vapour pressure (MacLeod, Morriss *et al.* 2001). As a group of compounds, aqueous solubility, Henry's law constant and vapour pressure decrease and K_{ow} increases with increasing molecular weight, indicating a greater partitioning to the particulate or solid phase of an environment with increasing molecular weight.

The preferential partitioning of the higher molecular weight PAHs (more than four rings) to particulate matter in the air (WHO 1998a) mean that these compounds are less likely to undergo long range atmospheric transport and may be expected to be deposited (through wet or dry deposition) in the vicinity of the discharge point (WHO 1998a). However, gas/particle partitioning is strongly dependent on the ambient conditions such as temperature and particle loading.

Levels of PAHs reported in soils are presented in Table 2.2 and 2.3.

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[2] It is recognised that stubble burning is no longer practiced in England and Wales. However residual levels of PAHs may remain in the soil from this activity.

Table 2.2 - Levels of PAHs reported in soils in industrialised areas

PAH	Concentration ($g.kg^{-1}$ dw)	Location	Reference
Naphthalene	0.048 5.2 0.0024 45 53	Near industrial site, Norway; Near waste processing site, USA; Site of abandoned coal gasification plant, USA Netherlands (waste disposal site) Spain (hazardous waste site, 2.4 m)	(WHO 1998a) (WHO 1998a) (WHO 1998a) (BRE 2001) (BRE 2001)
Acenaphthylene		Data not identified	
Acenaphthene	0.054 5090	Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO 1998a) (WHO 1998a)
fluorene	0.080 8600	Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO 1998a) (WHO 1998a)
phenanthrene	506 0.353 20000 0.040	Near coal gasification plant, Netherlands; Near industrial site, Norway; Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO 1998a) (WHO 1998a) (WHO 1998a) (WHO 1998a)
anthracene	144 1.6 0.070	Near coal gasification plant, Netherlands; Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO 1998a) (WHO, 1998c) (WHO, 1998c)
fluoranthene	340 0.573 234 0.2	Near coal gasification plant, Netherlands; Near industrial site, Norway; Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO, 1998c) (WHO, 1998c) (WHO, 1998c) (WHO, 1998c)
pyrene	208 0.459 16000 0.1	Near coal gasification plant, Netherlands; Near industrial site, Norway; Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO, 1998c) (WHO, 1998c) (WHO, 1998c) (WHO, 1998c)
chrysene	1210	Near waste processing site, USA;	(WHO, 1998c)
benzo(a)anthracene	79 200	Near coal gasification plant, Netherlands; Near waste processing site, USA;	(WHO, 1998c) (WHO, 1998c)

benzo(b)fluoranthene	0.2	Site of abandoned coal gasification plant, USA	(WHO, 1998c)
benzo(k)fluoranthene	130 0.1	Near waste processing site, USA; Site of abandoned coal gasification plant, USA	(WHO, 1998c) (WHO, 1998c)
benzo(a)pyrene	38 0.321 0.1	Near coal gasification plant, Netherlands; Near industrial site, Norway; Site of abandoned coal gasification plant, USA	(WHO, 1998c) (WHO, 1998c) (WHO, 1998c)
indeno(1,2,3-c,d)pyrene	0.1	Site of abandoned coal gasification plant, USA	(WHO, 1998c)
benzo(g,h,i)perylene	0.1	Site of abandoned coal gasification plant, USA	(WHO, 1998c)
dibenz(a,h)anthracene		Data not identified	
coronene		Data not identified	

Table 2.3 - Levels of PAHs reported in soils in rural areas

PAH	Concentration reported (μg.kg^{-1} dw)	Location	Reference
naphthalene	46	Norway (0-10 cm depth)^{B}	(WHO, 1998c)
	13-60	Norway	(WHO, 1998c)
	3.8, 11^{A}	Wales (5 cm depth)	(Jones, 1989)
	28^{A}	England (Rothamsted, 1956)	(BRE 2001)
	23^{A}	England (Rothamsted, 1980)	(BRE 2001)
	2.4	Wales (rural location)	(Jones, 1989)
	3.8	Wales (remote location)	(Jones, 1989)
	4-110	Norway (forested areas away from local pollution source)	(BRE 2001)
acenaphthylene	Nd-3.0	Wales (5 cm depth)	(Jones, 1989)
acenaphthene	1.7	Norway (0-10 cm depth)^{B}	(WHO, 1998c)
	<1-21	Norway	(WHO, 1998c)
fluorene	Nd	Norway (0-10 cm depth)^{B}	(WHO, 1998c)
	<1-10	Norway	(WHO, 1998c)
phenanthrene	30	Norway (0-10 cm depth)^{B}	(WHO, 1998c)
	17-21	Norway	(WHO, 1998c)
	18, 39^{A}	Wales (5 cm depth)	(Jones, 1989)
Anthracene	1.2, 4.2^{A}	Wales (5 cm depth)	(Jones, 1989)
Fluoranthene	22	Norway (0-10 cm depth)	(WHO, 1998c)
	8-28	Norway	(WHO, 1998c)
	35, 73^{A}	Wales (5 cm depth)	(Jones, 1989)
Pyrene	20	Norway (0-10 cm depth)	(WHO, 1998c)
	9-25	Norway	(WHO, 1998c)
	29, 42^{A}	Wales (5 cm depth)	(Jones, 1989)
Chrysene		Data not identified	
benzo(a)anthracene		Data not identified	
benzo(b)fluoranthene	14, 25^{A}	Wales (5 cm depth)	(Jones, 1989)
benzo(k)fluoranthene		Data not identified	
benzo(a)pyrene	15	Norway (0-10 cm depth)	(WHO, 1998c)
	6-12	Norway	(WHO, 1998c)
	13, 22^{A}	Wales (5 cm depth)	(Jones, 1989)
indeno(1,2,3-c,d)pyrene		Data not identified	
benzo(g,h,i)perylene	49, 28	Wales (5 cm depth)	(Jones, 1989)
dibenz(a,h)anthracene		Data not identified	
Coronene		Data not identified	

[A] single measurements

[B] soil samples from Norway study dried at 50-60°C prior to analysis. Therefore reported levels of the more volatile PAHs in these samples may be an underestimation of actual levels (due to losses by volatilisation during drying).

2.3 Physicochemical Properties

This section discusses the physicochemical parameters that will be used in the CLEA model. Justification is provided for the selection of a particular value for each parameter.

The physicochemical properties recommended for the PAHs addressed in this report are presented in Table 2.4. Information is presented for the following characteristics:

- molecular weight (g mol^{-1})
- boiling point (K)
- aqueous solubility (mg l^{-1} or g cm^{-3})
- vapour pressure (Pa)
- Henry's Law constant (Pa-m^3.mol^{-1})
- log K_{ow}
- log K_{oc}
- coefficient of diffusion (m^2 s^{-1})
- enthalpy of vapourisation (cal mol^{-1})
- critical temperature (K)

The information presented in Table 2.4 has been collated from four sources:

- Mackay, Shiu *et al*. 1991;
- Environmental Health Criteria document for PAHs (WHO 1998a);
- USEPA Soil Screening Level data (USEPA 2001a); and
- Syracuse Research Corporation databases (http://esc.syrres.com).

The data presented by Mackay, Shiu *et al*. (1991) are considered to be authoritative within the field. Therefore, although a wide range of values is reported for many of the physicochemical characteristics, specific values recommended by Mackay, Shiu *et al.* (1991) (referred to as default values) have been chosen. Where Mackay default values are not available, values from the other sources have been used and the source of the data identified, with priority given to WHO and USEPA reported values.

Table 2.4 - Recommended physicochemical values and parameters for CLEA, minimum and maximum literature ranges (CLEA and SI units)

Substance	Value	Mol. weight [a]	Boiling Point [b]	Aqueous Solubility [b] (all 25°C)	Vapour Pressure [b] (all 25°C)	Henry's Law Constants [# b] (all 25°C)			Log K_{ow} [b]	Log K_{oc}	Coefficient of Diffusion (25°C) [c]		Enthalpy of vapourisation [h]	Critical temp [h]
											Air	Water		
			K	mg l^{-1}	Pa[^]	Pa-m^3 mol^{-1}	atm-m^3 mol^{-1}	Dimension-less	-	-	m^2 s^{-1}	M^2 s^{-1}	cal mol^{-1}	K
Naphthalene	Recommended	128.17	491	31.0	36.81	43.01	4.24E-04	1.74E-02	3.37	3.11 [h]	5.90E-06	7.50E-10	10373 [m]	748.4 [m]
	Min		490.7	12.5	6.53	29.2			3.01	2.66 [b]				
	Max		491	137.35	111.0	123.95			4.70	3.91 [b]				
Acenaphthylene	Recommended	152.20	543	16.1	4.14	8.40	8.29E-05	3.40E-03	4.00	3.4-3.83 [b]	-	-	-	-
	Min		538	2.94	0.893				3.55					
	Max		553	16.1	4.14				4.08					
Acenaphthene	Recommended	154.20	552	3.8	1.52	12.17	1.20E-04	4.92E-03	3.92	3.85 [c]	4.20E-06	7.69E-10	-	-
	Min		550.5	2.42	0.122				3.32	3.59 [b]				
	Max		552	7.37	4.02				4.49	5.38 [b]				
Fluorene	Recommended	166.22	568	1.9	0.72	7.87	7.77E-05	3.18E-03	4.18	4.14 [c]	3.60E-06	7.88E-10	-	-
	Min		566	1.50	0.08				3.91	3.76 [b]				
	Max		571	10.98	1.66				4.47	5.47 [b]				
Phenanthrene	Recommended	178.23	612	1.1	0.113	3.24	3.20E-05	1.31E-03	4.57	4.36 [h]	-	-	-	-
	Min		611	0.0446	0.0127				3.60	3.58 [b]				
	Max		613	11.25	0.464				5.92	6.12 [b]				
Anthracene	Recommended	178.23	613	0.045	0.0778	3.96	3.91E-05	1.60E-03	4.54	4.47 [c]	3.20E-06	7.74E-10	13121 [m]	873.0 [m]
	Min			0.030	3.87E-07				4.15	2.96 [b]				
	Max			0.551	0.095				4.73	5.76 [b]				
Fluoranthene	Recommended	202.26	648	0.26	8.7E-03	1.04	1.02E-05	4.20E-04	5.22	5.03 [c]	3.00E-06	6.35E-10	13815 [m]	905.0 [m]
	Min		490	0.19	1.65E-04				4.78	4.0 [b]				
	Max		668	1.43	1.79				6.50	6.38 [b]				
Pyrene	Recommended	202.26	633	0.13	0.0119	0.92	9.08E-06	3.72E-04	5.18	5.02 [c]	2.70E-06	7.24E-10	14370 [m]	936.0 [m]
	Min		633	0.032	1.70E-04				4.45	3.11 [b]				
	Max		677	1.56	0.0119				6.70	6.51 [b]				
Chrysene	Recommended	228.30	721	0.0016 [c]	1.07E-04	0.065	6.41E-07	2.63E-05	5.70 [d]	3.66 [l]	2.50E-06	6.21E-10	16455 [m]	979.0 [m]
	Min		714	1.02E-03	5.7E-07				5.01	3.66 [b]				
	Max		761	0.017	1.07E-04				7.10	6.90 [b]				
Benzo(a) anthracene	Recommended	228.30	708	0.011	6.06E-04	0.581	5.73E-06	2.35E-04	5.91	4.0-7.3 [b]	5.10E-06	9.00E-10	16000 [n]	1004.79 [n]
	Min			0.0086	3.87E-07				5.48					
	Max			0.044	6.06E-04				7.50					
Benzo(b) fluroanthene	Recommended	252.32	754	0.0015	6.67E-05 [g]	0.43 [q]	4.26E-06	1.75E-04	5.80	5.74 [b]	2.60E-06	5.56E-10	17000 [n]	969.27 [n]
	Min			0.0015	5.0E-07				5.78	5.70 [b]				
	Max			0.014	6.70E-05				6.57	6.09 [d]				
Benzo(k) fluoranthene	Recommended	252.32	753	8.00E-04	4.12E-06	0.084 [c]	8.29E-07 [c]	3.4E-05 [c]	6.00	6.09 [c]	2.60E-06	5.56E-10	18000 [n]	1019.70 [n]
	Min		753	7.00E-03	5.20E-08				6.00	4.0 [b]				
	Max		754	0.008	6.70E-05				7.20	7.0 [b]				
Benzo(a) pyrene	Recommended	252.32	768	0.0038	2.13E-05	0.046	4.54E-07	1.86E-05	6.04	6.01 [c]	4.30E-06	9.00E-10	19000 [n]	969.27 [n]
	Min		584	1.7E-03	8.53E-10				4.05	4.0 [b]				
	Max		769	0.008	2.53E-05				8.50	8.3 [b]				

Substance	Value	Mol. weight [a]	Boiling Point [b]	Solubility[b] (all 25°C)	Vapour Pressure[b] (all 25°C)	Henry's Law Constants [# b] (all 25°C)			Log K_{ow} [b]	Log K_{oc}	Coefficient of Diffusion (25°C) [c] Air	Coefficient of Diffusion (25°C) [c] Water	Enthalpy of vapourisation [h]	Critical temp [h]
			K	mg l^{-1}	Pa[^]	Pa-m^3 mol^{-1}	atm-m^3 mol^{-1}	Dimension-less	-	-	m^2 s^{-1}	m^2 s^{-1}	cal mol^{-1}	K
Indeno(1,2,3-c,d) pyrene	Recommended	276.34	809 [a]	2.2E-05 [c]	1.30E-08 [f]	0.162 [c,f]	1.6E-06 [c,f]	6.56E-05 [c,f]	6.65 [d]	6.54 [c]	1.90E-06	5.66E-10	19000 [n]	1078.24 [n]
	Min			2.2E-05 [d]	1.30E-08				6.58	6.20 [f]				
	Max			2.30E-05 [f]	1.33E-08				6.65	6.54 [c]				
Benzo(g,h,i) perylene	Recommended	276.34	773 [a]	2.6E-04	2.25E-05	0.075	7.4E-07	3.03E-05	6.50	5.61 [f]	-	-	-	-
	Min			2.6E-04 [e]	1.40E-08				6.50	5.61 [f]				
	Max			2.6E-04 [e]	2.25E-05				7.10	6.26 [l]				
Dibenzo(a,h) anthracene	Recommended	278.36	797	6.0E-04	9.16E-08	1.49E-03 [c,f]	1.47E-08 [c,f]	6.03E-07 [c,f]	6.75	6.58 [c]	2.00E-06	5.18E-10	29995 [p]	990.41 [n]
	Min			5.0E-04	4.25E-10				5.80	5.0 [b]				
	Max			0.0025 [d,f]	1.33E-08				7.19	7.8 [b]				
Coronene	Recommended	300.36	798	1.40E-04	2.00E-10 [g]	-	-	-	6.75	5.0-7.8 [l]	-	-	-	-
	Min			0.0014	2.00E-10									
	Max			0.0054 [f]	2.00E-10									

[^] Conversion factor from mmHg to Pa, multiply by 133.32. The selected values presented are liquid vapour pressure values at 25°C

[#] Conversion factor from atm-m^3 mol^{-1} to Pa-m^3 mol^{-1} = multiply by 101325; atm-m^3 mol^{-1} to dimensionless = multiply by 41

[a] Chemfinder (http://chemfinder.cambridgesoft.com/)

[b] Values taken from Mackay (Mackay, Shiu et al. 1991)

[c] Value taken from USEPA Soil Screening Level data (USEPA 1996a). No summary value available from Mackay *et al.* (Mackay, Shiu et al. 1991)

[d] Value taken from USEPA Soil Screening Level data (USEPA 1996a);

[e] Value taken from the EHC document for PAHs and the SRC database.

[f] Value taken from SRC database.

[g] Value taken from EHC document (WHO 1998a);

[h] Value from Kenaga and Goring (Kenaga and Goring 1980b);

[i] Value from Abdul *et al.* (1986)(cited by (Baker, Mihelcic et al. 1997);

[k] Value from Hasset *et al.* (1980)(cited by (Baker, Mihelcic et al. 1997);

[l] Lancaster University POPs modelling reported value (http://www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html)

[m] Design Institute for Physical Property Data, The American Institute for Chemical Engineers online data search (1997). Cited by USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[n] USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[p] Lange's Handbook of Chemistry 15th Edition, MCGraw-Hill (1999). Cited by USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[q] Calculated using the vapour pressure and the solubility values given in the table.

For a number of the properties considered (aqueous solubility, vapour pressure, log K_{ow} and log K_{oc}) there are several published values. The range of values reported for these characteristics are discussed below and any clustering or consensus within the dataset identified. The references in these collations to Mackay are from Mackay *et al.* (1991), to USEPA from the USEPA Soil Screening Guidance: Technical Background Document (1996a), to SRC from the databases produced by the Syracuse Research Corporation, and the references to WHO are from the Environmental Health Criteria document for PAHs (WHO, 1998c). The 'Lancaster reported values' are taken from the Persistent Organic Pollutants (POPs) modelling database (POPs Fate Modelling 2003) produced by Lancaster University. The level of information presented in the databases varies for the different PAH compounds. For some PAHs such as naphthalene and benzo(a)pyrene there is a significant database of values reported. In these cases a consensus of the values has been provided, as well as the minimum and maximum values reported.

In many cases the minimum and maximum values listed in Table 2.4 are extreme outlying representatives of the published data. The following tabulated data summary provides information on the range of values available, along with the justification for the values selected.

Molecular Weight

Recommended values for molecular weight of PAH compounds were taken from Chemfinder. Ranges are not appropriate for this parameter.

Boiling Point

Recommended values and ranges for the boiling point of PAHs were obtained from Mackay.

Aqueous Solubility

Naphthalene

The minimum and maximum values presented in Table 2.4 were obtained using shake-flask UV and calculated from K_{ow} respectively. The majority of values reported by Mackay, Shiu *et al*. (1991) are between 30-35 mg l^{-1}. The value recommended for use within the CLEA model is 31.0 mg l^{-1} (Mackay default value). This value is also reported by SRC and USEPA. WHO report a value of 31.7 mg l^{-1}.

Acenaphthylene

Mackay and SRC reported 16.1 mg l^{-1} as the aqueous solubility for acenaphthylene. The minimum value of 2.94 is a predicted value reported by Mackay. The value recommended for use within the CLEA model is 16.1 mg l^{-1} (Mackay default value). Neither the WHO or USEPA report an aqueous solubility value for acenaphthylene.

Acenaphthene

The minimum and maximum values presented in Table 2.4 were obtained using shake-flask GC and shake-flask LSC respectively. The majority of values reported by Mackay are between 3.4 and 4.9 mg l^{-1}. The value recommended for use within the CLEA model is 3.8 mg l^{-1} (Mackay default value). WHO report a value of 3.93 mg l^{-1} and USEPA a value of 4.24 mg l^{-1}.

Fluorene

The minimum and maximum values presented in Table 2.4 were obtained by calculation. The majority of values reported by Mackay are between 1.6-2.0 mg l^{-1}. The value recommended for use within the CLEA model is 1.9 mg l^{-1} (Mackay default value). WHO and USEPA report a value of 1.98 mg l^{-1}.

Phenanthrene

The minimum and maximum values presented in Table 2.4 were obtained using vapour saturation UV and RP-HPLC respectively. The majority of values reported by Mackay are between 1.0 and 1.6 mg l^{-1}. The value recommended for use within the CLEA model is 1.1 mg l^{-1} (Mackay default value). USEPA do not list a value for phenanthrene. WHO report a value of 1.29 mg l^{-1}.

Anthracene

A large number of values are presented in Mackay. The majority of the values are between 0.04 and 0.075 mg l^{-1}. The value recommended for use within the CLEA model is 0.045 mg l^{-1} (Mackay default value). USEPA report a value of 0.0434 mg l^{-1} and WHO a higher value of 0.073 mg l^{-1}.

Fluoranthene

The majority of the values reported by Mackay are between 0.24 and 0.265 mg l^{-1}. The value recommended for use within the CLEA model is 0.26 mg l^{-1} (Mackay default value) which is the same as that reported by WHO. USEPA report a value of 0.206 mg l^{-1}.

Pyrene

Both the minimum and maximum values presented in Table 2.4 were obtained using shake flask UV. The majority of values reported are between 0.13-0.15 mg l^{-1}. The value recommended for use within the CLEA model is 0.13 mg l^{-1} (Mackay default value). Both USEPA and WHO report a value of 0.135 mg l^{-1}.

Chrysene

The majority of the values reported by Mackay are between 0.0015 and 0.002 mg l^{-1}. WHO (1998a) report a value of 0.002 mg l^{-1}. The value recommended for use within the CLEA model is 0.0016 mg l^{-1} (USEPA 1996a) since Mackay does not identify a default value.

Benzo(a)anthracene

The majority of the values reported by Mackay are between 0.01-0.014 mg l^{-1}. There are relatively few values reported outside this data range. The value recommended for use within the CLEA model is 0.011 mg l^{-1} (Mackay default value). The values reported by the WHO and USEPA are lower at 0.0038 and 0.0094 mg l^{-1} respectively.

Benzo(b)fluoranthene

Four values are reported by Mackay, ranging from 0.0015-0.014 mg l^{-1}. The USEPA and SRC report a value of 0.0015 mg l^{-1} and WHO gives a value of 1.2×10^{-3} mg l^{-1}. The value recommended for use within the CLEA model is 1.5×10^{-3} mg l^{-1} (Mackay default value).

Benzo(k)fluoranthene

Six values are reported by Mackay. Three of those values are between 7.60×10^{-4}-8.10×10^{-4} mg l^{-1}. A value of 8.00×10^{-4} mg l^{-1} is also reported by USEPA, WHO and SRC, and by Mackay as the default value. The value of 8.00×10^{-4} mg l^{-1} is therefore recommended for use within the CLEA model.

Benzo(a)pyrene

The consensus of the values reported by Mackay is between 0.0035-0.0045 mg l^{-1}. The value recommended for use within the CLEA model is 3.8×10^{-3} mg l^{-1} (Mackay default value). USEPA report a value of 1.6×10^{-3} mg l^{-1} and WHO report a higher value of 0.014 mg l^{-1}.

Indeno(1,2,3-c,d)pyrene

Three values for indeno(1,2,3-c,d)pyrene are reported. The USEPA list a value of 2.2×10^{-5} mg l^{-1} and SRC a value of 2.3×10^{-5} mg l^{-1}. The value reported by the USEPA is recommended for use within the CLEA model.

Benzo(g,h,i)perylene

Mackay, SRC and the WHO report a value of 2.60×10^{-4} mg l^{-1} for benzo(g,h,i)perylene. This value has therefore been recommended for use within the CLEA model.

Dibenzo(a,h)anthracene

The consensus of the values reported by Mackay is between 5.00×10^{-4} and 6.00×10^{-4} mg l^{-1}. The USEPA and SRC report a higher value of 0.0025 mg l^{-1}. The value recommended for use within the CLEA model is 6.00×10^{-4} mg l^{-1} (Mackay default value).

Coronene

Only two values for coronene are reported. Mackay report a value of 1.40×10^{-4} mg l^{-1}, and WHO a value of 5.40×10^{-3} mg l^{-1}. The value reported by Mackay has been recommended for use within the CLEA model.

Vapour Pressure

The values discussed below are liquid vapour pressure values at 25°C (unless otherwise stated).

Naphthalene

A large number of values are reported by Mackay. The consensus of values is between 10 and 12 Pa, although a value of 36.81 Pa is reported as the default summary value. WHO report a value of 10.4 Pa. The value recommended for use within the CLEA model is 36.81 Pa (Mackay default value). The reason for the relatively high value of the Mackay default value is unclear. The Lancaster database also cite a value of 36.81 for the vapour pressure for naphthalene at 25°C

Acenaphthylene

Values of 0.893-4.14 Pa are reported by Mackay. WHO report a value of 0.89 Pa. The value recommended for use within the CLEA model is 4.14 Pa (Mackay default value).

Acenaphthene

The majority of values reported by Mackay are between 0.2-0.4 Pa, although there are a cluster (four) values reported between 3.07-4.02 Pa. WHO report a value of 0.29 Pa and SRC a value of 0.33 Pa. The value recommended for use within the CLEA model is 1.52 Pa (Mackay default value).

Fluorene

The values reported by Mackay are spread between 0.08 and 1.66 Pa with no clustering or consensus within that range. WHO report a value of 0.09 Pa. The value recommended for use within the CLEA model is 0.72 Pa (Mackay default value).

Phenanthrene

The values reported by Mackay are spread between 0.018-0.134 Pa with no clustering or consensus within that range. WHO report a value of 0.016 Pa. The value recommended for use within the CLEA model is 0.113 Pa (Mackay default value).

Anthracene

The values reported by Mackay are spread between 3.87×10^{-7} and 0.095 Pa with little clustering or consensus within that range. WHO report a value of 8.00×10^{-4} Pa. The value recommended for use within the CLEA model is 7.78×10^{-2} Pa (Mackay default value).

Fluoranthene

Values reported by Mackay show little consensus between the maximum and minimum points (1.65×10^{-4} and 1.79 Pa). WHO report a value of 1.20×10^{-3} Pa. The value recommended for use within the CLEA model is 8.70×10^{-3} Pa (Mackay default value).

Pyrene
A cluster of values are reported by Mackay between 3.00x10^{-4} and 9.00x10^{-4} Pa, although the default value (recommended for use within the CLEA model) is given as 0.0119 Pa. WHO report a value of 6.00x10^{-4} Pa.

Chrysene
A limited number of values are reported by Mackay for vapour pressure, with a range between 5.7x10^{-7} and 1.07x10^{-4} Pa. WHO quote a value of 8.4x10^{-5} Pa and SRC a value of 8.3x10^{-7} Pa. The value recommended for use within the CLEA model is 1.07x10^{-4} Pa (Mackay default value).

Benzo(a)anthracene
Values reported by Mackay show little consensus between the maximum and minimum points (3.87x10^{-4} and 6.06x10^{-4} Pa). WHO report a value of 7.3x10^{-7} Pa. The value recommended for use within the CLEA model is 6.06x10^{-4} Pa (Mackay default value).

Benzo(b)fluoranthene
Mackay reports a limited number of values for vapour pressure. WHO quote a value of 6.70x10^{-5} Pa and SRC a value of 6.67x10^{-5} Pa. In the absence of a Mackay default value, the value reported by WHO is recommended for use within the CLEA model.

Benzo(k)fluoranthene
Mackay reports a limited number of values for vapour pressure, with a spread of figures between 5.20x10^{-8} and 6.70x10^{-5} Pa. WHO report a value of 1.3x10^{-8} Pa. The value recommended for use within the CLEA model is 4.12x10^{-6} Pa (Mackay default value).

Benzo(a)pyrene
Values reported by Mackay show little consensus between the maximum and minimum points (8.53x10^{-10} and 2.53x10^{-5} Pa). WHO report a value of 2.8x10^{-5} Pa. The value recommended for use within the CLEA model is 2.13x10^{-5} Pa (Mackay default value).

Indeno(1,2,3-c,d)pyrene
Only values reported by WHO (1.30x10^{-8} Pa) and SRC (1.33x10^{-8} Pa) are available. The WHO value has been recommended for use within the CLEA model.

Benzo(g,h,i)perylene
Only values reported by WHO (1.40x10^{-8} Pa), Mackay (2.25x10^{-5} Pa) and SRC (1.33x10^{-8} Pa) are available. The value reported by Mackay has been recommended for use within the CLEA model.

Dibenzo(a,h)anthracene
Mackay reports a limited number of values for vapour pressure. WHO quote a value of 1.30x10^{-8} Pa and SRC a value of 1.33x10^{-8} Pa. The value recommended for use within the CLEA model is 9.16x10^{-8} Pa (Mackay default value).

Coronene

Only a value of 2.0×10^{-10} Pa reported by WHO was identified, therefore this is recommended for use within the CLEA model.

Log octanol-water partition coefficient (K_{ow})

Naphthalene

The consensus of the values reported by Mackay is between 3.35-3.40. The value recommended for use within the CLEA model is 3.37 (Mackay default value). USEPA report a value of 3.36 and WHO a value of 3.40.

Acenaphthylene

The consensus of the values reported by Mackay is between 3.90-4.08. The value recommended for use within the CLEA model is 4.00 (Mackay default value). WHO report a value of 4.07. There is no value reported by USEPA for acenaphthylene.

Acenaphthene

The consensus of the values reported by Mackay is between 3.90-4.33. The value recommended for use within the CLEA model is 3.92 (Mackay default value). WHO and USEPA also report this value.

Fluorene

The majority of the values reported by Mackay give a log K_{ow} of 4.18. This value, which is also reported by WHO is recommended for use within the CLEA model (Mackay default value). USEPA report a slightly higher value of 4.21. The full range of values reported by Mackay is from 3.91 to 4.47.

Phenanthrene

A consensus of values are reported by Mackay of 4.45-4.60. The value recommended for use within the CLEA model is 4.57 (Mackay default value). No value is reported by USEPA but a figure of 4.60 is reported by WHO.

Anthracene

A consensus of values are reported by Mackay of 4.45-4.55. The value recommended for use within the CLEA model is 4.54 (Mackay default value). WHO report a value of 4.50 and USEPA a value of 4.55.

Fluoranthene

A consensus of values are reported by Mackay of 5.20-5.30, although there is a greater spread of values than for phenanthrene and anthracene. The value recommended for use within the CLEA model is 5.22 (Mackay default value). WHO also report a value of 5.22, USEPA report a lower value of 5.12.

Pyrene

A large spread of values are reported by Mackay of between 4.45 and 6.70. There is little consensus in the values reported. The value recommended for use within the CLEA model is 5.18 (Mackay default value). WHO also report a value of 5.18, USEPA report a lower value of 5.11.

Chrysene
A consensus of values are reported by Mackay of 5.61-5.91. The value recommended for use within the CLEA model is 5.70 (USEPA value, as no Mackay default value is available). WHO report a value of 5.91.

Benzo(a)anthracene
A consensus of values are reported by Mackay of 5.61-5.91. The value recommended for use within the CLEA model is 5.91 (Mackay default value). USEPA report a value of 5.70, WHO report a higher value of 6.50.

Benzo(b)fluoranthene
There is no consensus within the values reported by Mackay between the maximum (6.57) and minimum (5.78) values. The value recommended for use within the CLEA model is 5.80 (Mackay default value). WHO report a value of 6.12 and USEPA a value of 6.20.

Benzo(k)fluoranthene
There is no consensus within the values reported by Mackay between the maximum (7.20) and minimum (6.00) values. The value recommended for use within the CLEA model is 6.00 (Mackay default value). WHO report a value of 6.84 and USEPA a value of 6.20.

Benzo(a)pyrene
A consensus of values is reported by Mackay of 5.8-6.5 with a cluster of values between 6.04 and 6.06. The value recommended for use within the CLEA model is 6.04 (Mackay default value). USEPA report a value of 6.11 and WHO a value of 5.61.

Indeno(1,2,3-c,d)pyrene
Only values reported by WHO (6.58), USEPA (6.65) and SRC (6.58) are available. The value recommended for use within the CLEA model is 6.65 (USEPA).

Benzo(g,h,i)perylene
Values of 6.50 (Mackay *et al.* 1991), 6.58 (SRC) and 7.10 (WHO) are reported. The value recommended for use within the CLEA model is 6.50 (Mackay default value).

Dibenzo(a,h)anthracene
There is no consensus within the values reported by Mackay between the maximum (7.19) and minimum (5.80) values. The value recommended for use within the CLEA model is 6.75 (Mackay default value).

Coronene
The only value identified was that of 6.75 reported by Mackay.

Log organic carbon partition coefficient (K_{oc})

Naphthalene

Values of between 2.66 and 3.91 are reported by Mackay. The value recommended for use within the CLEA model is 3.11 (Lancaster reported value). The USEPA report a value of 3.30.

Acenaphthylene

Four values are reported by Mackay, ranging from 3.4-3.83. No single values for log K_{oc} for this PAH have been proposed by Mackay, USEPA or the Lancaster database. Therefore in the absence of such a value, the range of 3.4-3.83 is recommended for use within the CLEA model.

Acenaphthene

Five values are reported by Mackay ranging from 3.59-5.38 with a consensus of 3.59-3.79. No single Mackay default value is proposed, although a single value of 3.85 is reported by the USEPA. In the absence of other data the USEPA value is recommended for use within the CLEA model.

Fluorene

The values reported by Mackay range from 3.76-5.47 with a cluster of values between 3.76-4.21. The USEPA value of 4.14 is recommended for use within the CLEA model.

Phenanthrene

Values ranging from 3.58-6.12 are reported by Mackay, with a consensus of values between 4.15-4.42. In the absence of single values reported by Mackay or USEPA, the Lancaster value of 4.36 has been recommended for use within the CLEA model.

Anthracene

Values reported by Mackay range from 2.96-5.76. In the absence of a Mackay default value the USEPA reported value of 4.47 is recommended for use within the CLEA model.

Fluoranthene

Values reported by Mackay range from 4.0-6.38. In the absence of a Mackay default value the USEPA reported value of 5.03 is recommended for use within the CLEA model.

Pyrene

The values reported by Mackay range from 3.11-6.51 with a clustering of values between 4.8-4.95. In the absence of a Mackay default value the USEPA reported value of 5.02 is recommended for use within the CLEA model.

Chrysene

Five values are reported by Mackay ranging from 3.66-6.90 with no consensus within the range. The value recommended for use within the CLEA model is 3.66 (Lancaster reported value).

Benzo(a)anthracene
Values reported by Mackay range from 4.0-7.3, with little consensus within that range. In the absence of a Mackay default value, no single value is presented as the recommended for use within the CLEA model.

Benzo(b)fluoranthene
Only values of 5.70 and 5.74 are reported by Mackay. A value of 5.74 is also reported by the Lancaster database and a value of 6.09 is reported by USEPA. Based on the information available, the value of 5.74 is recommended for use within the CLEA model.

Benzo(k)fluoranthene
Values ranging from 4.0-7.0 are reported by Mackay. A value of 5.74 is reported by the Lancaster database and a value of 6.09 is reported by USEPA. In the absence of a Mackay default value the USEPA value of 6.09 is recommended for use within the CLEA model.

Benzo(a)pyrene
Values of between 4.0 and 8.3 are reported by Mackay. In the absence of other single values the USEPA value of 6.01 is recommended for use within the CLEA model.

Indeno(1,2,3-c,d)pyrene
A value of 6.54 is reported by USEPA, and a value of 6.20 reported by SRC. The USEPA value is recommended for use within the CLEA model.

Benzo(g,h,i)perylene
A value of 5.61 is reported by SRC, and a range of 6.2-6.26 reported in the Lancaster database. In the absence of other single values the value of 5.61 recommended for use within the CLEA model.

Dibenzo(a,h)anthracene
Only values of 5.0 and 7.8 are reported by Mackay. A value of 6.58 is reported by USEPA, and a range of 5.2-6.52 is reported in the Lancaster database. In the absence of a Mackay default value the USEPA value of 6.58 is recommended for use within the CLEA model.

Coronene
The only values reported are a range of 5.0-7.8 (Lancaster database). In the absence of other reported values, this range is recommended for use within the CLEA model.

2.4 Behaviour of PAHs in the Soil Environment

The purpose of this section of the report is to review the fate and behaviour of PAHs in the soil environment, and methods available for modelling behaviour in soil and exposure to biota.

On entering the soil environment, the PAH compounds are subject to sorption to the soil matrix, re-volatilisation back into the air, degradation through biotic or abiotic processes, or release to groundwater or surface water systems (Jones, Alcock et al. 1996). The behaviour of individual PAHs in the environment and the importance of each of the fate processes is determined, in part, by the physicochemical characteristics of the compounds under review which, in turn, is dictated largely by the molecular weight. The characteristics of the soil environment, particularly the soil organic matter (SOM) content, and the competence of the soil microbial community to degrade these chemicals is also important in determining their fate and behaviour.

For the compounds as a group, volatilisation is only relevant as a loss process for naphthalene, with volatilisation from soil reported as 30 percent in 48 h (WHO 1998a). However volatilisation is also likely to be significant for those PAHs with similar physicochemical properties to naphthalene (i.e. with two or three rings). For the other PAHs, i.e. those with four or more rings, volatilisation from soil surfaces is described as negligible (WHO 1998a). This is a consequence of the low Henry's law constant for these compounds and higher K_{ow} (relative to naphthalene), resulting in greater sorption to SOM. The importance of volatilisation as a loss process from soil will decrease with increasing soil organic matter content. This is applicable to naphthalene and other PAHs.

High K_{oc}, and therefore strong sorption to soil organic matter results in heavier PAHs being relatively immobile in the soil environment relative to other PAHs with lower K_{oc}. This, coupled with the low aqueous solubilities of these compounds, means that the transfer of these high molecular weight PAHs through soil into groundwater systems is unlikely, as is the partitioning from the particulate to the water phase in surface water systems (lakes and rivers).

As a consequence of the physicochemical characteristics of PAHs, soils and sediment act as a major sink for these chemicals in the environment. Once in soil or sediment, PAHs are known to persist for relatively long periods of time (compared to other pollutants such as chlorinated solvents and phenol), with persistence increasing with increasing molecular weight of the compound (Table 2.6). The recalcitrance of these compounds in the soil environment is due to:

(i) their inherent resistance to biodegradation – only microorganisms are capable of completely degrading aromatic ring structures (Imman, Strachan *et al.* 1984), albeit at relatively low rates. Although the biodegradation of many PAHs has been demonstrated in liquid culture (Heitkamp and Cerniglia 1998, Bogan, Lahner *et al.* 2003, Bogan and Lamar 1996, Fiebich, Thumm *et al.* 1995), poor bioavailability reduces both the rate and extent of their biodegradation in soil.

(ii) their poor bioavailability – biodegradation of PAHs in the soil environment is dependent on the bioavailability (defined here as the degree to which a compound is free to move into or onto organisms (Hamelink, Landrum *et al.* 1994), of the compounds in relation to microbial attack. Sorption (association of the chemical to the solid phase of the soil, MacLeod, Morriss *et al.* 2001) renders them less

> bioavailable to microorganisms, which are size excluded from micropores containing the sorbed compound. Therefore compounds are only biologically accessible (and consequently susceptible to biodegradation) when present on the surface of the solid phase or dissolved in the aqueous phase (McCarthy 1983, DiToro, Zarba *et al.* 1991). The low aqueous solubility of most of the PAHs means that the quantities present in the aqueous phase are likely to be limited.

The affect of sorption on bioavailability and biodegradation in the soil is compounded by a reduction in bioavailability of the contaminant with time (Alexander 1995). As the soil-chemical contact time increases, the bioavailable fraction decreases and the recalcitrant fraction increases. This process is referred to as 'ageing' of the pollutant (Alexander 1995, Reid, Jones *et al.* 2000, MacLeod, Morriss *et al.* 2001), and although thought to be controlled by sorption, may also involve entrapment within soil micropores or SOM (Steinberg *et al.* 1987; Xing and Pignatello 1997; both cited by Reid, Jones *et al.* 2000).

The effect of soil ageing with respect to biodegradation is that even the lower molecular weight molecules, such as naphthalene, are less susceptible to biodegradation if they have been in contact with the soil for a period of time. Long term contamination with the higher molecular weight PAHs, such as benzo(a)pyrene, results in the contaminant becoming almost completely resistant to biodegradative processes (USEPA 1999a).

As discussed in Section 2.1, the release of PAHs during the production of coal-gas means that these compounds are present, often at high concentrations, in soils at former gasworks sites (WHO, 1998c). The presence of oil in these sites however increases the mobility of PAHs in soil by decreasing their sorption to soil. Because the higher molecular weight PAHs are more mobile in oil than water (low aqueous solubility of these compounds), then at low oil concentrations (0.01 percent) only the less volatile PAHs are affected, whereas oil concentrations increase, the mobility of all PAHs are affected. Increased mobility of the PAH compound in soil may lead to the loss of this chemical from the soil environment through release to groundwater or surface water systems. Reduced sorption to soil will also increase the bioavailability of the compound and consequently the potential for biodegradation by microorganisms and/or plant uptake.

2.4.1. Degradation and loss in the soil environment

PAHs are susceptible to degradation in the environment through both biotic and abiotic processes. The compounds are transformed in surface waters by photo-oxidation, chemical oxidation, and microbial metabolism. In soil and sediments, microbial metabolism is the major process for degradation of PAHs (WHO, 1998c), although microbial degradation is limited to the bioavailable fraction in soil pore water or on the surfaces of the soil particles (Ogram, Jessup *et al.* 1985, Miller and Alexander 1991). PAHs with fewer than four aromatic rings are also degraded abiotically in soils through photolysis and oxidation, and may also be lost from the soil surface through volatilisation, although volatilisation may only be a significant for two and three ringed PAHs (ATSDR 1995; WHO 1998a). Hydrolysis is not a significant degradation process for PAHs due to the lack of reactive groups on these compounds (WHO, 1998c).

Volatilisation is reported to occur for some of the lighter PAHs such as naphthalene, acenaphthene, acenaphthylene, anthracene, fluorene and phenanthrene (Coover and Sims 1987; Wild and Jones 1992a). However, volatilisation as a significant loss process for PAHs from soil has only been reported for naphthalene, with 30 % of this PAH reported to be lost from soil through this pathway (Park, Simms *et al*. 1990, WHO, 1998c). Volatilisation was found not to be an important loss mechanism for fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, dibenz(a,h)anthracene, benzo(a)pyrene and indeno(l,2,3-c,d) pyrene (Park, Simms et al. 1990).

The rate and extent of the biodegradation of PAHs decrease with increasing molecular weight of the compound, and biodegradation occurs with much higher rates (for all PAHs) under aerobic compared to anaerobic conditions (USEPA 1999a). PAHs with two or three rings, such as naphthalene and fluorene for example have been found to be extensively degraded in soil (under aerobic conditions), whereas PAHs with four or five rings, such as pyrene and benzo(a)pyrene are much more recalcitrant with limited degradation in soil (WHO, 1998c). Biodegradation of all PAHs under anaerobic conditions is reported to be slow (WHO, 1998c).

The presence of other compounds in the soil environment, including other PAHs, is reported to have an effect of the rate and extent of biodegradation of the target compound (Heitkamp and Cerniglia 1998). This is likely to be due to the adverse effect of the other contaminants on the microorganisms involved in biodegradation of the target chemical, or by those chemicals altering the bioavailability of the PAH compounds i.e. oils.

With respect to degradation rates for PAHs in the soil environment, a number of studies have reported half-lives[3] for various PAHs in soil. These are presented in Table 2.5. The variation in the values reported for each individual PAH is indicative of the number of factors that affect the biodegradation of PAHs in soil, including concentration of the PAH, competence of the microbial community to degrade that PAH (prior exposure will probably result in a reduction in half-life) and bioavailability of the PAH (affected by soil organic matter content of the soil and ageing of the pollutant).

Because of the biphasic nature of the sorption of PAHs to soil organic matter (Jones, Alcock *et al.* 1996) and the effect that bioavailability has on biodegradation, it is not appropriate to view the degradation of PAHs in soil as a linear decay process.

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[3] defined as the time taken for half of the PAH to be lost from the soil, and therefore includes all degradation and loss processes and not just microbial degradation.

Table 2.5 - Reported half-lives for degradation of PAHs in soil

PAH	Half life	Test conditions	Reference
Naphthalene	<1-108 d	No information available	(USEPA 1999a)
	2 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.377 d^{-1}.	(WHO, 1998c)
	2.2 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.308 d^{-1}.	(WHO, 1998c)
	765 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
acenaphthylene	42.5-60 d	Aerobic soil column.	(WHO, 1998c)
acenaphthene	12-102 d	Aerobic soil column.	(WHO, 1998c)
	<1168 d	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
fluorene	2-385 d	No information available	(USEPA 1999a)
	32-60 d	Aerobic soil degradation.	(WHO, 1998c)
	<1168 d	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
phenanthrene	16 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0447 d^{-1}	(WHO, 1998c)
	35 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0196 d^{-1}.	(WHO, 1998c)
	9.7-14 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2080 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
anthracene	50-460 d	Aerobic soil column.	(WHO, 1998c)
	50 d	Aerobic sandy loam (McLaurin), initial test conc. 199 mg kg^{-1}. Degradation rate constant of 0.0138 d^{-1}.	(WHO, 1998c)
	>480 d	Degradation in soil. Loss of 33 % in 16 months.	(WHO, 1998c)
		Aerobic degradation in sandy loam, initial test conc.	

PAH	Half life	Test conditions	Reference
	17-45 d	5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2880 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
fluoranthene	15-462 d	No information available	(USEPA 1999a)
	140-440 d	Aerobic soil degradation.	(WHO, 1998c)
	377 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0018 d^{-1}	(WHO, 1998c)
	268 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0026 d^{-1}.	(WHO, 1998c)
	34-39 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2847 d	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
pyrene	5-1925 d	No information available	(USEPA 1999a)
	210-1941 d	Aerobic soil degradation.	(WHO, 1998c)
	260 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0027 d^{-1}.	(WHO, 1998c)
	199 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0035 d^{-1}.	(WHO, 1998c)
	48-58 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	3100 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
chrysene	19-1400 d	No information available	(USEPA 1999a)
	371-1000 d	Aerobic soil degradation.	(WHO, 1998c)
	371 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0019 d^{-1}	(WHO, 1998c)
	387 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0018 d^{-1}.	(WHO, 1998c)
	224-328 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2955 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
benzo(a)anthracene	6-21000 d^{B}	No information available	(USEPA 1999a)
	102-680 d	Aerobic soil degradation.	(WHO, 1998c)
	267 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0026 d^{-1}	(WHO, 1998c)
	130-240 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2955 d^{A}	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)

PAH	Half life	Test conditions	Reference
benzo(b)fluoranthene	360-610 d	Aerobic soil degradation.	(WHO, 1998c)
	294 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0024 d^{-1}.	(WHO, 1998c)
	211 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0033 d^{-1}.	(WHO, 1998c)
	3285 d	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
benzo(k)fluoranthene	910-2140 d	Aerobic soil degradation.	(WHO, 1998c)
	3175 d[A]	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
benzo(a)pyrene	12-11552 d	No information available	(USEPA 1999a)
	57-529 d	Aerobic soil degradation	(WHO, 1998c)
	309 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0022 d^{-1}.	(WHO, 1998c)
	229 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0138 d^{-1}.	(WHO, 1998c)
	218-347 d	Aerobic degradation in sandy loam, initial test conc. 5 and 50 mg kg^{-1}.	(WHO, 1998c)
	2993 d	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
indeno(1,2,3-c,d)pyrene	288 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0024 d^{-1}.	(WHO, 1998c)
	289 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0024 d^{-1}.	(WHO, 1998c)
benzo(g,h,i)perylene	590-650 d	Aerobic soil degradation.	(WHO, 1998c)
	3320 d[A]	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)
dibenzo(a,h)anthracene	361 d	Aerobic sandy loam (Kidman). Degradation rate constant of 0.0019 d^{-1}.	(WHO, 1998c)
	420 d	Aerobic sandy loam (McLaurin). Degradation rate constant of 0.0017 d^{-1}.	(WHO, 1998c)
coronene	6020 d[A]	Rural UK soil with metal-enriched sewage sludge (0.1-15.1 mg kg^{-1} PAH). Field test conditions.	(WHO, 1998c)

[A] Values reported in WHO (1998) in years. Converted to days in this table through multiplication by 365 and rounded to the nearest five days. .

[B] The large range for benzo(a)anthracene is a consequence of a number of studies that reported no degradation for this PAH in soil.

Table 2.6 - Summarised half-lives for PAHs in soil (Mackay, Shiu *et al.* 1991)

PAH	Mean half-life (h)	Range of half-lives (h)
Naphthalene	1700 (~2 months)	1000-3000
Acenaphthylene	Not listed	
Acenaphthene	5500 (~8 months)	3000-10000
Fluorene	5500 (~8 months)	3000-10000
Phenanthrene	5500 (~8 months)	3000-10000
Anthracene	5500 (~8 months)	3000-10000
Fluoranthene	17000 (~24 months)	10000-30000
Pyrene	17000 (~24 months)	10000-30000
Chrysene	17000 (~24 months)	10000-30000
benzo(a)anthracene	17000 (~24 months)	10000-30000
benzo(b)fluoranthene	Not listed	
benzo(k)fluoranthene	17000 (~24 months)	10000-30000
benzo(a)pyrene	17000 (~24 months)	10000-30000
indeno(1,2,3-c,d)pyrene	Not listed	
benzo(g,h,i)perylene	17000 (~24 months)	10000-30000
dibenzo(a,h)anthracene	17000 (~24 months)	10000-30000
Coronene	Not listed	

Degradation of naphthalene[4]

Naphthalene is reported to be relatively susceptible to biodegradation in soil (BRE 2001), with reported half-lives for this chemical ranging from <1 to 108 days (USEPA 1999a). The differences in degradation rate are likely to be a consequence of differing levels of organic matter in the soils (and consequently different levels of sorption and bioavailability of the naphthalene), different environmental conditions, variations in the competence of the microbial community present to degrade the PAH, and differences in the time naphthalene had been present in the soil before any degradation was assessed. These factors are of course relevant both to naphthalene and other PAH compounds.

Biodegradation of naphthalene in soil results in the formation of a number of metabolites, including the conversion of the naphthalene to *cis*-1,2-dihydroxy-1,2-dihydronaphthalene, and subsequent changes to 1-naphthol, salicylic acid and catechol (Heitkamp and Cerniglia 1987). It may be necessary to consider the toxicity of metabolites produced, in the assessment process.

Biodegradation of all PAHs in the environment occurs through a series of ring cleavage reactions, resulting in a range of metabolites and a reduction in the number of aromatic rings

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[4] The degradation of naphthalene is addressed in a separate section in this report because it is likely that this PAH will be given separate TOX and SGV reports.

of the parent compound. Many of these metabolites are formed at some point during the degradation of a number of PAHs. Biodegradation of the multiple ring PAHs such as benzo(a)pyrene is likely to result in the formation of two or three ring PAHs such as naphthalene and anthracene. These PAHs may be more toxic to aquatic organisms than the five ring parent compound (Nagdal 1993).

2.4.2. Implications of Behaviour in Soil for Modelling

The behaviour of the PAHs in soil (as discussed in section 2.4) has implications for exposure modelling for human health. There are usually insufficient data readily available to determine the actual exposure at a contaminated site. Additionally it is unlikely to be cost-effective to determine dermal exposure and detailed physicochemical parameters, such as contaminant vapour levels within the soil and in the boundary layer above it, at all but the most complex sites. Generic approaches to modelling are therefore likely to be required. These either relate behaviour to physicochemical properties of the contaminant and properties of the soil matrix, such as organic matter content, soil water content and particle size, or are empirical, based on observed relationships. For use in a tool for the derivation of generic assessment criteria, such as the CLEA model, such approaches will be in the "screening" category, using minimal data to predict exposure.

It may sometimes be possible to refine the approach for detailed quantitative risk assessment (DQRA). For instance, the likelihood of the effect of contaminant ageing on decreasing the availability of PAHs has been mentioned by a number of authors (e.g. Alexander 1995; USEPA 1999a; Reid, Jones *et al*. 2000; MacLeod, Morriss *et al.* 2001). This would be expected to affect several of the exposure modelling pathways in contrasting ways. Biodegradation would be expected to decrease, with the implication that the potential for exposure would be greater than biodegradation rates from laboratory studies might suggest. However, ageing would also result in a decrease in the availability for dermal penetration and inhalation of vapour (i.e. a decrease in exposure). For a generic approach the precautionary principle should be adopted. It is therefore assumed that degradation does not occur over time, so that PAH concentrations remain constant. However, at the same time, it is assumed that the PAHs remain available for volatilisation and penetration of the skin. Further, although the techniques routinely used for laboratory analysis of soils may be considered to give 'total' PAH concentrations rather than just the bioavailable fraction, this is an appropriate approach for all but the most detailed quantitative risk assessment.

Dermal Exposure

Dermal exposure models for soil may calculate absorption into the skin based on the skin structure, the properties of the chemical and the properties of the soil (e.g. McKone and Howd 1992; USEPA 1992). The dermal exposure model currently within the CLEA model (and described within CLR10, Defra and Environment Agency 2002d) is adapted from USEPA (1992). It requires soil/skin permeability coefficients, either taken directly from experimental work or, in the absence of data, by estimating a skin permeability coefficient for chemicals in aqueous solution using a relationship between K_{ow} and the molecular weight.

The skin permeability coefficient is then adjusted for soil, taking into account the soil matrix parameters and physicochemical properties of the substance.

It is likely that the dermal algorithm within the CLEA model will be changed to the approach within updated draft guidance on modelling dermal uptake from USEPA (2001a), (Martin, 2002 Pers. Comm.) This approach stresses that the validation data for modelling dermal absorption of chemicals from soils are very limited and presents dermal absorption factors from soil for ten chemicals based on well-designed studies, which it states will be added to as further research is conducted. It recommends using a dermal absorption fraction of the applied dose rather than a flux through the skin to model dose. The lipophilicity of the PAHs means that they are able to penetrate skin. USEPA (2001a) advocates the use of dermal absorption fractions derived from experimental studies involving soil for PAHs. The absorbed fraction proposed for benzo(a)pyrene and other PAHs is 0.13. It was considered that there were insufficient available data to differentiate based on soil type. It is recommended that this approach is adopted for the CLEA model and for DQRA, unless appropriate information on other PAHs and/or information relating to specific soil types becomes available. Users should be aware that this is a screening approach, giving a general indication of uptake, especially for PAHs other than BaP. Given the wide range of K_{ow} values for the list of PAHs in this report (log~3-7), it may not be appropriate to use one value for 'absorbed fraction' for all PAHs and it is recommended that these be the subject of further review in the future.

Inhalation of Dust (derived from contaminated sites)

Enrichment factors[5] for sand, loam and organic rich soils are already included as defaults within the CLEA model for benzo(a)pyrene. Aeolian derived particles from these soil types will therefore reflect the repetitive PAH burden. In the urban and background atmosphere ~70-90 percent of the PAH mass is associated with the smaller particles (<3 µm diameter) (Smith and Jones 2000) which can be inhaled into the deeper regions of the lung. Consequently dust inhalation is considered to be an important pathway for PAHs and it is therefore recommended that the enrichment factors be retained.

Inhalation of Vapours

The literature review suggests that volatilisation from the soil, and hence inhalation of soil vapours, is unlikely to be a significant pathway for PAHs with more than two rings. It is possible that generic algorithms for modelling vapour intrusion may be conservative for some forms of PAH contamination. As discussed above, it is likely that the effect of ageing (discussed by Alexander 1995; USEPA 1999a; Reid, Jones *et al.* 2000; MacLeod, Morriss *et al.* 2001) will decrease the availability for volatilisation from soil. However, there is insufficient information to justify departure from generic algorithms and these are therefore

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[5] CLR10 (Defra and Environment Agency 2002) describes the use of enrichment factors for certain soils. This is because certain contaminants bind preferentially to the finer fraction of soils, and this fraction is also the one most likely to be inhaled and adhere to skin. Thus coarser soils will have a higher enrichment factor, because the finer fraction will be atypical of the matrix. The EFs have already been used in the derivation of SGVs for metal contaminants, and are reviewed on a substance by substance basis for other contaminants.

considered to be appropriate for a generic assessment tool such as the CLEA model. Other approaches, such as monitoring of soil vapour levels, could be undertaken as part of a DQRA if the volatilisation pathways were perceived to be risk drivers. From the literature review, it would appear unlikely that volatilisation from groundwater would be expected to be a major pathway, because solubility in water of the PAHs is limited. However, if measurements show high concentrations of PAHs in groundwater, this pathway would need to be considered as part of a DQRA.

2.5 Dietary Uptake of PAHs

The mechanisms by which PAHs are released into the environment, coupled with their environmental persistence and ability to accumulate in biota, mean that dietary exposure is an important pathway for human exposure to PAHs. The bioaccumulation potential of these chemicals in biota, and hence the food chain, increases with increasing molecular weight (and can be quantified by increase in K_{ow}). However, the ingestion of plant material (leafy and root crops) that has been exposed to PAHs through contaminated soil or atmospheric deposition onto leaves is probably the most significant pathway in terms of dietary uptake of these chemicals, rather than exposure through bioaccumulated PAHs.

Plants cover a large proportion of the surface of the terrestrial environment (both above and below ground). They are therefore exposed to chemicals already present and released to the atmosphere and the soil environment. They also occupy the bottom trophic level of many foodchains and therefore represent the key link between the abiotic and biotic environments. The exposure of plants to PAHs is therefore a key component in determining dietary uptake (and subsequent exposure) of these chemicals in the foodchain. The air-leaf-cattle-milk (and other dairy products, and beef) pathway is described as the most significant route to human exposure for polychlorinated biphenyls (PCBs), another group of substances with high $\log K_{ow}$ (AEAT 1999). However, because of the relatively poor biomagnification potential of PAHs in the foodchain, the air-leaf-cattle-milk pathway is less significant than the ingestion of plant material (leafy or root) with surface-associated PAHs.

2.5.1. Key processes of plant uptake and accumulation into the foodchain

Plants are exposed to PAHs through their foliar tissues (leaves, shoots and stems) and roots following (Simonich and Hites 1995, Welsch-Pausch, McLachlan *et al.* 1995, Smith and Jones 2000, Wilcke 2000):

- uptake from the soil, directly by plant roots or indirectly by volatilisation from the soil, and uptake into aerial parts of the plant following vapour transfer through plant tissue[6] (Jones, Johnston *et al.* 1995);
- dry vapour phase transfer (also referred to as dry deposition) of vapour phase chemicals;
- dry deposition of particulate matter onto aerial parts of the plant; and
- wet deposition or washout of vapour phase chemicals (likely to be extremely limited) or particulate matter onto aerial parts of the plant.

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[6] Volatilisation from the soil in this way is also described as ‘soil outgassing’ (Jones *et al.* 1995)

Uptake of PAHs into Plants

Uptake from the Atmosphere

As discussed, the uptake of PAHs into the plant directly from the atmosphere has been identified by a number of studies as the key uptake pathway for these persistent organic pollutants into vegetation (Smith and Jones 2000, Simonich and Hites 1995, Wilcke 2000). PAHs may be taken up through aerial parts of the plant following vapour transfer through stomatal tissue, or dry or wet deposition onto leaf and stem surfaces. The total amount of uptake (through transfer or deposition) involved per plant will be dependent on:

- surface area and physiology of the leaves;
- partitioning of PAHs between the vapour/gas phase and particulate phase in air;
- physicochemical characteristics of the PAHs (vapour pressure, lipophilicity and aqueous solubility); and
- meteorological conditions.

The potential for vapour phase transfer will be determined largely by the fraction of PAH in the vapour phase, with partitioning between the vapour and particulate phases determined by either the vapour pressure or the K_{oa} of the chemical. The less volatile compounds exhibit greater partitioning to the particulate phase (WHO, 1998c). Vapour phase exchange is therefore likely to be a more significant uptake pathway for the lower molecular weight PAH compounds.

Sorption to plant surfaces of chemicals in the vapour phase can be described by the octanol-air partition coefficient (K_{oa}) partition coefficient. The K_{oa} values for PAHs increase with increasing molecular weight, indicating that the higher molecular weight compounds are more likely to be deposited to leaf surfaces through this route. Dry particulate deposition involves the chemical becoming bound to particulate matter in the atmosphere and then being deposited subject to the behaviour of the particles. Due to greater partitioning to the particulate phase (WHO, 1998c), the uptake into plants through dry particulate deposition is likely to be a more significant pathway for the higher molecular weight compounds. The amount of dry particulate deposition that actually occurs will depend on the settling rate of the particle load from the air, with a higher rate occurring with larger sized particles or during periods of lower wind speeds.

Wet deposition involves the washout of chemicals present in either the vapour or particulate phase by precipitation (including via dew, mist and fog). Washout of chemicals in the vapour phase will be determined by the air-water partition coefficient (K_{aw})(dimensionless Henry's law constant) for the particular PAH compound. This decreases with increasing molecular weight and therefore the lower molecular weight compounds will be preferentially washed out of the vapour phase during precipitation events. Washout of chemicals in the particulate phase is determined by the particle scavenging efficiency of precipitation (Bidleman 1988), with different types and intensities of precipitation event likely to have differing ability to remove particulate matter from the air.

With respect to the differing importance of each uptake pathway, vapour phase transfer through the surfaces of foliar tissues is likely to be an important uptake pathway for PAHs into plants. Dry particulate deposition is also likely to be significant. For wet deposition processes, wet deposition of particulate bound chemical is a more significant process than wet deposition of vapour phase (Poster and Baker 1996).

Uptake from Soil

The uptake of PAHs into plants from the soil can occur either directly through root uptake (Kipopoulou, Manoli *et al.* 1999), or indirectly following volatilisation of the chemical from the soil surface and subsequent vapour phase sorption onto the aerial part of the plant (Jones, Johnston *et al.* 1995).

The direct uptake of PAHs from soil into plant roots (other than just uptake into epidermal cells) has been reported as limited (Jones, Johnston *et al.* 1995; Simonich and Hites 1995). The pollutants tend to partition to the epidermis of the root or to soil particles on the root surface and are not drawn into the inner root or xylem (Simonich and Hites 1995). Because the lower molecular weight compounds may be less sorbed to soil organic matter, relative to heavier ones, these chemicals are more likely to undergo root uptake. However, it should be noted that some compounds secreted by plants into the rhizosphere may act as biosurfactants and consequently improve the bioavailability (and possible uptake) of any persistent organic chemicals present (Smith, 2001 Pers. Comm.).

The indirect uptake of PAHs from soils into plants through volatilisation and uptake into the foliar part of the plant is dependent on the volatilisation of the congener from the soil surface. This uptake pathway is most likely to be realised for the lower molecular weight, and therefore more volatile, PAH compounds.

It is also noted that whilst pollutant ageing has an adverse effect on bioavailability, it has been reported (for PCBs) not to have an effect on soil-air partition coefficients (Cousins, Mclachlan *et al.* 1998a). According to this study the exposure of plants through volatilisation from soil and subsequent foliar exposure is not affected by the length of time the PCB congener has remained in the soil environment.

Concentrations of PAHs in Plants

The uptake of PAHs from soil to plants and the subsequent biomagnification is generally quite low (Sims and Overcash 1983; Wilcke 2000). Ratios of PAH concentrations in vegetation to those in soil have been reported to range from 0.001 to 0.18 for total PAHs and from 0.002 to 0.33 for benzo(a)pyrene (Edwards 1983). In a study of PAH uptake from cropland soils (repeated sewage sludge application over the years) conducted in the UK, elevated concentrations of PAHs in soils were not correlated with concentrations in plant tissues (Wild, Berrow *et al.* 1992b). Tissues from plants grown in the treated soils were relatively enriched with low molecular weight PAHs, but increased PAH concentrations (relative to tissues from plants grown in control plots that did not receive sludge amendments) were not consistently detected. The PAH concentrations in above ground plant parts were not strongly related to soil PAH levels but were probably the result of atmospheric deposition. The presence of PAHs in root crop tissues was probably due to adsorption of the compounds to root surfaces.

The uptake of PAHs from sewage sludge-amended soils by carrots (*Daucus carota*) was investigated by Wild and Jones (Wild and Jones 1992a). Carrots were grown in control soils and sludge amended soils[7]. Carrot foliage, root peels and root cores were analysed for 15 PAH compounds. Foliage PAH concentrations were unaffected by sludge applications (PAH loadings), but root peel PAH concentrations increased with increasing soil PAH levels. The PAH concentrations detected in the root peels were all significantly lower than in the foliage, which receives PAH inputs from the atmosphere. Carrot core total PAH concentrations were unaffected by sludge application, implying little or no transfer of PAHs from the peels to the core. About 70% of the PAH burden found in carrots was associated with the peels. Fresh weight carrot core concentrations were all < 4.2 ìg kg^{-1}. Simonich and Hites (Simonich and Hites 1994a) found that the partitioning of PAHs between vegetation and the atmosphere was dependent primarily upon the atmospheric gas-phase PAH concentration and ambient temperature.

Kipopoulou *et al*. (1999) determined the PAH content of cabbage (*Brassica oleracea capitala*), carrot (*Daucus carota*), lettuce (*Latuca sativa*), leek (*Allium prorrum*) and endive (*Chochorium endiva*) and their growing environment (soil and atmosphere) in the industrial area of Thessaloniki, northern Greece. Concentrations were found to be low, with total PAH values between 25 and 294 ìg kg^{-1} dry weight. The lower molecular weight PAHs dominated in both vegetable leaves and roots. The highest PAH burden was found for leafy vegetables with large surface areas (lettuce and endives), further demonstrating the importance of atmospheric inputs. Cabbage had the lowest loading, despite growing above ground, possibly due to its closed internal structure. Carrot roots, although peeled, had a higher PAH content than cabbage, in particular low molecular weight PAHs. The high lipid content and oil channels in roots of carrots are reported to give greater potential for uptake of non-polar chemicals. The PAH mixture in inner vegetable tissue was very similar to that in air vapour, thus suggesting gaseous transfer or deposition as the principal pathway for the accumulation of PAHs. Soil-to-vegetation and air-to-vegetation bioconcentration factors were calculated and their relationships with physicochemical properties of PAHs were investigated. Solubility and K_{ow}, as well as vapour pressure were proved to be good predictors for the accumulation of PAHs in inner root and leaf tissue, respectively.

Soil samples, great plantain (*Plantago major*) leaves and grass (mixed species) from the vicinity of an oil refinery in Belgium, were analysed for seven PAHs (Bakker, Casado *et al*. 2000). The samples adjacent to the site contained very high PAH concentrations, 300, 8 and 2 ìg kg^{-1} dry weight for soil, plantain and grass respectively. Concentrations at sites up to 4 km away were 10-30 times lower. The PAH profile of the plant samples, in contrast with soil, suggested higher contributions of gaseous PAHs with increasing distance from the refinery. This is due to particle-bound PAHs being deposited closer to the source. Concentrations were higher in *P. major* than grass, a result of differences in surface

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[7] Sludge contained 17.2 mg-total PAH kg^{-1}, a typical concentration for sludge derived from a rural area.

roughness, leaf orientation and/or leaf age. However the ratio of concentrations at different sites for *P. major*/grass were not constant, varying from 1.2 to 8.8.

Fismes *et al.* (2002) carried out a study to determine whether PAHs present in contaminated soils are transferred to edible parts of lettuce (*Latcuca sativa*), potato (*Solanum tuberosum*) and carrot (*Daucus carota*). Soil samples from a former gasworks and private garden contained levels of PAHs of 4-53 to 172-1263 (for gasworks soil) and 2526 mg kg^{-1} soil (for garden soil) (all dry weight data). PAHs were detected in all plants grown in contaminated soils. However, their concentrations were low compared with the initial soil concentration, and hence bioconcentration factors were low, ranging from $13.4x10^{-4}$ in potato and carrot pulp to $2x10^{-2}$ in potato and carrot leaves. With the exception of peeled potatoes, the PAH concentration in vegetables increased with the PAH concentration in soils. The PAH distribution profiles in plant tissues and in soils suggested that root uptake was the main pathway for high molecular weight PAHs. In contrast lower molecular weight PAHs were probably taken up from the atmosphere through the leaves as well as by roots.

2.5.2. Implication of literature base for modelling plant uptake

The recommendation of this report on the basis of the literature review is that there are insufficient measured concentrations for PAHs in soils to provide substance specific concentration factors for adaptation of the CLEA model. There is sufficient information, however, to inform the selection of algorithms.

The review shows that the major pathway for plant uptake is atmospheric deposition/transfer onto aerial plant parts - this is more likely to arise from a point source of contamination than for soil contamination. The literature review suggests that concentration within root vegetables, especially the outer peel, can be correlated to soil concentrations, especially for the lighter PAHs. However there appears to be little translocation from the roots into the stems and foliage. The Briggs Ryan algorithm is currently the default within the CLEA model (Defra and Environment Agency 2002d), although the algorithm for uptake of root vegetables for benzo(a)pyrene in CLEA 2002 has been adjusted to calibrate it against measured data (Martin, 2002 Pers. Comm.).

The original papers (Briggs, Bromilow *et al.* 1982 and 1983) state that calibration of the algorithm beyond a log K_{ow} of approximately 4.5 has not taken place. The log K_{ow} of many of the PAHs considered in this review are either close to (phenanthrene and anthracene) or exceed (fluoranthene, pyrene, chrysene, benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(ghi)perylene, dibenzo(ah) anthracene and coronene) this limit. Furthermore, the Briggs and Ryan approach focuses on root uptake and translocation to above ground parts, but does not account for outgassing or atmospheric deposition of site-derived dust, which the literature base suggests are more critical processes. It is therefore suggested that another screening approach is adopted if possible. It is of particular importance to establish whether the Briggs Ryan algorithm predicts significant translocation into stem and foliage as this would be in contradiction to the literature base.

The BP RISC model uses the Travis Arms regression for above ground vegetables and the Briggs Ryan algorithm for below ground vegetables, with a modification for lipophilic compounds such as PAHs, of 0.01 (Briggs, Bromilow *et al.* 1982 and 1983; Travis and Arms 1988). This is because it is considered that over-prediction by Briggs Ryan will occur for lipophilic compounds. This approach may be a possibility but might be considered somewhat arbitrary.

The current Dutch Intervention Values were derived using the Briggs approach with a soil correction factor based on the fugacity approach (Lijzen, Baars *et al.* 2001). However the proposed new Dutch Serious Risk Concentrations for humans (SRC_{human}) are based on the approach of Trapp and Matthies (also used within the EUSES model and UMS model) (Lijzen, Baars *et al.* 2001; Rikken, Lijzen *et al.* 2001). For below ground vegetable parts, they found that the predicted soil-plant concentration ratios reflected experimental values more closely, especially for contaminants with high log K_{ow}. For above ground vegetable plants it was considered that the Trapp and Matthies approach better described the "relevant processes and parameters". This is because it includes diffusive transfer from the air above the soil into the plant. Although this may be relevant to some of the more volatile PAHs, it will not be as important a factor as for more volatile substances such as the chlorinated solvents and BTEX compounds. However, Trapp and Matthies (1995) explicitly state that "The soil-air-plant path that is of significance for volatile and semivolatile lipophilic chemicals needs a different solution". The PAHs, especially the lighter compounds such as naphthalene, fluorene, acenaphthene, and acenaphthylene, could be considered to fall into this category, and this would present a drawback to using this approach.

Another plausible screening level approach is that of Dowdy and McKone (1997). This uses a "molecular connectivity index" derived from the nature of the bonding within a compound, rather than a log K_{ow} approach to predict uptake into vegetation and the food chain. The empirical relationship was derived from concentration factors within the literature base, including BaP. It should, however, be noted that the authors did not develop this approach further and it has not been incorporated by McKone into his CalTOX Model.

It is possible that there may not be a generic screening approach that it totally suited to the Conceptual Model within the CLEA model and which addresses PAHs. It may be necessary to "tailor" an approach to fit the available data. It is therefore suggested that the current approach within the CLEA model be revised to reflect the data in the experimental literature. In particular, an approach which explicitly addresses uptake from the soil by outgassing, should be considered for the lighter PAHs. Atmospheric deposition of PAHs to leaves is often considered to be the most critical plant uptake process where it occurs. Although deposition from a point source is not considered within the Conceptual Model within the CLEA model, it may be appropriate to consider whether the levels of dust calculated as occurring within the model are sufficiently high for consideration to be given to wet and dry deposition via this mechanism.

2.6 Key conclusions

2.6.1. Recommendations for Detailed Quantitative Risk Assessment (DQRA)

There is a range of physicochemical properties across the PAHs with a consequent variation in environmental behaviour. This combined with the different toxicological criteria, means that it is therefore essential that a DQRA is conducted for the compounds that are actually detected in the soil and not for total PAHs (as was the case for comparison with ICRCL trigger levels).

Variation in both calculated and measured K_{oc} values has been noted. K_{oc} is critical for a number of exposure pathways and for some methods of calculating plant uptake which may be a significant for some of the PAHs It may therefore be appropriate to select a value for a similar soil if available, or otherwise to determine the fraction of organic material experimentally on a site specific basis.

The effect of ageing is likely to decrease the rate of degradation within the soil. Therefore, it is essential that half lives encompass all abiotic and biotic processes for a DQRA. If the decision is made to consider degradation when undertaking exposure modelling, this should be measured in the field for the site in question.

It is recognised that the laboratory methods routinely used for the analysis of soils consider "total" content, rather than the bioavailable fraction. However, for all but the most detailed quantitative risk assessments, it is recommended that the "total" content is considered, as issues of relating bioavailability to existing toxicological criteria are complex.

There is insufficient information for the recommendation of adaptation of generic approaches to dermal modelling of PAHs for DQRA, unless very detailed studies for the site in question involving skin transfer are available. This will be highly unlikely. It is therefore recommended that generic approaches, such as that in USEPA 2001, are used but that the risk evaluation clearly states that the dermal absorption factor was derived for B(a)P. The results therefore only represent a screening approach for other PAHs and soil conditions other than those in the experimental set up in the dataset used by USEPA (2001a).

Plant uptake may be a critical pathway for PAHs, especially those with a higher solubility and lower log K_{ow}. It should be noted that some transfer pathways (such as uptake through meat and milk products) are viewed within the literature as relatively unimportant. The generic approaches to modelling plant uptake may not fully consider the processes which are important for PAHs, especially the lighter fractions for which sorption may be important. They may also over predict translocation from roots into stem and foliage. Therefore, in contexts where a screening approach has indicated that exposure via the plant uptake pathway is likely to occur, analysis of available produce or vegetables grown in field trials or, if this is not possible due to the management context of the site, pot trials are recommended.

It is not considered likely that human exposure to vapours will be a critical pathway for the majority of PAHs compared with exposure from soil ingestion, dermal contact and consumption of food. It is therefore recommended that in general the burden of effort, when undertaking a DQRA, is focused on other pathways, rather than on the vapour pathway. However, for the lighter PAHs, especially naphthalene, inhalation of vapours may constitute a more significant pathway, and if this is indicated by the generic screening model, measurements within soil gas may be appropriate.

2.6.2. Recommendations for the CLEA Model

There are insufficient data available in the literature to enable replacement of the plant uptake algorithms within the CLEA model with specific concentration factors. However the literature review provides sufficient information to inform the selection of approach and suggests that the Briggs Ryan algorithm may not be the most appropriate approach for the PAHs. This is particularly the case for PAHs with either a high potential to volatilise from the soil, such as naphthalene, or a log K_{ow} of above 4.5.

The literature base suggests that plant soil concentration factors may be derived for root vegetables (especially peels) but that this is problematic for stems and foliage, where translocation to above ground compartments by plants appears to be less important than outgassing from the soil. It is recommended that a modelling approach that specifically addresses outgassing from the soil should be considered for the lighter PAHs, such as naphthalene. Where atmospheric deposition of PAHs to leaves occurs, it is often considered to be the most critical plant transfer process. Although deposition from a point source is not considered within the Conceptual Model within the CLEA model, it may be appropriate to consider whether the levels of dust calculated as occurring within the model are sufficiently high for consideration to be given to wet and dry deposition via this mechanism.

It is recommended that the USEPA (2001a) dermal absorption factor currently proposed for use within the CLEA model is adopted but that the situation is kept under review if studies pertaining to PAHs other than BaP, or which may be related to soil conditions, become available.

There are insufficient data in the literature to suggest any substance-specific modifications of the approach to the vapour pathways within the CLEA model. It is likely however that generic approaches may over predict the significance, due to the effects of ageing. The literature review suggests that volatilisation pathways will only be important for the lighter PAHs, in particular for naphthalene. It is suggested that careful consideration is given to whether an enrichment factor for dust particles should be included.

2.6.3. Summary of Recommended Values

Table 2.7 provides a summary of the physicochemical parameter values recommended for inclusion in the CLEA Model.

Table 2.7 - Recommended physicochemical values and parameters for the PAHs for inclusion in the CLEA model (CLEA units only)

Substance	Mol. weight [a]	Boiling Point [b]	Solubility [b] (all 25°C)	Vapour Pressure [b] (all 25°C)	Henry's Law Constants [# b] (all 25°C)			Log K_{ow} [b]	Log K_{oc}	Coefficient of Diffusio (25°C) [c]	
										Air	Water
		K	mg l^{-1}	Pa[^]	Pa-m^3 mol^{-1}	atm-m^3 mol^{-1}	Dimension-less	-	-	m^2 s^{-1}	m^2 s^{-1}
Naphthalene	128.17	491	31.0	36.81	43.01	4.24E-04	1.74E-02	3.37	3.11 [h]	5.90E-06	7.50E-1
Acenaphthylene	152.20	543	16.1	4.14	8.40	8.29E-05	3.40E-03	4.00	3.4-3.83 [b]	-	-
Acenaphthene	154.20	552	3.8	1.52	12.17	1.20E-04	4.92E-03	3.92	3.85 [c]	4.20E-06	7.69E-1
Fluorene	166.22	568	1.9	0.72	7.87	7.77E-05	3.18E-03	4.18	4.14 [c]	3.60E-06	7.88E-1
Phenanthrene	178.23	612	1.1	0.113	3.24	3.20E-05	1.31E-03	4.57	4.36 [h]	-	-
Anthracene	178.23	613	0.045	0.0778	3.96	3.91E-05	1.60E-03	4.54	4.47 [c]	3.20E-06	7.74E-1
Fluoranthene	202.26	648	0.26	8.7E-03	1.04	1.02E-05	4.20E-04	5.22	5.03 [c]	3.00E-06	6.35E-1
Pyrene	202.26	633	0.13	0.0119	0.92	9.08E-06	3.72E-04	5.18	5.02 [c]	2.70E-06	7.24E-1
Chrysene	228.30	721	0.0016 [c]	1.07E-04	0.065	6.41E-07	2.63E-05	5.70 [D]	3.66 [l]	2.50E-06	6.21E-1
Benzo(a) anthracene	228.30	708	0.011	6.06E-04	0.581	5.73E-06	2.35E-04	5.91	4.0-7.3 [b]	5.10E-06	9.00E-1
Benzo(b) fluroanthene	252.32	754	0.0015	6.67E-05 [f]	0.43 [q]	4.26E-06	1.75E-04	5.80	5.74 [b]	2.60E-06	5.56E-1
Benzo(k) fluoranthene	252.32	753	8.00E-04	4.12E-06	0.084 [c]	8.29E-07 [C]	3.4E-05 [c]	6.00	6.09 [c]	2.60E-06	5.56E-1
Benzo(a) Pyrene	252.32	768	0.0038	2.13E-05	0.046	4.54E-07	1.86E-05	6.04	6.01 [c]	4.30E-06	9.00E-1
Indeno(1,2,3-c,d) pyrene	276.34	809 [a]	2.2E-05 [c]	1.30E-08 [f]	0.162 [c,f]	1.6E-06 [c,f]	6.56E-05 [c,f]	6.65 [d]	6.54 [c]	1.90E-06	5.66E-1
Benzo(g,h,i) perylene	276.34	773 [a]	2.6E-04	2.25E-05	0.075	7.4E-07	3.03E-05	6.50	5.61 [f]	-	-
Dibenzo(a,h) anthracene	278.36	797	6.0E-04	9.16E-08	1.49E-03 [c,f]	1.47E-08 [c,f]	6.03E-07 [c,f]	6.75	6.58 [c]	2.00E-06	5.18E-1
Coronene	300.36	798	1.40E-04	2.00E-10 [g]	-	-	-	6.75	5.0-7.8 [l]	-	-

[^] Conversion factor from mmHg to Pa, multiply by 133.32. The selected values presented are liquid vapour pressure values at 25°C

[#] Conversion factor from atm-m^3 mol^{-1} to Pa-m^3 mol^{-1} = multiply by 101325; atm-m^3 mol^{-1} to dimensionless = multiply by 41

[A] Chemfinder (http://chemfinder.cambridgesoft.com/)

[b] Values taken from Mackay *et al.* 1991 (Mackay, Shiu et al. 1991)

[C] Value taken from USEPA Soil Screening Level data. No summary value available from Mackay *et al.* 1991

[D] Value taken from USEPA Soil Screening Level data.

[E] Value taken from the EHC document for PAHs and the SRC database.

[F] Value taken from SRC database.

[G] Value taken from EHC document (WHO 1998a)

[h] Value from Kenaga and Goring (Kenaga and Goring 1980b)

[i] Value from Abdul *et al.* (1986)(cited by Baker *et al.* (Baker, Mihelcic et al. 1997))

[k] Value from Hasset *et al.* (1980)(cited by Baker *et al.* (Baker, Mihelcic et al. 1997))

[L] Lancaster University POPs modelling reported value (http://www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html)

[M] Design Institute for Physical Property Data, The American Institute for Chemical Engineers online data search (1997). Cited by USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[N] USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[P] Lange's Handbook of Chemistry 15th Edition, MCGraw-Hill (1999). Cited by USEPA (2000) User's Guide for the Johnson and Ettinger (1991) Model for Subsurface Vapour Intrusion into Buildings (Revised).

[q] Calculated using the vapour pressure and the solubility values given in the table.

3. CHLORINATED SOLVENTS

3.1 Introduction

Chlorinated solvents have been used by industry since the early 20th century for a variety of purposes, including metal degreasing, as dry cleaning agents and in the manufacture of plastics and consumer products, such as propellant aerosols and paints. However, since the mid-20th century, concerns over the effects of particular solvents on human health and the environment have led to the banning or restriction of the use of specific solvents. For example, carbon tetrachloride was withdrawn from use in the 1950's due to its high toxicity, and was replaced by tri- and tetrachloroethene for dry cleaning applications. The main chlorinated solvents in use in the UK today are dichloromethane, tri- and tetrachloroethene (pers comm., André Orban, ECSA).

Seven chlorinated solvents were selected by the Environment Agency for assessment in this report: trichloroethene, tetrachloroethene, trichloroethane, tetrachloroethane, carbon tetrachloride, 1,2-dichloroethane and vinyl chloride[8].

3.1.1. Major sources to the environment

The selected solvents and their specific uses are listed below:

- Trichloroethene (TCE) is the second most widely used solvent in the UK (pers comm., André Orban, ECSA). More than 80% is used for vapour degreasing and cleaning of metal parts; it is also used in adhesives, in chemical synthesis e.g. HCFC production, and as a solvent (ESCA 2002).
- Tetrachloroethene (PCE) is commercially important as a solvent and as a chemical intermediate. It is used widely in dry cleaning and degreasing operations (ATSDR 1997a; ESCA 2002).
- 1,1,1-trichloroethane (TCA) had applications in metal degreasing processes and as a solvent in many industrial and consumer products, including adhesives, spot removers, and aerosol cans (WHO 1992a). However, due to concerns over its role in ozone depletion, production for emissive uses in Europe was phased out under the Montreal Protocol by 1995 (ESCA 2002). The main current use of TCA is as feedstock for HCFCs and fluoropolymer resins (ESCA 2002).
- Tetrachloroethane's (PCA) only significant use today is as a feedstock in the manufacture of TCE, PCE, and 1,2-dichloroethene (ESCA 2002). In the past it was mainly used as a chemical intermediate and as an industrial solvent, but also for cleaning and degreasing metals, and in paints and pesticides. (Kirk-Othmer 2003).
- Carbon tetrachloride (CT) was previously used in metal degreasing, as a refrigerant and as a chemical intermediate. However in 1986, it was identified as a compound which may deplete the stratospheric ozone layer. Under the Montreal Protocol the use of CT was phased-out by 1994, with the exception of some essential and feedstock uses e.g. production of CFC 11 and 12.

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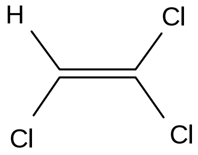
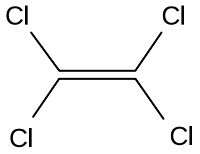
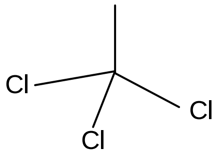
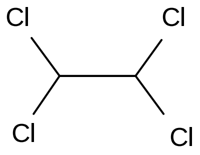
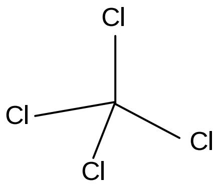
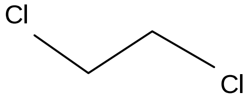
[8] At the request of the Agency, dichloromethane has not been assessed.

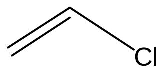
- 1,2-dichloroethane (DCA) is today used mainly as a chemical intermediate for the manufacture of vinyl chloride (VC). In the past, it was used in metal cleaners and degreasers, domestic cleaning solutions and pesticides; adhesives, paint, varnish, and finish removers (ATSDR 2001b).
- Vinyl chloride (VC) is mainly used as the monomer in the production of poly vinyl chloride (PVC). It is also used in the manufacture of building and construction products, electrical wire insulation and cables, piping, industrial and household equipment (HSDB 2002).

3.1 Identity

Table 3.1 presents information on the nomenclature, structure, CAS number and IUPAC name of the chlorinated solvents addressed in this report.

Table 3.1 **Information on nomenclature, structure, CAS number and IUPAC name of selected chlorinated solvents**

Substance name (IUPAC name if different)	Structure	CAS Number	Common names
Trichloroethene		79-01-6	TCE, Tri Ethylene trichloride 1,1-dichloro-2-chloroethylene 1-chloro-2,2-dichloroethylene Trichloroethylene
Tetrachloroethene		127-18-4	PCE, Perc Perchloroethylene Ethylene tetrachloride Tetrachloroethylene
1,1,1-Trichloroethane		71-55-6	TCA Methyl chloroform Methyl trichloromethane
1,1,2,2-Tetrachloroethane		79-34-5	PCA 1,1-dichloro-2,2-dichloroethane Acetylene tetrachloride
Carbon tetrachloride (Tetrachloromethane)		56-23-5	CT Carbon tet Methane tetrachloride tetrachlorocarbon
1,2-Dichloroethane		107-06-2	DCA 1,2-Ethylene dichloride

Substance name **(IUPAC name if different)**	**Structure**	**CAS Number**	**Common names**
Vinyl chloride **(Chloroethene)**		75-01-4	VC Ethylene monochloride Monochloroeth(yl)ene

3.2 Occurrence in Soil

The chlorinated solvents do not occur naturally and are only present in the environment as a consequence of anthropogenic activities. One of the primary reasons for environmental pollution with chlorinated solvents is their improper historic disposal. As a consequence of the high volatility of these chemicals, it was originally thought that pouring them onto dry ground was a safe and efficient disposal practice; however, due to infiltration and diffusion of the solvent into the subsurface, serious pollution resulted (DNAPL 2002).

Trichloroethene

TCE has been found in concentrations exceeding 100 µg kg^{-1} in soils and sediments near production sites, however, samples taken further away (distance not given) from production sites show lower levels; for example concentrations measured in Liverpool Bay (an urban and industrialised area) ranged from a few ng kg^{-1} to 10 µg kg^{-1} (WHO 1985). Soils from an industrial area in Germany were found to contain TCE at levels of 3 to 4 ìg kg^{-1}; riverside soil from the Roth Main contained 0.06 ìg kg^{-1} TCE (EU 2001a). The mean concentration in soil samples from a small catchment area used for agriculture was 13 ìg kg^{-1} (EU 2001a).

Tetrachloroethene

PCE may occur in soil due to spills, runoff and leaching, however it is not likely to persist due to its high mobility and potential for degradation (ATSDR 1997a). The concentration in soil air samples taken in Germany is reported to be between 2.1 and 4.5 ìg m^{-3} (EU 2001b). No other reports of levels in soil have been identified. In a UK survey, the maximum level of PCE in groundwater was 13 ìg l^{-1} (EU 2001b).

Trichloroethane

Concentrations of 1,1,1-TCA in soil interstitial water and on soil particles in samples from an industrial area in Germany were near to or less than the detection limits (0.1 µg l^{-1} and 0.1 µg kg^{-1}, respectively) (WHO 1992a). Samples of soil air contained 1,1,1-TCA levels ranging from 0.2 to 10 µg m^{-3}. In the same study, soil air samples from over 1,000 bore holes in various locations were analysed, concentrations ranging from 1 µg m^{-3} in a rural area, to over 2.2 µg m^{-3} in agricultural and forest soils near industrial sources and up to 9 µg m^{-3} in urban areas (WHO 1992a).

Tetrachloroethane

No reports on the occurrence of PCA in soil have been identified. It is considered by the author that levels may be expected to be <1 ìg kg^{-1} in unpolluted areas, up to ~10 ìg kg^{-1} in industrial areas.

Carbon Tetrachloride

CT may occur in soil due to spills, runoff and leaching, however in one US survey in the 1980's only 1% of soil/sediment samples analysed contained the compound; the concentration of CT was always less than 5.0 mg kg^{-1} dry weight soil or sediment (WHO 1999a) which suggests that volatilisation to air is usually swift.

Dichloroethane

1,2-DCA was not detected (detection limit 0.01 mg kg^{-1}) in 30 soil samples from "typical" urban residential and parkland locations in southern Ontario, Canada (WHO 1995). The mean 1,2-DCA concentration in soil near 20 homes in "uncontaminated" areas of the Netherlands was 11 mg kg^{-1}, while samples of soil in the vicinity of a garage and a waste site contained <5 and 30 mg kg^{-1}, respectively (WHO 1995).

Vinyl Chloride

Environmental contamination with VC arises from its formation during the degradation of TCE, PCE and 1,1,1-TCA (through anaerobic dechlorination, see Section 5) as well as emissions from primarily PVC manufacturing facilities (ATSDR 1997c). Subsurface soil samples near a solvent disposal pit in southern Finland showed VC concentrations as high as 900 mg kg^{-1} (WHO 1999b). After an accidental spillage of VC into snow in 1980, VC concentrations as high as 500 mg kg^{-1} were measured in the soil at up to 2 m depth (WHO 1999b).

3.3 Physicochemical Properties

This section discusses the range of physicochemical parameters that are recommended for use in the CLEA model and aims to justify a particular selection. The recommended physicochemical properties of individual solvents to be used in the CLEA model are presented in Table 3.2, together with the minimum and maximum values. Where SI units are different to CLEA model units, these are also given. The various physical and chemical properties of chlorinated solvents which contribute to their contamination of soil are summarised below. The introductory chapter describes how these parameters are used within environmental modelling and the CLEA model in particular.

Characteristics such as molecular weight, molecular structure, aqueous solubility and the octanol-water partition coefficient (K_{ow}) will determine the behaviour of the solvent in the environment and its potential for degradation through biotic and abiotic processes. Solvents with a low molecular weight, high aqueous solubility, low K_{ow} and a high resistance to degradation processes are most likely to be mobile in soil and leach to groundwater.

A hierarchical approach to the selection of physicochemical parameters has been applied. EU risk assessments have been carried out for TCE and PCE, and where possible, the EU recommended physicochemical data have been selected for these chemicals in the CLEA model. The EU values are felt to be most applicable to CLEA, since the UK (the Environment Agency and Health and Safety Executive) was the rapporteur for the assessments. The approach followed by the rapporteur for selection of physicochemical data was to take the most appropriate values from chemical handbooks and databases for use in modelling.

Where a chemical or specific parameter has not been covered by EU risk assessments, the aforementioned approach used in the EU risk assessments was applied, i.e. selection from peer reviewed sources, databases or encyclopaedias. Values were selected from the most appropriate of the following sources, taking into account the publication date of the source, how well referenced the quoted value is and the temperature at which the quoted value was recorded:

(i) EU risk assessment documents;
(ii) WHO Environmental Health Criteria documents, which have been prepared by a panel of international experts;
(iii) USEPA soil screening level (SSL) guidance document (USEPA 1996a);
(iv) Syracuse Research Centre (SRC) Chemfate database;
(v) Other chemical encyclopaedias or reference books used by the EU rapporteur.

The values recommended for use in the CLEA model lie within the literature range identified, are referenced and, where feasible, are provided with possible measurement conditions.

With the exception of values for air and water diffusivity and certain K_{oc} values in the USEPA SSL, all of the values used in the development of USEPA SSLs were derived from the most recent version of the Superfund Chemical Data Matrix (SCDM)[9]. SCDM generally uses data from the following references (in order of preference):

- USEPA FATE Database (USEPA 1995).
- SRC CHEMFATE Database (SRC and Syracuse Research Corporation 1995).
- CHEMCALC values, calculated according to Lyman *et al.* (1982 and 1990), as described in RTI (1996).
- GSC Corporation CHEMEST Database (GSC Corporation 1990).

To avoid repetitious referencing in this section, abbreviations (given in brackets below) are used in the following section:

- Syracuse Research Corporation CHEMFATE Database. SRC, Syracuse, NY. (SRC)
- WHO Environmental Health Criteria document (WHO)
- US National Library of Medicine Hazardous Substances Data Bank (HSDB)
- USEPA Soil Screening Guidance Technical Background Document (USEPA 1996)
- European Union Risk Assessment Report for TCE/PCE (EU 2001a)
- Kirk-Othmer Encyclopaedia of Chemical Technology (Kirk-Othmer)
- Lide, D.R. (Ed.). 1994. CRC Handbook of Chemistry and Physics, 75th ed. CRC Press, Boca Raton, FL (CRC)

The above sources often cite references and these are mentioned in the text where available, with the full reference given after the table of values.

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[9] http://www.epa.gov/superfund/resources/scdm/scdm-pf.pdf

The recommended physicochemical data for use in the CLEA model are shown in Table 3.2. The values have been selected according to the hierarchy discussed in above. The table presents selected values, and the minimum and maximum values identified from the literature. Where numbers are less than one i.e. x10^{-1}, the values have been entered as E-01 etc. so that numbers can be copied directly into the CLEA model spreadsheet.

Table 3.2 Recommended physicochemical values and parameters for use in the CLEA model, minimum and maximum literature ranges (CLEA units, temperature (°C) in brackets)

Substance	Value	Mol. weight [a]	Boiling Point [a,h]	Aqueous Solubility		Vapour Pressure		Henry's Law Constants [#]					Log K_{ow}	Log K_{oc}	K_{oc}	Coefficient of Diffusion (25°C) [e]		Enthalpy of vapourisation (25°C)	Critical temp
																Air	Water		
			K	mg l^{-1}		Pa[^]		Pa-m^3 mol^{-1}		atm-m^3.mol^{-1}		Dimen-sionless (cm^3/cm^3)	-	-	$l.kg^{-1}$	$m^2.s^{-1}$	$m^2.s^{-1}$	$cal.mol^{-1}$	K
TCE	Recommended	131.39	360.45	1070	(20)[a]	8600	(20)[c]	1044	(25)[b,c,e]	0.0103	(25)[b,c,e]	0.418	2.29 [c]	2.21	162 [†]	7.90E-06	9.10E-10	7474 [a]	573.2 [a]
	Min	-	-	1070	(20)[a]	6240	(17.8)[c]	1044	(25)[b,c,e]	0.0103	(25)[b,c,e]	0.418	2.29 [c]	1.76	57 [e]	-	-	7474 [a]	544.2 [h]
	Max			1472	(25)[b]	9794	(25)[b]	1333	(13.8)[a]	0.0132	(13.8)[a]	0.726	2.71 [e]	2.96	921 [c]			7505 [h]	573.2 [a]
PCE	Recommended	165.83	394.35	149	(ns)[c]	1900	(20)[c]	2128	(20)[c]	0.0211	(20)[c]	0.865	2.53 [c]	2.34	219 [†]	7.20E-06	8.20E-10	8293 [a]	620.1 [a]
	Min	-	-	149	(20/25)[a,c,d]	1333	(13.8)[a]	1864	(25)[b]	0.0184	(25)[b]	0.754	2.53 [c]	1.64	44 [c]	-	-	8288 [h]	620.1 [a]
	Max			400	(25)[b]	2473	(25)[b]	2128	(20)[c]	0.0211	(20)[c]	0.865	3.40 [b]	2.72	525 [c]			8293 [a]	620.2 [h]
TCA	Recommended	133.40	347.0	1334	(25)[b]	13330	(20)[a,d]	1743	(24.8)[b]	0.0172	(24.8)[b]	0.705	2.47 [d]	2.30	200 [†]	7.80E-06	8.80E-10	7911 [a]	584.5 [a]
	Min	-	-	300	(20)[d]	13330	(20)[a,d]	811	(ns)[f]	0.0080	(ns)[f]	0.328	2.47 [d]	2.04	106 [e]	-	-	7136 [h]	545.0 [h]
	Max			4400	(25)[b]	16532	(25)[b]	1743	(24.8)[b]	0.0172	(24.8)[b]	0.705	2.68 [b]	2.26	183 [b]			7911 [a]	584.5 [a]
PCA	S Recommended	167.85	419.3	3200	(20)[a]	647	(20)[a]	35	(25)[b]	0.000345	(25)[b]	0.014	2.39 [b]	2.26	182 [†]	7.10E-06	7.90E-10	9247 [a]	661.0 [a]
	Min	-	-	2962	(25)[b]	616	(25)[b]	35	(25)[b]	0.000345	(25)[b]	0.014	2.39 [b]	1.90	79 [e,b]	-	-	8996 [h]	661.0 [a]
	Max			3200	(20)[a]	647	(20)[a]	-	-	-	-	-	-	1.97	93 [e]			9247 [a]	661.2 [h]
CT	Recommended	153.82	349.7	793	(25)[b]	12172	(20)[d]	2330	(24.8)[d]	0.023	(24.8)[d]	0.943	2.83 [b]	2.49	309 [†]	7.80E-06	8.80E-10	7158 [a]	556.2 [a]
	Min	-	-	757	(25)[b]	11940	(20)[a]	2330	(24.8)[d]	0.023	(24.8)[d]	0.943	2.64 [d]	1.38	24 [b]	-	-	7127 [h]	556.2 [a]
	Max			800	(25)[a]	15332	(25)[b]	3060	(25)[b]	0.0302	(25)[b]	1.238	2.83 [b]	2.35	224 [b]			7158 [a]	556.6 [h]
DCA	Recommended	98.96	356.7	8524	(20)[b]	8500	(20)[a,d]	111	(25)[d]	0.0011	(25)[d]	0.045	1.48 [b]	1.79	62 [†]	10.4E-06	9.90E-10	7418 [a]	563.0 [a]
	Min	-	-	8524	(20)[b]	8500	(20)[a,d]	99	(25)[b]	0.00098	(25)[b]	0.040	1.47 [e]	1.23	17 [e]	-	-	7418 [a]	561.0 [h]
	Max			8690	(20)[a,d]	10519	(25)[b]	111	(25)[d]	0.0011	(25)[d]	0.045	1.76 [d]	1.90	76 [b]			7643 [h]	563.0 [a]
VC	Recommended	62.50	259.3	1100	(20)[d]	333000	(20)[d]	1960	(17.5)[d]	0.01935	(17.5)[d]	0.779	0.60 [b]	1.80	63 [†]	10.6E-06	12.3E-10	5250 [h]	432.0 [a,h]
	Min	-	-	60	(20)[b]	309306	(20)[b]	1960	(17.5)[d]	0.01935	(17.5)[d]	0.779	0.60 [b]	1.15	14 [d]	-	-	5250 [h]	432.0 [a,h]
	Max			8800	(25)[b]	394366	(25)[b]	18880	(20)[g]	0.180	(20)[g]	7.380	1.58 [d]	2.38	240 [d]			-	-

[^] Conversion factor from mmHg to Pa = multiply by 133.32. Values with zero's at end have been rounded up from literature values quoted in kPa.

[#] Conversion factor from atm-m^3 mol^{-1} to Pa-m^3 mol^{-1} = multiply by 101325; atm-m^3 mol^{-1} to dimensionless = multiply by 41

[†] K_{oc} calculated from recommended K_{ow} using the following equation for non-hydrophobic compounds from (EU 1996): $\log K_{oc} = 0.52 \log K_{ow} + 1.02$

[a] Kirk-Othmer (Kirk-Othmer 2003)

[b] SRC Chemfate

[c] EU Risk Assessment

[d] WHO EHC document for that chemical

[e] (USEPA 1996a)

[f] (HSDB 2002)

[g] (ECSA 2002)

[h] (USEPA 2000). Values from CRC (1994) except VC (Design Institute for Physical Properties Data, American Institute of Chemical Engineers, on line data search 1997) and CT (estimated from QSAR data).

Molecular Weight

The molecular weight of the chlorinated solvents affects their transport and partitioning in the soil environment. Higher molecular weight compounds are less mobile in soil due to their greater potential to be adsorbed by soil organic matter. Molecular weights for use in the CLEA model have been taken from Kirk-Othmer. Ranges are not appropriate for this parameter.

Boiling Point

Trichloroethene

The boiling point of TCE reported in the literature ranges from 85.9 to 88°C. The EU risk assessment uses a range of 86 to 88°C, which is consistent with that expected from the vapour pressure. WHO (1985) quotes a value of 86.7°C (at 760 mmHg) while CRC (2000-2001) and Kirk Othmer (2003) quote 87.2°C and 87.3°C respectively.

Tetrachloroethene

A value of 121.2°C (reported by Kirk-Othmer, 2003) is the value used in the EU risk assessment since the method of determination is known (constant fractionation through a Young column) and the value is consistent with that which would be expected from vapour pressure studies. The IUCLID database and WHO (1984) both quote 121°C.

Kirk Othmer has been used as the source of values for all the solvents, since that is source used by the UK rapporteur for the EU risk assessment of PCE.

Water Solubility

The chlorinated solvents generally have low solubilities in water, typically a few grams per litre (g l^{-1}) or less. This will reduce their potential for degradation in the environment.

Trichloroethene

TCE is described as being practically insoluble (Merck 1989), slightly soluble (CRC Handbook 2000-2001) or soluble (IUCLID 2000). This difference in opinions is due to the subjective nature of qualifying solubility. The EU risk assessment employs a value of 1100 mg l^{-1}, which is the value quoted in the IUCLID dataset (from Horvath, 1982). Kirk-Othmer (2003) quotes 1070 mg l^{-1} at 20°C. This latter value is recommended for use in the CLEA model since the temperature is given, and when rounded is the same as the EU value.

Tetrachloroethene

PCE is described as sparingly soluble or insoluble (CRC Handbook 2000-2001). Values of 149 mg l^{-1} (IUCLID 2000, from Horvath, 1982), 150 mg l^{-1} (WHO 1984, at 20°C; Kirk-Othmer, at 25°C, Kirk-Othmer 2003) and 160 mg l^{-1} (Merck 1989) have been identified. The EU risk assessment employs 149 mg l^{-1} (at 20°C) and this value is recommended for use in the CLEA model.

Trichloroethane

TCA is described in WHO (1992a) as slightly soluble in water. WHO (1992a) quotes values of 300 mg l^{-1} (IARC 1979, at 20°C), 480 mg l^{-1} (at 20°C) and 950 mg l^{-1} (25°C, Kirk-Othmer 2003). The SRC recommended value is 1.33 g l^{-1} (measured at 25°C, Banerjee *et al*. 1980) and is also the value used in USEPA (1996a). This value has been chosen for use in the CLEA model as it is fully referenced with measurement conditions given.

Tetrachloroethane

PCA is slightly soluble in water with values of 3200 mg l^{-1} (20°C, Kirk-Othmer 2003), 2960 mg l^{-1} (measured at 25°C, SRC recommended value, Horvath 1982) and 2970 mg l^{-1} (25°C, used in USEPA, 1996a). The value from Kirk-Othmer is chosen for use in the CLEA model as it is the source used by the EC and is similar to the measured SRC value.

Carbon Tetrachloride

The solubility recommended by SRC of 793 mg l^{-1} (measured at 25°C; Horvath 1982) is the same value quoted in USEPA (1996a). Kirk Othmer (2003) and WHO (1999a) quote values of 800 mg l^{-1} and 785 mg l^{-1} at 25°C respectively. The SRC/USEPA value is chosen for use in the CLEA model, as it is a measured value from a referenced source, and is within the range identified.

Dichloroethane

WHO (1995) quotes a solubility of 8.69 g l^{-1} (20°C; Kirk-Othmer 2003). The SRC recommended value is 8524 mg l^{-1} (20°C, measured by Horvath 1982) and is the same as the value used in USEPA (1996a). This latter value is recommended for use in the CLEA model.

Vinyl Chloride

WHO (1999b) describes VC as having a relatively low solubility and quotes an ESCA value of 1100 mg l^{-1} at 20°C. USEPA (1996a) uses a value of 2760 mg l^{-1} at 25°C. Both values fall within the literature range identified in the SRC Chemfate database of 60 to 8800 mg l^{-1}, however, the WHO value is recommended for use in the CLEA model since it is from a recent EU source at a more appropriate temperature.

Vapour Pressure

The chlorinated solvents have relatively high vapour pressures compared to other substances considered in this report, hence they readily volatilise from the subsurface to indoor and outdoor air spaces. They are expected to exist solely as a vapour in air (HSDB 2002).

Trichloroethene

The EU risk assessment (2001a) uses the IUCLID value of 8.6 kPa at 20°C. This value is taken from Verschueren (1983). The risk assessment also reports values of 6.24 and 9.55 kPa (measured at 17.8°C and 25.5°C respectively). 73.46 mmHg (9.79 kPa) (measured at 25°C) is the SRC's recommended value. The EU value is recommended for use in the CLEA model.

Tetrachloroethene
The EU risk assessment (2001b) employs a value of 1.9 kPa at 20°C, as quoted in the IUCLID dataset and WHO (1984). 18.55 mmHg (2.47 kPa) is the recommended SRC value (measured at 25°C, Daubert and Danner 1989). Kirk-Othmer (2003) quotes a value of 1.33 kPa at 13.8°C, which may be a more appropriate temperature for soils. The EU value is recommended for use in the CLEA model.

Trichloroethane
The vapour pressure of TCA reported in WHO (1992a) is 13.3 kPa (measured at 20°C, cited in CRC (2000-2001), the same value as in Kirk-Othmer (2003). The SRC recommended value is 124 mmHg (16.53 kPa) (measured at 25°C, Daubert and Danner 1989). Since both cited references are relatively dated, the former value of 13.3 kPa, measured at the lower temperature, is recommended for use in the CLEA model.

Tetrachloroethane
The vapour pressure of PCA recommended by SRC is 4.62 mmHg (0.616 kPa) measured at 25°C by Daubert and Danner (1989). Kirk-Othmer (2003) quotes a value of 0.647 kPa at 20°C. The lower temperature value is recommended for use in the CLEA model.

Carbon Tetrachloride
The vapour pressure recommended by SRC is 114 mmHg (15.20 kPa) (at 25°C, Daubert and Danner 1989). Kirk Othmer (2003)quotes 11.94 kPa and WHO (1999a) quotes 91.3 mmHg (12.17 kPa) both at 20°C. The latter value from WHO is recommended for use in the CLEA model according to the hierarchy.

Dichloroethane
The vapour pressure given by WHO (1995) is 8.5 kPa (20°C). 78.9 mmHg (10.52 kPa) is the recommended SRC value (measured at 25°C, Daubert and Danner 1989). The WHO value, given for a lower temperature, is recommended for use in the CLEA model.

Vinyl Chloride
The SRC recommended vapour pressure of VC is 2958 mmHg (394 kPa) (measured value for 25°C, based on extrapolation; Boublik, Fried *et al*. 1984). WHO (1999b) quotes a value of 333 kPa at 20°C; this value is recommended for use in the CLEA model in the absence of an EU value.

Henry's Law Constant

Due to their relatively low solubilities and high vapour pressures, the chlorinated solvents will exhibit high values of K_H. A large K_H (i.e. greater than 10^{-3}) indicates a strong tendency to partition to the gas phase and limited dissolution in water. The chlorinated solvents are expected to evaporate rapidly from moist soil surfaces based on their K_H. The range of K_H for individual solvents is a consequence of the range of vapour pressures and solubilities. Table 3.2 shows values in both units and also as a dimensionless Henry's Constant.

Trichloroethene

The EU risk assessment uses a value of 0.0103 atm-m^3 mol^{-1} (1044 Pa-m^3 mol^{-1}), calculated from the ratio of vapour pressure to solubility. This is the same as the SRC recommended value (measured at 25°C, Munz and Roberts 1987) and the value used in USEPA (1996a). This value is therefore recommended for use in the CLEA model.

Tetrachloroethene

The EU risk assessment employs a value of 0.021 atm-m^3 mol^{-1} (2128 Pa-m^3 mol^{-1}), calculated using molecular weight, vapour pressure and solubility. The SRC recommended value is 0.0184 atm-m^3 mol^{-1} (1864 Pa-m^3 mol^{-1}), (measured at 25°C, Munz and Roberts 1987) which is the same as that used in USEPA (1996a). The EU value is recommended for use in the CLEA model, as it is suitably close to the other values identified.

Trichloroethane

The SRC recommended value is 0.0172 atm-m^3 mol^{-1} (1743 Pa-m^3 mol^{-1}) (measured at 24.8°C, Gossett 1987), and is the same as that employed in USEPA (1996a). HSDB (2002) reports a value of 0.008 atm-m^3 mol^{-1} (811 Pa-m^3 mol^{-1}) (Lyman, Reehl *et al.* 1982 and 1990). In the absence of any EU or WHO recommended value, the SRC/USEPA value is recommended for use in the CLEA model.

Tetrachloroethane

The SRC recommended value is 3.45×10^{-4} atm-m^3 mol^{-1} (35 Pa-m^3 mol^{-1}) (calculated for 25°C), and is the same as that employed in USEPA (1996a). In the absence of any EU or WHO recommended value, this value is recommended for use in the CLEA model.

Carbon Tetrachloride

The SRC recommended value is 0.0302 atm-m^3 mol^{-1} (3060 Pa-m^3 mol^{-1}) (25°C, Warner, Cohen J.M *et al.* 1987) and is the same as that employed in USEPA (1996a). WHO (1999a) quotes a value of 0.023 atm-m^3 mol^{-1} (2330 Pa-m^3 mol^{-1}) at 24.8°C. The WHO value is recommended for use in the CLEA model according to the hierarchy given earlier.

Dichloroethane

The SRC recommended value is 9.79×10^{-4} atm-m^3 mol^{-1} (99.2 Pa-m^3 mol^{-1}) (25°C, Dilling 1977), and is the same as that employed in USEPA (1996). WHO (1995) quotes 111.5 Pa-m^3 mol^{-1} (1.1×10^{-3} atm-m^3 mol^{-1}) (25°C). The WHO value is recommended for use in the CLEA model, as it is suitably close to the other value identified.

Vinyl Chloride

The SRC recommended value is 0.027 atm-m^3 mol^{-1} (2736 Pa-m^3 mol^{-1}) (24.8°C, Gossett 1987), the same as that employed in USEPA (1996a). WHO (1999b) quotes values of 1.96 kPa-m^3 mol^{-1} (0.019 atm-m^3 mol^{-1}) at 17.5°C (Gossett 1987) and 18.8 kPa-m^3 mol^{-1} (0.18 atm-m^3 mol^{-1}) at 20°C (ESCA 2002). The first WHO value is recommended for use in the CLEA model as it is recorded at the most appropriate temperature for soil, and is from the same author as the SRC/USEPA recommended values at 25°C.

Octanol-water partition coefficient

The chlorinated solvents have relatively low octanol-water partition coefficient (K_{ow}) values and are considered to be fairly hydrophilic with a low potential to bind to soil. They are therefore not expected to persist in the soil environment. The more chlorinated solvents tend to have higher values, for instance log K_{ow} (USEPA 1996a) for VC (a monochlorinated alkene) is 1.36 and 3.40 for PCA (a tetrachlorinated alkane). For K_{ow}, SCDM uses Log K_{ow} data from Research Triangle Institute (1996), followed by USEPA (1995), SRC (2003) and GSC Corporation (1990).

Trichloroethene

The EU risk assessment uses a measured log K_{ow} value of 2.29 (quoted in IUCLID and SRC, from Rogers and McFarlane 1981). IUCLID also quotes a calculated value of 2.42 (Hansch and Leo 1985), the same as that quoted in WHO (1985) from Banerjee, Yalkowsky et al. (1980). The recommended value from SRC is 2.47 (estimated, Hansch and Leo 1985). A value of 2.71 is used in USEPA (1996a). The EU value of 2.29 is recommended for the CLEA model in order to be consistent with the EU risk assessment and because it is a measured value.

Tetrachloroethene

The EU risk assessment employs a value of 2.53 (measured using the shake flask method at 23±1.5°C, (Banerjee, Yalkowsky *et al.* 1980). This same value (measured by Veith, Macek *et al.* 1980) is also reported in the IUCLID dataset. The SRC recommended value is 3.4 (measured, Hansch and Leo 1985). WHO (1984) quotes a log K_{ow} of 2.86. Although the lowest of the identified values, the EU value is recommended for the CLEA model to be consistent with the European risk assessment and because its method of determination is reported.

Trichloroethane

The value of Log K_{ow} quoted in WHO (1990) is 2.47 (measured, Veith, Macek *et al.* 1980) which is very close to both the SRC recommended value and the value in USEPA (1996a), 2.49 (measured, Hansch and Leo 1985) and 2.48 respectively. The WHO value is chosen for use in the CLEA model.

Tetrachloroethane

The SRC recommended value is 2.39 (measured (Hansch and Leo 1985) and is the same as that used in (USEPA 1996a). The absence of any EU or WHO value means that this value is selected for use in the CLEA model.

Carbon Tetrachloride

WHO (1999a) quotes a value of 2.64. The SRC recommends a value of 2.83 (measured, Hansch and Leo 1985) while USEPA (1996a) employs a value of 2.73. In the absence of any EU data, the SRC recommended value is recommended for use in the CLEA model, based on referenced data.

Dichloroethane

The Log K_{ow} reported in WHO (1995) is 1.76 (it is notable that this has changed from the recommended value of 1.48 quoted in the 1987 edition of the same document). The SRC recommended value is 1.48 (measured, Hansch and Leo 1985). A value of 1.47 is used in USEPA (1996a). The SRC measured value is recommended for inclusion in the CLEA model as it is close to both the WHO (1995) and USEPA (1996a) values, and is from a referenced source.

Vinyl Chloride

WHO (1999b) quotes Log K_{ow} values of 1.36 (calculated, BUA 1989) and 1.52 (Gossett, Brown *et al*. 1983) and 1.58 (measured at 22°C, BUA 1989). SRC recommended values are 0.6 (measured, Callahan, Slimak *et al.* 1979) and 1.36 (estimated, SRC and Syracuse Research Corporation 1995). USEPA (1996a) uses a value of 1.5. In the absence of any EU value, a value of 1.5 is recommended for use in the CLEA model, as this is the middle of the WHO values and the value used by USEPA (1996a).

Organic carbon partition coefficient

Organic carbon partition coefficient (K_{oc}) values for individual solvents can vary significantly in the literature, with reported measured values for a compound sometimes varying over several orders of magnitude. This can be attributed to several factors, including differences in soil or sediment properties, differences in experimental and analytical approaches used to measure the values, and experimental or measurement error (USEPA 1996a).

The Karickhoff expression (Karickhoff, Brown *et al.* 1979) is often used within the literature to calculate K_{oc} from $K_{ow.}$ USEPA (1996a) uses the relationship of Di Toro (as explained within the introductory chapter) for non- volatile solvents. However, USEPA (1996a) does not consider the experimental data to fit the established relationships; instead the following expression is used: $\text{Log } K_{oc} = 0.7919 \text{ Log } K_{ow} + 0.0784$. This relationship is based on a range of soils and sediments, some of which may not be appropriate to the UK. For this reason, USEPA calculated values are not recommended for use in CLEA. However where USEPA experimental data from soils appropriate to the UK are available, this may be considered.

USEPA (1996a) measured K_{oc} values were obtained from SCDM (1997), which reports that an extensive literature survey was carried out to determine the available measurements and methods of determination. The results of the survey are provided in Appendix K, Chapter 5 of USEPA (1996a). Where K_d or K_p were reported with the organic carbon (OC) content of the soil, K_{oc} was computed by dividing K_d by the fractional soil organic carbon content (foc, g/g). Collected values were qualitatively reviewed by the USEPA, and some values were excluded - values measured for low-carbon-content sorbents (i.e. foc <0.001) were mostly rejected, while anomalous values and those outside the range of other measured values were also eliminated (USEPA 1996a).

As discussed in the introduction, where possible SGVs will be derived using a K_{oc} derived directly from the K_{ow}. The EU risk assessment reports derive K_{oc} from K_{ow} according to a range of relationships, varying according to class of compound as recommended in the Technical Guidance Document (EU 1996):

• Predominantly hydrophobics	$\log K_{oc} = 0.81 \log K_{ow} + 0.10$
• Nonhydrophobics	$\log K_{oc} = 0.52 \log K_{ow} + 1.02$

The recommended log K_{oc} values in Table 3.2 have been calculated from the recommended log K_{ow} values using the equation for nonhydrophobic compounds. Most values are within the range identified from the literature, with the exception of TCA, PCA and CT. This may be a consequence of the smaller dataset available for these substances. Nonetheless, the values are within 0.5 log K_{oc} units of the literature range.

The literature values for the individual solvents are discussed briefly below and presented in Tables 3.3 to 3.5. Tables 3.3 and 3.4 present the K_{oc} values for TCE and PCE respectively. Table 3.5 presents the values (measured and calculated) identified in literature reviews of USEPA (1996a), WHO EHC documents and the SRC and HSDB databases for all other solvents.

Trichloroethene

The EU risk assessment presents the results of laboratory studies on the adsorption of TCE by various types of soils. These results are shown in Table 3.3 below as K_{oc} values. The USEPA (1996a) literature review of K_{oc} values are also shown in Table 3.3. The average of the USEPA values is 97 (geometric mean 94). The EU recommends that K_{oc} is calculated from K_{ow} using the Karickhoff equation[10] (this gives a value of 1.90). Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, log K_{oc} is estimated to be 2.21 (K_{oc} 162 – within the literature range given in Table 3.3).

Tetrachloroethene

The EU risk assessment recommends a value of 251 l kg^{-1} at 20°C based on the measured and calculated coefficients identified in a literature search, the results of which are presented in Table 3.4. The K_{oc} values from the USEPA (1996a) literature review are also presented in Table 3.4. The average of the USEPA values gives a log K_{oc} of 272 l kg^{-1} (geometric mean 265). Using the equation given in the TGD for

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[10] Karickhoff equation is given in the introductory chapter. For the purposes of consistency in this report, all recommended K_{oc} values have been calculated using the equation from EC (1996) given above

nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 2.34 (log K_{oc} 219 – within the literature range given in Table 3.4).

Trichloroethane

No EU or WHO value was identified for TCA. The USEPA (1996a) measured average value is 139 l kg^{-1} (geometric mean 135). Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 2.30 (log K_{oc} 200 – just outside the literature range given in Table 3.5).

Tetrachloroethane

No EU or WHO value was identified. The USEPA measured value of 79 l kg^{-1} is also the SRC suggested value. Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 2.26 (log K_{oc} 182 – outside the literature range given in Table 3.5, possibly due to the small dataset).

Carbon Tetrachloride

WHO (1999a) quotes a calculated K_{oc} value of 110 l kg^{-1}. The USEPA average value is 158 (geometric mean 152) is within the SRC range of 71-224. Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 2.49 (log K_{oc} 309 – outside the literature range given in Table 3.5, possibly due to the small dataset).

Dichloroethane

The value recommended by WHO is 19 (no further details given). The USEPA average measured K_{oc} value is 44 l kg^{-1} (geometric mean 38) and is close to the SRC suggested value of 32. Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 1.79 (log K_{oc} 62 – within the literature range given in Table 3.5).

Vinyl Chloride

The value of 57 l kg^{-1} from HSDB lies within the WHO literature range of 14-240. Using the equation given in the TGD for nonhydrophobics and the previously recommended log K_{ow} value, K_{oc} is estimated to be 1.80 (log K_{oc} 63 – within the literature range given in Table 3.5).

Table 3.3 **K_{oc} (l kg^{-1}) for TCE adsorption on soil (EU and USEPA literature review data)**

K_{oc}	Soil and conditions	Source	Reference
57	Peat, 57% OC	(USEPA 1996a)	Rutherford & Chiou (1992)
58	Average of 18 values for various soils, as K_{som}	(EU 2001a)	Friesel et al (1984)
63	Soil, 4.02% OC, vapour phase expt	(USEPA 1996a)	Smith et al (1990)
65	Eq'm batch expts, aquifer material, 1.05% OC	(EU 2001a) (USEPA 1996a)	Abdul et al (1987)
69	Sandy aquifer material, 0.13% OC	(USEPA 1996a)	Brusseau & Rao (1991)
72.5 95.8 142	Forest soil (0.2% OC) 0.5 ìgg^{-1} TCE, pH 5.6 Agr. soil (2.2% OC) 0.5 ìgg^{-1} TCE, pH 7.4 Forest soil (3.7% OC) 0.5 ìgg^{-1} TCE, pH 4.2	(EU 2001a) (USEPA 1996a)	Seip et al. (1986)
84	Soil, 1.4% OC, pH 3.2	(USEPA 1996a)	Stauffer & MacIntyre (1986)
84	Aquifer solid, 0.19% OC	(USEPA 1996a)	Piwoni & Banerjee (1989)
87	Silty clay loam, 1.8% OC	(USEPA 1996a)	Rogers & McFarlane (1981)
92	Lincoln sand, 0.087% OC, 20°C	(USEPA 1996a)	Wilson et al (1981)
99	Av 2 values, soil, 2.57% OC	(USEPA 1996a)	Pignatello (1990)
101	Average of 32 soils, as $K_{som,}$ range of %OC	(USEPA 1996a)	Friesel et al (1984)
103	Top 20 cm Eerd soil, 4% OC	(USEPA 1996a)	Loch et al (1986)
123	Av 3 values, soil, 0.85% OC, column study	(USEPA 1996a)	Hutzler et al (1986)
127-183	Three soils (0.76-3.56% OC)	(EU 2001a)	Scheubel (1984)
188	Av of 2 values, clay loam, 2.6% and 1.8% OC	(EU 2001a)	Rogers & MacFarlane (1981)
316-921	Three soils (0.76-3.56% OC), OECD Test Guideline no.106 (12/5/81)	(EU 2001a)	Korte and Freitag (1984)

Table 3.4 K_{oc} ($l\ kg^{-1}$) **values for PCE adsorption on soil (EU and USEPA literature review data)**

K_{oc}	Derivation		Reference
44-51	Measured	(EU 2001b)	Lee et al. (1989)
135	Measured	(EU 2001b)	Friesel et al. (1984)
138	Calculated	(EU 2001b)	TGD Method
209 229	Measured Calculated	(EU 2001b)	Giger et al. (1983)
120, 525 372	Measured Calculated	(EU 2001b)	Zytner et al. (1989)
177 205 348	Forest soil, 0.2% OC Agricultural soil, 2.2% OC Forest soil, 3.7% OC	(USEPA 1996a) (EU 2001b)	Seip et al. (1986) column study
225	Lincoln sand, 0.087% OC	(USEPA 1996a)	Wilson et al (1981)
235	Av. 8 values, core sediment, 0.15-0.89% OC	(USEPA 1996a)	Piwoni & Banerjee (1989)
237	Av. 32 soils, K_{som}, range foc	(USEPA 1996a)	Friesel et al. (1984)
240	Calculated	(EU 2001b)	Kenaga (1980)
263	Eq'm batch expts, aquifer material, 1.05% OC	(USEPA 1996a) (EU 2001b)	Abdul et al. (1987)
268	Av 2 values, fine sandy loam, 2.57% OC	(USEPA 1996a)	Pignatello (1990)
269	Sandy aquifer material, 0.13% OC	(USEPA 1996a)	Brusseau & Rao (1991)
311	Top 20 cm Podzol soil, 0.87% OC	(USEPA 1996a)	Loch et al. (1986)
356	Coarse sand, 0.09% OC	(USEPA 1996a)	Paviostathis & Mathavan (1992)
362	Silt loam, 0.93% OC, 20°C	(USEPA 1996a)	Chiou et al (1979)
363	Calculated	(EU 2001b)	Mabey et al (1982)
373	Av. 6 measurements, 0.15% OC	(USEPA 1996a)	Schwarzenbach & Westall (1981)

Table 3.5 K_{oc} ($l\ kg^{-1}$) values for TCA, PCA, DCA, CT and VC adsorption on soil

K_{oc}	Derivation	Source	Reference
TCA			
105.9	Top 20 cm Eerd soil, 4% OC	(USEPA 1996a)	Loch et al. (1986)
172	Top 20 cm Podzol soil, 0.87% OC		
107	K_{som}, range foc	(USEPA 1996a)	Friesel et al (1984)
110	Calculated	(USEPA 1996a)	-
129	Cyanopropyl column, HPLC	(USEPA 1996a)	Hodson & Williams (1988)
179	Silt loam, 0.93% OC, 3.5°C	(USEPA 1996a)	Chiou et al (1979)
183	Measured	(SRC 2002)	Chiou et al (1979)
PCA			
79	Measured, silt loam, 0.93% OC, 20°C	(SRC 2002) (USEPA 1996a)	Chiou et al (1979)
93	Calculated	(USEPA 1996a)	-
CT			
23.8, 65.6	Two silty clay loams	(SRC 2002)	Rogers & McFarlane (1981)
110	Calculated	(WHO 1999a)	Kenaga (1980)
123	Sorption coefficient (assume K_{om})	(USEPA 1996a)	Koch (1983)
127	Extracted peat, 64% OC	(USEPA 1996a)	Rutherford et al. (1992)
224	Not given	(USEPA 1996a; SRC 2002)	Abdul et al. (1987)
DCA			
17	Calculated	(USEPA 1996a)	-
19	Not given	(WHO 1995)	Chiou et al (1979)
22	Soil, selected	(USEPA 1996a)	Jury et al (1990)
32	Silt loam, 0.93% OC, 20°C	(SRC 2002)	Chiou et al (1979)
43	Calculated	(SRC 2002)	Kenaga (1980)
76	Lincoln sand, 0.087% OC	(USEPA 1996a; SRC 2002)	Wilson et al (1981)
VC			
19	Calculated	(USEPA 1996a)	-
57	Calculated	(HSDB 2002)	Lyman et al. (1990)
14-240	-	(WHO 1999b)	Various

Coefficients of Diffusion

Organic vapour transport in the unsaturated zone is important in understanding the distribution of organic contaminants in the subsurface and their exchange between the subsurface environment and the atmosphere

Apart from the diffusion coefficients (0.0053 to 0.0609 $cm^2 s^{-1}$) measured for TCE in undisturbed soil samples (Bartlet-Hunt and Smith 2002) no other recent literature describing diffusion coefficients has been identified. Coefficients of diffusion for the solvents in air (Di_a) and water (Di_w) are held on the USEPA's CHEMDAT8 database, and are quoted in USEPA (1996a). These values are recommended for use in the CLEA model, in the absence of EU or WHO values.

Molar enthalpy of vapourisation

Values for the molar enthalpy of vapourisation were obtained from Kirk-Othmer and a recent USEPA publication (USEPA 2000). No other source for this parameter was identified. The values from the two sources are relatively close and in some cases are identical. Values from Kirk-Othmer are recommended for use in the CLEA-Model.

Critical temperature

Values for critical temperature were obtained from Kirk-Othmer and a recent USEPA publication (USEPA 2000). No other source for this parameter was identified. The values from the two sources are relatively close and in some cases are identical. Values from Kirk-Othmer are recommended for use in the CLEA-Model.

3.4 Behaviour of Chlorinated Solvents in the Soil Environment

This section considers volatilisation pathways, adsorption mechanisms and degradation processes for the chlorinated solvents in soil. The chlorinated solvents have relatively high vapour pressures so will volatilise from soil surfaces. As a result of their density and low interfacial tension, the fundamental tendency of the solvents in the subsurface is to sink through the unsaturated (vadose) zone of soil to the groundwater table, sinking through the aquifer until an impermeable layer is reached. The mobility of the solvents in the subsurface is a function of their sorption to organic (and some mineral) matter, as is indicated by their K_{oc} values. In soil, the higher chlorinated solvents are degraded more easily than their lower chlorinated counterparts.

3.4.1. Adsorption to Soil

The adsorption of a compound to soil is related to the K_{oc} value of that compound. Many researchers have found that the sorptive capacity of a soil for chlorinated solvents can be correlated to the soil organic matter (SOM) content of the soil (Diamadopoulos, Askellariadis *et al*. 1998). Generally, the greater the SOM content, the greater the sorptive capacity of the soil. From the K_{oc} values identified, the chlorinated solvents exhibit moderate to high mobility in soil compared to the non-aliphatic chlorinated hydrocarbons.

The mobility of chlorinated solvents in soil is likely to decrease with increasing molecular weight and with increased organic matter content of the environment (due to greater sorption of the solvent to the organic matter). For instance, in experiments, PCE was retarded by the soil to a greater extent than TCE under the same experimental conditions (Diamadopoulos, Askellariadis *et al.* 1998).

The SOM composition and morphology may vary, leading to a variation in the K_{oc} for a particular chlorinated solvent. For instance, K_{oc} values of chlorinated solvents for humic acid can be 6 to 13 times higher than for fulvic acid . An increase in the humic acid content of soil pore water decreases retardation by soils, though each chlorinated solvent shows different characteristics, probably due to differences in K_{oc} (Diamadopoulos, Askellariadis *et al.* 1998).

In a soil profile, a 10 fold decrease in K_{oc} may occur due to depth related changes in the composition, conformation and accessibility of SOM. Further down the soil profile, fulvic acid becomes more dominant in the SOM fraction and iron oxyhydroxide and clay particles show an increase in size. This appears to decrease the K_{oc}, probably as a result of decreasing accessibility of SOM as it becomes incorporated into the growing soil particles (Njoroge, Ball *et al.* 1998).

SOM can become associated with mineralogical phases, which may affect the ability to adsorb chlorinated solvents (Njoroge, Ball *et al.* 1998). However only when SOM was <0.1%, did sorption onto the mineral fraction of soil become significant (Njoroge, Ball et al. 1998). Pore water conditions, including pH and ionic strength may also affect adsorption to soil (Njoroge, Ball *et al.* 1998).

It has been hypothesised (Werth and Hansen 2002) that the kinetics of desorption of chlorinated solvents from soils is related to the vapour pressure of the solvent and the exposure time. Only physical characteristics of the soil were considered in assessing the kinetics of desorption. At low concentrations of solvent, only soil micropores were found to take up TCE, while at higher concentrations, larger pores also became available for sorption.

The length of time for which the solvent has been present in the soil (soil 'ageing') has an important effect on solvent desorption from SOM. The longer a contaminant is resident in soil the more resistant it becomes to desorption and biodegradation (Sheremata, Yong *et al.* 2000).

In summary, the mobility of the chlorinated solvents in soil is determined primarily by physical processes i.e. adsorption to organic matter, and to a lesser extent mineral matter. Pore water conditions, including pH and ionic strength may also affect adsorption to soil, as well as vapour pressure of the solvent and exposure time.

Removal of Chlorinated Solvents from Soils

The chlorinated solvents are subject to both abiotic and biotic degradation processes in the soil environment. Degradation will occur to various degrees, dependent upon the degree of chlorination and saturation, and soil conditions.

3.4.2. Degradation and Loss in the Soil Environment

Volatilisation

The relatively high volatility of the chemicals means that in water and soil, volatilisation is the primary abiotic fate process for the chlorinated solvents, with fairly rapid loss of the chemical from the surface (ATSDR 1997c).

TCE, in common with other chlorinated solvents, has a relatively high vapour pressure and will readily volatilise from the subsurface to indoor and outdoor air spaces (HSDB 2002). Volatilisation from wet soil surfaces may be limited by the aqueous solubility, as some of the chemical present may be expected to leach through the porewater to groundwater, rather than volatilise to the atmosphere (Cowfer and Magistro 1985). However, similar losses have been reported for TCA from both wet and dry soils (HSDB 2002).

The rate of flow is influenced by diffusive and advective processes. The organic carbon content of soils can have a significant impact on volatilisation rates as chlorinated solvents, in common with most other organic contaminants, will adsorb to organic matter. Whilst there is evidence to suggest that mass transfer is slower for long term contaminated soils (Culver, Hallisey *et al*. 1997), such adsorption is generally reversible. More permeable soils such as sands and gravels will have a relatively high effective porosity which will facilitate volatilisation.

As moisture content increases, pore spaces will become filled until only the largest pore spaces remain, requiring volatilisation to occur by increasingly more complex pathways. With increasing discontinuity of the vapour phase, volatilisation will be increasingly inhibited as diffusion through the aqueous phase will become rate limiting. However, as moisture content increases, water molecules can displace contaminant molecules, decreasing the sorptive capacity of the soils, thus acting to increase volatilisation of TCE vapours. Whilst these two factors offset one another in terms of their effect on volatilisation rate, in the case of TCE with its high vapour pressure, the air-filled effective porosity is the dominant factor (Arands, Lam *et al*. 1997, McCarthy and Johnson 1995, Smith, Tisdale *et al*. 1996).

In practice, even in conditions of very low moisture content, most soil particles are covered as a minimum by an adsorbed layer of water molecules and thus there will generally be competition for binding sites as discussed above (Arands, Lam *et al*. 1997). However, it is possible for the top few centimetres of soils to have extremely low moisture content to the extent that there are more potential binding sites available which have not been covered by water molecules. Under such circumstances, there is potential for greater concentrations of VOCs to be adsorbed thus restricting the release of VOCs (Petersen, El-Farhan *et al.* 1996). In certain circumstances, volatilisation may temporarily increase with increasing moisture content and this would be consistent with increased competition for binding sites on extremely dry soils as they become saturated. This is considered to be a minor effect although it may contribute to temporal variation in emission rates associated with rainfall events.

Biodegradation

Compounds with low chlorine content are degradable under aerobic conditions, while completely chlorinated compounds are more persistent (Zhuang and Pavlostathis 1995).

Chlorinated solvents may undergo aerobic co-metabolism. This process requires the presence of oxygen and reducing equivalents and is catalysed by soil microbial oxygenase enzymes (Alvarez and Vogel 1991). The rate of co-metabolic degradation may be limited by competitive or non-competitive inhibition of enzymes by growth or other co-metabolic substrates, toxicity of chlorinated solvent breakdown product, shortage of reducing energy or reductant (Alvarez and Vogel 1991).

Under anaerobic conditions, the biodegradation of chloroalkenes via reductive dechlorination reactions is a well documented route (e.g. Vogel and McCarty 1985; Simms, Suflita *et al.* 1991). The transformation pathways are shown in Figure 3.1. As a result of the similarities in chemical structure, the dechlorination of PCE, TCE, 1,1,1-TCA, 1,2-DCA and VC are linked, with all five compounds ultimately degraded to chloroethane.

Figure 3.1 indicates that some of the solvents may be present in the environment as a consequence of the degradation of another chlorinated solvent, and not solely due to initial pollution with that particular substance. This has implications in modelling the occurrence of these chemicals in the environment as the total inputs from waste streams or other emission points will not represent total inputs of those chemicals into the environment. This point is of particular relevance for chemicals such as VC and TCE, and the di-chlorinated compounds which are formed during the degradation of a number of the more highly chlorinated solvents.

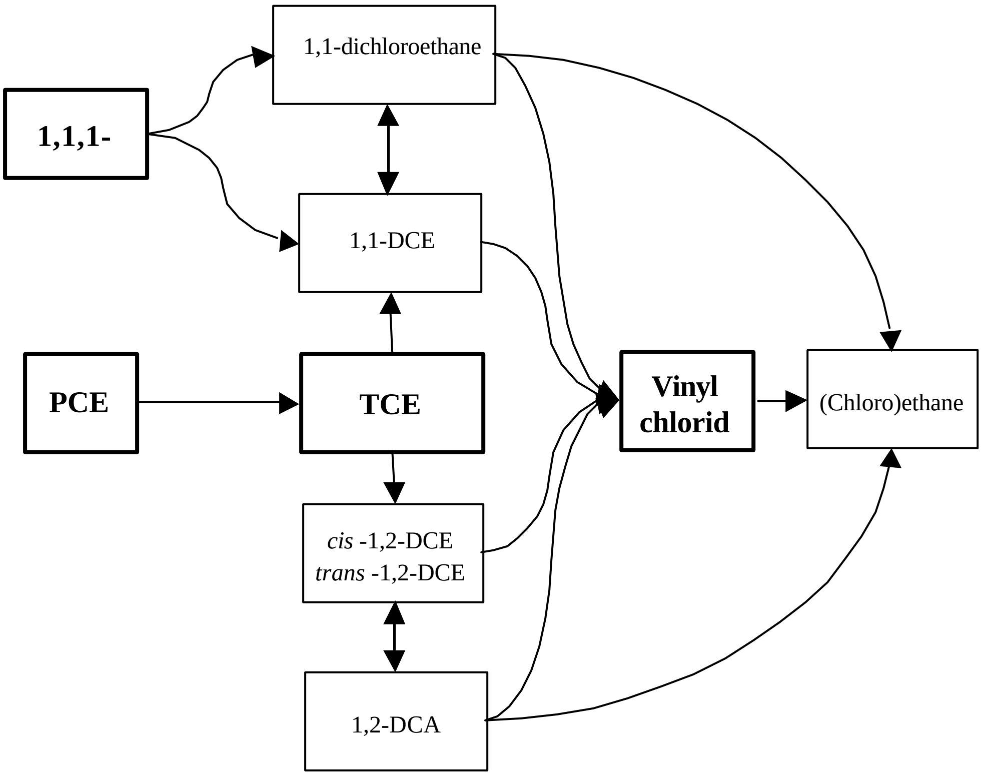

Figure 3.1 Transformation pathways for chlorinated solvents in soil (Simms, Suflita et al. 1991)

Trichloroethene
The volatilisation of TCE from soil surfaces is an important abiotic fate pathway for this chemical. However, because TCE is denser than water, it is more likely to move downward through the subsurface into the vadose zone until lower permeability features impede its progress (Russell, Matthews *et al*. 1992).

TCE is a highly oxidised molecule with three chlorine atoms attached to a carbon-carbon double bond. It is therefore largely resistant to degradation through oxidative processes, although it can readily accept electrons. Overall, the biodegradation of TCE in soil is slow and has led to the chemical being described as relatively persistent (ATSDR 1997b). The rate of biodegradation of TCE increases with the organic content of the soil, and occurs faster in vegetated compared with non-vegetated soils (Anderson and Walton 1995).

According to OECD test methods TCE is not readily biodegradable (EU 2001a), although rates may increase in the presence of certain substrates. Under anaerobic conditions, such as those that occur in soil microsites, flooded soils or aquifer sites, TCE may be slowly biodegraded by reductive dechlorination to 1,1-dichloroethene (DCE) and VC. The extent and rate of degradation will depend upon the strength of the reducing environment. There are concerns over the breakdown product VC due to its toxicity. However, several studies have shown that reductive dechlorination may continue to produce ethene and ethane (EU 2001a).

In a batch culture experiment, increased levels of electron donor (acetate) were found to increase the rates of TCE reductive dechlorination and methane production (Zhuang and Pavlostathis 1995). Optimum conditions for TCE degradation were at a neutral pH and temperature of 35°C.

Biodegradation under aerobic conditions is also limited. Aerobic biodegradation is reported only to occur through co-metabolism and under very specific conditions, although unlike anaerobic dechlorination it does not result in the formation of undesirable metabolites such as 1,1-DCE and VC (Fan and Scow 1993). This is a consequence of the balance required between enough co-substrate to induce the degrading enzymes and too much co-substrate, which would out-compete the TCE and inhibit its decomposition (Ensley 1991).

Hoekstra, de Leer *et al*. (1998) have shown that under oxidative conditions, which may be present in the soil surface layer, TCE may be converted to a variety of compounds including trichloroacetaldehyde, 2,2,2-trichloroethanol and dichloroacetic acid. Reports from studies conducted on the aerobic degradation of TCE in the rhizosphere found that TCE can be co-metabolised with ammonia, isoprene, propane or toluene as the primary substrate (Mu and Scow 1994). These aerobic transformations result in the formation of a highly reactive epoxide which may be further transformed to dichloroacetic acid, trichloroethanol and trichloroacetic acid (HSDB 2002). The observation that TCE is biodegraded aerobically in the rhizosphere may explain previous reports that found faster degradation of TCE in vegetated compared to non-vegetated soils.

Biodegradation is reported to be influenced by the length of time the solvent has been present in the soil (described as soil ‘ageing’). The longer a contaminant is resident in soil the more resistant it becomes to desorption and biodegradation. TCE present in soil for 30 days was found to be 75% less biodegradable than TCE that had only been present for 2 days (Sheremata, Yong *et al*. 2000). Overall there was a decrease in the rate of TCE degradation with ageing and an increase in resistance to desorption (from soil particles?) to SOM. However, the resistance of the breakdown product 1,2-DCE decreased with ageing i.e. it became more mobile with time, the opposite of TCE.

Tetrachloroethene

The fate of PCE in soil is similar to that described for TCE. Volatilisation from soil surfaces is likely to be an important abiotic process, although the high aqueous solubility and density of this chemical means that some movement through the soil column and into groundwater may be expected to occur (Piet, Morra *et al*. 1981). The residence time of PCE in surface environments is not expected to be more than a few days based on its high mobility in soil (ATSDR 1997a).

PCE readily undergoes reductive dechlorination by specific soil organisms, however it is resistant to aerobic degradation (Bagely and Gossett 1990). Vogel and McCarty (1985) found evidence of PCE degradation in soil by sequential reductive dechlorination to TCE, DCE, VC and finally chloro(ethane) under anaerobic conditions (Figure 3.1). TCE and VC were the major metabolites. This process is thought to require the absence of oxygen or nitrate (Zhuang and Pavlostathis 1995, USEPA 1996a) i.e. it occurs under anaerobic conditions.

The rate of anaerobic biodegradation is also improved in the presence of acclimated microorganisms (HSDB 2002). Therefore the rate of biodegradation is likely to be greater in previously contaminated environments, where the microorganisms present will have had an opportunity to adapt to the presence of the chemical. Equally, biodegradation in previously uncontaminated environments will be very limited to begin with, although improved degradation rates may be expected with time.

Biodegradation is expected to be slow under aerobic conditions, with some studies reporting negligible aerobic degradation (Zhuang and Pavlostathis 1995). Hoekstra *et al.* (1998) found that under oxidative conditions in the soil surface layer PCE did not degrade.

Trichloroethane

In addition to volatilisation, 1,1,1-TCA is also subject to abiotic removal from soil by hydrolysis or dehydrohalogenation, forming acetic acid and 1,1-DCE respectively (Aronson and Howard 1997). As illustrated in Figure 3.1, DCE is subject to further dechlorination to form VC.

The biodegradation of 1,1,1-TCA in soils is reported to be very slow (WHO 1992a; HSDB 2002), with a half-life of several years reported at many contaminated sites (Aronson and Howard 1997), although biologically-mediated degradation is reported to be at least an order of magnitude higher than abiotic degradation mechanisms (Klecka, Gonsior *et al.* 1990). Wing (1997) studied the degradation of 1,1,1-TCA in an otherwise uncontaminated aquifer at a manufacturing facility. An overall dissipation half-life including abiotic and biotic processes was measured as 2.3 years, while abiotic transformation to 1,1-DCE and acetic acid at the site exhibited first-order kinetics with half-life of 2.9 years.

No aerobic degradation of 1,1,1-TCA at a concentration of 1 mg l^{1} was found to have occurred in soil samples collected just above and below the groundwater table (Wilson, McNabb *et al.* 1983) which suggests that aerobic degradation is limited.

The actual rate of degradation that occurs is likely to depend on the activity of the microbial community present, since microbially-mediated reductive dechlorination is reported to be the main degradative pathway for 1,1,1-TCA. Acclimation of microorganisms is important in achieving significant degradation.

1,1,1-TCA has been shown to undergo biotransformation under methanogenic conditions via reductive dechlorination to 1,1-DCE and chloroethane (Vogel and McCarty 1987). Anaerobic biotransformation has also been observed under sulphate reducing conditions (Naranyan, Davis *et al.* 1995).

Tetrachloroethane

Limited information was available on the degradation of PCA in soil. Abiotic as well as biotic reactions may be important in the fate of PCA in the environment. It is likely to biodegrade, as do all the highly chlorinated aliphatic hydrocarbons, under strong reducing conditions i.e. methanogenic, sulphate reducing and iron reducing conditions with the initial formation of TCE, DCE with smaller amounts of TCA and DCA appearing later (Aronson and Howard 1997). Some abiotic transformation to TCE may occur.

Carbon Tetrachloride

The low K_{oc} of CT indicates that it will be highly mobile in soil and may leach to groundwater. Volatilisation of CT from moist soil surfaces is expected to be an important fate process given its value of K_H. The potential for volatilisation from dry soil surfaces may also exist.

Anaerobic degradation occurs through reductive dechlorination. This results in the conversion of CT to TCA and subsequently to dichloromethane (DCM) and finally carbon dioxide:

$$CCl_4 \rightarrow CHCl_3 \rightarrow CH_2Cl_2 \rightarrow CO_2$$

Complete dechlorination will depend on the environmental conditions (de Best, Salminem *et al*. 1998). CT degrades relatively rapidly under methanogenic and sulphate/iron reducing conditions, with dissipation half lives ranging from 4 days (mean adjusted vale for field/in-situ data set) to 187 days (for iron-reducing conditions) (Aronson and Howard 1997).

Under methanogenic conditions, CT is biodegraded to low levels with carbon dioxide as the primary (or only) major degradation product (WHO 1999a). Under denitrifying conditions, CT was found to be degraded rapidly with no detectable lag period, producing DCA and carbon dioxide. Reductive dehalogenation of CT to DCA has been reported to occur in aquifer material (WHO 1999a). There is also evidence of reductive dehalogenation by naturally occurring iron porphyrins and other reducing agents in aqueous solution under anaerobic conditions (WHO 1999a). Bioremediation studies have shown that anaerobic biodegradation of CT is enhanced by increasing the concentration of primary substrates (such as glucose and acetate) and by lowering the redox potential (providing a relatively higher electron activity which facilitates dechlorination) (WHO 1999a).

Degradation under anaerobic conditions through co-metabolism has been found to result in the complete removal of CT, the major transformation products being DCA and DCM, although some unknown products are also reported to be formed (de Best, Salminem *et al*. 1998). Other studies have reported the formation of carbon disulphide following the degradation of CT under anaerobic degradation (Devlin 1997).

CT is reported to be resistant to aerobic biodegradation (McCarty 1997; de Best, Salminem *et al.* 1998). However, the half-life of CT in soil has more recently been estimated at 6 to12 months, based on the estimated aqueous aerobic biodegradation half-life (ATSDR 1994). The studies considered in this assessment demonstrate that aerobic degradation will vary from site to site.

Dichloroethane
No reports on the degradation of 1,2-DCA have been identified, however degradation processes are likely to be similar for other chlorinated alkanes. For instance, it may be expected to undergo reductive dechlorination to VC and chloroethane.

Vinyl Chloride
On release to the environment, VC is subject to degradation through both biotic and abiotic processes (Freedman, Danko *et al.* 2001). Most of the VC released to the environment is eventually transported to the atmosphere through volatilisation, with a small percentage transported to groundwater (Smith and Dragun 1984). In the atmosphere, the chemical is degraded abiotically through reactions with hydroxyl radicals. The half-life in air is reported to be between one and two days (ATSDR 1997c).

Transfer of VC to groundwater is also likely to occur following releases to soil because VC has a low sorption tendency to organic matter and is therefore highly mobile in the soil (ATSDR 1997c). The mobility of VC may be increased further still in the presence of other organic solvents that are often present at hazardous waste sites (Cowfer and Magistro 1985).

Several laboratory-based studies have indicated that VC is subject to biodegradative processes in soils, under both aerobic and anaerobic conditions (Barrio-Lage, Parsons *et al.* 1990; Castro, Riebeth *et al.* 1992a; Davis and Carpenter 1990; Castro, Wade *et al.* 1992b).

Under aerobic conditions, VC undergoes oxidative dechlorination to ethanoic acid, eventually forming carbon dioxide, carbon monoxide and water (Vogel and McCarty 1987). The rate of dechlorination under anaerobic conditions is slow (Vogel and McCarty 1985) compared to the other compounds considered in this report.

Hydrolytic degradation is a further possible degradation pathway, and in theory will occur under aerobic and anaerobic conditions (Deipser 1998). Biodegradation of VC may occur with or without the presence of a primary substrate e.g. methane, propane, ammonia, toluene (Davis and Carpenter 1990).

Biodegradation is however reported to be relatively slow, indicating that abiotic processes such as volatilisation are the key fate pathways for this chemical in soil (ATSDR 1997c). Reported losses for VC in soil due to biodegradation were 20% over 4 weeks and 55% over 11 weeks (HSDB 2002).

3.4.3. Implications of Behaviour in Soil for Modelling

The expected rapid rate of volatilisation from soil, based on the high vapour pressure and K_H, combined with the relatively low K_{oc} (see evaluative triangle in introductory chapter) will dictate the nature of the exposure of the chlorinated solvents from soil.

Dermal exposure models for soil calculate absorption into the skin based on the skin structure, the properties of the chemical and the properties of the soil (e.g. McKone and Howd 1992, USEPA 1992). The dermal exposure model currently within the CLEA model (and described within CLR10) is adapted from USEPA (1992). It requires soil/skin permeability coefficients (Kps), either taken directly from experimental work or, in the absence of data, by estimating a skin permeability coefficient for chemicals in aqueous solution using a relationship between K_{ow} and the molecular weight. The skin permeability coefficient is then adjusted for soil type, taking into account the soil matrix parameters and physicochemical properties of the substance.

It is likely that the dermal algorithm within the CLEA model will shortly be changed to the approach within USEPA (2001a) (Martin, 2002 Pers. Comm.). This approach stresses that the data for dermal absorption of chemicals from soils is very limited and presents dermal absorption factors from soil for ten chemicals based on well-designed studies, which it states will be added to as further research is conducted. No default dermal absorption values are presented for volatile organic compounds on the basis that “in the considered soil exposure scenarios, volatile organic compounds would tend to be volatilised from the soil on the skin”. If the approach of the USEPA (2001a) was followed, exposure via the dermal pathway would not be modelled within the CLEA model for volatile contaminants. Given that residual chlorinated solvents are still present within the soil on historically contaminated sites, it would appear prudent to consider including consideration of this pathway, especially as the US criterion for the significance of a pathway (10%) is different from that used in CLR10 (1%). Moreover the USEPA exposure scenarios included water pathways, which would have the effect of further decreasing the significance of exposure via dermal contact.

Experimental work concerning uptake of some of the chlorinated solvents, specifically PCE and TCE from soil has been conducted since the last consultation draft of USEPA (2001a). Poet *et al.* (2002)have conducted experimental work on the percutaneous absorption of PCE from the soil matrix for both human volunteers and rats and fitted this to a model, predicting the behaviour of the chemical within the body. The paper also refers to earlier work conducted by the same authors employing the same experimental approach using TCE.

The studies have been co-authored by researchers whose work was used to provide the initial default dermal absorption fraction within USEPA (2001a). As this work has been conducted in a similar way to the earlier studies, it is likely to meet the criteria outlined by USEPA (2001a) for “well-designed studies”. It might therefore be reasonable to assume that this work would meet the USEPA criteria for the derivation of new dermal absorption fractions for PCE and TCE.

The Poet, Weitz *et al*. (2002) work considers it more appropriate to derive soil/skin permeability coefficients (K_ps) than absorbed doses for the human participants (although it would be possible to derive an estimated dermal absorption fraction from the work by making some assumptions). The rationale given is that K_ps are not affected by factors such as exposure conditions (for instance soil loading), length of exposure and exposure concentration, whereas dermal absorption fractions are influenced by all these factors. For instance, they demonstrated that the higher the dermal loading on the rats within the study, the lower the absorbed fraction. Further, trapping the PCE on the skin resulted in an average of approximately 50% absorption, whereas allowing volatilisation to occur resulted in an average of approximately 10% absorption. The authors noted that in a typical exposure scenario, volatilisation would be able to occur and that in an aged sample (as opposed to their freshly prepared sample) bioavailablity would be likely to be reduced.

The K_p for PCE for humans was estimated to be 0.0009 cm/hr[11]. It was noted that "the low K_p and the expected volatilisation of PCE from the soil would indicate that dermal exposures would not result in significant uptake of PCE" (Poet, Weitz *et al.* 2002). The research also noted that PCE is less volatile and more lipophilic than TCE and that the K_ps for rats were higher for PCE than for TCE. Thus the assumption about the lack of significant exposure could also be applied to TCE and the other chlorinated solvents with a higher volatility and lower log K_{ow} such as VC. It should be noted, however, that some of the other chlorinated organic solvents, however, have either lower volatilities (e.g. TCA) or higher log K_{ow} (e.g. CT) and for these substances such an approach may not be appropriate. Caution is required when considering the application of this approach. As mentioned above, the USEPA criteria (2001a) for significance of exposure is different from that in CLR10, and a slightly different exposure scenario was considered.

Therefore it is recommended that as a preliminary approach a dermal absorption fraction of 0.1 (10% is used) as a conservative first screen for all chlorinated solvents. This is the approach recommended in USEPA (2001a) for semi volatile organic compounds and could therefore be considered to be conservative if applied to volatile organic contaminants, such as the chlorinated solvents. 10% is also the estimated absorbed dose for PCE for rats when volatilisation was allowed to occur. An alternative approach would be to continue to model dermal absorption from chemical and soil properties, but this approach is considered by the authors of this report to be over-complicated in a screening model such as the CLEA model.

The high vapour pressure and Henry's Law Constants of the chlorinated solvents indicate that they are likely to volatilise from soils and groundwater into indoor and outdoor air spaces. The rate of flow is influenced by diffusive and advective processes. Diffusive processes are generally more continuous and are determined by concentration gradients. Advective influences tend to be more temporally variable, examples include barometric

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[11] This could either be used directly within the current approach within CLR10, or converted to a DAF by setting up a "typical scenario" with contact time and soil loading rates and calculating the percentage absorbed.

pressure changes and displacement of vapours by water infiltration. Diffusive transport of chlorinated solvent vapours can determine the removal rate of VOCs under certain circumstances (Arands, Lam *et al.* 1997) whereas the diffusive contribution to total vapour flux may be negligible in other situations (Smith, Tisdale *et al.* 1996). It is therefore not possible from the available data to make generic predictions as to whether advective or diffusive flow will be the dominant factor for chlorinated solvents as this will be determined by local conditions. However, where further detailed quantitative risk assessment (DQRA) is undertaken, the most appropriate course of action will be to undertake a survey of concentrations within the soil air and within the boundary layer directly above the soil surface.

Currently an enrichment factor is included within the CLEA model for the inhalation of dust pathway (DEFRA and the Environment Agency 2002)[12]. However, the literature review has revealed no specific information on differential partitioning of chlorinated solvents to the finer soil fraction. The key factor for sorption appears to be the presence of SOM rather than particle size. Therefore the recommendation of this report would be that there is insufficient evidence to apply an enrichment factor to the chlorinated solvents within the CLEA model.

3.5 Dietary Uptake of Chlorinated Solvents

The mechanisms for uptake into the food chain will be primarily dictated by the high K_H, and relatively low K_{oc} (see evaluative triangle in introductory chapter).

3.5.1. Key processes of plant uptake and accumulation into the foodchain

The uptake of chemicals from soil by plants occurs through one of four pathways (although pathways three and four are only significant in specific applications) (Wang and Jones 1994):

(i) root uptake and subsequent translocation to the above-ground (foliar) part of the plant by the transpiration stream;
(ii) foliar uptake of vapour from the surrounding air (significant particularly for volatile and semi-volatile chemicals);
(iii) uptake by external contamination of leaves and shoots by soil and dust, followed by retention in the plant cuticle or permeation through it; and
(iv) uptake and transport of the solvent into the plant in oil cells (specific to oil containing plants such as carrots and cress).

The total amount of any particular chemical in a plant is usually the result of uptake through a combination of these pathways minus the losses incurred through volatilisation from the leaves and metabolism by the plant (Wang and Jones 1994; He, Sun *et al.* 1996).

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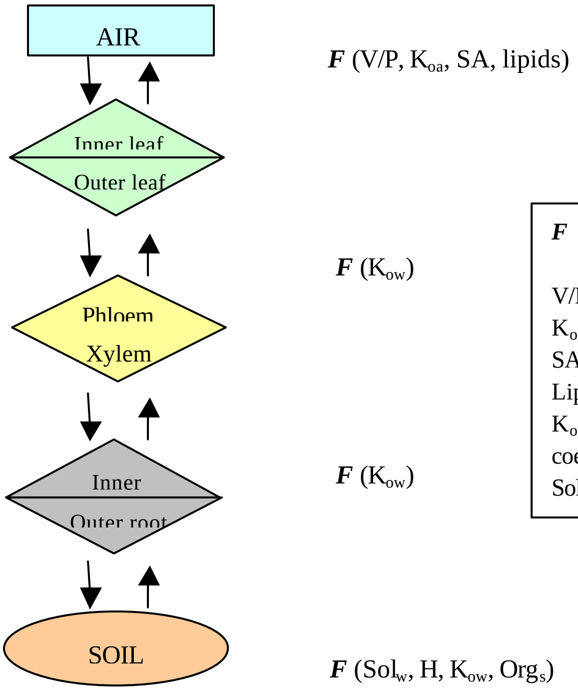
[12] Enrichment factors are used for coarser soils when there is evidence that contaminants are preferentially sorbed to the finer fraction, which is also likely to adhere to skin and pass into the lung.

The sorption and uptake of contaminants is determined by the physicochemical properties of the contaminants. The uptake of solvents by plants will depend on the K_{ow} of the chemical, as this will influence the amount of solvent that will be available to the plant. Uptake of hydrophilic compounds is likely to occur predominantly through the plant's root system, due to their high solubility in water, and low values of K_H and K_{ow}. The main accumulation pathway for lipophilic compounds is from the air to the leaf surface, which is dependent on vapour-particle partitioning in the atmosphere, the octanol-air partition coefficient (K_{oa}) and the plant species (Simonich and Hites 1995). This is illustrated in Figure 3.2.

Moderately hydrophobic chemicals (log K_{ow} 1.0 to 3.5) are most likely to be available to rooted, vascular plants, while plant uptake by transpiration is considered to be important for chemicals with a log K_{ow} less than 2.5 and a log air-water partition coefficient (log K_{aw}) less than -1 (Cousins and MacKay 2001; Dietz and Schnoor 2001). The chlorinated solvents in this study have Log K_{ow} values ranging from 1.47 to 2.73, hence they would be expected to be available to plants via both the root uptake and transpiration pathways.

As well as being dependent upon the solvent properties, uptake is also determined to some extent by the characteristics of the soil and of the plant. Plant uptake in soils with a high organic carbon content will be limited due to the increased adsorption of the solvent to soil, hence the solvent being in a less bioavailable form. Plants with a high leaf surface area and lipid content will exhibit increased foliar uptake, as these characteristics will facilitate transfer across the leaf surface.



F	***Uptake factor***
V/P	vapour-particle partitioning
K_{oa}	octanol-air partition coefficient
SA	plant surface area
Lipids	plant lipid concentration
K_{ow}	octanol-water partition coefficient
Sol_w	water solubility

Figure 3.2 Simplified mechanism of pollutant uptake by vegetation (from Simonich and Hites 1995)

Trichloroethene

Much of the research on the uptake of TCE by plants is related to the potential for plants such as poplar trees to bioremediate contaminants in the environment (in a process known as phytodegradation) (e.g. Newman, Strand *et al.* 1997, Walton and Anderson 1990, Anderson and Walton 1995). However, this research is not within the scope of the current work and is therefore not presented here.

The uptake of TCE by edible garden plants was studied using carrots, spinach and tomatoes grown inside continuous air-flow bioreactors (Schnabel, Dietz *et al.* 1997). The plants were regularly irrigated with synthetic groundwater containing a mixture of 14C-labelled and unlabelled TCE. Radiolabel recoveries ranged from about 50% for low-dose reactors to about 70% for high-dose reactors. Most of the recovered 14C label was found to have volatilised while a portion of the recovered label (5-25%) was sorbed to the soil. The concentration of 14C label in edible plant tissue was higher than in the surrounding soil. Bioconcentration factors (BCFs) ranged from 2.6 in high-dose tomato reactors to 32 in low-dose spinach reactors on a harvest weight basis. The concentrations in edible tissue were estimated to range from 152 ìg kg^{-1} for high-dosed tomatoes to 580 ìg kg^{-1} for high-dosed spinach. However, neither TCE nor its commonly reported transformation products were detected, which suggests that TCE was taken up, transformed, and bound to plant tissue. Bound residues are generally believed to have lower toxicological effects than the parent compound.

Potential mechanisms for the uptake and transformations of TCE in a tomato plant are shown in Figure 3.3.

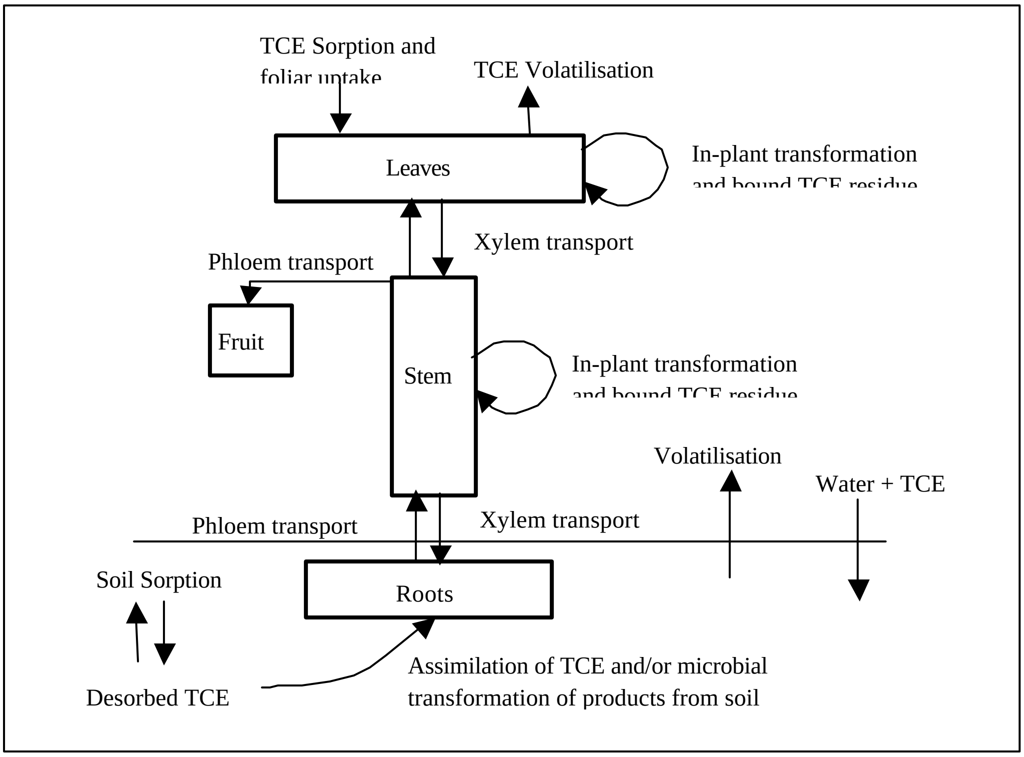


Figure 3.3 Potential fate of TCE added to soil surrounding a tomato plant (from Schnabel, Dietz et al. 1997)

The uptake of TCE from soil by agricultural plants was studied in a closed aerated laboratory soil-plant system which allowed differentiation between uptake via the roots and via the leaves after evapouration (Schroll, Bierling *et al.* 1994). Studies on carrot and radish plants revealed that uptake occurred mainly through the foliage as opposed to the roots, although subsequent translocation resulted in substantial distribution throughout the plants. The largest part of 14C residues was bound to plant material as unextractable residues. The authors determined fairly moderate BCFs of 4.4 to 63.9.

To predict the fate of TCE in plants, Hu, Davis *et al.* (1998)conducted diffusion experiments to estimate contaminant diffusivity within plant roots, while adsorption experiments were used to investigate the adsorption of contaminant in stems. TCE diffusivity was $9.8x10^{-7}$ cm^2 s^{-1}, $8.12x10^{-7}$ cm^2 s^{-1} and $5.23x10^{-7}$ cm^2 s^{-1} for 8-day-old soybean roots, 3-month-old cottonwood seedling roots and 1-year-old alfalfa roots respectively. These results indicate that TCE diffusivity is smaller in older and bigger roots. The adsorption coefficient for TCE was between 27 and 32.

Tetrachloroethene

It is likely that, due to similarities in structure and properties, PCE will be taken up by plants in a similar fashion to TCE. Since TCE is formed in soil via reductive dechlorination of PCE, the TCE pathways are relevant.

PCE was detected in fruit and vegetables (potatoes, apples, pears and tomatoes) in the range 0.7 to 2.0 µg kg^{-1} (McConnell, Ferguson *et al.* 1975). However, although uptake by plants may be indicated by the presence of PCE in fruits and vegetables, it should be noted that uptake of PCE in fruit and vegetables could take place either during growth or after harvesting i.e. as a consequence of packaging or distribution processes.

Trichloroethane

As with TCE, the uptake of 1,1,1-TCA by plants is used as a treatment process for TCA-contaminated sites. The K_{ow} value for TCA suggests that uptake will be primarily into the leaf or root lipid phase. 1,1,1-TCA has been detected in fruits and vegetables at levels of 1 to 4 µg kg^{-1} (McConnell, Ferguson *et al.* 1975) although the source of the TCA is not defined. Coefficient values for the adsorption of the chemical onto plant biomass, determined for chlorinated aliphatic hydrocarbons, include a value of 15 for 1,1,1-TCA (Hu, Davis *et al.* 1998).

Tetrachloroethane

There are no recent literature reports on the uptake of PCA by plants, nor any reported measured concentrations in fruit and vegetables.

Carbon Tetrachloride

Some plants, due to their lipid content, will take up CT from the air. Studies of the equilibrium partitioning of CT between the gas phase and conifer needles (*Pinus sylvestris* and *Picea abies*) and hexane-extractable leaf waxes showed partition ratios (g m^{-3} needle; gm^{-3} air) of 9 to 17 and 90 to 400, respectively (Brown, Cape *et al.*

1998). While it is likely that this mechanism will also apply to leafy vegetables, no experimental studies have been found.
Low levels of CT have been found in grain, or food products derived from such grain, at concentrations typically of 1 to 100 mg kg^{-1} (ATSDR 1994) however this is due to its use as a fumigant, rather than plant uptake. Concentrations of CT in such products today are unlikely following the ban in this use of CT.

Dichloroethane
A survey of recent literature did not reveal any papers on the uptake of 1,2-DCA by plants. Uptake by plants is not considered to be a significant pathway, based on its low value of K_{ow}. Historically 1,2-DCA has been identified in market basket samples fruits, vegetables, oils and spices at 1 to 10 ìg kg^{-1}, however it was not detected in more recent food surveys in the US, Japan and Canada (WHO 1995; ATSDR 1996b).

Vinyl Chloride
Based on its low value of K_{ow}, root uptake of VC is unlikely. Wild and Jones (1992c) classified VC as having a low potential for retention by the root surface, moderate potential for uptake and translocation, and high potential for foliar uptake.

3.5.2. Summary

Uptake of chlorinated solvents may occur through the roots (in particular for the more lipophilic compounds with higher log K_{ow} values) or across the leaf surface (for the more hydrophilic compounds). Based on the K_{ow} values of the chlorinated solvents, the potential for plant uptake would be expected to be low, however BCFs for TCE uptake by garden plants are quite high.

Studies looking at the uptake of chlorinated solvents by edible garden plants are limited to TCE. No other chemicals have been studied in such detail, although it is likely that similar mechanisms will apply for the higher chlorinated compounds, i.e. TCA and PCE. Uptake of the vapour across the leaf surface was considered to be the dominant mechanism for TCE, although root uptake will also occur. The degree of foliar uptake is dependent upon leaf surface area and lipid content, as well as physicochemical characteristics of the solvent. Since DCA and VC have lower log K_{ow} values compared to the other solvents studied, they are not expected to be taken up to the same extent as TCE.

Given the paucity of data on uptake of chlorinated solvents into garden vegetables, it is not possible to recommend specific bioconcentration (uptake) factors for use within the CLEA model. At best, the studies revealed by the literature search may be used as a "reality check" when assessing the different plant uptake models available. The Briggs Ryan algorithm, which is described within CLR10, is currently the default approach within the CLEA model (Defra and Environment Agency 2002d). The chlorinated solvents considered all fall within the model constraints with regard to log K_{ow}. However experimental studies do appear to show that uptake from air through above ground parts maybe an important pathway, especially for the most volatile chlorinated solvents such as CT (Brown, Cape *et al.* 1998). Furthermore volatile substances may be lost to the environment. The Briggs Ryan model does not explicitly include consideration of this pathway.

It may therefore be more appropriate to use a fugacity approach, such as the simplified Hung and Mackay model (Hung and Mackay 1997), based on the Patterson McKay model (Paterson and Mackay 1989), or the Trapp and Matthies model (Trapp and Matthies 1995) for this aspect of plant uptake. The simplified Patterson McKay model is currently used within the CalTox model (CalTox 1993) and has been adopted within GasSim (Environment Agency 2002a). The Trapp and Matthies model is used within the German UMS model (UMS 1997), the EUSES model (EC 1996a) and has been proposed for the new Dutch Serious Risk Concentrations for human health (SRChuman).

It should be recognised that generic modelling is likely to be conservative because there is evidence that the aliphatic chlorinated hydrocarbons (list) maybe biotransformed into less toxic products once taken into the plant (Schnabel, Dietz *et al*. 1997). However caution is required about the findings of some authors that plant uptake of volatile organic contaminants is unlikely to occur because contaminant in the soil will be lost to the system (Wild and Jones 1992c; Schnabel, Dietz *et al*. 1997). This is because aged samples may behave differently from fresh samples.

Given the physicochemical properties of the chlorinated solvents, the volatilisation pathways are likely to dominate exposure. It is therefore unlikely that plant uptake would be a focus for DQRA. However, should the decision be made to undertake further DQRA on this pathway, it is suggested that either available garden produce is analysed or that field trials, or if this is not possible due to the management context of the site, pot trials are conducted, to minimise the uncertainty from this pathway.

3.5.3 Uptake into the Rest of the Food Chain

The K_{ow} values of the chlorinated solvents suggest that some bioaccumulation in the food chain is likely. TCE and PCE have both been detected at levels of a few ìg kg^{-1} or ìg l^{-1} in solid and liquid foodstuffs. (McConnell, Ferguson *et al*. 1975) detected levels of TCE at up to 60 ìg kg^{-1} in tea and 16-22 ìg kg^{-1} in meat, and levels of PCE at up to 5 ìg kg^{-1} in meat and 0.3 to 13 in dairy products.

Pfannhauser, Gombos *et al*. (1988) detected 1,1,1-TCA at levels mostly below 10 µg kg^{-1} in olive oil, cheese, and chocolate; only one sample of olive oil contained over 100 µg kg^{-1}. The authors suggested that cleaning solvents in production areas and packaging materials were possible sources for contamination.

1,2-DCA has been identified in market basket samples including oils, meats, fruits and vegetables and spices at 1 to 10 ìg kg^{-1}. When used as a grain fumigant, DCA could be detected in wheat and wheat products (1 out of 281 wheat samples contained 1,2-DCA at 290 mg kg^{-1}, WHO 1995). However, it was not detected in a USA survey of 234 table ready foods, nor in a survey of foods from Japan (ATSDR 2001b) nor in any samples of 34 food groups collected in Canada in 1991 (detection limit 50 µg kg^{-1} for solids and 1.0 µg l^{-1} for liquids) or 1992 (detection limit 5 µg kg^{-1} for solids and 1 µg/litre for liquids) (WHO 1995).

Foodstuffs are not considered to represent significant sources of exposure to PCA, based on its volatility and low potential for bioaccumulation (ATSDR 1996b). PCA was not detected in three surveys of foodstuffs in Canada and the USA (detection limits 1 µg l^{-1} for liquids and 5 to 50 µg kg^{-1} for solids) (ATSDR 1996b; WHO 1998b).

Low levels of CT have been found in grain, or food products derived from such grain, at concentrations typically of 1 to 100 mg kg^{-1} (ATSDR 1994) however this is due to its use as a fumigant, rather than plant uptake. High concentrations in such products today are unlikely due to the ban in use of CT as a fumigant. It is possible that certain foods may absorb small amounts of CT from the air during processing (ATSDR 1994; WHO 1999a).

Therefore most of the chlorinated solvents have been detected in foodstuffs at least at trace levels, and sometimes elevated levels. However it is not possible to say from these results whether the contamination is present as result of transfer through the food chain following plant uptake of the chlorinated compounds from soil by plants, or if it is due to exposure of food products to the solvents during manufacture, preparation or packaging.

3.6 Key Conclusions

3.6.1. Recommendations for DQRA

Considerable variation in both calculated and measured K_{oc} values has been observed. Indeed USEPA (1996a) noted that the relationship with log K_{ow}, often used within environmental modelling literature, appeared to be inappropriate for volatile organic contaminants. The presence of SOM is a key factor but other aspects of soil type also play a part. K_{oc} is critical for a number of exposure pathways, including the volatilisation pathways, which are likely to be dominant. It may therefore be appropriate to select a value for a similar soil if available, or otherwise to determine K_{oc} experimentally on a site specific basis.

Based on their physicochemical properties and degradation pathways, the chlorinated solvents should be rapidly lost from the soil and groundwater. However their presence on historically contaminated sites indicates that there are circumstances in which this may not be the case and generic screening models will therefore be based on the more conservative viewpoint. It may therefore be advisable to conduct further DQRA on concentrations within the soil air and within the air in the boundary layer above the soil surface. In addition, particularly if there are issues of groundwater contamination at the site, it may be possible to conduct long term monitoring as to site specific rates of loss from the soil. Care should be taken to monitor the degradation products, such as VC, as this is more toxic than many of the other chlorinated solvents. Volatilisation would be expected to occur from contaminated groundwater as well as from soils, so where groundwater contamination is encountered, an appropriate risk assessment tool which can model this pathway should be selected.

Plant uptake is unlikely to be a critical pathway for chlorinated solvents, because of the expected dominance of the inhalation of vapour pathways. However there may be occasions where the analysis of available produce or plants grown in field or pot trials is appropriate.

3.6.2. Recommendations for the CLEA Model

There are insufficient data available in the literature to make specific recommendations for the substance specific calibration of generic vapour models for the chlorinated solvents. The literature review appears to show that the behaviour of chlorinated solvents within the soil at high concentrations differs from that at low concentrations. It may be appropriate to include a check within the model to indicate that concentrations nearing saturation have been reached.

There are insufficient data available in the literature to replace the plant uptake algorithms within the CLEA model with specific concentration factors. However the literature review indicates that the uptake of chlorinated solvents from the air in the boundary layer is likely to be the critical pathway. It would therefore be appropriate to select an approach to plant uptake modelling which accounts for this pathway, such as the simplification of the Patterson Mackay model (Paterson and Mackay 1989) derived by Hung and Mckay (1997), or the Trapp and Matthies model (Trapp and Matthies 1995) for this aspect of plant uptake.

It is recommended that consideration is given to modelling the dermal pathway for chlorinated solvents, although the current proposed approach would omit it. This is because it is considered that in certain circumstances it might constitute a significant pathway.

3.6.3. Summary of Recommended Values

The recommended physicochemical data for use in the CLEA model (taken from Table 3.2) are summarised in Table 3.6.

Table 3.6 Recommended physicochemical values and parameters for use in the CLEA model

Substance	Mol. Weight ^{a}	Boiling Point ^{a}	Aqueous Solubility	Vapour Pressure	Henry's Law Constants $^{\#}$		Log K_{ow}	K_{oc} †	Coefficient of Diffusion (25°C) ^{e} Air	Coefficient of Diffusion (25°C) ^{e} Water	Enthalpy of vapourisation ^{a,h}	Critical temp ^{a,h}
		K	mg l^{-1}	Pa$^{\wedge}$	Pa-m^3 mol^{-1}	Dimen-sionless (cm^3/cm^3)	-	$l.kg^{-1}$	$m^2.s^{-1}$	$m^2.s^{-1}$	$cal.mol^{-1}$	K
TCE	131.39	360.45	1070 (20)^{a}	8600 (20)^{a}	1044 (25)^{b,c,e}	0.418	2.29 ^{c}	162	7.90E-6	9.10E-10	7474	573.2
PCE	165.83	394.35	149 (ns)^{c}	1900 (20)^{a}	2128 (20)^{c}	0.865	2.53 ^{c}	219	7.20E-6	8.20E-10	8293	620.1
TCA	133.40	347.0	1330 (25)^{b}	13300 (20)^{a,d}	1743 (24.8)^{b}	0.705	2.47 ^{d}	200	7.80E-6	8.80E-10	7911	584.5
PCA	167.85	419.3	3200 (20)^{a}	647 (20)^{a}	35 (25)^{b}	0.014	2.39 ^{b}	182	7.10E-6	7.90E-10	9247	661.0
CT	153.82	349.7	793 (25)^{b}	12172 (20)^{a,d}	2330 (24.8)^{d}	1.238	2.83 ^{b}	309	7.80E-6	8.80E-10	7158	556.2
DCA	95.96	356.7	8524 (20)^{b}	8500 (20)^{d}	111 (25)^{b}	0.045	1.48 ^{b}	62	10.4E-6	9.90E-10	7418	563.0
VC	62.50	259.3	1100 (20)^{d}	333000 (20)^{d}	1960 (17.5)^{d}	0.793	1.50 ^{e}	63	10.6E-6	12.3E-10	5250	432.0

$^{\wedge}$ Conversion factor from mmHg to Pa = multiply by 133.32

$^{\#}$ Conversion factor from atm-m^3 mol^{-1} to Pa-m^3 mol^{-1} = multiply by 101325; atm-m^3 mol^{-1} to dimensionless = multiply by 41

† K_{oc} calculated from recommended K_{ow} using the following equation for non-hydrophobic compounds from (EU 1996): $\log K_{oc} = 0.52 \log K_{ow} + 1.02$

[a] Kirk-Othmer encyclopaedia (Kirk-Othmer 2003)

[b] SRC Chemfate database (SRC 2002)

[c] Calculated from K_{ow}

[d] EHC document for that chemical (WHO 1984; WHO 1985; WHO 1992a; WHO 1995; WHO 1999a; WHO 1999b)

[e] USEPA (1996) Soil Screening Level Guidelines (USEPA 1996a)

[f] HSDB Toxnet database (HSDB 2002)

[g] ESCA (ESCA 2002)

[h] (USEPA 2000). Values from CRC (1994) except VC (Design Institute for Physical Properties Data, American Institute of Chemical Engineers, on line data search 1997) and CT (estimated from QSAR data).

4. BTEX

4.1 Introduction

Benzene, toluene, ethylbenzene and xylene are often referred to collectively as BTEX compounds or simply BTEX. They are used individually in a number of industrial processes and are collectively present in crude oil and light petroleum products, which account for their highest usage. Consequently, the individual BTEX compounds are often released contemporaneously where they coexist in the environment by virtue of similarities in their physicochemical properties. There are therefore trends in their occurrence and behaviour which merit collective consideration. For this reason the fate and transport of these monocyclic aromatic hydrocarbons has been considered in a combined literature review.

A further reason for considering these compounds collectively is that there are some areas of exposure modelling, such as plant uptake and dermal exposure, where there are limited discrete experimental data relating to the specific behaviour of individual BTEX constituents. In these circumstances a more generic approach to modelling may be required although, where sufficient information is available, separate reviews have been conducted for each BTEX compound.

The BTEX compounds are an important family of contaminants on account of their established toxicity, their high environmental mobility relative to the majority of the constituents of petroleum derived products and the widespread use and storage of the products that contain them. Of particular relevance is their greater solubility in water relative to the majority of hydrocarbon compounds, which facilitates lateral migration towards receptors that may otherwise be remote from a spill source area.

The BTEX chemicals are commonly found together in crude oil and light petroleum products. Concentration ratios of the various BTEX constituents in products such as gasoline will vary according to the source of the crude, the product grade and national regulations. Table 4.1 provides an indication of the concentration of BTEX compounds in the more commonly encountered petroleum based products.

Table 4.1 **Indicative composition* (% wt) of several petroleum products that contain BTEX constituents (TPHCWG 1998)**

	Benzene	**Toluene**	**Ethylbenzene**	***o*-Xylene**	***m*-Xylene**	***p*-Xylene**
Gasoline	1.9 (1.6-2.3)	8.1 (6.4-10.0)	1.7 (1.4-2.0)	2.5 (2.1-3.1)	4.6 (3.9-5.4)	1.9 (1.6-2.3)
Kerosene	0.47 (0.47-0.5)	1.6 (1.3-1.6)	0.66 (0.37-0.69)	1.0	0.96	0.35
Diesel	0.029 (0.0026-0.1)	0.18 (0.0069-0.7)	0.068 (0.007-0.2)	0.043 (0.0012-0.085)	0.22 (0.018-0.51)	
Lubricating oils	0.0096 (0.0059-0.0096)	0.22 (0.1-0.22)	Not reported	0.34 (0.2-0.34)		

* The detailed breakdown in this table is based on US fuels. UK fuel compositions may differ, most significantly gasoline. Typical BTEX constituent concentrations in UK gasoline are 3% benzene, 1% toluene, 4% xylenes and 2% ethylbenzene (MAFF 1997).

In addition to their collective presence as constituents of petroleum based fuels, the BTEX compounds are produced and used individually:

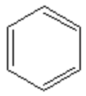
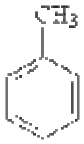
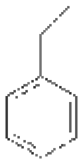
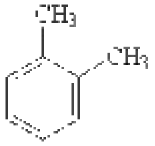
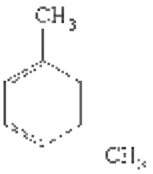
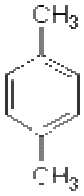
- Benzene was being isolated from coal tar as early as the mid 19th century and later from the petrochemical and petroleum industries which now account for the majority of the commercial production. It is a colourless liquid at room temperature and ambient pressure and has a characteristic aromatic odour. The primary use is as a chemical intermediate in the manufacture of other chemicals and end products and as a gasoline additive. It was used extensively as a solvent in the chemical and drug industries although this use has declined in most developed countries (<2%) as safer alternatives have been identified (ATSDR 1997d) (WHO 1993).
- Toluene occurs naturally in crude oil and in the tolu tree. It is also produced in the process of making gasoline and certain other fuels (e.g. jet fuel) from crude oil and making coke from coal. Toluene is used in the manufacture of paint, in paint thinners, fingernail polish, lacquers, adhesives, rubber and in some printing and leather tanning processes (ATSDR 2000a).
- Ethylbenzene is found in natural products such as crude oil and in petroleum fuels, coal tar and products such as inks, insecticides, and paints. Ethylbenzene is used primarily to make styrene; other uses include as a solvent and in the manufacture of other chemicals (ATSDR 1999).
- Xylene is found in natural products such as crude oil and smoke from forest fires and volcanoes (these latter being rapidly transformed in the troposphere by photo-oxidation). Production methods include manufacture from crude oil or coal tar and transalkylation of toluene which can lead to benzene impurities in the final product. It is used in a variety of solvent applications, particularly in the paint and printing ink industries and as a chemical intermediate in the plastics and pharmaceutical industries (ATSDR 1995a).

4.2 Identity

The BTEX compounds are volatile monocyclic aromatic hydrocarbons, based on a single benzene ring with varying degrees of alkylation. Their structures are shown in Table 4.2.

It is also worth noting that “mixed xylenes” is a commonly used name for a catalytic reformate of petroleum which is used as a solvent in paints and coatings and blended into fuels, although the majority is purified into the individual isomers. It consists of approximately 44% *m*-xylene, 20% *o*-xylene, 20% *p*-xylene and 15% ethylbenzene (current formulations of mixed xylenes are relatively free of benzene (<0.001%) (ATSDR 1995a).

Table 4.2 **Chemical structure and nomenclature of BTEX compounds**

Substance **(IUPAC name)**	**Structure**	**CAS number**	**Other names**
benzene		71-43-2	benzol, cyclohexatriene
toluene (methylbenzene)		108-88-3	methylbenzol, toluol
ethylbenzene		100-41-4	ethylbenzol
o-xylene (1,2-dimethylbenzene)		95-47-6	*o*-xylol
m-xylene (1,3-dimethylbenzene)		108-38-3	*m*-xylol
p-xylene (1,4-dimethylbenzene)		106-42-3	*p*-xylol

4.3 Occurrence in Soil

BTEX compounds can occur naturally in crude oil and be generated from forest fires. Given the UK geology and the rapid tropospheric destruction of BTEX from forest fires and associated releases, soils in the United Kingdom would not be expected to contain naturally occurring BTEX compounds. The presence of BTEX in soils and groundwater is attributable to man-made releases and detected concentrations will vary widely according to the magnitude and type of spill in conjunction with the local environmental conditions.

A background benzene soil concentration of 0.02 ìg kg^{-1} has been calculated from all of the releases of benzene into the environment (EU 2002). This relates to natural soils which have not been contaminated as a result of direct spillage and are not in the immediate vicinity of an industrial source.

Several studies of background soil concentrations of toluene are reported (EU 2001c) although the information presented is not accompanied by any indication of soil type or organic matter content. Toluene concentrations in unspecified Dutch soils averaged 1ìg kg^{-1}.

In the absence of significant natural background soil concentrations, BTEX concentrations may vary from near zero in uncontaminated soils to highly elevated concentrations when free phase hydrocarbons are present in localised areas on contaminated sites. Therefore, rather than quote concentrations that have been detected in association with historic spills and which may bear little resemblance to other site conditions, it is more instructive to consider the relative abundance of the BTEX compounds at the source of the spill. By applying Raoult's Law which considers the mole fraction of each of the constituents of the mixture, the relative dissolution and adsorption of the BTEX compounds can be estimated.

This is covered further in Section 4.5 which discusses the behaviour of BTEX in the soil environment.

4.4 Physicochemical Properties

This section reviews the physicochemical parameters that are required for use in the CLEA model. It aims to justify the selection of a particular value for each parameter in the CLEA model. The various physical and chemical properties of BTEX which contribute to their contamination of soil are summarised below. The introductory chapter describes how these parameters are used within environmental modelling and the CLEA model in particular.

Characteristics such as molecular weight, molecular structure, aqueous solubility and the octanol-water partition coefficient (K_{ow}) will determine the behaviour of the compound in the environment and its potential for degradation through biotic and abiotic processes. Although low in absolute terms (ranging between 160 and 1770 mg l^{-1} at 25°C), the aqueous solubility of the BTEX compounds is significant in terms of environmental fate and behaviour. With a low molecular weight, significant aqueous solubility, low K_{ow} and resistance to degradation processes (whilst not as recalcitrant as MTBE, PAHs and PCBs, the environmental persistence of BTEX compounds is a material issue) BTEX compounds are likely to be mobile in soil and leach to groundwater.

A hierarchical approach to the selection of parameter values has been applied, as outlined in the introductory chapter. EU Risk Assessments have been carried out to a draft stage for benzene and toluene and, where valid, recommended physicochemical data in these EU reports have been selected for the CLEA model. The EU assessment for ethylbenzene has reached the draft stage and is currently available in the form of the German Chemical Society Publication BUA Report 178 (October 1995), published 1997. No similar documents have been identified for isomers of xylene. Other references quoted in this section include WHO Environmental Health Criteria documents, USEPA Soil Screening Guidance (and its contributory databases, such as CHEMFATE, which are presented in the Superfund Chemical Data Matrix (SCDM), available to download through the USEPA website) and authoritative chemistry reference texts.

To avoid repetitive referencing in this section, abbreviations for the following commonly consulted sources (given in brackets below) are used throughout the following sections:

- Syracuse Research Corporation (2003) CHEMFATE Database. SRC, Syracuse, NY. (SRC 2002)
- WHO Environmental Health Criteria documents for benzene (WHO 1993), toluene (WHO 1986), ethylbenzene (WHO 1996) and xylene (WHO 1997)
- US National Library of Medicine Hazardous Substances Data Bank (HSDB 2002)
- USEPA Soil Screening Guidance Technical Background Document (USEPA 1996a)
- European Union DRAFT Risk Assessment Report for Benzene (EU 2002) and Risk Assessment Report for Toluene (EU 2001c)
- German Chemical Society BUA Report 178 (October 1995), published 1997 (GCS 1997)
- Kirk-Othmer Encyclopaedia of Chemical Technology (Kirk-Othmer 2003)
- IUCLID International Uniform Chemical Information Database, European Commission Joint Research Centre, 2000 (IUCLID 2000)

The above sources often cite references and these are mentioned in the text and included in the references for this chapter.

The recommended physicochemical data for use in the CLEA model are shown in Table 4.3. The values have been selected according to the hierarchy discussed above and in the introductory chapter. The table presents selected values, and the minimum and maximum values identified from the literature.

Table 4.3 Recommended physicochemical values and parameters for use in the CLEA model, minimum and maximum literature ranges (CLEA units, temperature (°C) in brackets)

Substance	Value	Mol. Weight	Boiling Point	Aqeous Solubility		Vapour Pressure		Henry's Law Constant				Log K_{ow}	Log K_{oc}	K_{oc}	Coefficient of Diffusion (25°C)[k]		Critical temp[u]	Enthalpy of Vapourisation[u]
															Air	Water		
			K	$mg\ l^{-1}$ or $g\ m^{-3}$ (temp°C)		Pa (temp°C)		temp°C	$Pa\text{-}m^3\ mol^{-1}$	$atm\text{-}m^3\ mol^{-1}$	unitless	-	-	$l\ kg^{-1}$	$m^2\ s^{-1}$	$m^2\ s^{-1}$	K	$cal\ mol^{-1}$
Benzene	Recommended	78.11[a]	353.25[a,b]	1770	(25)[h]	9970	(20)[a]	(20)	442.5[*]	$4.37E^{-03}$	0.182	2.13[a,k,l,m]	2.13[a]	134.1	$8.80E^{-06}$	$9.80E^{-10}$	562.05	7342.1
	Min			1760	(20)[h]	6069	(10)[m]	(10)	270.5[a]	$2.67E^{-03}$	0.115	1.56[p]	1.23[t]	17				
	Max			1810	(30)[h,i]	24,397	(40)[m]	(25)	570[o]	$5.63E^{-03}$	0.230	2.25[p]	3.00[a]	1023				
Toluene	Recommended	92.15[b,c,d]	383.75[b,d]	535	(25)[c,d]	3000	(20)[d]	(20)	537[d]	$5.30E^{-03}$	0.221	2.65[d,k,l,m]	2.25[d]	178	$8.70E^{-06}$	$8.60E^{-10}$	591.8	7930.0
	Min			515	(20)[d]	1000	(1.5)[n]	(20)	537[d]	$5.30E^{-03}$	0.221	1.83[k]	1.57[r,d]	371				
	Max			535	(25)[c,d]	12,000	(50)[o]	(25)	680[n]	$6.71E^{-03}$	0.275	2.79[k]	2.39[k]	247				
Ethyl-benzene	Recommended	106.16[e,f]	409.35[b,e]	169	(25)[j]	950	(20)[f]	(20)	663.5[*]	$6.55E^{-03}$	0.273	3.13[e,f]	2.64[s**]	432	$7.50E^{-06}$	$7.80E^{-10}$	617.2	8501.2
	Min			152	(20)[e,f]	931	(20)[f]	(20)	478.7[f]	$4.72E^{-03}$	0.197	3.07[f]	1.98[p,q]	95.5				
	Max			181	(25)[j]	10,000	(67.1)[n]	(25)	887[e,n]	$8.75E^{-03}$	0.358	3.15[f,l,m]	3.04[p,q]	1096				
o-xylene	Recommended	106.16[g]	417.55[b,g]	173	(25)[j]	660	(20)[g]	(25)	534[o]	$5.27E^{-03}$	0.216[m]	3.12[g,l,m,o]	2.63[s**]	424	$8.70E^{-06}$	$1.00E^{-09}$	630.3	8661.4
	Min			142	(??)[g]	340	(10)[m]	(25)	520	$5.13E^{-03}$[l]	0.210	3.12[g,l,m,o]	2.34[g]	219				
	Max			179	(25)[j]	3200	(50)[o]	(25)	565[n]	$5.58E^{-03}$	0.228	3.13[k,o]	2.63[s**]	424				
m-xylene	Recommended	106.16[g]	412.25[b,g]	160	(25)[j]	790	(20)[g]	(20)	493.3[*]	$4.87E^{-03}$	0.203	3.20[g,k,l,m,o]	2.69[s**]	492	$7.00E^{-06}$	$7.80E^{-10}$	617.0	8522.7
	Min			134	(25)[j]	660	(20)[o]	(20)	493.3[*]	$4.87E^{-03}$	0.203	3.20[g,k,l,m,o]	2.11[g]	129				
	Max			173	(25)[j]	1333	(28.3)[o]	(25)	753	$7.43E^{-03}$[m]	0.304	3.20[g,k,l,m,o]	2.69[s**]	492				
p-xylene	Recommended	106.16[g]	411.45[g]	180	(25)[j]	860	(20)[g]	(25)	699	$6.9E^{-03}$[l]	0.282	3.15[g,l,m,o]	2.65[s**]	448	$7.69E^{-06}$	$8.44E^{-10}$	616.2	8525.1
	Min			156	(25)[j,o]	461	(10)[m]	(25)	578[n]	$5.70E^{-03}$	0.233	3.15[o]	2.41[k]	260				
	Max			200	(25)[j]	2645	(40)[m]	(25)	776	$7.66E^{-03}$[m]	0.309	3.17[g,l,m,o]	2.65[s**]	448				

[*] Calculated from relevant soil and vapour pressures following EU risk assessment approach (EU 2001c; EU 2002).

[**] Calculated from selected log K_{OW} using regressions established by (Sabljic and Gusten 1995) presented in (EU 1996) and applied in EU risk assessments (EU 2001c; EU 2002).

[a] (EU 2002)

[b] (Kirk-Othmer 2003)

[c] (WHO 1986)

[d] (EU 2001c)

[e] (WHO 1996)

[f] (GCS 1997)

[g] (WHO 1997)

[h] (IUPAC 1989a)

[i] (SCDM 1997)

[j] (IUPAC 1989b)

[k] (USEPA 1996a)

[l] (HSDB 2002)

[m] (SRC 2002)

[n] (Lide 1997)

[o] (IUCLID 2000)

[p] (Mackay, Shiu et al. 1991)

[q] (WHO 1993)

[r] (ATSDR 2000a)

[s] (EU 1996)

[t] (Risk Science Programme (RSP) 1994)

[u] (Lide 2000)

Molecular Weight

The molecular weight of the BTEX compounds affects their transport and partitioning in the soil environment. By scientific convention molecular weight is reported in units of g mol^{-1}; these are also the units required by the CLEA Model. Therefore, all units stated below are g mol^{-1}.

Molecular weights for use in the CLEA model have been researched from Kirk-Othmer, WHO EHC reports and where available EU Risk Assessment documents. Ranges are not appropriate for this parameter; variation in quoted values identified within the consulted texts was largely due to the number of significant digits selected by the authors. For use within CLEA two decimal places is considered sufficiently sensitive for this parameter; this is consistent with EU Risk Assessments.

The molecular weights of the BTEX compounds, in increasing order, are benzene, toluene, ethylbenzene and xylene. The lighter compounds (benzene, toluene) will be relatively more mobile in soil because sorption to soil organic matter is considered to be less. In the absence of other major structural differences a lower molecular weight will also result in a greater potential for skin absorption.

Benzene
The molecular weight identified within the EU Risk Assessment is 78.11 (EU 2002). This value has been recommended to be used within the CLEA model as it is derived from an authoritative EU source.

Toluene
The molecular weight of toluene (C_7H_8) is reported as 92.14 (± 0.01) (Kirk-Othmer 2003, WHO 1986; EU 2001c). For consistency, and according to the hierarchy of data sources set out in CLEA, the value of 92.15 (EU 2001c) has been recommended to be used within the CLEA model. The small variation in the quoted values is unlikely to have a significant effect on potential model sensitivity.

Ethylbenzene
The molecular weight for ethylbenzene (C_8H_{10}) identified within the GCS report (1997) and WHO (1996) is 106.16. This value has been recommended to be used within the CLEA model as it is derived from an authoritative EU source.

Xylene
The molecular weight of each of the xylene isomers (C_8H_{10}) is reported as 106.16 (WHO 1997). A value of 106.16 has been recommended to be used within the CLEA model as according to the hierarchy, in the absence of EU sources, a WHO source is considered appropriate.

Boiling Point

The following section presents values in °C, for ease of comparison with scientific literature; Tables 4.3 and 4.12 present values in K. A major factor in the variability of reported literature values for boiling point is the pressure at which the experiment was undertaken. This is commonly reported either as hPa (100 Pa) or mmHg. For ease of comparison of values for a wide range of compounds, boiling points have been reported in this document at 1013 hPa (equivalent to 760 mmHg).

Ranges are not appropriate for this parameter although some variation in quoted values was identified within the consulted texts, largely due to the number of significant digits selected by the source literature. In the context of selection for intended use within CLEA one decimal place is considered sufficiently sensitive for this parameter, and is consistent with the approach within the WHO EHC documents.

Benzene

The EU Risk Assessment (EU, 2002) proposes an experimentally derived value of 80.1°C at 1013 hPa (source Römmp 1995) which is consistent with the figure of 80.1 (reported as 80.094 at 101.3 kPa in Kirk-Othmer 2003 and WHO 1993). The value of 80.1 is recommended for use within the CLEA model as it is derived from authoritative and EU sources.

Toluene

The value used in the EU Risk Assessment (EU 2001c) is 110.6°C at 1013 hPa (Merck 1989) which is consistent with Kirk-Othmer, and WHO (1986, cited from Weast 1977). The value of 110.6°C is recommended for use within the CLEA model as it is consistently derived from authoritative sources, including the relevant EU Risk Assessment report.

Ethylbenzene

Values derived from three studies (Hoechst 1976; Coty, Welch *et al.* 1987 and Griesbaum, Stretter *et al.* 1977) are quoted in the GCS BUA report, ranging from 136.1°C to 136.2°C, all measured at 1013 mbar (mbar is directly comparable to hPa). Kirk-Othmer (2003) and WHO (1996) also quote values within this range. A value of 136.2°C is recommended for use within the CLEA model as this value is consistently reflected in the authoritative literature and decimal place is considered appropriate.

Xylene

Kirk-Othmer (2003) states 139.12°C for *m*-xylene, 144.41°C for *o*-xylene and 138.37°C for *p*-xylene, although the pressure is not provided. WHO (1997) quotes comparable boiling points of 139.1°C for *m*-xylene, 144.4°C for *o*-xylene and 138.3°C for *p*-xylene at 101.3 kPa (1013 hPa), however, the source of these values is not clear as a reference list is provided for the entire table of physical properties, rather than for each individual property. The WHO values are recommended for use within the CLEA model, despite the lack of clear referencing, as experimental conditions (pressure) are provided.

Aqueous Solubility

The solubility of BTEX compounds has been measured at various temperatures by a wide range of studies adopting many different techniques. A comprehensive and critical review of this work (IUPAC 1989a) is available and has been used as a foundation for much of the following discussion. In the process of the IUPAC review, several proposed values, which differed significantly from the bulk of the experimental results, were discarded as unreliable.

Within scientific literature, aqueous solubility is typically reported at a temperature of 25°C, although for well studied chemicals such as BTEX aqueous solubility is also available over a range of temperatures. Whilst it is conceded that 25°C does not represent a standard temperature for UK soils, within this report aqueous solubility is reported at this temperature to enable future comparison with less well studied chemicals.

Aqueous solubility has also been supplied at 20°C. This is required to facilitate calculation of Henry's Law Constants (K_H) in conjunction with vapour pressures, which are presented at 20°C. Other data provided within this report can be used to convert K_H to more plausible UK soil temperatures if needed. There are very limited data available beyond these temperatures and therefore 20°C is the closest temperature with reasonable quantities of measured data from which parameters can be extrapolated to UK ambient environmental temperatures. Where reliable values at other temperatures are available, these have been provided.

The BTEX compounds all have significant aqueous solubility, which will allow them to leach from contaminated soils into groundwater. Benzene is more soluble than toluene, which in turn is more soluble than ethylbenzene and xylenes.

The solubilities quoted in this section relate to behaviour of chemicals in pure form. In the majority of cases involving land contamination by BTEX, they will be present in mixtures with other hydrocarbon compounds and/or other organic chemicals. Consequently, the effective solubility of the various contaminant constituents may be considerably lower in practice.

Consideration of the indicative compositions of different fuel types and calculation of the respective mole fractions of BTEX within the mixture will give an indication of the likely relative solubilities of BTEX compounds for fresh spills. However, effective solubilities in the environment can evolve rapidly as fuel constituents volatilise and the contaminant mixture changes, so effective solubility estimates should take account of measured petroleum hydrocarbon constituents in the zone of interest.

Benzene

IUPAC (1989a) indicates that benzene has an aqueous solubility minimum at approximately 17°C. Recommended solubility values at various temperatures quoted in this study are provided below in Table 4.4.

Table 4.4 **Solubility Values for Benzene at Varying Temperature (after IUPAC 1989a)**

Temp (K)	Temp (°C)	No. of values	Solubility (mg l^{-1})	95% CI (± mg l^{-1})
278	5	4	1800	50
283	10	5	1780	40
288	15	5	1760	40
293	20	6	1760	30
298	25	20	1770	20
303	30	6	1810	50

The EU Risk Assessment (2002) proposes a solubility of 1.8 g l^{-1} (1800 mg l^{-1}) at 25°C (cited from Freier 1976). This appears to be atypical as within the IUPAC study a solubility of 1800 mg l^{-1} lies at either extreme of the range identified, consistent with temperatures of <10°C or >25°C. USEPA (1996b) suggests a value of 1750 mg l^{-1} at 20 to 25°C. As the EU value is obtained from a single study from the 1970's, and appears at odds with the findings of more recent authoritative studies, the value recommended for the CLEA model is the IUPAC value of 1770 mg l^{-1} at 25°C. Also derived from this study is a suggested solubility at 20°C of 1760 mg l^{-1}. Values for different temperatures are provided in the table, above, should these be required.

Toluene

A review of 14 independent studies (where data that were more than three standard deviations from the average value were rejected) recommended a value of 530 mg l^{-1} at 25°C (IUPAC 1989a). An estimated uncertainty of 20 mg l^{-1} associated with this value was provided although this was not presented as a statistically significant uncertainty. The experimental results at other temperatures were considered too inconclusive to derive recommended values, although the results suggest that the aqueous solubility of toluene has a similar temperature dependent relationship to that of benzene, albeit with a less well defined solubility minimum between tentative values of 590 mg l^{-1} at 5°C and 30°C.

The solubility of toluene in water has been recorded as 515 mg l^{-1} at 20°C (EU 2001, cited from IUCLID 1994) and 535 mg l^{-1} at 25°C (EU 2001, cited from Hansch and Leo 1985), however, the methodology behind the value quoted by IUCLID is not known and the study is not well referenced. The WHO provides a figure of 535 mg l^{-1} at 25°C in freshwater (source Sutton and Calder 1975). USEPA (1996a) suggests a value of 526 mg l^{-1}, at 20 to 25°C. These data are all consistent with the ranges of solubility presented in the IUPAC study. The value of 535 mg l^{-1} at 25°C is recommended for use within the CLEA model, as it is referenced by both the EU Risk Assessment and WHO. In the absence of alternative values for the lower temperature, the IUCLID figure of 515 mg l^{-1} at 20°C is also recommended.

Ethylbenzene

A review of eleven independent studies, which included aqueous solubility results ranging from 152 to 181 mg l^{-1} at 25°C, recommended a value of 169 mg l^{-1} at this temperature (IUPAC 1989b). An estimated uncertainty of 9 mg l^{-1} associated with this value was provided although this was not presented as a statistically significant uncertainty. The data suggested the occurrence of a solubility minimum at approximately 20°C.

The solubility of ethylbenzene in water has been stated to be 152 mg l^{-1} at 20°C by GCS 1997 and WHO 1996 (both cite Verschueren 1983); according to the IUPAC study this is consistent with the lowest solubility determined at 25°C. The methodologies behind several varying values quoted by IUCLID are not known and as the studies are not well referenced, these are not presented here. USEPA (1996a) suggests a value of 169 mg l^{-1}, at 20 to 25°C. The value of 169 mg l^{-1} is recommended as a representative value for solubility at 25°C for use within the CLEA model; this is suggested by both the IUPAC study and USEPA. Also recommended for the purposes of calculation of a Henry's Law constant at a lower temperature (should this be required) is the GCS (1997) sourced value of 152 mg l^{-1} at 20°C.

o-xylene

No EU Risk Assessment is available for xylene isomers. IUPAC (1989b) recommended a value for the aqueous solubility of *o*-xylene at 25°C of 173 mg l^{-1}, based on results ranging from 167 to 179 mg l^{-1}. The WHO (1997) references a value outside this range (142 mg l^{-1} - temperature unknown), but the source of this value is not clear and without a quoted temperature it is of limited use.

A range of solubility values at various temperatures are provided by IUCLID, ranging from 142 mg l^{-1} at 0°C (Polak and Lu 1973), to 196 mg l^{-1} at 35°C (Sanemasa, Araki *et al*. 1982). A value of 1800 mg l^{-1} (1.8g l^{-1}) at 20°C is also reported (cited from Deutsche Exxon, with no further details on reference provided), although an outlier of this magnitude has to be viewed with scepticism. USEPA (1996a) suggests a value of 178 mg l^{-1}, at 20 to 25°C. HSDB (2002) gives 178 mg l^{-1} at 25°C (Sanemasa, Araki *et al*. 1982). A value of 173 mg l^{-1} (derived from IUPAC 1989b) is recommended as a representative value for solubility at 25°C for use within the CLEA model; this is thought applicable as it is from an authoritative source and reflects the range of experimental values identified. Data have been found to be too limited to derive an experimental value for a temperature of 20°C, although with further research, and perhaps some data interpolation, this may be possible.

m-xylene

IUPAC (1989b) found insufficient data to recommend an aqueous solubility of *m*-xylene in a typical environmental temperature range, but offered indicative values of 160 +/-20 mg l^{-1} based on results ranging from 134 to 173 mg l^{-1} at 25°C. Additional tentative values reported at other temperatures were 170 mg l^{-1} at 20°C and 200 mg l^{-1} at 10°C.

The WHO (1997) references a value of 146 mg l^{-1}. However, the source of this value is not clear and without a quoted temperature it is of limited use. A solubility value of 146 mg l^{-1} is also quoted at 25°C in IUCLID, cited from Sutton and Calder, 1975. USEPA (1996a) suggests a value 161 mg l^{-1}, at 20 to 25°C. HSDB gives 162 mg l^{-1} at 25°C (Yalkowsky and Dannenfelser 1992). A value of 160 mg l^{-1} (derived from IUPAC 1989b) is recommended as a representative value for solubility at 25°C for use within the CLEA model, as it is from an authoritative source and agrees with the ranges presented within a number of other sources. From the same study, a tentative 170 mg l^{-1} at 20°C is suggested.

p-xylene

The solubility of *p*-xylene at 25°C reported in IUPAC (1989b) was 180 +/- 20 mg l^{-1} based on results ranging from 156 to 200 mg l^{-1}. The WHO (1997) references a value of 185 mg l^{-1} but the source of this value is not clear and without a quoted temperature it is of limited use. IUCLID quotes a solubility of 156 mg l^{-1} at 25°C (cited from Howard 1990). HSDB (2002) reports a water solubility of 198 mg l^{-1} at 25°C (Yalkowsky and Dannenfelser 1992).

More so than the other isomers, research into *p*-xylene has identified a wide range of quoted solubility values. A value of 180 mg l^{-1} (derived from IUPAC 1989b) is recommended as a representative value for solubility at 25°C for use within the CLEA model, as it is from an authoritative source which critically reviewed a full range of studies. Data have been found to be too limited to derive an experimental value for a temperature of 20°C, although with further research, and perhaps some data interpolation, this may be possible.

Vapour Pressure

The vapour pressure is used within the CLEA Model together with the aqueous solubility to estimate the Henry's Law Constant where measured values are not available. Vapour pressure alters with temperature and a range for different temperatures is provided where found in the literature. Whilst it is noted that 20°C is warmer than would be expected for typical UK soils, use of these vapour pressure values will allow temperature-consistent Henry's Law Constants to be calculated despite the limitations of physicochemical literature for these compounds.

The literature review has indicated that if released to air, the vapour pressures of each of the BTEX compounds are such that they will exist solely as a vapour in the ambient atmosphere (HSDB 2002). However, there is an order of magnitude variation between the values across the BTEX compounds which will influence their behaviour relative to one another. Benzene has the highest vapour pressure, toluene will demonstrate intermediate properties while ethylbenzene and all xylene isomers have a similar range of vapour pressure at the lower end of the BTEX range and consequently will have lower volatility.

Benzene

Several vapour pressure study results have been reported at a temperature of 25°C with values ranging from 12,100 to 12,700 Pa and a mean of 12,530 Pa (McKay, Shiu *et al.* 1991). The saturated vapour pressure of benzene has been reported as 6070 Pa (at 10°C) and 24,400 Pa (at 40°C) (SRC 2002). Benzene vapour pressure at 20°C is reported as 10,000 Pa (Lide 1997) whilst a value of 13,300 at 26°C is provided by the WHO (1993). Kirk-Othmer (2003) reports a value of 12,600 Pa at 25°C, while the EU Risk Assessment proposes 9970 Pa at 20°C (EU, 2002, source Folkins 1985). The SRC (2002) recommends a saturated vapour pressure of 95 mmHg (12,664 Pa) at 25°C, citing Daubert and Danner 1989, which is an evaluated database arising from a data compilation exercise. SRC (2002) also report a measured value of 95 Torr (12,664 Pa) at 25°C (Thibodeaux 1981) and 95.2 Torr (12,690 Pa) at 25°C (Boublik, Fried *et al.* 1984). Calculated values, using the Antoine equation, at three different temperatures are also provided (Zwolinski and Wilhoit 1971). These results, along with other values noted above, are presented in Table 4.5.

Table 4.5 Values of vapour pressure for benzene at varying temperatures

Temp °C	Vapour Pressure (Pa)	Source
10	6069 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
20	9970	(Folkins 1985; EU 2002)
20	10,000	(Lide 1997)
25	12,530 (average)	(Mackay, Shiu et al. 1991)
25	12,664	(SRC 2002) (Daubert and Danner 1989)
25	12,664	(Thibodeaux 1981; SRC 2002)
25	12,600	(Kirk-Othmer 2003)
25	12,687 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
25	12,690	(Boublik, Fried et al. 1984; SRC 2002)
26	13,300	(WHO 1993)
40	24,367 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)

A value of 9970 Pa at 20°C is recommended from the EU Risk Assessment as a representative value for use within the CLEA model, as it is from a reputable European source and is consistent with the range of values (tabulated above) derived by various studies over different temperatures. Should a value at 25°C be required, then the SRC (2002) value of 12,664 Pa is suggested to be sufficiently representative.

Toluene

A range of vapour pressures are quoted in the literature, over a variety of temperatures. The vapour pressure has been reported as between 1000 Pa (at 1.5°C) and 24,400 Pa (at 45.2°C) by Lide 1997. A value of 28.7 mmHg (3826 Pa) at 25°C is provided by the WHO (1986 cited from Weast 1977). The EU Risk Assessment proposes 3000 Pa at 20°C (EU 2001c), measured, cited from IUCLID 1994, and 3800 Pa at 25°C (EU, 2001 cited from Mackay, Shiu *et al.* 1991; one further value is provided, although no experimental temperature is given. Within IUCLID there are several additional values, although the source and reliability of these is not always clear. These include 2890 Pa at 20°C (calculated, no further data), 2930 Pa at 20°C (cited from, BASF AG, 1997 with no further details on reference provided), 3000 Pa at 20°C (measured, cited from Deutsche Shell, with no further details on reference provided, date unknown) and 12,000 at 50°C (cited from BASF AG, 1995, with no further details on reference provided). The saturated vapour pressure of toluene has also been reported 28.4 mmHg (3786 Pa) at 25°C by SRC (2002), citing Daubert and Danner 1989, an evaluated database arising from a data compilation exercise. These results, along with other values noted above, are presented in Table 4.6.

Table 4.6 - Values of vapour pressure for toluene at varying temperatures

Temp °C	Vapour Pressure (Pa)	Source
1.5	1000	(Lide 1997)
20	2890	(IUCLID 2000) (no further data)
20	2930	(IUCLID 2000) (BASF AG 1997)
20	3000	(EU 2001c) (IUCLID 1994)
25	3786	(Daubert and Danner 1989; SRC 2002)
25	3800	(EU 2001c) (Mackay, Shiu et al. 1991)
25	3826	(WHO 1986) (Weast 1977)
45.2	24,400	(Lide 1997)
50	12,000	(IUCLID 2000) (BASF AG, 1995)

The EU Risk Assessment measured value of 3000 Pa at 20°C, referenced from IUCLID, is recommended for use in the CLEA model. This is consistent with the CLEA hierarchy of accepting robust European data, where available. Should a value at 25°C be required, then the SRC value of 3786 Pa is suggested to be sufficiently representative.

Ethylbenzene

In the absence of an EU Risk Assessment, the GCS draft report on ethylbenzene has been consulted. Within this document a number of values for vapour pressure are provided, as follows: 950 Pa at 20°C (source, Stoye D 1978), 931 Pa at 20°C (source, Hoechst 1976), 950 Pa at 20°C (source, BASF AG 1988a, with no further details on reference provided) and 4600 Pa at 38°C (source BASF AG 1990 with no further details on reference provided). IUCLID provides an additional value of 1359 Pa at 25.9°C (Repsol, no date and with no further details on reference provided). Lide (1997) provides values of 1000 Pa at 21.1°C and 10,000 Pa at 67.1°C. A value of 1240 Pa at 20°C is provided by the WHO (1996), however the source of this value is not clear. The SRC (2002) recommends a saturated vapour pressure of 9.6 mmHg (1280 Pa) at 25°C, citing Daubert and Danner 1985, an evaluated database arising from a data compilation exercise. SRC also reports a measured value of 9.571 Torr (1276 Pa) at 25°C (Driesbach 1955) and calculated values, using the Antoine equation, at four different temperatures (Zwolinski and Wilhoit 1971). These values, and a summary of the others mentioned above, are presented in Table 4.7.

Table 4.7 - **Values of vapour pressure for ethylbenzene at varying temperatures**

Temp °C	Vapour Pressure (Pa)	Source
20	931	(Hoechst 1976; GCS 1997)
20	950	(Stoye D 1978; GCS 1997)
20	950	(GCS 1997) (BASF AG, 1988a)
20	1240	(WHO 1996)
21.1	1000	(Lide 1997)
25	1276	SRC, 2003 (Driesbach 1955)
25	1280	SRC, 2003 (Daubert and Danner 1989)
25	1267 (calc. Antoine eqn.)	SRC, 2003 (Zwolinski and Wilhoit 1971)
25.9	1359	IUCLID, 2000 (Repsol)
38	4600	(GCS 1997)(BASF AG, 1990)
38.6	2666 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
52.75	5332 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
74.105	13,330 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
67.1	10,000	(Lide 1997)

A vapour pressure of 950 Pa at 20°C, referenced from the GCS Report, is recommended for use in the CLEA model. This is consistent with the CLEA hierarchy of accepting robust European data, where available, and is a more recent value than the Hoechst reference, cited by the same source. Should a value at 25°C be required, the SRC value of 1280 Pa is suggested to be sufficiently representative.

o-xylene

No EU Risk Assessment is available for xylene isomers. However, the IUCLID database offers the following values; 670 Pa at 20°C, 1200 Pa at 30°C and 3200 Pa at 50°C (cited from Auer Technikum, 1989 with no further details on reference provided). WHO (1997) provides a value of 660 Pa for *o*-xylene at 20°C; the source of this value is not clear. Lide (1997) does not provide data for *o*-xylene, but extrapolates data to give 1000 Pa at 27°C. The SRC (2002) recommends a saturated vapour pressure of 6.61 mmHg (881 Pa) at 25°C, citing Daubert and Danner 1989, an evaluated database arising from a data compilation exercise. SRC (2002) also reports calculated values, using the Antoine equation, at three different temperatures (cited from Zwolinski and Wilhoit 1971). Values are tabulated below.

m-xylene

The IUCLID database offers the following values; 660 Pa at 20°C (SICREM, no further information available) and 1333 Pa at 28.3°C (Weast, Lide *et al.* 1989). WHO (1997), provides a value of 790 Pa for *m*-xylene at 20°C, however the source of this value is not clear. Lide (1997) provides a value of 1000 Pa at 23.4°C. The SRC (2002) recommends a measured saturated vapour pressure of 8.454 mmHg (1127 Pa) at 25°C, citing Daubert and Danner 1989, an evaluated database arising from a data compilation exercise. SRC also reports a value of 8.29 mmHg (1105 Pa) at 25°C (Chao, Lin *et al.* 1983) and a calculated value, using the Antoine equation of 8.3 Torr (1107 Pa) cited from Zwolinski and Wilhoit 1971. Values are tabulated below.

p-xylene

The IUCLID database offers the following values; 1200 Pa at 24°C (from Intercontinental Quimca) and 1150 Pa at 25°C (ICI) (no further details are provided). WHO (1997) provides a value of 860 Pa for *p*-xylene at 20°C, but the source of this value is not clear. CRC provides a value of 1000 Pa at 22.4°C. The SRC recommends a measured saturated vapour pressure of 8.9 mmHg (1186 Pa) at 25°C, citing Daubert and Danner (1989), an evaluated database arising from a data compilation exercise. SRC also reports a value of 8.84 mmHg (1179 Pa) at 25°C (Chao *et al.,* 1983) and calculated values, using the Antoine equation, at three different temperatures (Zwolinski and Wilhoit 1971). These results and others noted above are presented in Table 4.8.

Table 4.8 - Values of vapour pressure of xylene isomers at varying temperatures

Temp °C	**Vapour Pressure (Pa)**	**Source**
o-xylene		
10	340 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
20	660	(WHO 1997)
20	670	(IUCLID 2000) (Auer Technikum, 1989[13])
25	881	(SRC 2002) (Daubert and Danner 1989)
25	883 (calc. Antoine eqn.)	(SRC 2002) (Zwolinski and Wilhoit 1971)
27	1000	(Lide 1997)
30	1200	(IUCLID 2000) (Auer Technikum, 1989)
40	2045 (calc. Antoine eqn.)	(SRC 2002) (Zwolinski and Wilhoit 1971)
50	3200	(IUCLID 2000) (Auer Technikum, 1989)
m-xylene		
20	660	(IUCLID 2000) (SICREM)
20	790	(WHO 1997)
23.4	1000	(Lide 1997)
25	1105	(SRC 2002) (Chao, Lin et al. 1983)
25	1107 (calc. Antoine eqn.)	(Zwolinski and Wilhoit 1971; SRC 2002)
25	1127	(SRC 2002) (Daubert and Danner 1989)
28.3	1333	IUCLID (Weast, Lide et al. 1989)
p-xylene		
10	461 (calc. Antoine eqn.)	(SRC 2002) (Zwolinski and Wilhoit 1971)
20	860	(WHO 1997)
22.4	1000	(Lide 1997)
24	1200	(IUCLID 2000)

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[13] no details provided

25	1150	(IUCLID 2000)
25	1179	(SRC 2002) (Chao, Lin et al. 1983)
25	1168 (calc. Antoine eqn.)	(SRC 2002) (Zwolinski and Wilhoit 1971)
25	1186	(SRC 2002) (Daubert and Danner 1989)
40	2645 (calc. Antoine eqn.)	(SRC 2002) (Zwolinski and Wilhoit 1971)

In the absence of clearly referenced EU data (values cited in the IUCLID database are not well supported and are obtained from a variety of sources, at inconsistent temperatures), WHO values are recommended for xylene isomers for input to the CLEA model. These are available for the target temperature of 20°C for each isomer. One limitation is that these are subject to some ambiguity as to the source documents, due to the referencing system used; further research could improve certainty in this aspect. Should values at 25°C be required, the SRC values cited from Daubert and Danner are suggested to be sufficiently representative.

Henry's Law Constant

Henry's Law Constant may either be determined experimentally or calculated from the solubility and vapour pressure, as discussed in more detail in the introductory section.

Ryan, Bell *et al*. (1988) cite the volatilisation categories of Jury, Farmer *et al*. (1984) according to dimensionless Henry's Law Constant. The BTEX all fall into the category of 2.5×10^{-3} (6.2 Pa-m^3 mol^{-1}) and above, and according to Jury are thus likely to volatilise easily from soil solution. In common with other parameters discussed in this document, the most mobile of the BTEX compounds is benzene which has the highest Henry's Law Constant, and therefore is the most likely to volatilise from soil. The isomers of xylene are less volatile than other members of this group of compounds but will still readily volatilise from permeable soils.

Benzene

The EU Risk Assessment provides calculated values of Henry's Law Constant of 270.5 Pa-m^3 mol^{-1} at 10°C and 557.1 Pa-m^3 mol^{-1} at 25°C (cited from Mackay and Leinonen 1975). The report also calculates a Henry's Law Constant (utilising suggested solubility and vapour pressure figures derived earlier in the assessment), resulting in a value at 20°C of 432.6 Pa-m^3 mol^{-1}, this has been adopted as the recommended value throughout the EU document. The calculation used by the EU Risk Assessment is presented in the EU Technical Background Document (TBD) (EU 1996).

However, in the case of benzene the vapour pressure used within the EU assessment is valid at 20°C while the solubility is that quoted at 25°C. Therefore it does not appear to be appropriate to state that the Henry's Law Constant developed is valid at 20°C.

Using the calculation presented in the TBD, substituting the recommended solubility at 20°C of 1,760 mg l^{-1} and vapour pressure of 9970 Pa at 20°C (as derived in the preceding sections of the EURA), results in an estimated Henry's Law Constant of 442.5 Pa-m^3 mol^{-1}.

Other values quoted in the literature are 557 Pa-m^3 mol^{-1} at 25°C (Lide 1997) and 5.56x10^{-3} atm-m^3 mol^{-1} (563.4 Pa-m^3 mol^{-1}) (HSDB 2002), cited from Mackay, Shiu *et al.* 1979 also at 25°C. SRC (2002) refers to a number of *measured* values, expressed as unitless constants, which convert to 561, 556 and 551 Pa-m^{3}mol^{-1} (Mackay and Leinonen 1975; Shen 1982 and Green and Frank 1979, respectively), no temperatures are stated although the same (Mackay and Leinonen 1975) figure is variously quoted elsewhere as being at 25°C (ATSDR 1997d, or 20°C, WHO 1993). The recommended value within the SRC database is 5.55x10^{-3} atm-m^3 mol^{-1} (562 Pa-m^3 mol^{-1}) at 25°C, cited from Mackay, Shiu *et al.* (1979).

The IUCLID database references Mackay and Leinonen (1975) giving the same values for 10°C and 25°C as the EU Risk Assessment, and Mackay, Shiu *et al.* (1991) which it states is a 'compilation of the literature' giving a range of 533 to 570 Pa-m^3 mol^{-1} at 25°C, an experimental value at 562 Pa-m^3 mol^{-1} and a recommended value of 550 Pa-m^3 mol^{-1}. This reference is more up to date than Mackay *et al.*, 1979 from which the recommended value in the SRC database is derived.

Clearly, there is minor variation in literature values for Henry's Law Constant of benzene, particularly at 25°C. This is considered to be mainly due to conversion between different units and unitless constants. The choice is based on preference of data source and calculated or measured values. Without recourse to the original documents, there are further difficulties in interpreting the data, for instance, values from Mackay and Leinonen (1975) are classed as calculated by EU and measured by SRC.

For the purpose of recommending a value for use in the CLEA model it is suggested that the approach outlined throughout the EU Risk Assessment is followed, that is to calculate Henrys Law Constant for 20°C. This has been undertaken based upon the recommendations made earlier in this document for vapour pressure and solubility at this temperature, resulting in 442.5 Pa-m^3 mol^{-1}.

Toluene

A value of 537 Pa-m^3 mol^{-1} at 20°C is given by the EU, 2001 (calculated based on a 'measured' vapour pressure of 3000 Pa and the water solubility of 515 mg l^{-1}). This calculation appears to be soundly based upon vapour pressure and solubility consistently derived for 20°C, values which are also in agreement with those suggested in this document, above.

Other values quoted in the literature are 680 Pa m^3 mol^{-1} at 25°C (Lide 1997) and 6.64x10^{-3} atm-m^{-3} mol^{-1} (672.8 Pa-m^3 mol^{-1}) (HSDB 2002), cited from Mackay, Shiu *et al.* (1979). The IUCLID (2000) database includes no mention of Henry's Law Constant. SRC refers to a *measured* value, expressed as a unitless constant, which converts to 615 Pa-m^3 mol^{-1} (NRC 1980). A recommended value within this database of 6.64x10^{-3} atm-m^3 mol^{-1} (672.8 Pa-m^3 mol^{-1}) at 25°C is cited from Mackay, Shiu *et al.* (1979).

The recommended value for use in the CLEA model is the EU Risk Assessment (EU 2001c) calculated Henry's Law Constant for 20°C of 537 Pa-m^3 mol^{-1}. This is based on the most relevant solubility and vapour pressure data as reviewed earlier in this document, and reflects the preferred EU approach for deriving this parameter.

Ethylbenzene

In the absence of an EU Risk Assessment for ethylbenzene, the GCS BUA publication (GCS 1997) has been consulted. This gives information on Henry's Law Constants from a number of studies, the majority calculated. At 20°C, cited studies are Mabey, Smith *et al.* (1982) which calculated 668.7 Pa-m^3 mol^{-1} and Thomas (1990) which calculated 881.5 Pa-m^3 mol^{-1}. At 25°C, Shen (1982) returned a value of 652.5 Pa-m^3 mol^{-1} and Harkins, Bohm *et al.* (1987) calculated 721.9 Pa-m^3 mol^{-1}. Data from Mackay, Shiu *et al.* (1979) indicates a measured value of 854.2 Pa-m^3 mol^{-1} and a calculated Henry's Law Constant of 884.6 Pa-m^3 mol^{-1}, both at 25°C.

Based upon the ranges of solubility and vapour pressure at 20°C identified earlier in the GCS report, a range of 478.7 to 664.3 Pa-m^3 mol^{-1} is derived using the same equation as in the EU Risk Assessment reports (GCS 1997). This approach has been adopted using the most relevant solubility and vapour pressure data as reviewed earlier in this document (solubility at 20°C of 152 mg l^{-1} and vapour pressure of 950 Pa at 20°C), resulting in a Henry's Law Constant of 663.5 Pa-m^3 mol^{-1}.

The IUCLID database references a number of studies, including Shen (1982) which provides 6.64x10^{-3} atm-m^3 mol^{-1} (652.3 Pa-m^3 mol^{-1}) at 25°C and Mackay, Shiu *et al.* (1979) which again provides 854.2 Pa-m^3 mol^{-1}. SRC (2002) refers to a number of *measured* values, expressed as unitless constants, which convert to 650 and 914 Pa-m^3 mol^{-1} (Shen 1982 and Lyman, Reehl *et al.* 1982 and 1990, respectively). Mackay, Shiu *et al.* (1979) is also referenced. The recommended value within this database is 7.88x10^{-3} atm-m^3 mol^{-1} (798 Pa-m^3 mol^{-1}) at 25°C, cited from Sanemasa, Araki *et al.* (1982). Other values quoted in the literature were 887 Pa-m^3 mol^{-1} (WHO 1996), no temperature or clear reference is stated, however this is consistent with 887 Pa-m^3 mol^{-1} at 25°C (Lide 1997).

The recommended value for use in the CLEA model is the calculated Henry's Law Constant for 20°C of 663.5 Pa-m^3 mol^{-1}. This is based on the most relevant solubility and vapour pressure data as reviewed earlier in this document, and reflects the preferred EU approach for deriving this parameter, as demonstrated in the benzene and toluene risk assessment reports.

o-xylene

SRC refers to a *measured* value, expressed as a unitless constant of 0.216 (cited in Mackay and Leinonen 1975), which converts to 534 Pa-$m^3$$mol^{-1}$. A further (calculated) unitless constant converts to 541 Pa-$m^3$$mol^{-1}$ (NRC 1980). The recommended value within this database is 5.19x10^{-3} atm-m^3 mol^{-1} (526 Pa-m^3 mol^{-1}) at 25°C, cited from Sanemasa, Araki *et al.* (1982).

IUCLID provides a Henry's Law Constant of 534 Pa-$m^3$$mol^{-1}$ from Mackay and Leinonen (1975). The HSDB offers a single value of 5.13x10^{-3} atm-m^3 mol^{-1} at 25°C (520 Pa-m^3 mol^{-1}), again cited from Sanemasa, Araki *et al.* (1982). One further value, a slight outlier, is 565 Pa-m^3 mol^{-1} at 25°C (Lide 1997).

Calculating values for *o*-xylene at 20°C, as was carried out for benzene, toluene and ethylbenzene, is more problematic than for the other BTEX compounds. This is mainly due to the paucity of solubility data at this temperature. In the absence of required data to calculate a value at 20ºC, the measured value of 534 Pa-m^3mol^{-1} at 25°C (Mackay and Leinonen 1975) has been presented; this is cited by IUCLID and the SRC and is therefore considered a valid authoritative value.

m-xylene

IUCLID provides no data on the Henry's Law Constant of *m*-xylene. The recommended value within the SRC (2003) is $7.43x10^{-3}$ atm-m^3 mol^{-1} (753 Pa-m^3 mol^{-1}) at 25°C, calculated by SRC (2002) using the calculation of vapour pressure divided by aqueous solubility in mol m^{-3}. The HSDB (2002) offers a single value of 0.00718 atm-m^3 mol^{-1} at 25°C (728 Pa-m^3 mol^{-1}), again cited from Sanemasa, Araki *et al.* (1982), one further value is 730 Pa-m^3 mol^{-1} at 25°C (Lide 1997).

A value of Henry's Law Constant for *m*-xylene at 20°C can be calculated as solubility data at this temperature are available. The most relevant solubility and vapour pressure data as reviewed earlier in this document (solubility at 20°C of 170 mg l^{-1} and vapour pressure of 790 Pa at 20°C) result in a Henry's Law Constant of 493.3 Pa-m^3 mol^{-1}.

p-xylene

IUCLID provide no data on Henry's Law Constant of *p*-xylene. The recommended value within the SRC database is $7.66x10^{-3}$ m^3 mol^{-1} (776 Pa-m^3 mol^{-1}) at 25°C, calculated by SRC using the calculation of vapour pressure divided by aqueous solubility in mol m^{-3}. The HSDB offers a single value of 0.0069 atm-m^3 mol^{-1} at 25ºC (699 Pa-m^3 mol^{-1}), cited from Foster *et al* (1994). One further value is 578 Pa-m^3 mol^{-1} at 25°C (Lide 1997).

Calculating values for *p*-xylene at 20°C, as was carried out for benzene, toluene ethylbenzene and *m*-xylene, is more problematic than for the other BTEX compounds. This is mainly due to the paucity of solubility data at this temperature. In the absence of required data for this calculation to be carried out, the value of 699 Pa-m^3mol^{-1} (Foster *et al* 1994) at 25ºC is adopted. This is cited from HSDB and is therefore considered a valid authoritative value; it is also from a recent study and lies in the mid-range of other literature-derived values.

Octanol-water partition coefficient

The octanol-water partition coefficient (K_{ow}) is a measure of a chemical's tendency to partition into the lipid phase. A low log K_{ow} tends to indicate high polarity and aqueous solubility, whereas a high log K_{ow} is an indication of highly lipophilic substances, usually with low aqueous solubility.

The literature review has indicated that each of the BTEX compounds can be thought of as moderately lipophilic to lipophilic, according to an adaptation of the scheme proposed in Bromilow and Chamberlain (1995) and described within the introductory chapter. However, the BTEX do present a range of values across this classification which will influence their relative behaviour in the soil. Benzene has the lowest log K_{ow} and thus theoretically the highest aqueous solubility and lowest tendency for partitioning into plants and animal tissues. Of the TEX compounds, toluene will demonstrate intermediate properties while ethylbenzene and all xylene isomers have similar log K_{ow} at the upper end of the BTEX range and consequently will have the lowest aqueous solubility and be most highly lipophilic.

Benzene

WHO (1993) presents a range of log K_{ow} values for benzene of 1.56 to 2.25. The EU Risk Assessment uses a measured log K_{ow} value of 2.13, cited from Sangster (1989), which is consistent with the USEPA value (USEPA 1996a). The HSDB references this figure to Hansch and Leo (1985), while the recommended value from SRC is also 2.13 (Hansch and Leo 1985). The EU value of 2.13 is recommended for the CLEA model primarily in order to be consistent with the EU Risk Assessment. It also appears to be a consistently adopted as representative across various databases.

Toluene

The range of log K_{ow} values for toluene given in Mackay, Shiu *et al.* (1991) is 1.83 to 2.79. USEPA (1996a) quotes a value of 2.75. The HSDB references 2.73 to Hansch and Leo (1985), likewise, the SRC recommended value is also 2.73 (Hansch and Leo 1985). Sangster (1989), cited by the EU for the selected benzene log K_{ow}, provides a figure for toluene of 2.73. A value of 2.69 is presented by the WHO (1986), citing Tute, 1971. The USEPA selected value is 2.65 (USEPA 1996a).

The EU Risk Assessment employs a value of 2.65, referenced from IUCLID, 1994. The only further information provided by the original reference is that it is a measured value obtained from Deutsche Shell Chemie. Further values quoted in this document range from 2.66 (calculated) and 2.69 (calculated at 20ºC) to an apparent outlier of 5 (no further data are provided and this value is excluded from this exercise). Although the lowest of the commonly reported range of values (2.65 to 2.75), the EU value of 2.65 is recommended for the CLEA model following the accepted CLEA hierarchy as an EU sourced figure. It is also consistent with the USEPA value.

Ethylbenzene

USEPA (1996a) quotes a log K_{ow} of 3.14. The HSDB references a value of 3.15 (Hansch and Leo 1985), likewise, the value recommended by the SRC is also 3.15 (Hansch and Leo 1985). Sangster (1989), cited by the EU for the selected benzene log K_{ow}, provides a figure for ethylbenzene which is also 3.15. A value of 3.13 is presented by the WHO (1996), although the source of this value is not clear.

A range of 3.07 to 3.15 is provided by the GCS report (GCS 1997), derived from a number of studies, the most commonly quoted figure is 3.13 (Schantz and Martire 1987), measured by GC-RPLC at 25ºC; (Yalkowsky and Valvani, 1976, methodology unknown and Tewari, Miller *et al*. 1982, measured by HPLC at 25ºC). Of the lower values (3.07 to 3.11), the majority are calculated rather than measured. The log K_{ow} value recommended for the CLEA model is 3.13 as this is the most common of a range of values presented in the GCS study and is the figure quoted by the WHO.

Xylene

Data from USEPA (1996a) indicate log K_{ow} values of 3.13 for *o*-xylene, 3.20 for *m*-xylene, and 3.17 for *p*-xylene. In most other literature sources consulted log K_{ow} values are consistently stated to be 3.12 (*o*-xylene), 3.20 (*m*-xylene) and 3.15 (*p*-xylene) (HSDB 2002, SRC 2002, WHO 1997 and Sangster 1989). HSBD and SRC once more reference studies by Hansch and Leo (1985). The source of the WHO values is not clear.

The IUCLID database (2000), as referenced for the log K_{ow} values used in the EU Risk Assessment for toluene, was interrogated for *m*-, *o*- and *p*-xylene. The stated value for *m*-xylene is 3.20 at 25ºC, referenced from Miller, Wasik *et al*. (1985). For *o*-xylene stated log K_{ow} values are 3.12 (measured by the slow stir approach proposed by De Bruijn), referenced from Van Leeuwen, Van der Zandt *et al.* (1992), and 3.13 (measured) at 25ºC by generator column HPLC, referenced from Tewari, Miller *et al.* (1982). A single value is provided for *p*-xylene, this is 3.15 (measured), sourced from Lyman, Reehl *et al*. (1981).

In the absence of an EU Risk Assessment, IUCLID values are recommended for inclusion in the CLEA model, according to the hierarchy of sources. The selected values are therefore 3.12 (*o*-xylene), 3.20 (*m*-xylene) and 3.15 (*p*-xylene). This is considered a robust decision given that it also reflects the consensus of the published literature reviews (including that of the WHO), is consistent with the source for the log K_{ow} in the EU risk assessment review of benzene (Sangster 1989) and with the IUCLID database which was used as the basis for log K_{ow} in the EU risk assessment review of toluene.

Organic carbon partition coefficient

Organic carbon partition coefficient (K_{oc}) values for individual BTEX can vary significantly in the literature, with reported measured values for a compound sometimes varying over orders of magnitude. This can be attributed to several factors, including differences in soil or sediment properties, differences in experimental and analytical approaches used to measure the values, and experimental or measurement error (Gustafson, Griffith Tell *et al.* 1997). As a result of the number of factors which can affect experimental K_{oc} values, it is not possible to group derived values by any single factor. For instance, the range of reported values within a particular soil type is likely to be as great as the variation between soil types. Log K_{oc} may either be calculated from measured Log K_{ow} values or determined experimentally as described within the introductory chapter.

The general recommendation of this report is that, where possible, Soil Guideline Values (SGVs) are derived using a K_{oc} derived directly from the Log K_{ow}. This is because values of K_{oc} taken from the experimental literature will vary according to soil properties and SGVs may be developed for different soil types and conditions. Nevertheless, the range of literature quoted values for experimental K_{oc} is discussed, for comparison with the calculated values. The adopted approach is important as the selected value should be consistent with the conservative conceptual site model specified for SGV development. This includes the specification of the physical properties of a sandy soil. For this reason, the value calculated from K_{ow} has been particularly compared with K_{oc} values derived from experimental studies of 'typical' sandy soils (where available).

Individual experimentally-derived K_{oc} values are listed in the literature by the USEPA and, where available EU Risk Assessment and chemical reports. USEPA (1996a) measured K_{oc} values were obtained from Superfund Chemical Data Matrix (SCDM 1997), which reports that an extensive literature survey was carried out to determine the available measurements and methods of determination. The results of the survey are provided in Appendix K, Chapter 5 of USEPA (1996a).

Benzene

WHO (1993) cites the log K_{oc} of benzene as being 1.8 to 1.9. The source of the values is not clear but they are consistent with the ATSDR toxicological profile, which is one of the named references. Later in the same WHO document K_{oc} values of 60 to 83 (log K_{oc} 1.78 to 1.92) are cited (Kenaga and Goring 1980b; Karickhoff 1981) (which are also the original references given in the ATSDR toxicological profile), leading to the assumption that benzene is fairly mobile in soil.

The EU Risk Assessment (2002) provides a wide range of measured K_{oc} values in soils, ranging between 18.2 $l.kg^{-1}$ (log K_{oc} 1.26) (silt loam soil, Chiou, Porter *et al.* 1983) and 1,023 $l.kg^{-1}$ (log K_{oc} 3.00) (Uchrin and Mangels 1987). The variation is assigned to test conditions and soil characteristics. Two studies on Dutch soil and sediments returned results ranging between 42 and 900 $l.kg^{-1}$ (log K_{oc} 1.62 to 2.95) (Larson, Kjeldsen *et al.* 1992a and 1992b).

The USEPA (1996a) review of experimentally derived K_{oc} values identified thirteen studies on a range of soil types, ranging between 31 and 100 (log K_{oc} 1.49 to 2.00). The lowest referenced value is from the same study as the EU (Chiou, Porter *et al.* 1983), although the value quoted differs.

A further US appraisal is provided by Risk Science Programme (RSP) 1994, this appraises seventeen studies, including some of which duplicate those in the USEPA report, with K_{oc} ranging between 17 and 124 (log K_{oc} 1.23 to 2.09). Interestingly, this provides slightly more background data and the reason for the discrepancy in the reported low end result of Chiou *et al.*, becomes evident; the EU study quotes the value directly, reported as 18.2, while the USEPA and RSP transform the value from K_{om} to K_{oc} using a conversion of 1.724. Within this study, of particular relevance to the selection of a value for CLEA is the inclusion of a sandy vadose zone study with a fraction organic carbon (f_{oc}) of 1% (Abdul, Gibson *et al.* 1987), which returned a K_{oc} of 49 (log K_{oc} 1.69).

Clearly, there is a wide variation in quoted experimentally measured K_{oc} values for benzene with the widest range provided within the EU Risk Assessment, which is the highest tier resource within the CLEA hierarchy. As outlined in the introductory section, above, there are alternative methods for defining a log K_{oc} based upon conversion from the log K_{ow}, which is usually a more tightly constrained parameter. Both the USEPA and EU commence from a measured log K_{ow} value of 2.13.

The USEPA (1996a) calculates a K_{oc} of 58.9 (log K_{oc} of 1.77) derived from the log K_{ow} of 2.13, using the modified Di Toro regression for VOC compounds. The EU Risk Assessment (2002) suggests a K_{oc} of 134.1 (log K_{oc} of 2.13) derived from the log K_{ow} of 2.13, using the relationship for non-hydrophobic chemicals presented in Technical Guidance Document (EU 1996) as proposed by Sabljic and Gusten (1995). The difference in derived K_{oc} can be attributed solely to the theoretical conversion adopted. Were benzene to be classed by the ECB as a 'predominately hydrophobic' chemical (it is not clear what solubility cut-off was used) then a K_{oc} of 66.9 (log K_{oc} of 1.82) is derived using the alternative equation, which is closer to the USEPA result. It is of note that the regression used to derive the values is stronger for the USEPA ($r^2 = 0.97$) than the ECB ($r^2 = 0.63$), however this may be explained by differences in approach to selecting raw data.

The higher K_{oc} recommended by the EU (log K_{oc} of 2.13) is recommended for use in the CLEA model as it is from an authoritative data source and follows the accepted CLEA hierarchy as an EU sourced figure. In addition, it reflects the larger range of experimentally determined values (primarily from European studies) quoted in the ECB report compared to the USEPA analysis. The proposed value of 2.13 is consistent with the consensus of opinion that benzene is mobile in soil (WHO 1993; HSDB 2002), and will not undergo significant geoaccumulation. It should be noted, however, that a study of a sandy vadose zone soil type consistent with the CLEA default conceptual site model derived a log K_{oc} of 1.69, which would suggest less affinity to soil organic matter, and therefore potentially greater availability. This lower figure is more consistent with the USEPA calculated value.

Toluene

ATSDR (2000a) cites the log K_{oc} of toluene as being 1.57 to 2.25 (source Howard 1990), which convert to K_{oc} values of 37 to 178. The EU Risk Assessment provides three K_{oc} values in silt soils from a single study, ranging between 37 $l.kg^{-1}$ (log K_{oc} 1.57) and 160 $l.kg^{-1}$ (log K_{oc} 2.2) (Nathwani and Philips 1977).

The USEPA (1996a) review of experimentally derived K_{oc} values identified twelve studies on a range of soil types. These studies reported values for K_{oc} ranging between 94 and 247 (log K_{oc} 1.97 to 2.39). Within this study, of potential relevance to the selection of a value for CLEA, is the inclusion of a study of aquifer material with an f_{oc} of approximately 0.01 (Abdul, Gibson *et al.* 1987), for which a K_{oc} of 115 was calculated (log K_{oc} 2.06), and a study of a sandy soil (Wilson, Enfield *et al.* 1981) with an f_{oc} of 0.087, which derived a K_{oc} of 150 (log K_{oc} 2.18).

The USEPA (1996a) calculates a K_{oc} of 182 (log K_{oc} of 2.26) derived from the log K_{ow} of 2.65 using the modified Di Toro regression for VOC compounds. The EU (2001c) suggests a K_{oc} of 177 (log K_{oc} of 2.25) derived from the log K_{ow} of 2.65 using the relationship for predominately hydrophobic chemicals presented in Technical Guidance Document (EU 1996) as proposed by Sabljic and Gusten (1995). The minor difference in derived K_{oc} between these sources can be attributed solely to the theoretical conversion adopted. These calculated values are at the upper end of the ranges identified by experimental studies.

The calculated K_{oc} recommended by the EU (log K_{oc} of 2.25) is recommended for use in the CLEA model as it is from an authoritative data source and follows the accepted CLEA hierarchy as an EU sourced figure, and the approach is consistent with the selection of a K_{oc} for benzene.

Ethylbenzene

WHO (1993) cites a range of values for the K_{oc} of ethylbenzene as being 95.5 to 1,096 (log K_{oc} 1.98 to 3.04). The source of the WHO values is not clear, although they agree with the range presented in Mackay *et al.*, 1991. No EU Risk Assessment is available for ethylbenzene. The GCS BUA report (1997) details a number of studies, four of which used relevant measurement techniques, the range of reported values is 165 to 195 (log K_{oc} 2.22 to 2.47).

The USEPA (1996a) review of experimentally derived K_{oc} values identified five studies on a range of soil types, ranging between 165 and 255 (log K_{oc} 2.22 to 2.41). Three of the five values are referenced from the same primary data sources as the GCS BUA report, and are also referenced by ATSDR, 1999, which presents no further values.

The USEPA (1996a) calculates a K_{oc} of 363 (log K_{oc} of 2.56) derived from the log K_{ow} of 3.14 using the modified Di Toro regression for VOC compounds. Although no EU Risk Assessment is available, the methodology used within the benzene and toluene EU documents for deriving K_{oc} from log K_{ow} can be followed in the case of ethylbenzene. This approach is presented in Technical Guidance Document (EU 1996) and is based on a study by Sabljic and Gusten (1995). For ethylbenzene, the regression relationship developed by Sabljic and Gusten for predominately hydrophobic chemicals is appropriate (ethylbenzene has a lower solubility than toluene, which is classed by the ECB as predominately hydrophobic). When applied to the suggested log K_{ow} of 3.13 (see above) the regression results in a calculated K_{oc} of 432 (log K_{oc} of 2.64). The calculated values by both the USEPA and EU methods are beyond the upper end of the ranges identified for the majority of the experimental studies, with the exception of the WHO and Mackay.

The log K_{oc} of 2.64, calculated using the equation recommended by the EU, is recommended for use in the CLEA model, as the approach is consistent with the EU approach to selection of K_{oc} values for benzene and toluene. This is appropriate within the accepted CLEA hierarchy, and in addition it is also within the range of measured values quoted by the WHO. This K_{oc} is consistent with moderate mobility in soil (HSDB 2002), however, it should be noted that a number of the experimental studies indicate a somewhat lower range of K_{oc}, thus suggesting a higher mobility.

Xylene

Compared to the data availability for the previously addressed BTEX compounds, information on the K_{oc} of individual isomers of xylene is fairly scarce. No EU Risk Assessment is available and, in the absence of this, the IUCLID database was consulted. However, its treatment of K_{oc} is limited to a few studies that are not well defined.

The WHO is inconsistent in their sources and presentation of K_{oc} values, citing Vowles and Mantoura (1987) for *o*-xylene, giving a figure of 8.9 (thought to require conversion from K_{OM}); Siep, Alstad *et al.* (1986) for *m*-xylene, providing a range of K_{oc} from 129 to 289 (log K_{oc} 2.11 to 2.46); for *o*-xylene a further value of 219 (log K_{oc} of 2.34) Pussemier, Szabó *et al.* (1990) is presented.

The USEPA (1996a) review of experimentally derived K_{oc} values identified the following ranges for each isomer:

- xylene - a K_{oc} range of 222 to 258 (log K_{oc} 2.35 to 2.41) is derived from four studies
- *m*-xylene - a K_{oc} range of 158 to 289 (log K_{oc} 2.20 to 2.46) is derived from three studies;
- *p*-xylene - a K_{oc} range of 260 to 347 (log K_{oc} 2.41 to 2.54) derived from three studies.

ATSDR reference a log K_{oc} for each isomer from Abdul, Gibson *et al.* (1987) (*o*-xylene 2.11, *m*-xylene 2.22, *p*-xylene 2.31), of these, only *m*-xylene is included in the USEPA dataset reviewed above, the remaining two lie outside (lower than) the range given by the USEPA database.

For each of the xylene isomers the USEPA (1996a) calculate K_{oc} using the modified Di Toro regression for VOC compounds. The results for each isomer are presented below:

- *o*-xylene - a K_{oc} of 363 (log K_{oc} of 2.56) is derived from the log K_{ow} of 3.13;
- *m*-xylene - a K_{oc} of 407 (log K_{oc} of 2.61) is derived from the log K_{ow} of 3.20; and
- *p*-xylene - a K_{oc} of 389 (log K_{oc} of 2.59) is derived from the log K_{ow} of 3.17.

Although no EU Risk Assessment is available, the methodology used within the benzene and toluene ECB documents for deriving K_{oc} from log K_{ow} can be followed in the case of xylene isomers. This approach is presented in Technical Guidance Document (EU 1996) and is based on a study by Sabljic and Gusten (1995). For xylene isomers, the regression relationship developed by Sabljic and Gusten for predominately hydrophobic chemicals is appropriate (each isomer has a lower solubility than toluene, which is classed by the ECB as predominately hydrophobic). The regression results for each isomer are presented below:

- *o*-xylene - a K_{oc} of 424 (log K_{oc} of 2.63) is derived from the log K_{ow} of 3.12;
- *m*-xylene - a K_{oc} of 492 (log K_{oc} of 2.69) is derived from the log K_{ow} of 3.20; and
- *p*-xylene - a K_{oc} of 448 (log K_{oc} of 2.65) is derived from the log K_{ow} of 3.15.

The calculated values by both the USEPA and EU methods are beyond the upper end of the ranges identified for the majority of the experimental studies. There is obviously a choice between;

a) retaining consistency with the ECB approach by adopting the calculated values, with the possibility of overestimating the K_{oc}, or

b) adhering more closely to the available measured values.

It is noted that the range of benzene K_{oc} identified in European (Dutch) studies in the ECB report included far higher values than those cited in the USEPA study. This, in part, was used in the justification for the selection of the ECB calculated value. In consideration of the requirement for a consistent approach it is recommended that the log K_{oc}'s calculated using the equation recommended by the EU, are selected for use in the CLEA model. Further consideration of the validity and potential effects this may have on the physicochemical behaviour of the xylenes within the CLEA model is recommended.

Coefficients of Diffusion in Air and Water

Diffusion coefficients express the transfer rate of a substance by random molecular motion along a concentration gradient. Rate of diffusion is affected by the size and weight of individual molecules, the diffusion coefficients in air and water being inversely related to molecular weight. These parameters are used in CLEA in equations that simulate diffusive transport in the vadose zone in order to predict atmospheric emission rates of volatile compounds to points of inhalation exposure.

Coefficients of diffusion for the solvents in air (Di_a) and water (Di_w) are held on the USEPA's CHEMDAT8 database, and are quoted in USEPA (1996a). In the absence of EU or WHO data, these values are recommended for use in the CLEA model. No other recent literature describing diffusion coefficients has been identified. USEPA values are presented in Table 4.9. The summary table shows the values converted into the correct units for the CLEA model.

Table 4.9 **Values of Coefficients of Diffusion in Air and Water (25° C) (after USEPA 1996a)**

Compound	Diffusion Coefficient in air, $D_{i,a}$ ($cm^2\ s^{-1}$)	Diffusion coefficient in water, $D_{i,w}$ ($cm^2\ s^{-1}$)
Benzene	8.80×10^{-2}	9.80×10^{-6}
Toluene	8.70×10^{-2}	8.60×10^{-6}
Ethylbenzene	7.50×10^{-2}	7.80×10^{-6}
o-xylene	8.70×10^{-2}	1.00×10^{-5}
m-xylene	7.00×10^{-2}	7.80×10^{-6}
p-xylene	7.69×10^{-2}	8.44×10^{-6}

Critical Temperature

Critical temperature (in degrees Kelvin) is used to adjust the enthalpy of vapourisation to the soil/groundwater system temperature. These are well established data and the slight variations (maximum 0.09 K) between quoted values will not have a significant effect on the temperature adjustment of Henry's Law Constants for which these values have been compiled. All values in Table 4.10 are taken from the CRC Handbook (2000-2001) which agree with those quoted in Yaws (1999).

Table 4.10 **Critical Temperatures of BTEX compounds**

Compound	Benzene	Toluene	Ethylbenzene	*o*-xylene	*m*-xylene	*p*-xylene
T_c (K)	562.05	591.8	617.2	630.3	617.0	616.2

Enthalpy of Vapourisation

Enthalpy of vapourisation is a temperature dependent variable which is used in the Clapeyron equation for temperature adjustment of the Henry's Law constant, details on this conversion were presented in the Introduction chapter. For this application it should be quoted at the respective boiling temperatures of the individual chemical species.

Standard values for enthalpy of vapourisation (Ä$_{vap}$H$_{tb}$) are provided in Table 4.11 below, derived from Lide (2000) and Yaws (1999). Literature quoted values are expressed in kJ mol^{-1} while CLEA requires units of cal mol^{-1}, therefore necessitating a conversion between kJ and cal whereby 1 kJ equals 239 cal. Table 4.11 presents values in kJ mol^{-1} while Table 4.3 presents values in cal mol^{-1}.
The values given in the CRC handbook (2000-20001) from Lide (2000) have been selected for derivation of temperature corrected Henry's Law Constants as this is a recent peer reviewed source.

Table 4.11 **Enthalpy of Vapourisation (D vapHtb) at the respective boiling temperatures of BTEX compounds**

Compound	Benzene	Toluene	Ethylbenzene	*o*-xylene	*m*-xylene	*p*-xylene
$\Delta_{vap}H(t_b)$ (kJ mol^{-1})	30.72^{a} 30.75^{b}	33.18^{a} 33.59^{b}	35.57^{a} 35.91^{b}	36.24^{a} 37.00^{b}	35.66^{a} 36.33^{b}	35.67^{a} 35.82^{b}

^{a} (CRC Handbook 2000-2001)
^{b} (Yaws 1999)

4.5 Behaviour of BTEX Compounds in Soil

This section briefly considers adsorption mechanisms, volatilisation pathways and degradation processes for the BTEX compounds in soil. Given their significant aqueous solubilities (in the context of environmental behaviour), leaching is also an important pathway which should be considered in any evaluation of fate and transport. However, detailed assessment of groundwater pathways is beyond the scope of this study, although the relative quantities of BTEX lost from soils by various phase transfers/reaction mechanisms are briefly referred to in the adsorption and volatilisation sections. BTEX compounds have relatively high vapour pressures so will volatilise readily from soil surfaces. The introductory chapter presents an evaluative triangle which provides an example of how the relative partitioning of substances between the air, water and octanol (used to represent organic carbon, and especially lipid) can be used to predict the behaviour of a number of contaminants, including BTEX.

As a result of their density, the fundamental tendency of the solvents in the subsurface is to sink through the unsaturated (vadose) zone of soil to the groundwater table, where the higher density of water will prevent further downward migration of free phase hydrocarbon. Further downward migration will only be possible by water table fluctuation or in the dissolved phase. The mobility of BTEX compounds in the subsurface is a function of their sorption to organic (and some mineral) matter, as indicated by their K_{oc} values (Lyman, Reidy *et al*. 1992).

4.5.1. Adsorption to Soil

The adsorption of BTEX compounds to soils is one of the most influential soil characteristics with respect to contaminant migration. BTEX compounds (in common with other organic contaminants) adsorb to soil organic matter which hinders onward migration. Adsorption is reversible and contaminants are retarded rather than destroyed by this process. It has also been noted that mass transfer is slower for long term contaminated soils (Culver, Hallisey *et al*. 1997).

The retardation of contaminant transport increases travel times providing greater opportunity for biodegradation of BTEX before they can migrate to points of receptor exposure. As discussed in the section on K_{oc}, sorption potential varies considerably depending on environmental conditions and discussion of adsorption potential without expansive discussion of the general environmental context will not be particularly instructive. However, a review of over 600 studies of dissolved phase hydrocarbon plumes throughout the United States (Newell and Connor 1998) found that benzene rarely migrated more than 200 to 300 ft (60 to 90 m) following leaching to groundwater. Toluene, ethylbenzene and xylenes would be expected to sorb more strongly to soil and in conjunction with their lower solubilities would have shorter plume attenuation lengths.

Presence of colloidal matter within groundwater will also affect contaminant transport. Whilst much of this colloidal matter will be filtered out of solution during transport, BTEX and other contaminants can sorb to the remaining free colloidal matter and increase transfer via groundwater pathways (Lyman, Reidy *et al*. 1992).

The adsorptive capacity of any soil is finite and in instances where BTEX contaminants are present at high concentrations, there will be competition for soil adsorption sites. Once these have been exhausted (occupied by BTEX or other contaminants) free phase product will appear. This affects subsequent behaviour and would mean that application of many of the algorithms in CLEA and other risk assessment tools would be invalidated.

4.5.2. Degradation and loss of BTEX from soil

Volatilisation

BTEX compounds have high vapour pressure and will readily volatilise from the subsurface to indoor and outdoor air spaces. The rate of flow is influenced by diffusive and advective processes. Diffusive processes are generally more continuous and are determined by concentration gradients. Advective influences tend to be more temporally variable, examples including barometric pressure changes, pressure gradients induced by central heating in dwellings and displacement of vapours by water infiltration.

All BTEX compounds will readily volatilise from surface soils although the rate of volatilisation will decrease at greater depths (ATSDR 1995a; ATSDR 1997d; ATSDR 1999; ATSDR 2000a). Benzene and toluene will volatilise more rapidly on account of their higher vapour pressures and lower K_{oc} values. The relative mass transfer rates of BTEX compounds present collectively will also be affected by their mole fraction in the contaminant mixture.

The rate of flow is influenced by diffusive and advective processes. The organic carbon content of soils can have a significant impact on volatilisation rates as BTEX compounds preferentially adsorb to organic matter. Whilst there is evidence to suggest that mass transfer is slower for long term contaminated soils (Culver, Hallisey *et al*. 1997), such adsorption is generally reversible. More permeable soils such as sands and gravels will have a relatively high effective porosity which will facilitate volatilisation. As moisture content increases, pore spaces will become filled until only the largest pore spaces remain, requiring volatilisation to occur by increasingly tortuous pathways. With increasing discontinuity of the vapour phase, volatilisation will be increasingly inhibited as diffusion through the aqueous phase will become rate limiting. However, as moisture content increases, water molecules can displace contaminant molecules, decreasing the sorptive capacity of the soils, thus acting to increase volatilisation of BTEX vapours. Whilst these two factors offset one another in terms of their effect on volatilisation rate, in the case of BTEX compounds with their high vapour pressure, the air-filled effective porosity is the dominant factor (McCarthy and Johnson 1995; Smith, Tisdale *et al.* 1996; Arands, Lam *et al.* 1997).

In practice, even in conditions of very low moisture content, most soil particles are covered as a minimum by an adsorbed layer of water molecules and thus there will generally be competition for binding sites as discussed above (Arands, Lam *et al.* 1997). However, it is possible for the top few centimetres of soils to have extremely low moisture content to the extent that there are more potential binding sites available which have not been covered by water molecules. Under such circumstances, there is potential for greater concentrations of VOCs to be adsorbed thus restricting the release of VOCs (Petersen, El-Farhan *et al.* 1996). This study also suggested that in certain circumstances, volatilisation may temporarily increase with increasing moisture content and this would be consistent with increased competition for binding sites on extremely dry soils as they become saturated. This will be a minor effect although it may contribute to temporal variation in emission rates associated with rainfall events.

Abiotic degradation

Degradation of BTEX contaminants in the environment is predominantly biologically mediated as ambient temperatures are generally too low to provide the activation energy necessary for degradation reactions to proceed. Photolysis of BTEX compounds does occur and is an important mechanism in the atmospheric degradation of these chemicals. However, UV penetration will be limited to near surface soils and the high vapour pressures of BTEX compounds mean that concentrations in this section of the soil profile would be quickly depleted via volatilisation.

Furthermore, BTEX compounds do not possess readily hydrolysable functionality and pH conditions in most natural environments would be insufficiently extreme to promote abiotic degradation.

Biodegradation

Microorganisms use enzymes to lower the activation energy necessary to effect ring cleavage. Biodegradation of BTEX compounds occurs under both aerobic and anaerobic conditions. Biodegradation in aerobic conditions is generally more rapid as contaminant breakdown using oxygen as an electron acceptor is the mechanism which yields most energy to the microbes which facilitate the degradation.

However, utilisation of oxygen by microbes during aerobic degradation may lead to significant depletion of oxygen levels in the soil environment which can cause conditions in contaminated soil to become progressively more anaerobic. Consequently, whilst degradation will not cease when oxygen is depleted, the degradation rates may change by virtue of the different reaction mechanisms involved.

The kinetics of BTEX biodegradation are site specific, and influences include the type and population of microbes present, the environmental temperature, the concentration of hydrocarbon contamination, the presence of other compounds that may act as a substrate or inhibit metabolic processes, and the availability of oxygen and other potential electron acceptors (Ostendorf and Kampbell 1991; De Vaull, Ettinger *et al.* 1997). Soil permeability will affect the rate of replenishment of dissolved oxygen as it will influence processes such as rainfall infiltration and capillary fringe aeration (Arands, Lam *et al.* 1997).

Assuming ready availability of the following species and a microbial community that is acclimatised to the conditions, electron acceptors will be preferentially utilised in the following order (Environment Agency 2000a):

Aerobic	O_2 to O^{2-}
Nitrate-reducing	NO_3^- to NO_2^- (then to N_2O or N_2 - Denitrification)
Iron-reducing	Fe^{3+} to Fe^{2+}
Sulphate-reducing	SO_4^{2-} to S^{2-}
Methanogenic	CO_2 to CH_4

Dissolved oxygen and redox measurements can be used to indicate whether degradation appears to be taking place in the subsurface, although they will not inform the user as to whether individual BTEX species are being degraded. Notwithstanding this, the information in conjunction with literature values can be useful in estimating potential rates of degradation in soils. Addition of nitrate generally increases the degradation rate for BTEX (Aronson and Howard 1997; De Vaull, Ettinger *et al.* 1997)

Degradation rates for BTEX compounds are predominantly presented as first-order rate constants or half-lives, where rate of degradation is proportional to the contaminant concentration. Microbial biodegradation kinetics are more complex than the first-order rate constant approach may imply and it has been proposed that Monod-type kinetics may provide more reliable estimates of degradation rate (De Vaull, Ettinger *et al.* 1997). In Monod-type kinetics, the rate of substrate utilisation is both proportional to the concentration of the microorganisms present and is a function of the substrate concentration.

In aerobic conditions and over broad ranges in soil pore water concentrations, Monod-type kinetics provide a good fit with much of the published experimental data (De Vaull, Ettinger *et al.* 1997). As contaminant concentrations reduce, and in the absence of other factors, one would expect degradation to follow first order kinetics more closely as the reducing concentrations will become the rate limiting factor. At soil pore water concentrations below approximately 0.2 mg l^{-1} first-order kinetics apply.

It should also be acknowledged that some values reported in the literature relate to mineralization rather than primary degradation of the parent compound. Reporting rate constants in this form tends to underestimate the rate of loss of BTEX compounds and can incorporate an unreasonable degree of conservatism into risk assessments. However, whilst it is beyond the scope of this paper to discuss degradation kinetics in detail, it is important to establish that there is a danger in assuming that a single first order degradation rate constant can be applied indiscriminately.

Such an approach assumes an inexhaustible supply of electron acceptors, which could lead to overestimates of BTEX degradation when degradation of high concentrations of petroleum based fuels alters local conditions from aerobic to anaerobic with an associated reduction in degradation rate. High concentrations of BTEX compounds can also inhibit biodegradation on account of the inherent toxicity of these chemicals. Breakdown may therefore be restricted to the periphery of contaminant source zones where dilution and other processes result in the concentrations being reduced. Inhibitory thresholds vary according to experimental set up but indications of such concentrations have been provided where possible. These concentrations should not be considered as absolute as differences in the host microbial population, soil type and the presence of other contaminants may serve to lower such thresholds.

The following sections discuss the degradability of the individual BTEX compounds in both aerobic and anaerobic conditions, in terms of persistence and toxicity of daughter products and rate of degradation.

First-order rate constants have been adopted for this review as a practical approximation of degradation kinetics. Whilst they are most relevant to conditions where there is no growth of the microbial population and contaminant concentration is low, they still represent a reasonable approximation for other conditions and allow comparability across a wide range of compounds for which such rate constants have been reported.

Whilst detailed metabolic pathways vary according to environmental conditions and chemical structure of the BTEX compounds, it is helpful to note the following general reaction mechanisms. In aerobic conditions microorganisms use oxygenases to break down BTEX compounds via catechol intermediates (see Figure 4.3).

In anaerobic conditions the mechanisms are less well understood but benzoyl-CoA is a metabolite that is common to toluene and ethylbenzene degradation (see Figure 4.4).

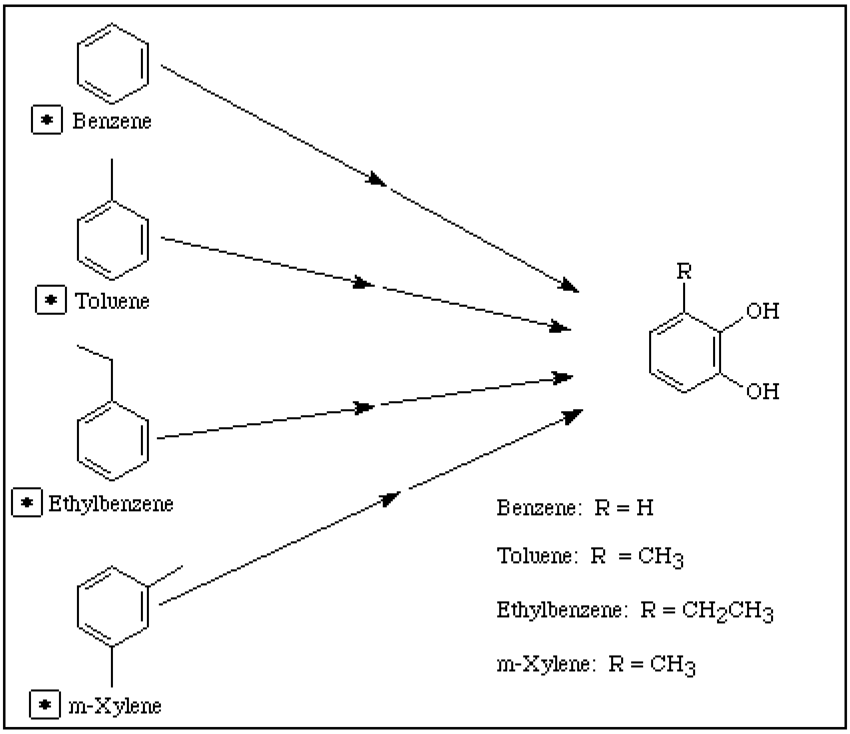

Figure 4.3 Aerobic degradation of BTEX compounds (UMN 2002) cited at http://umbbd.ahc.umn.edu)

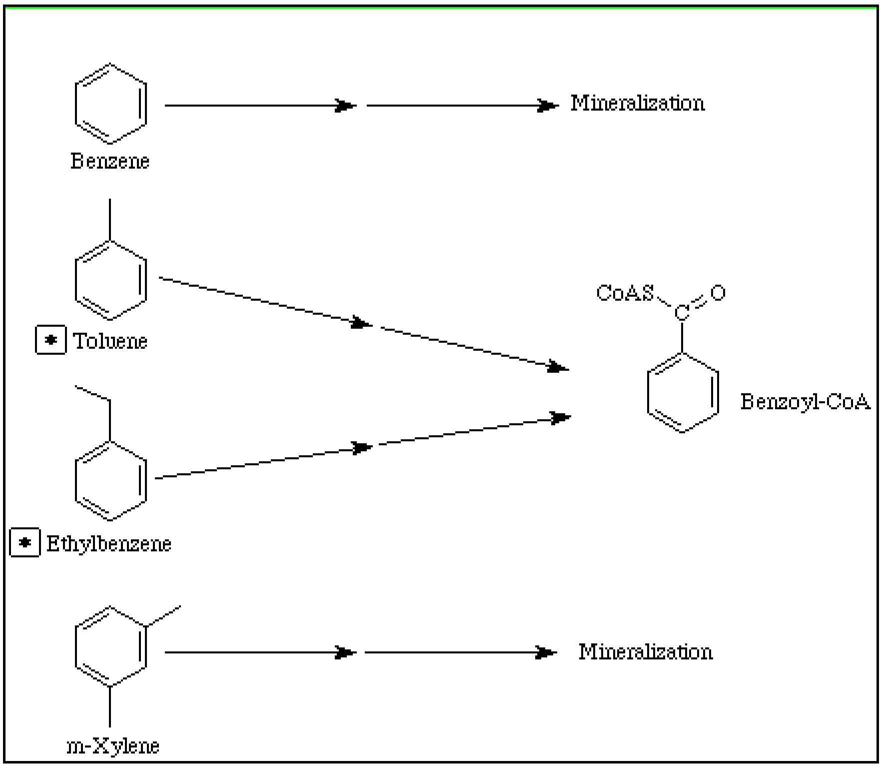

Figure 4.4 Anaerobic degradation of BTEX compounds (UMN 2002) cited at http://umbbd.ahc.umn.edu)

Benzene

Benzene is expected to biodegrade fairly readily under most aerobic environmental conditions, molecular breakdown occurring via cis-1,2-dihydroxy-1,2-dihydrobenzene to form catechol with subsequent ring cleavage (Hopper 1978, Aronson, Citra *et al*. 1999, WHO 1993). The catechol will be transformed into acetaldehyde and pyruvate which are assimilated by microorganisms or completely mineralised (Fig A1, App.A). These degradation daughter products of benzene are not environmentally persistent, since oxygen present in aerobic soils acts as a terminal electron acceptor for degradation of the ring cleavage products (ATSDR 1997d).

Soil aerobic half lives of benzene are reported in Howard, Boethling *et al*. (1991) which, following a review of a range of experimental studies (i.e. field and laboratory), estimates high and low aerobic degradation values in soil of 5 days and 16 days respectively. These values are derived from studies where abiotic losses were not factors in determining the results. A median value for the primary biodegradation rate constant of benzene from consideration of a wide range of studies is 0.096 day^{-1} (Aronson, Citra *et al*. 1999).

A study of the fate of benzene on soil utilising composting waste (Korte and Klein 1982) cited in WHO (1993) noted that of benzene applied to the waste only 2-2.5% remained in situ whereas 35% volatilised. A modelling study (Tucker, Huang *et al*. 1986) in ATSDR (1997d) based on a shallow sandy soil predicted that only 1% of benzene lost from an underground tank gasoline spill would be degraded within 17 months, the majority (67%) being volatilised and 29% leached to groundwater.

Some *Pseudomonas* bacteria are able to oxidise benzene to catechol whilst other species isolated from benzene contaminated sites have been found to be able to utilise benzene as a direct source of carbon and energy under both aerobic and anaerobic conditions (Morikawa and Imanaka 1993). *Nocardia sp*. and *Pseudomonas sp*. bacteria have been shown to be able to degrade benzene completely to carbon dioxide within 7 days (45-90%), although the greater degree of degradation only occurred after acclimation to the chemical (ATSDR 1998a, Lee, Roh *et al*. 1994). The soil bacterium *Nitrosomonas europaea* is also reported to be able to degrade benzene to phenol and hydroquinone (Keener and Arp 1994).

De Vaull, Ettinger *et al*. (1997) reports first order benzene degradation rate constants ranging from 0.00025 to 0.003 day^{-1} for gasoline vapours in unsaturated soils.

Under strictly anaerobic conditions, benzene is believed to be recalcitrant (Colberg and Young 1995) cited in Aronson and Howard (1997). This seems to be supported by the work of Battersby and Wilson (1989) cited in WHO (1993) who examined the degradation of benzene under methanotrophic conditions and noted that benzene, at a concentration of 50 mg carbon l^{-1}, remained undegraded after 11 weeks of digestion. However, studies over an extended time period by Wilson, Smith *et al*. (1986b) cited in WHO (1993) showed that whilst no significant benzene biodegradation occurred during the first 20 weeks of incubation of samples of landfill leachate under methanogenic conditions, benzene concentrations were reduced by 72% after 40 weeks.

No single organism has been shown to mineralize benzene completely under anaerobic conditions, although limited anaerobic degradation was found in chemical biotransformation studies under nitrate- and sulphate-reducing conditions (HSDB 2002). However, it has been shown that benzene is transformed under anaerobic conditions by methanogenic cultures containing multiple organisms.

The other BTEX compounds are certainly more readily degradable and it has been hypothesised that anaerobic degradation of benzene may occur in the field once other carbon sources have been removed and redox starts to recover. Following removal of more readily degradable carbon sources, one would anticipate an increase in the dissolved oxygen content of the pore water which could be used for aerobic benzene metabolism.

There is limited understanding of the anaerobic transformation of benzene (Harwood and Gibson 1997) and consequently reaction intermediates and daughter products have not been presented in this document. However, although there is some debate as to whether anaerobic degradation could be more accurately attributed to the presence of localised aerobic microsites or co-metabolism, there is evidence to demonstrate the removal of benzene in these conditions. First order rate constants for field and *in situ* microcosm studies have a mean of 0.0036 day^{-1} although there is potential for some of the values contributing to this mean value not to represent strictly anaerobic degradation. Mean first-order rate constants for nitrate-reducing, iron-reducing, sulphate-reducing and methanogenic environments are 0.0023 day^{-1}, 0.0035 day^{-1}, 0.016 day^{-1} and 0.0050 day^{-1} respectively (Aronson and Howard 1997).

Concentrations of between 50 and 200 mg l^{-1} of benzene in sewage sludges have been reported as inhibitory to anaerobic digestion (Jackson and Brown 1970, cited in WHO 1993).

Toluene

Toluene is reported to be biodegraded by a variety of soil micro-organisms such as *Pseudomonas sp.* and *Achromobacter sp.* (Fewson 1981). Aerobic degradation of toluene proceeds via 3-methylcatechol to acetaldehyde and the pyruvate ion (Fig 2 App. A: taken from UMN, 2002) which can be readily biodegraded and/or assimilated in either aerobic or anaerobic conditions. The daughter products of toluene degradation are not likely to persist in the soil environment and therefore should not constitute a secondary source of toxicity.

Soil aerobic half lives of toluene are reported in Howard, Boethling *et al.* (1991), which provides high and low aerobic degradation values in soil of 4 days and 22 days respectively. These values are derived from studies where abiotic losses were not factors in determining the results. Studies by Davis and Madsen 1996 indicated that no toluene biodegradation occurred in air dried soils over a period of 30 days, whereas toluene added to the same soil with 100% moisture biodegraded with a half-life of less than 1 day. The study concluded that availability of water in soil is only likely to be rate limiting at very low moisture contents (soils with 50% of their field capacity did not exhibit markedly lower biodegradation rates).

In situ microcosm studies (Nielsen, Bjerg *et al.* 1996 in Aronson, Citra *et al.* 1999) indicated that toluene half-lives in sediments were significantly lower than those in the groundwater. Half-lives of 1 to 7 days are typical in aerobic environments (ATSDR 2000a).

An experiment to investigate the rate of aerobic degradation of toluene during transport through soil (Jin, Streck *et al.* 1994) determined the aerobic half-life to be approximately 2 hours. This result has more relevance to the modelling of degradation during BTEX volatilisation in the vadose zone than application to depletion of soil or groundwater source terms.

In some circumstances, the presence of other carbon sources can reduce degradation rate either by competitive inhibition or toxic effects. In a 16-day incubation study by (Dyreborg, Arvin *et al.* 1996, cited in EU 2002)) it was observed that the presence of thiophene, pyrrole, methylpyrrole and benzofuran in creosote-contaminated groundwater reduced the degradation of toluene from 100% to 10% after 4 days.

Biodegradation half-lives varying from 83 to 92 days in various soil systems were reported by Sloof and Blokzijl (1988). The EU Risk Assessment document proposes a conservatively derived aerobic half-life of 90 days (equivalent to a first-order rate constant of 0.0077 day^{-1}) for use in the estimation of soil concentrations.

De Vaull, Ettinger *et al.* (1997) reported first-order rate constants for degradation of toluene in aerobic soils of 0.004 to 0.06 day^{-1} in diffusive soil column studies.

From an extensive review of aerobic degradation studies (Aronson, Citra *et al.* 1999), the median primary degradation rate constant of toluene was 0.2 day^{-1} with a corresponding median mineralization rate constant of 0.00895 day^{-1}. Toluene is expected to degrade readily under most aerobic environmental conditions.

Toluene concentrations of 250 mg kg^{-1} in soil are reported to be inhibitory to biodegradation by soil micro-organisms (Davis and Madsen 1996).

The anaerobic decay of toluene can be initiated by the addition of the methyl group to the double bond of fumarate to synthesise a benzylsuccinate metabolite. The enzymatically catalysed reaction proceeds to generate benzoyl-CoA (Fig A3, App A; (UMN 2002). Benzoyl-CoA is in turn metabolised and used as a growth substrate.

Under anaerobic conditions, nitrate or sulphate can act as the terminal electron acceptor in the degradation of toluene (ATSDR 2000a). It has been noted that other mechanisms may also occur; under sulphate-reducing conditions, it has been found that less than 10% of the toluene carbon was metabolised via benzylsuccinic acid, whereas >80% was mineralised to CO_2 (Beller, Grbic-Galic *et al.* 1992)

EU (2002) suggests a half life of 900 days in anaerobic sediments which is an estimate based on 10% of the aerobic half life rather than data from anaerobic studies.

The rate of anaerobic degradation of toluene in aquifer environments is influenced by the redox potential. Mean first-order rate constants for nitrate-reducing, iron-reducing, sulphate-reducing and methanogenic studies are 0.63 day^{-1}, 0.021 day^{-1}, 0.049 day^{-1}, and 0.029 day^{-1} (Aronson and Howard 1997). This literature review reports a mean value for all experimental data of 0.059 day^{-1} (corresponding to a half-life of 12 days) which was judged to provide a relatively conservative value for the first-order rate constant under anaerobic conditions.

Ethylbenzene

Ethylbenzene is moderately degradable under most aerobic environmental conditions (Aronson, Citra *et al.* 1999). Several aerobic degradation pathways have been suggested all using dioxygenases to catalyse the reaction (UMN 2002) which can be undertaken by various *Pseudomonas sp* (Figure A4, Appendix A). One such pathway closely resembles the toluene aerobic degradation, proceeding via 3-ethylcatechol to acetaldehyde and pyruvate and ultimately to complete mineralization. Other potential intermediates include styrene (which can in turn be mineralized by pseudomonas bacteria) and 2-hydroxy-acetophenone (generated during metabolism by *Nocardia tartaricans*) the environmental persistence and toxicity of which is unclear.

In addition to the potential for cometabolism (ATSDR 1999), a number of studies have indicated that ethylbenzene can be utilised as a sole carbon source by some *Pseudomonas* bacteria (WHO 1996). White-rot fungus *Phanerochaete chrysosporium* has also been shown to degrade ethylbenzene together with other BTEX compounds, when these chemicals are present individually or as a composite mixture (Yadav and Reddy 1993 cited in WHO 1996).

Aerobic half lives of ethylbenzene are reported in Howard, Boethling *et al.* (1991) which estimates high and low aerobic degradation half lives in soil of 3 days and 10 days respectively.

De Vaull, Ettinger *et al.* (1997) reported first-order rate constants for degradation of ethylbenzene in aerobic soils of 0.04 to 0.1 day^{-1} in diffusive soil column studies.

The median primary biodegradation rate constant reported by Aronson, Citra *et al.* (1999) is 0.113 day^{-1} with a range of 0.003 to 4.8 day^{-1} (although it should be noted that the value of 0.003 day^{-1} (half-life of 231 days) related to a study where 85% methanol was present. A parallel study where methanol was not present indicated a half-life of 22 days.

Anaerobic biodegradation is postulated to occur by a dehydrogenation reaction that generates acetyl-CoA and benzoyl-CoA, which can be assimilated and used as growth substrates (UMN 2002). Degradation in anaerobic conditions is therefore not believed to generate environmentally persistent and/or metabolites.

Anaerobic degradation of ethylbenzene is much slower than aerobic degradation (ATSDR 1999). First order rate constants for field and in situ groundwater anaerobic microcosm studies provided a collective mean value of 0.015 day^{-1}. Mean first-order rate constants for nitrate-reducing, iron-reducing, sulphate-reducing and methanogenic studies were reported as 0.28 day^{-1}, 0.0011 day^{-1}, 0.0098 day and 0.05 day^{-1} respectively (Aronson and Howard 1997). This review suggests a fairly conservative range of anaerobic first-order rate constants for ethylbenzene of 0.0006 day^{-1} (lowest measured field value) to 0.015 day^{-1}. In general, ethylbenzene is not degraded as rapidly as toluene but appears to be degraded at a similar rate to xylene isomers.

Xylene

Biodegradation is an important fate process for xylenes and all isomers are expected to degrade fairly readily under most environmental conditions (Aronson, Citra *et al*. 1999). Although the degradation pathways for each isomer are similar (using monooxygenases to initiate the reaction and proceeding via the respective methylbenzoates to give methyl catechols) different strains of microorganism may be required to degrade the different isomers (Figures A6, A7 and A8).

The position of the methyl group is important in the breakdown of xylene isomers, with microorganisms pre-exposed to one isomer being unable to degrade one or more of the other isomers. For instance, *Pseudomonas* sp. cultures grown on *p*-xylene were capable of oxidizing both *m*-xylene and toluene, but neither *p*-xylene-grown cultures nor *m*-xylene-grown cultures were capable of oxidizing *o*-xylene (ATSDR 1996a). In the vast majority of instances of soil contamination, the isomers will not be present in isolation and, whilst different forms may be degraded by different species within the microbial population, it is highly unlikely that any individual isomer will be excluded from the process. Furthermore, the various metabolic pathways all yield daughter compounds that are not environmentally persistent and this process should not generate any secondary risk.

Evaluation of the biodegradation kinetics of BTEX mixtures is very complex and will vary according to site-specific conditions. Degradation of *p*-xylene is assisted by the presence of other BTEX compounds, although the presence of the *p*-xylene may delay the onset of degradation of benzene and toluene (Alvarez and Vogel 1991 in WHO 1997)

Aerobic half lives of xylene are reported in Howard, Boethling *et al*. (1991) as the same for each isomer, providing high and low aerobic degradation values in soil of 168 hours and 672 hours respectively.

Aerobic soil specific studies by De Vaull, Ettinger *et al.* (1997) reported first-order rate constants for degradation of xylenes ranging from 0.002 to 0.1 day^{-1} in diffusive soil columns.

When considering biodegradability of individual isomers as sole carbon sources, it appears that *o*-xylene is more resistant to degradation than the meta- and para- forms (WHO 1997). However, consideration of the median primary biodegradation rate constants from field and laboratory studies (Aronson, Citra *et al.* 1999) which quotes 0.054 day^{-1}, 0.057 day^{-1} and 0.052 day^{-1} for ortho-, meta- and para-xylene respectively suggests that biodegradation rates should be comparable.

All xylene isomers have been shown to degrade in nitrate-reducing, sulphate-reducing, methanogenic and iron-reducing environments (Aronson and Howard 1997). The mechanisms of degradation are unclear but all xylene isomers have been shown to be completely mineralised under sulphate reducing conditions within a gasoline contaminated sediment (Edwards and Grbic-Galic 1992 cited in WHO 1997). The anaerobic biodegradation of xylenes is not anticipated to generate environmentally persistent and toxic daughter products.

In most of the studies quoted in WHO (1997), long lag periods were observed prior to commencement of degradation in anaerobic conditions. Varying initial resistance to degradation may account for some of the apparent differences in degradation potential of the different isomers, particularly where studies have been conducted over short time periods. In soil (and water), *m*- and *p*-xylene are reported to be readily biodegradable under a wide range of aerobic and anaerobic denitrifying conditions, although *o*-xylene is much more persistent under similar conditions (WHO 1997).

There are a limited number of organisms that are capable of anaerobically metabolising xylene. Those that are include strains of denitrifying bacteria, which can use *m*-xylene as a growth substrate {Harwood, 1997 #35}. The *o*-xylene isomer has been reported to be biodegraded under anaerobic methanogenic conditions (WHO 1997). No significant degradation of *o*-xylene occurred over the first 20 weeks, but after 40 weeks the concentration was reduced to 22% of the original concentration. Less than 1% remained after 120 weeks (Wilson, Smith *et al.* 1986b).

However, when reviewed collectively (Aronson and Howard 1997), the experimental evidence suggests that anaerobic degradation proceeds at a similar rate to ethylbenzene for each of the three isomers. Mean values for first-order rate constants from field and in situ studies were 0.021 day^{-1}, 0.016 day^{-1} and 0.015 day^{-1} for ortho, meta and para-xylene respectively.

4.5.3. Implications of Behaviour in Soil for Modelling

The expected rapid rate of volatilisation from soil, based on the high vapour pressure and K_H, combined with the relatively low K_{oc} (see evaluative triangle in introductory chapter) will dictate the nature of the exposure of the BTEX contaminants from soil. Thus a volatilisation pathway is likely to be active, and of importance. As this is the case, model approaches should include robust treatment of this pathway.

Volatilisation from soils and groundwater can result in migration into indoor and outdoor air spaces. The rate of flow is influenced by diffusive and advective processes. The Johnson and Ettinger model which is to be adopted by the CLEA methodology (Environment Agency 2001) accounts for both advective and diffusive influences, with diffusion dominating vapour transport away from building influences. Advective processes tend to be more temporally variable but can dominate vapour transport in certain conditions (Smith, Tisdale *et al.* 1996). Rapid initial rates of BTEX volatilisation have been reported but removal via volatilisation from sorbed or dissolved phase at depth can take considerably longer; e.g. 90% of toluene released to surface soils has been shown to volatilise within 24 hours whilst the same contaminant reduced by <3% in a year at depths of 1-1.3 m below ground level (ATSDR 2000a). The potential for extremely rapid volatilisation is clearly limited to certain specific environmental or experimental conditions as this is not generally borne out by the relative persistence of BTEX contaminants in real life situations.

Biodegradation has been shown to be a significant process for removal of contaminant mass from soils, and will apply to phases other than contaminant sorbed to solids. For instance, given the importance of volatilisation as a pathway from soil, (and the likely significant contribution to human exposure via this pathway) it is important to consider the likelihood of biodegradation within the vapour phase.

It is difficult to incorporate degradation into the derivation of generic assessment criteria, such as SGVs; however this likely level of conservatism should be explicitly stated within the accompanying SGV reports. When undertaking Detailed Quantitative Risk Assessment (DQRA), site specific degradation rates for the sorbed and vapour phases would produce a more realistic modelling approach to BTEX in soil. It should be noted that the Johnson and Ettinger model which is to be incorporated within the CLEA model does not account for biodegradation in the vapour phase. (Hers, Zapf-Gilje *et al*. 2000) consider that within DQRA, application of biodegradation in vapour phase modelling can reduce the point of exposure concentration by orders of magnitude.

Various studies have examined, and in some cases quantified, the effect of biodegradation of vapour-phase BTEX in the unsaturated zone. (Ostendorf and Kampbell 1991) measured and modelled the vapour phase component over a free-phase aviation fuel source at a depth of approximately 4.0m. Volatilisation was found to be a significant long-term transport mechanism, although biodegradation prevented the escape of appreciable contamination to the atmosphere. (Hers, Zapf-Gilje *et al.* 2000) studied the transport of benzene, toluene and xylene vapours over a shallow (c. 2.0m) vadose zone, again with an underlying free-phase source. Significant attenuation was identified over a relatively small depth interval, with this being inferred as primarily due to biodegradation. Homogeneous sandy soils were present in both studies.

DeVaull *et al.*(1997) review the requirements for, and existing data on, vadose-zone biodegradation and present conservative ranges of biodegradation rates. This paper states that diffuse vapour transport models which neglect biodegradation may overestimate the flux of hydrocarbons at the surface.

With regards to understanding the behaviour of BTEX volatilisation on a subject site, where DQRA is undertaken, the most appropriate course of action may be to undertake a survey of BTEX concentrations within the soil air and within the boundary layer directly above the soil surface. The measurement of oxygen and carbon dioxide in soil air can also provide a useful indication of the status of biodegradation processes.

The BTEX compounds are more likely to exist in the atmosphere in the vapour phase than in dust because of their high vapour pressures, although they can partition to organic matter so this pathway cannot be completely excluded. No specific information is available on differential partitioning of BTEX compounds to the finer soil fraction. Therefore careful consideration is required before an enrichment factor is applied to these substances.

The dermal exposure model currently within the CLEA model (and described within CLR10) is adapted from USEPA (1992). It requires soil/skin permeability coefficients, either taken directly from experimental work, or, in the absence of data, by estimating a skin permeability coefficient for chemicals in aqueous solution using a relationship between K_{ow} and the molecular weight. The skin permeability coefficient is then adjusted for soil, taking into account the soil matrix parameters and physicochemical properties of the substance.

It is likely that the dermal algorithm within the CLEA model will shortly be changed to the approach within USEPA (2001a), (Martin, 2002 Pers. Comm.). USEPA (2001a) stresses that the data for dermal absorption of chemicals from soils is very limited and presents dermal absorption factors from soil for ten chemicals based on well-designed studies, which it states will be added to as further research is conducted. No default dermal absorption values are presented by the USEPA for volatile organic compounds, such as BTEX compounds, on the basis that "in the considered soil exposure scenarios, volatile organic compounds would tend to be volatilized from the soil on the skin", and as a result would not be available for dermal uptake.

If the approach of USEPA (2001a) was followed, exposure via the dermal pathway would not be modelled within CLEA for the BTEX compounds. The literature review has not revealed any studies on dermal uptake of BTEX compounds conducted since the publication of the USEPA report. There is some reservation about adopting the USEPA approach of neglecting this pathway completely, since their criterion for "significance" of a pathway is a 10% contribution to exposure, which is much higher than the criterion of 1% selected in CLR10 (Defra and Environment Agency 2002d). In addition the scenarios considered included water pathways, which are not considered in the derivation of SGVs; in their absence, it is likely that dermal contact pathways become relatively more significant. The preliminary recommendation of a default dermal absorption factor of 0.1 is therefore made for each of the BTEX. This is the current USEPA (2001a) default for semi-volatile organic compounds and was the previous default recommended for all organic compounds in USEPA (1992); applying this to volatiles, such as the BTEX, retains conservatism over the most recent USEPA guidance. This approach is still used within some other risk assessment tools such as BP RISC (BP Oil 1997). While it is possible that inclusion of the dermal pathway for the BTEX compounds may be considered over-conservative, the recommendation of this report is that it is appropriate for a generic screening tool, especially as the definition as to what constitutes a significant pathway differs between the Environment Agency and the USEPA.

Spillages of pure BTEX compounds occur only in a minority of cases. In the majority of contaminated land scenarios encountered, BTEX are likely to be present in the soil as a mixture with other organic substances. This contrasts with the necessary treatment herein, where physicochemical and environmental constants are presented for pure phase compounds. Partitioning and environmental behaviour will be influenced by the presence of other compounds in the mixture. This mixture can evolve rapidly as constituents volatilise, leach or adsorb preferentially. Modelling based on pure phase properties may, therefore, not reflect the behaviour of contaminants in the field.

It may be considered appropriate to model the *m*, *p* and *o*-xylene isomers separately because of differences in their physicochemical properties. However, it is likely that for practical purposes it will be necessary to provide a single combined SGV because *m*- and *p*-xylene co-chromatograph on GC analysis and as a result are reported together by laboratories. Quantification of these individual isomers is rare due to the analytical costs involved. However, depending on the laboratory technique selected, *o*-xylene may be reported separately. As the differences in the physicochemical parameters between all three isomers are relatively slight, it is possible that differences between individually derived SGVs may be insignificant. The toxicological review of these isomers will also influence a decision as to the appropriate course of action, and as a minimum a sensitivity analysis exercise should be undertaken to establish the effects of the possible approaches.

4.6 Dietary Uptake of BTEX

4.6.1. Uptake by plants

The uptake of chemicals from soil by plants occurs through one of four pathways (although pathways three and four are only significant in specific applications) (Wang and Jones 1994):

1. root uptake and subsequent translocation to the above-ground (foliar) part of the plant by the transpiration stream;
2. foliar uptake of vapour from the surrounding air (significant particularly for volatile and semi-volatile chemicals);
3. uptake by external contamination of leaves and shoots by soil and dust, followed by retention in the plant cuticle or permeation through it; and
4. uptake and transport of the solvent into the plant in oil cells (specific to oil containing plants such as carrots and cress).

The total amount of any particular chemical in a plant is usually the result of uptake through a combination of these pathways minus the losses incurred through volatilisation from the leaves and metabolism by the plant (Wang and Jones 1994).

Many studies have identified that the sorption and uptake of contaminants by plants is primarily determined by the physicochemical properties of the contaminants. Generally speaking, the uptake of BTEX by plants will depend on the K_{ow} of the chemical, as this will influence the amount that will be available to the plant. Uptake of hydrophilic compounds is likely to occur predominantly through the plant's root system, due to their high solubility in water, and low values of K_H and K_{ow}. Once a chemical has penetrated the root it will enter the xylem and be transported in the transpiration stream. The main accumulation pathway for lipophilic compounds is from the air to the leaf surface, which is dependent on vapour-particle partitioning in the atmosphere, the octanol-air partition coefficient (K_{oa}) and the plant species (Simonich and Hites 1995).

Dietz and Schnoor (2001) propose that moderately hydrophobic chemicals (log K_{ow} 1.0 to 3.5) are most likely to be available to rooted, vascular plants. Similarly, Cousins and MacKay (2001), through a fugacity modelling approach, consider plant uptake by transpiration to be important for chemicals with a log K_{ow} less than 2.5 and a log air-water partition coefficient (log K_{aw}) less than -1. For root uptake, chemicals with a log K_{ow} of around 2 are transported in the transpiration stream (xylem), while those with a log K_{ow} of around 1 are xylem and phloem mobile (Collins, Laturnus *et al.* 2002). Phloem mobility is important as it is this flow of nutrients to growing portions of the plant that can contribute to loading in fruit.

Compounds with a log K_{ow} of > 2 are increasingly retained by lipid-containing root epidermis and the mucilage surrounding the root as a result of their hydrophobicity (Collins, Laturnus et al. 2002). Peak uptake of organic contaminants to the transpiration stream has been quoted at a log K_{ow} of 2.4 (Burken and Schnoor 1998, cited from Collins, Laturnus *et al.* 2002).

Of the BTEX compounds in this study, benzene has a log K_{ow} of 2.13, hence would be expected to be available to plants via root uptake and subsequent transpiration pathways through the plant. The remaining BTEX compounds have Log K_{ow}'s of 2.65 to 3.20, suggesting they are also likely to be available to rooted, vascular plants, but may be more likely than benzene to have a component which is retained in the root.

Once in the transpiration stream, chemicals may react with or partition into plant tissues, be metabolized by plant enzymes, or escape by gaseous diffusion through stomata in leaves (Chard, Ferro *et al.* 2001).

As well as being dependent upon the chemical properties, uptake is also determined to some extent by the characteristics of the soil and of the plant. Plant uptake in soils with a high organic carbon content will be limited due to the increased adsorption to soil. Plants with a high leaf surface area and lipid content will exhibit increased foliar uptake, as these characteristics will facilitate transfer from the atmosphere across the leaf surface.

Potential mechanisms for the uptake and transformations of BTEX in a plant are shown in Figure 4.5 (after Collins, Laturnus *et al.* 2002, adapted from Schnabel, Dietz *et al.* 1997).

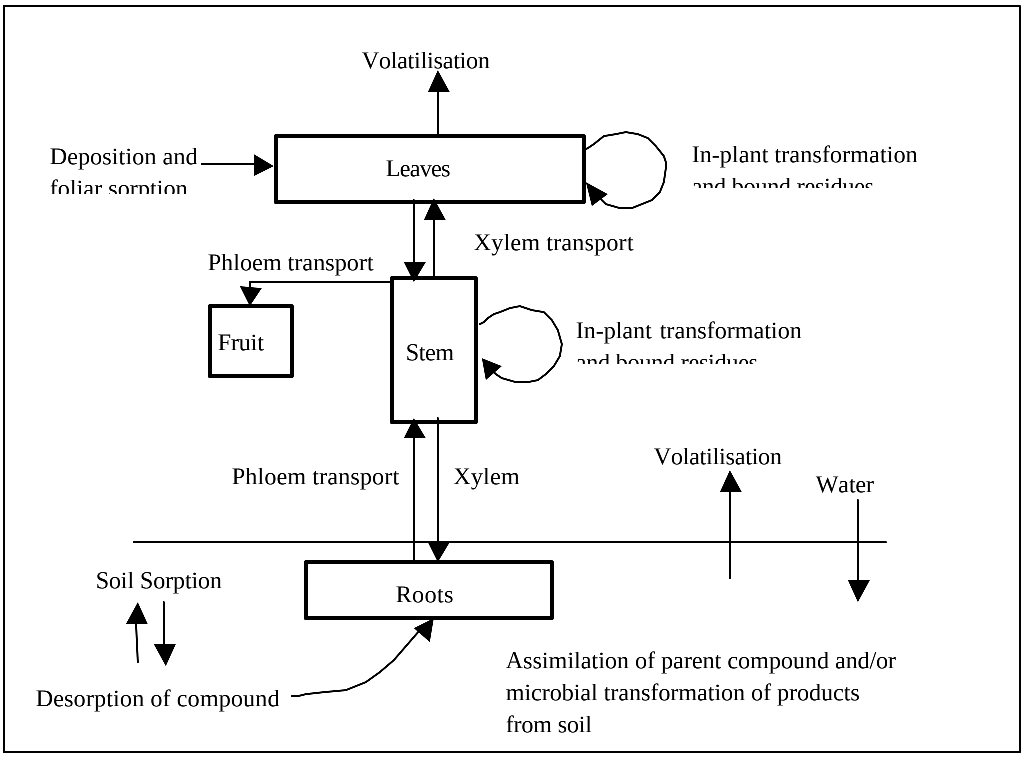

Figure 4.5 **Mechanisms for the uptake and transformations of BTEX in a plant (after Collins, Laturnus *et al*. 2002), adapted from Schnabel, Dietz *et al.* 1997).**

The tendency for lipophilic substances to become more concentrated in plant (or animal) tissues after their uptake from the environment (air, water, soil) is known as bioconcentration. This is expressed as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in its surrounding environment, and is commonly referred to as the BCF (bioconcentration factor). This is a measure of the bioaccumulation potential of a chemical in organisms in the environment. BCFs of 100 to 1000 are thought to be indicative of modest bioaccumulation (ATSDR 1995a).

BTEX compounds are moderately lipophilic (as classified by their K_{ow} after Bromilow and Chamberlain, 1995), which indicates some potential for bioaccumulation in fatty plant tissues. Where information has been located on plant studies alone, this is noted in the sections below. More commonly, BCF is quoted from animal studies; in these cases discussion is included in Section 6.2.

Benzene

The majority of the accumulation of benzene in vegetation is considered to result from air-to-leaf transfer (ATSDR 1997d, Ugrekhelidze, Korte *et al.* 1997). The EU Risk Assessment (EU 2002) also states that binding of benzene in a plant occurs through exchange at the air/leaf interface, and that root uptake is unlikely given the low concentration in soil (a statement which is not well supported, but is presumably based upon the Henry's Law Constant).

Evidence does exist for the uptake of benzene from soil by cress and barley plants (Scheunert, Topp *et al*. 198), Topp, Scheunert *et al*. 1989, both cited from ATSDR 1998a). Plant BCFs for barley plants after 12, 33, 71, and 125 days were 17, 2.3, 2.9, and 4.6, respectively; BCFs for cress plants after 12, 33, and 79 days were 10, 2.3, and 1.9, respectively. The relative decrease in the BCFs over experimental duration was attributed to growth dilution (Topp, Scheunert *et al.* 1989, cited from ATSDR 1998a), although it has been suggested by others (Cape, Binnie *et al*. 2000, Collins, Laturnus *et al*. 2002, Collins, Bell *et al*. 2000, Ugrekhelidze, Korte *et al*. 1997) that metabolism takes place within the plant. The BCFs derived by this study are not considered to represent a significant potential for accumulation.

A further soil to plant study (Ferro, Kennedy *et al*. 1997) subirrigated (i.e. from below) alfalfa crops with an aqueous solution containing radiolabelled [^{14}C]benzene. This resulted in a maximum soil concentration of 0.62mg kg^{-1}. By analysing for [^{14}C] benzene in air every 12 hours and in alfalfa tissue at the end of the test the it was possible to determine root and foliar uptake of benzene from the system and also efflux to the atmosphere. Mass recovery of [^{14}C]benzene was 90%; of this less than 2% was associated with the plant shoots and 2 to 8% in the root fraction (in the root and rhizosphere soil). Clearly, this study indicates that volatilisation from the soil is the primary control on fate of benzene, with low potential for mass concentration in plant tissue.

Apple, blackberry and cucumber crops were exposed to elevated levels of benzene in air (1 mg m^{-3}) in a chamber experiment at 20°C for 80 days (Collins, Bell *et al*. 2000). Partitioning factors from air to fruit (K_{fa}) and leaves (K_{1a}) were derived. Benzene was found to be retained in fruits, with a maximum K_{fa} in blackberries of 400 (average blackberry K_{fa} 235.6, average cucumber K_{fa} 18.5, a K_{fa} was not calculated for apples, which did not produce fruit until after a second exposure at 8.78 mg m^{-3} benzene in air). Assuming an atmospheric concentration of 5 ppb benzene (the air standard at the time the paper was written) the maximum K_{fa} would result in a fruit concentration of 24 µg kg^{-1}. With the air standard dropping to 1 ppb, the authors of the paper concluded that in terms of potential toxicity to a population, crop exposure to ambient air and subsequent ingestion was not likely to be a significant issue.

Benzene accumulated in leaves of blackberries and apples (average K_{la} of 5.5 in apples and 349 (259 with outlier removed) in blackberries), although there was little evidence of uptake in cucumber leaves. The authors suggested that where there was no significant uptake of benzene this appeared to be related to the density of the tissue. This appears to be supported by an earlier study, in which after plants were removed from a benzene-rich atmosphere desorption was dependent on the path length from the interior, e.g. cabbage leaves desorbed in 10 minutes, while apple fruits took 2 hours (Collins, J *et al.* 1998, cited in Collins, Bell *et al*. 2000). In addition, Ugrekhelidze, Korte *et al.* (1997) (cited in EU 2002) suggests that, in general, the number of stomata and the structure of the cuticle affect uptake to leaves. Keymeulen, Schamp *et al*. (1993, cited in Collins, Bell *et al.* 2000) also suggests that inter-species variability could be related to the composition of the cuticle. A less well-studied possibility is that metabolism occurs in the leaf (Collins, Bell *et al.* 2000).

EU (2002) cites a study by Behrent and Bruggeman (1994) which calculated a partitioning factor from air to leaves (K_{1a}) of 10.6. Given an air concentration of 1 µg m^{-3} and a leaf density of 0.5g cm^{-3}, the resulting concentration in the leaf is calculated to be 0.021 µg kg^{-1} wet weight. No information on the plant species or experimental conditions is given.

Produce studies have detected benzene in fruit and vegetables. However, although this may indicate uptake by plants, it should be noted that uptake could have taken place either during growth or after harvesting i.e. as a consequence of packaging or distribution processes. Example produce studies for BTEX are presented in a later section.

Toluene
There are no recent literature reports on the uptake of toluene by plants from soil or air during growth under controlled experimental conditions. It is likely that, due to similarities in structure and properties, toluene will be taken up by plants in a similar fashion to benzene, with a high proportion being through the leaf/air interface. Keymeulen, 1993 (cited from Collins, Bell *et al.* 2000) found that there was relatively more toluene present in urban roadside leaves compared to benzene. The reasons for this could not be ascertained from the citation; however it could be due to relatively greater lipid affinity, hence retention, in the leaf.

According to the review presented at the beginning of this chapter, one potential area where toluene will differ relative to benzene is that the slightly higher log K_{ow}, may affect uptake from soil and the subsequent transport mechanism within the plant. This slightly increased lipophilicity may result in less ready movement through transpiration, thus toluene is more likely than benzene to have a component which is retained in the root. However, studies have indicated that in chambers containing alfalfa in sand dosed with toluene (Narayanan, Davis *et al.* 1998) the loss of chemical can be correlated with transpiration.

The bioconcentration factor of toluene is expected to be relatively low (ATSDR 2001a). Produce studies have detected toluene in fruit and vegetables. However, although uptake by plants may be indicated by the presence of toluene in fruit and vegetables, it should be noted that uptake could take place either during growth or after harvesting i.e. as a consequence of packaging or distribution processes. Example produce studies for BTEX are presented in a later section.

Ethylbenzene
There are no recent literature reports on the uptake of ethylbenzene by plants from soil or air during growth under controlled experimental conditions. It is likely that, due to similarities in structure and properties, ethylbenzene will be taken up by plants in a similar fashion to benzene and toluene, with a high proportion being through the leaf/air interface.

Compared to toluene and benzene the higher log K_{ow} of ethylbenzene may affect uptake from soil and the subsequent transport mechanism within the plant. This slightly increased lipophilicity may result in less ready movement through transpiration, thus ethylbenzene is more likely than benzene and toluene to have a component which is retained in the root. Ethylbenzene is more lipophilic than benzene and toluene, so will be more likely to bioaccumulate. A study on soil and grain residues reported that grain residues adsorbed a greater amount of ethylbenzene as compared with surface soil (ATSDR 1999, cited from Boyd, Xiangcan *et al.* 1990). The author suggested that this was because the highly lipophilic plant cuticle provides the sorptive component. Despite this, the ATSDR document goes on to say that the bioaccumulation factor is unlikely to be of great concern, with the majority of reported values for plant and animal studies less than 100.

Produce studies have detected ethylbenzene in fruit and vegetables. However, although uptake by plants may be indicated by the presence of ethylbenzene in fruits and vegetables, it should be noted that uptake could take place either during growth or after harvesting i.e. as a consequence of packaging or distribution processes. Example produce studies for BTEX are presented at the end of this section.

Xylene

A survey of recent literature did not reveal any papers on the uptake of xylene isomers by plants. Based on similar physicochemical properties, the plant uptake is considered to be similar to that of ethylbenzene. Xylene is within the upper extreme of the range of log K_{ow} chemicals (the quoted range is 1.0 to 3.5, xylene isomers log K_{ow} is 3.12 to 3.20) which are likely to be available to rooted, vascular plants (Dietz and Schnoor 2001).

The increased lipophilicity of xylene over the other BTEX compounds may result in less ready movement through transpiration; hence xylene is more likely than benzene and toluene to be retained in the root and, subsequent to transport processes within the plant, is likely to bioaccumulate in plant tissues. Despite this, ATSDR (1995a) consider that significant bioconcentration is unlikely, with the majority of reported values for plant and animal studies less than 100, and all less than 500.

4.6.2. Uptake into the Rest of the Food Chain

Produce Studies

A number of ‘food-basket’ produce studies have been undertaken to establish the uptake of BTEX into the food chain, primarily for the purposes of toxicological appraisal. In the majority of these studies, information was not provided in relation to the soil conditions or atmospheric BTEX concentrations during crop production, or other environmental sources of contamination from harvest onwards, simply because it was impossible for the authors to determine, and in any case was not the stated aim of the study. As this is the case the studies provide general indications of the potential for uptake of the BTEX by various food crops (including meat and animal derivatives) and incorporation into the food chain in the period of growing, harvest, distribution, packing and sale, but specific routes of uptake are unable to be determined. Data on likely concentrations of BTEX compounds in food products is covered within the toxicological data and intake value (TOX) reports, produced under the CLR9 framework (Defra and Environment Agency 2002d).

A recent literature survey was undertaken by De Wolf and van den Beld (2000) on behalf of CONCAWE into the background levels of hydrocarbons in food purchased from petrol station shops. This includes a useful summary of an earlier literature compilation (TNO, 1996, cited from De Wolf and van den Beld 2000) of volatile compounds found in general food studies. This identified that benzene, toluene and xylene isomers had been identified in food items. In 1995 the US Food and Drug Administration (FDA) surveyed 234 foods for benzene, toluene and xylenes (Heikes, Jensen *et al*. 1995, cited from De Wolf and van den Beld 2000). Raw fruits and vegetables were excluded. The survey showed a close correlation between levels of BTX and the fat content of the foods analysed. This indicates that the lipophilic nature of the BTX is resulting in their concentration in high fat foods. As ethylbenzene was not considered by de Wolf and van den Beld details are not available for this substance, however, in view of its similar physiochemical properties, ethylbenzene would be expected to show a similar pattern in foods.

Górna-Binkul, Keymeulen *et al*. (1996), analysed fruit and vegetables from shops for the presence of various monoaromatic hydrocarbons. Benzene was only found in three species of fruit (apple, kiwifruit and orange) at low concentrations (27 to 56 µg kg^{-1} dry mass). Benzene was not detected in any of the 14 species of vegetables examined and toluene in only a few (cabbage, tomato, paprika and sprouts). Toluene was detected in eight of the fruits, with the highest concentrations (169-771 µg kg^{-1}) in citrus varieties. Xylenes were only detected in orange peel extract at low concentrations, and in two vegetables (parsley and paprika) although at notably high concentrations (max 1890 µg kg^{-1}).

The results showed that uptake by plants is dependent on species and particularly morphological structure, for example orange peel absorbed all compounds of interest while no BTEX compounds were detected in avocado peel and celery leaves. Higher toluene concentrations were found in peel than pulp, this is possibly due to the higher levels of lipophilic components in peel (wax, essential oils).

No detectable concentrations of BTEX were identified in underground portions of plants which are not exposed to air (while growing). This would tend to support the theory that the primary uptake of BTEX is through the plant-air interface, and in addition suggests that distribution from the leaves throughout the plant may not be significant. However, alternatively the marked difference could be due to the low fat contents of these root crops. The growth medium is also unlikely to have been contaminated, whereas air pollution is more ubiquitous.

In the UK, Total Diet Studies (TDS) are undertaken by the Food Standards Agency (FSA, formerly the Ministry of Agriculture, Fisheries and Food (MAFF) to establish the average concentrations of chemicals taken in through the diet. The studies provide information on the contribution to the diet from each food group. Similarly to the US Food and Drug Administration (FDA) study concentrations are highest in the categories of meat, poultry, oils and fats, nuts and fish (those foodstuffs which have high fat contents), and low (majority non-detectable) in vegetables and fruit.

All of the BTEX compounds have been detected in foodstuffs at least at trace levels, and sometimes elevated levels, with the lipophilic nature of the compounds apparently contributing to their presence in foods, particularly those foodstuffs with high fat contents. However it is not possible to say from these results whether the contamination is present as a result of transfer through the food chain following plant uptake of the compounds from soil by plants, or if it is due to exposure of food products to the chemicals during manufacture, preparation or packaging. Generally, vegetables and fruits which would be expected to be grown in UK gardens have not indicated high potential for uptake and accumulation.

Bioconcentration

Within the Environmental Health Criteria series of documents the WHO review studies on bioconcentration and bioaccumulation of BTEX in aquatic and terrestrial organisms. These present no data derived from edible garden or indeed (with the exception of algae) any other plants, however, the conclusions of the WHO as to the potential of these substances to accumulate in the food chain are considered below. As previously stated, BCFs of between 100 to 1,000 are thought to be indicative of modest bioaccumulation (ATSDR 1995a). The WHO documents are reviewed below.

The WHO state that benzene is not expected to bioconcentrate to any great extent in aquatic or terrestrial organisms given the reported value for BCF of 24 (cited from Miller, Wasik *et al.* 1985). Experimental BCFs quoted from a number of studies were 4.3 to 225.

WHO state that bioaccumulation of toluene has not been studied adequately, but consider that according to a quoted log K_{ow} of 2.69, slight to moderate accumulation may take place. However, various studies are consulted for experimental BCFs, from which it is concluded that it is unlikely that toluene accumulates in an ecosystem food chain.

A quoted log K_{ow} for ethylbenzene of 3.13 indicates that bioaccumulation of ethylbenzene could take place. Using this partition coefficient, an estimated BCF of 145 can be calculated (Bysshe 1982). Measured values are similarly low, and the report concludes that biomagnification of ethylbenzene through the aquatic food chain is unlikely.

Using the formula of Veith, Macek *et al.* (1980), BCFs of 138 for o-xylene, 158.5 for m-xylene and 144.5 for p-xylene are calculated. Measured values are found to be up to an order of magnitude less, hence it is concluded that biomagnification of ethylbenzene through the aquatic food chain is unlikely.

4.7 Key Conclusions

4.7.1. Recommendations for DQRA

Considerable variation in both calculated and measured K_{oc} values has been noted for each of the BTEX. Indeed, USEPA (1996a) notes that the relationship with log K_{ow}, often used within environmental modelling literature, appeared to be inappropriate for volatile organic compounds. Of particular importance to the BTEX, significant disagreement is noted between the K_{oc} derived from modified Di Toro equation by the USEPA and the approach of Sabljic and Gusten used in the EU risk assessment. The primary factor influencing the K_{oc} is soil organic matter (SOM), although other aspects of soil type also play a part such as particle size and pH. K_{oc} is critical for a number of exposure pathways, including the volatilisation pathways, which are likely to be dominant. For application of a ‘representative’ K_{oc} within

DQRA it may be possible to justify the use of a K_{oc} derived from a similar soil if available, or otherwise to determine K_{oc} experimentally on a site specific basis.

Plant uptake is unlikely to be a critical pathway for the BTEX compounds, because of the expected dominance of the inhalation of vapour pathways. However there may be occasions where the analysis of available produce or plants grown in field or pot trials is appropriate.

Based on their physicochemical properties and degradation pathways, the BTEX contaminants should be rapidly lost from the soil and groundwater. However their presence on some historically contaminated sites indicates that there are circumstances in which this may not be the case and generic screening models will therefore be based on the more conservative viewpoint. However, biodegradation has been shown to be a significant process for removal of contaminant mass from many soils. Where SGVs were exceeded, it would therefore be advisable to conduct DQRA. Consideration of biodegradation in the vapour phase is also likely to be a valid assumption in DQRA for BTEX contamination from soil (and groundwater) and would involve alternatives to the approach of Johnson and Ettinger. Example models which do include a degradation term are Jury (Jury, Spencer *et al*. 1983; Jury, Russo et al. 1990, cited in De Vaull, Ettinger *et al*. 1997), and the Dominant Layer Model of Johnson, Kemblowski *et al*. (1998). Volatilisation would be expected to occur from contaminated groundwater as well as from soils, so where groundwater contamination is encountered, an appropriate risk assessment tool which can model this pathway should be selected.

Further DQRA might include measurements of concentrations within the soil, air and within the air in the boundary layer above the soil surface. In addition, particularly if there are also issues of groundwater contamination at the site, it may be possible to conduct long term monitoring as to site specific rates of loss from the soil.

4.7.2. Recommendations for the CLEA Model

As mentioned above, considerable variation in both calculated and measured K_{oc} values has been noted for each of the BTEX. USEPA (1996a) notes that the relationship with log K_{ow}, often used within environmental modelling literature, appeared to be inappropriate for volatile organic compounds. Of particular importance to the BTEX, significant disagreement is noted between the K_{oc} derived from modified Di Toro equation by the USEPA and the approach of Sabljic and Gusten used in the EU risk assessment. The uncertainty around the differences in approach should be evaluated when deriving the SGVs for these substances.

Application of a ‘representative’ K_{oc} in determining an SGV is also in question due to the inherent variability of this parameter between sites. The primary factor influencing the K_{oc} is the nature of the SOM, although other aspects of soil type also play a part. K_{oc} is important for a number of exposure pathways, including the volatilisation pathways, where it has a significant impact on the source vapour concentrations. For a screening level assessment the selection should reflect appropriate SOM and soil matrix for the generic conservative conceptual site model.

There are insufficient data available in the literature to replace the plant uptake algorithms within the CLEA model with specific concentration factors. The literature search has revealed a few relevant studies (almost exclusively on benzene) and it is suggested that these should be used as a "reality check" when assessing the different plant uptake models available. The Briggs Ryan algorithm, which is described within CLR10 (Defra and Environment Agency 2002d), is currently the default approach within the CLEA model. All of the BTEX compounds fall well within the model constraints with regard to log K_{ow}. However it is considered that due to the volatility of the BTEX compounds, air-to-leaf transfer is the most important uptake mechanism, (Ugrekhelidze, Korte *et al*. 1997; ATSDR 1997d). The Briggs Ryan model does not explicitly include consideration of the air-to-leaf pathway. It may therefore be more appropriate to use a fugacity approach, such as the simplified Patterson McKay model (Paterson and Mackay 1989), or the Trapp and Matthies model (Trapp and Matthies 1995) for this aspect of plant uptake.

The simplified Patterson McKay is currently used within the CalTox model (CalTox 1993) and has been adopted within GasSim (Environment Agency 2002a). The Trapp and Matthies model is used within the German UMS model (UMS 1997), the EUSES model (EC 1996a) and has been proposed for the new Dutch Human Serious Risk Concentrations (Lijzen, Baars *et al.* 2001). The Trapp and Matthies model is considered to be more suitable than the Patterson McKay model for air-to-leaf transfer. This is because the Patterson McKay model was calibrated against bromacil which has a low vapour pressure, whereas the Trapp and Matthies model was calibrated against nitrobenzene, amongst other substances.

The work of Scheunert, Topp *et al.* (1985) and Topp, Scheunert *et al.* (1989) considered uptake of benzene from soil, and the possibility of using the regression that they developed may also be considered. A challenge in the modelling will be to make a decision about the initial assumption on how long the benzene is considered to be within the plant before harvesting. This is because a general decline in the levels within barley and cress plants appeared to occur over the course of the experiments. A literature search has identified that once in the transpiration stream, a reduction in contaminant mass in the plant may result from a combination of the following processes; chemicals may react with plant tissues, be metabolized by plant enzymes, or escape by gaseous diffusion through stomata in leaves (Chard, Ferro *et al.* 2001).

The expected rapid rate of volatilisation from soil, based on the high vapour pressure and K_H, combined with the relatively low K_{oc} (see evaluative triangle in introductory chapter) will dictate the nature of the exposure of the BTEX from soil. Thus a volatilisation pathway is likely to be active, and of importance. There are insufficient data available in the literature to make specific recommendations for the substance specific calibration of generic vapour models for the BTEX compounds. It may be appropriate to include a check within the model to indicate that concentrations nearing saturation have been reached. The SGV reports should include caveats about the likely effects of not considering degradation processes in solid, aqueous and vapour phases, or a check for mass balance.

It is recommended that consideration is given to modelling the dermal pathway for BTEX, although the current proposed approach (application of the USEPA, 2001 methodology) would omit it. Therefore, an approach based on a default dermal absorption factor of 0.1 (see Section 5.4) is recommended for each of the BTEX.

It may be considered appropriate to model the *m*, *p* and *o*-xylene isomers separately because of differences in their physicochemical properties. However, it is likely that for practical purposes it will be necessary to provide a single combined SGV because *m*- and *p*-xylene co-chromatograph on GC analysis and as a result are reported together by laboratories. Quantification of these individual isomers is rare due to the analytical costs involved. However, depending on the laboratory technique selected, *o*-xylene may be reported separately. As the differences in the physicochemical parameters between all three isomers are relatively slight, it is possible that differences between individually derived SGVs may be insignificant. The toxicological review of these isomers will also influence a decision as to the appropriate course of action, and as a minimum a sensitivity analysis exercise should be undertaken to establish the effects of the possible approaches.

4.7.3. Summary of Recommended Values

The recommended physiochemical data for use in the CLEA model (taken from Table 4.4) are summarised in Table 4.12.

Table 4.12 - Recommended physicochemical values and parameters for use in the CLEA model (CLEA units)

Substance	Mol. weight	Boiling Point	Solubility	Vapour Pressure	Henry's Law Constants	Log K_{ow}	Log K_{oc}	Coefficient of Diffusion (25°C)$^{\bullet}$		Critical temp ^{o}	Enthalpy of vapourisation ^{p}
								Air	Water		
		K	mg l^{-1} or g m^{-3}	Pa$^{\wedge}$	Pa-m^3 mol^{-1}	-	-	m^2 s^{-1}	m^2 s^{-1}	K	cal mol^{-1}
Benzene	78.11^{a}	353.25^{a,b}	1770 (25)^{h}	9970 (20)^{a}	442.5 (20)*	2.13^{a,k,j,l}	2.13^{a}	8.80E-06	9.8E-10	562.05	7342.1
Toluene	92.15^{b,c,d}	383.75^{b,d}	535 (25)^{c,d}	3000 (20)^{d}	537 (20)^{d}	2.65^{j,d,k,l}	2.25^{d}	8.70E-06	8.6E-10	591.8	7930.0
Ethylbenzene	106.16^{e,f}	409.35^{b,e}	169 (25)^{i}	950 (20)^{f}	663.5 (20)*	3.13^{e,f,l}	2.64^{n**}	7.50E-06	7.8E-10	617.2	8501.2
o-xylene	106.16^{g}	417.55^{b,g}	173 (25)^{i}	660 (20)^{g}	534 (20)^{l,m}	3.12^{g,k,l,m}	2.63^{n**}	8.70E-06	1.00E-09	630.3	8661.4
m-xylene	106.16^{g}	412.25^{b,g}	160 (25)^{i}	790 (20)^{g}	493.3 (20)*	3.20^{g,j,k,l,m}	2.69^{n**}	7.00E-06	7.80E-10	617.0	8522.7
p-xylene	106.16^{g}	411.45^{g}	180 (25)^{i}	860 (20)^{g}	699 (20)^{k}	3.15^{g,k,l,m}	2.65^{n**}	7.69E-06	8.44E-10	616.2	8525.1

[*] Calculated from relevant soil and vapour pressures following EU risk assessment approach { (EU 2001c); EU, 2002 #495}.

[**] Calculated from selected log K_{OW} using regressions established by (Sabljic and Gusten 1995) presented in (EU 1996) and applied in EU risk assessments { (EU 2001c); EU, 2002 #495}.

[a] (EU 2002)
[b] (Kirk-Othmer 2003)
[c] (WHO 1986)
[d] (EU 2001c)
[e] (WHO 1996)
[f] (GCS 1997)
[g] (WHO 1997)
[h] (IUPAC 1989a)
[i] (IUPAC 1989b)
[j] (USEPA 1996a)
[k] (HSDB 2002)
[l] (SRC 2002)
[m] (IUCLID 2000)
[n] (EU 1996)
[o] (Lide 2000)

5. PHENOL

5.1 Introduction

This chapter reviews the environmental behaviour of phenol and recommends appropriate parameter values for use within the CLEA model. Information is provided on the major sources of this chemical to the environment, reported levels in the soil environment and the key physicochemical characteristics such as solubility, Henry's Law constant and octanol-water partition coefficient that will determine the fate and behaviour of phenol in the environment.

5.1.1. Major Sources of Phenol to the Environment

Although phenol does occur naturally as a constituent of coal tar and is formed during the natural decomposition of organic materials, the presence of this chemical in the environment is a consequence primarily of anthropogenic activities. The major commercial use of phenol is in the formation of phenolic resins, bisphenol A and caprolactam. (WHO 1994a) It is also used in the manufacture of nylon and other synthetic fibres, in slimicides[14], as a disinfectant, as an antiseptic and in medicinal and pharmaceutical products such as cough drops and mouth wash (ATSDR 1998c; HSDB 2002). The release of phenol during the manufacture of these materials and products accounts for the majority of phenol present in the environment. Other sources to the environment include vehicle exhaust (both directly and following the photochemical degradation of the benzene released in the exhaust), pulp manufacture and landfill leachate (ECB 2002).

Production and use of phenol and its products, especially phenolic resins and caprolactam, exhaust gases, residential wood burning and cigarette smoke are potential sources of contamination, as is the atmospheric degradation of benzene under the influence of light. Benzene and phenol derivatives may, by *in vivo* conversion, form a source of endogenous human phenol. (WHO 1994a) It should be noted however that only exposure of phenol from soil is considered in this report. Information on exposure to the atmosphere or aquatic environment is provided for completeness and to describe the major sources of phenol to the environment.

5.2 Identity

Phenol (CAS 108-95-2; IUPAC name Phenol) is a colourless to light pink crystalline solid which melts at 43 °C and liquefies upon contact with water. It is moderately volatile at room temperature and has a very low odour threshold. Phenol has a characteristic acrid odour and a sharp burning taste. It is soluble in most organic solvents and at temperatures above 68 °C it is entirely water-soluble. It is a weak acid, and in its ionised form is very sensitive to electrophilic substitution reactions and oxidation. (WHO 1994a)

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[14] Slimicides are products used to kill or remove algal or fungal growths

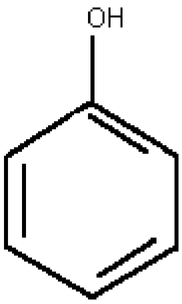

Figure 5.6 Chemical structure of phenol (WHO 1994a)

5.3 Occurrence in Soil

The majority of the phenol present in the soil environment is a consequence of anthropogenic activities. Phenol may be released to the soil during its manufacturing process, loading and transport when spills occur, and when it leaches from hazardous waste sites and landfills. (ATSDR 1998c)

Levels of 0.01-53 mg l^{1} of phenol have been reported in effluents from industrial processes (WHO 1994a) with the highest levels associated with the iron and steel industry.

Information on levels of phenol in soil is limited, with WHO (1994a) for example reporting an absence of data for the presence of phenol in soil. Although phenol is likely to be released into the soil environment through emissions from the anthropogenic activities discussed above, the poor persistence of this chemical in soil is reported to explain its limited detection in the soil environment.

Phenol is however reported as likely to be found in soils that receive continuous or consistent releases from a point source, although details of the concentrations involved are not reported (ATSDR 1998c).

5.4 Physicochemical Properties

The physicochemical properties for phenol are presented in Table 5.1. Values for the physicochemical properties for phenol have been obtained from six key sources:

- European Chemicals Bureau (ECB 2002) – Draft environmental risk assessment for phenol.
- WHO (1994a) – Environmental Health Criteria document for phenol.
- USEPA (1996a) – Soil screening guidance.
- HSDB (2002) – Hazardous substances database managed by the US National Library of Medicine.
- Chemfate (2002) – Chemfate database managed by the Syracuse Research Corporation (http://esc.syrres.com/efdb/Chemfate.htm).
- ASTDR (1998c) – Toxicological profile for phenol.

With respect to the selection of a recommended value for the CLEA model, data from the ECB have been used where available. Where these are not available, values reported by WHO (1994a) have been taken as the recommended values for the CLEA model.

Molecular Weight

The recommended relative molecular weight for use in the CLEA physicochemical data base is 94.11. (ECB 2002, WHO 1994a). This value is reported by both the ECB and WHO databases.

Aqueous Solubility

Generally phenols have a high solubility within water. Solubilities range from 67 g l^{-1} at 16°C (WHO 1994a) to 84 g l^{-1} at 20ºC (ECB 2002). The recommended solubility for use in the CLEA model is the value from the ECB (2002)

Vapour Pressure

Reported values for vapour pressure at 25ºC vary from 36.79 Pa (0.276 mmHg) (Chemfate 2002) to 46.83 Pa (0.3513 mmHg), (HSDB 2002) and 47.59 Pa (0.357 mmHg) at 20ºC (WHO 1994a). The recommended value for use in the CLEA model is 47.59 Pa (0.357 mmHg) at 20ºC (WHO 1994a).

Henry's Law Constant

Chemfate (2002) reports a calculated value at an unknown temperature of $3.97\text{x}10^{-7}$ atm-m^3 mol^{-1} (0.040 Pa m^3 mol^{-1}); this value has also been reported by the USEPA (1996a) at 25ºC. Chemfate (2002) also report a measured value of $3.33\text{x}10^{-7}$ atm-m^3 mol^{-1} (0.034 Pa m^3 mol^{-1}) at 25ºC. The recommended value for use in the CLEA model is the value in USEPA (1996a)

K_{ow}

There are a limited number of values reported for the log K_{ow} of phenol. Chemfate (2002), ATSDR (1998c) and WHO (1994a) have reported a value of 1.46, whilst ECB report a value of 1.47. The recommended value for use in the CLEA model is the value in ECB of 1.47 (ECB 2002).

K_{oc}

Reported K_{oc} values vary from 9 to 3100 (log K_{oc} 0.95-3.49) (Chemfate 2002). The recommended value for use in the CLEA model is the calculated K_{oc} as reported by USEPA (1996a) of 28.8 (log K_{oc} 1.46).

Diffusivity

The recommended values for diffusivity of phenol in air and water have been taken from the ChemDAT8 model database, cited in USEPA (1996a). These are $8.20\text{x}10^{-6}$ and $9.10\text{x}10^{-10}$ m^2 s^{-1} respectively.

Enthalpy of vapourisation

Values reported for the enthalpy of vapourisation at boiling point (454 K) range from 10920 cal mol^{-1} (CRC Handbook 2000-2001) to 11299.8 cal mol^{-1} (Chemical Properties Handbook 1999). A value of 13809.98 kJ mol^{-1} at a much lower temperature of 25°C has also been reported (CRC Handbook 2000-2001). The recommended value for use in the CLEA model is 10920 cal mol^{-1} at (454 K). This is the most recent value reported.

Critical temperature

Two values for critical temperature for phenol have been identified. These are 694.2 K (CRC Handbook 2000-2001) and 694.25 K (Chemical Properties Handbook 1999). The recommended value for use in the CLEA model is 694.2 K as this is the most recent value reported.

Table 5.1 Recommended physicochemical values and parameters for use in the CLEA model, minimum and maximum literature ranges (CLEA units)

Value	**Mol. weight**	**Boiling Point**	**Solubility**	**Vapour Pressure**	**Henry's Law Constants (25°C)**		
	-	**K**	**$g\ l^{-1}$**	**Pa[^]**	**$Pa\text{-}m^3mol^{-1}$**	**$atm\text{-}m^3mol^{-1}$**	**Dimensionless**
Recommended	94.11[a]	454.75[a]	84 [h] (20°C)	47.59 [a] (20ºC)	0.040 [b]	3.97E-07[b]	1.63E-05[b]
Min			67 [a] (16°C)	36.79 [c] (25ºC)	0.034 [c]	3.33E-07[c]	1.37E-05[c]
Max			84 [h] (20°C)	47.59 [a] (25ºC)	0.040 [b]	3.97E-07[b]	1.63E-05[b]

Value	**Log K_{ow}**	**K_{oc}**	**Coefficient of Diffusion (25 °C)**		**Enthalpy of vapourisation (454 K)**	**Critical temp**
			Air	**Water**		
	-	-	**$m^2\ s^{-1}$**	**$m^2\ s^{-1}$**	**cal mol^{-1}**	**K**
Recommended	1.47 [h]	28.8 [b]	8.20E-06[e]	9.10E-10[e]	10920 [f]	694.2 [f]
Min	1.46 [a,c,d]	9.0[c]	-	-	10920[f]	694.2 [f]
Max	1.48 [b]	3100 [c]			11299.8[g]	694.25 [g]

[^] Conversion factor from mmHg to Pa = multiply by 133.3

[#] Conversion factor from $atm\text{-}m^3\ mol^{-1}$ to $Pa\text{-}m^3\ mol^{-1}$ = multiply by 101325; $atm\text{-}m^3\ mol^{-1}$ to dimensionless = multiply by 41

[a] WHO reported value (WHO 1994a)

[b] USEPA reported value (USEPA 1996a)

[c] Chemfate reported value (Chemfate 2002)

[d] ASTDR reported value (ATSDR 1998c)

[e] data from the ChemDAT8 model database, cited by USEPA (USEPA 1996a)

[f] data from CRC Handbook (CRC Handbook 2000-2001)

[g] data from Chemical Properties Handbook (Chemical Properties Handbook 1999)

[h] data from European Chemicals Bureau (ECB 2002)

5.5 Behaviour of Phenol in the Soil Environment

Phenol is shown on the evaluative triangle within the introductory chapter, which provides an indication of its likely behaviour in the soil. The evaluative triangle shows that phenol is likely to be highly mobile in soil and may leach to groundwater (as demonstrated by its low K_{oc}). Based on its vapour pressure and low adsorptivity to soil, volatilisation from dry soil and other surfaces may also occur (HSDB 2002). Field scale and laboratory microcosm experiments have demonstrated that phenol is readily biodegraded under aerobic conditions in all environmental media, including soil and sediment (Aronson, Citra *et al*. 1999; HSDB 2002; WHO 1994a; WHO 1994b). Phenol may also be removed from soil as a result of surface-catalysed reaction or oxidative processes (HSDB 2002).

Under aerobic conditions, phenol may be completely mineralised by microbial biodegradative processes to carbon dioxide and water and, under anaerobic conditions, to carbon dioxide and methane (WHO 1994a). Benzoate, catechol, cis-cis-muconate, ß-ketoadipate, succinate and acetate have all been identified as intermediates in the biodegradation of phenol in the environment (WHO 1994a).

Biodegradation can be hindered or even precluded by high concentrations of phenol which exceed toxicity thresholds of the competent microbial community (ATSDR 1998c). This indicates the importance of the soil microbial community in the degradation of phenol, as inhibition of this activity has a negative effect on the removal of the phenol. Similar reductions in phenol degradation may also occur in the presence of other chemicals that have an inhibitory effect on soil microorganisms, or in the absence of necessary nutrients (WHO 1994a). Laboratory experiments have demonstrated that biodegradation is effective at phenol concentrations in soil of up to 1000 mg kg^{-1} (Aronson, Citra *et al.* 1999).

The half-life of phenol in soil is usually less than 5 days, even in subsurface soil and aquifer material, although for acid soils and some surface soils the half-life may be of the order of 20-25 days and in the case of a till subsoil, 116 days (Aronson, Citra *et al.* 1999, HSDB 2002). This is probably as a consequence of lower microbial activity in these soils. Under aerobic conditions microbial acclimation times are rapid and are reported to be 11 hours in laboratory scale tests (Packwood and Lerner 1999).

Degradation is slower under anaerobic conditions than under aerobic conditions and acclimation times are longer (ATSDR 1998c, HSDB 2002). A review of biodegradation studies in groundwater (Aronson and Howard 1997) indicates that phenol is degraded under methanogenic, sulphate-reducing, iron-reducing and nitrate-reducing conditions, with a half-life range of 22 to 533 days.

5.5.1. Implication of Behaviour in Soil for Modelling

The evaluative triangle within the introductory chapter shows that phenol is likely to exist mainly in solution within the porewater, with a strong tendency to leach to groundwater. Exposure pathways connected with the use of water would therefore be expected to be significant where they occur. For instance, where there is an on-site source of water, used for washing and/or drinking, this exposure is likely to be more important than direct contact with soil. In addition, phenol may permeate plastic pipes, so that even if there is no on-site source, mains water may become contaminated. The Henry's Law Constant indicates that volatilisation is usually unlikely to be a major pathway, once correction for soil temperature is taken into account. However, volatilisation from dry soils may occur, hence volatilisation from soil should still be included in the modelling process.

Dermal Exposure

The dermal exposure approach for soil currently within the CLEA model described within CLR10 is adapted from USEPA (1992). It requires soil/skin permeability coefficients, either taken directly from experimental work or in the absence of data, derived by estimating a skin permeability coefficient for chemicals in aqueous solution using a relationship between the K_{ow} and molecular weight. The skin permeability coefficient is then adjusted for soil, taking into account the soil matrix parameters and physicochemical properties of the substance. No experimental skin permeability coefficient for phenol in either soil or aqueous solution is provided in the 1992 USEPA review of dermal exposure. However, a value for phenol from aqueous solution of 0.008 cm h^{-1} is predicted and this is currently used within the CLEA model.

It is likely that the dermal algorithm within the CLEA model will shortly be changed to the approach used by USEPA (2001a), (Martin, 2003 Pers. Comm.). USEPA (2001a) stresses that the data for dermal absorption of chemicals from soils is very limited and presents dermal absorption factors from soil for ten chemicals based on well-designed studies, which it states will be added to as further research is conducted. Phenol is not included within the current USEPA list and there does not appear to have been any work suitable for the derivation of dermal absorption factor specific to phenol.

The USEPA (2001a) suggests a default dermal absorption factor (DAF) of 0.1 for semi-volatile organic contaminants (SVOCs) for which there are no experimental studies. However, it is noted (USEPA 2001a) that this default position may not be sufficiently protective of dermal exposure to some SVOCs. The SVOC most similar to phenol for which an experimental dermal absorption factor is provided is pentachlorophenol. The DAF of 0.25 is the highest in the dataset. It is unlikely that a DAF for monohydric phenol would be as high as this because pentachlorophenol is significantly more polar, and has a much higher log K_{ow} in the region of 5 rather than 1.5. However, phenol is a relatively small molecule (MW approximately 94) and is extremely soluble. It is therefore possible that the default DAF of 0.1 may underestimate dermal uptake. This should be made clear in the evaluation of uncertainties within the SGV report for phenol and the risk evaluation accompanying a DQRA.

The CLEA model does not currently include consideration of dermal exposure to contaminated water, either from use of an on-site source of water or from permeation of plastic pipes. However, these may both be significant exposure pathways, where they occur, and should be considered when undertaking a detailed quantitative risk assessment (DQRA).

Inhalation of Dust (derived from contaminated sites)

Currently an enrichment factor is included within the CLEA model for the inhalation of dust pathway (DEFRA and the Environment Agency 2002)[15]. No specific information is available on differential partitioning of phenol to the finer soil fraction. However, the position of phenol on the evaluative triangle suggests that, due to the relatively low log K_{oc} and the relatively high solubility it is more likely to be dissolved within the pore water than sorbed to the surface of the soil particles. It is the recommendation of this report that an enrichment factor is not included within the CLEA model for phenol.

Inhalation of Vapours

As indicated by the evaluative triangle, phenol is more likely to partition to water than air; it is therefore unlikely that inhalation of vapours from soil would be a significant pathway, providing that this partitioning was accounted for. However, there is the potential for volatilisation to occur from dry soils and therefore this pathway should still be evaluated when developing screening criteria. The CLEA model does not currently perform environmental partitioning prior to modelling, and this is one of the reasons why it predicts vapour concentrations which are higher than might be expected. However, it is likely that environmental partitioning will be incorporated into the CLEA model before the derivation of the SGV for phenol is derived (Martin, 2003 Pers. Comm.).

There are insufficient data available in the literature to make specific recommendations for the substance specific calibration of generic vapour models for phenol. The CLEA model does not consider soil degradation processes; as discussed above it is likely that this will occur in the majority of cases. Therefore when undertaking a DQRA, the most appropriate course of action for modelling soil vapour is likely to be to undertake a soil vapour survey, and if this indicates a potential problem, to determine whether *in situ* degradation is occurring and if so at what rate.

The behaviour of phenol means inhalation of groundwater vapours is unlikely to constitute a significant pathway; however it is possible that at sufficiently high concentrations, exposure could occur. Pathways associated with the inhalation of groundwater vapours are not currently included within the CLEA model, but should be considered on a site-specific basis, and included within a DQRA if groundwater could be significantly contaminated.

5.6 Dietary Uptake of Phenol

5.6.1. Uptake by Plants

Phenol is not expected to bioaccumulate significantly (WHO 1994a). Studies have reported its uptake and storage in the cuticle membranes of various plants, including tomatoes and green pepper fruits, and rubber leaves (Schafer and Schönherr 1985). Radio-labelled phenol was demonstrated to be taken up by soybean roots, remaining in the roots and not being

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[15] Enrichment factors are used for coarser soils when there is evidence that contaminants are preferentially sorbed to the finer fraction, which is also likely to adhere to skin and pass into the lung.

transported to the shoots or leaves of the plant. The findings from this study concluded that following its uptake into plant roots, phenol is converted by the plants into a more immobile compound (McFarlane, Pfleeger *et al*. 1987).

Other studies have reported that plants are able to metabolise phenol readily (ATSDR 1998c). Therefore human exposure from eating plants grown in phenol-contaminated soil is probably minimal (ATSDR 1998c). Phenol is unlikely to bioaccumulate, with studies of aquatic organisms indicating rapid elimination of the chemical from the organism (HSDB 2002). A half-life of 3.5 h for phenol has been reported for humans (HSDB 2002). On the basis of the poor persistence of phenol in the environment (ECB 2002) and its rapid elimination from biota, then human exposure through pathways connected with the consumption of food, such as ingestion of poultry, eggs, meat and dairy produce are therefore not predicted to be significant.

5.6.2. Implication of Literature Base for Modelling Plant Uptake

There is a paucity of data on uptake of phenol into plants and no specific studies relating to garden vegetables were found. However, the literature review of uptake into other plants suggests that the phenol does not readily bioaccumulate. A "reality check" may therefore be necessary when assessing the different plant uptake models available.

The Briggs Ryan algorithm, which is described within CLR10, is currently the default approach within the CLEA model; a correction factor is used for phenol because otherwise its high solubility gives rise to results that are improbable in view of the relationship between the phenol content of the soil and the soil solution. The log K_{ow} for phenol is within the log K_{ow} limits by which the algorithm is constrained within the original study by Briggs *et al.* (1982). However, given the possibility that phenol may volatilise, it may be appropriate to consider uptake from air through above ground parts. The Briggs Ryan model does not explicitly include consideration of this pathway. It may therefore be more appropriate to use a fugacity approach, such as the simplified Patterson McKay model, (Paterson and Mackay 1989) or the Trapp and Matthies model (Trapp and Matthies 1995) for this aspect of plant uptake. The simplified Patterson McKay model is currently used within the CalTox model (CalTox 1993) and has been adopted within GasSim (Environment Agency 2002a). The Trapp and Matthies model is used within the German UMS model; (UMS 1997) the EUSES model[16] and has been proposed for the new Dutch human Serious Risk Concentrations (Rikken, Lijzen *et al*. 2001).

Metabolism of the contaminant by the plant is only taken into account by the most sophisticated plant uptake models. However, as discussed above, the literature base indicates that plants readily metabolise phenol. Thus, if a screening approach indicates that plant uptake is likely to be the major exposure pathway, measurement of actual concentrations of phenol in either available produce or produce grown specifically for the purpose in field trials or pot plant studies, is likely to generate higher site-specific assessment criteria.

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[16] Europena Union System for the Evaluation of Substances (1996). Available from European Chemical Bureau (EC/DGXI), Ispra, Italy.

5.7 Key conclusions

5.7.1. Recommendations for Detailed DQRA

The literature base on the environmental behaviour of phenol suggests that, in the majority of cases, it degrades fairly rapidly within soils and is metabolised rapidly by plants. Neither of these observations may be readily incorporated into the derivation of generic assessment criteria. If initial risk assessment suggests that exposure to soils is likely to constitute a risk, it would therefore be appropriate to undertake further DQRA where measured in situ degradation rates, soil vapour levels and plant concentrations were taken into account.

In the environment, phenol partitions mainly to the water compartment. Where there is use of water from an on-site source, or there are plastic pipes used for carrying mains water on site, exposure to phenol from water pathways (particularly by direct ingestion of drinking water and dermal contact when washing) should be included within a DQRA. Where high concentrations are found within groundwater, the potential for inhalation of vapours should also be considered.

Phenol does not appear to bioaccumulate or biomagnify because it is readily metabolised by plants. The literature review also suggests that it may be eliminated from biota. If the results of a DQRA suggest that food pathways other than the consumption of vegetables are a significant source of exposure, it is recommended that analysis of foodstuffs is undertaken.

5.7.2. Recommendations for the CLEA Model

There are insufficient data available in the literature to make specific recommendations for the substance specific calibration of generic vapour models for phenol. It is important to consider partitioning between the water and air compartments within the model to ensure that unrealistic estimates of vapours generated from soil are not produced.

There are insufficient data to replace the plant uptake algorithms within the CLEA model with specific concentration factors. However, given the possibility of volatilisation from dry soils at sufficiently high concentrations, volatilisation may occur, especially within dry soils, it is recommended that an approach to plant uptake modelling is selected which accounts for intake of phenol by the plant from the air in the boundary layer, as discussed in detail above[17] (Environment Agency ongoing).

It is considered that dermal exposure could constitute a significant pathway for phenol. There does not appear to be an appropriate study within the literature to recommend a DAF for phenol according to the revised USEPA 2001 methodology. However, the default DAF for SVOCs of 0.1 advocated by the USEPA approach may be on the low side for phenol,

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[17] The purpose of ongoing Environment Agency report is to carry out an authoritative review of soil-plant models and to collate a set of parameters to undertake generic / screening level modelling as part of a wider assessment of human exposure. The output of this study will recommend specific algorithms to be used in the CLEA model.

because of the small molecule size and high solubility. It is recommended that this should be made clear within the SGV report for phenol.

5.7.3. Summary of Recommended Values

A summary of the values recommended for phenol for use in the CLEA model is provided in Table 5.2.

Table 5.2 **Recommended physicochemical values and parameters for CLEA (CLEA units)**

Value	Mol. weight	Boiling Point	Solubility	Vapour Pressure	Henry's Law Constants (25°C)		
	-	K	G l^{-1}	Pa[^]	Pa-m^3 mol^{-1}	atm-m^3 mol^{-1}	Dimensionless
Recommended	94.11[a]	454.75[a]	84[h] (20°C)	47.59[a] (20°C)	0.040[b]	3.97E-07[b]	1.63E-05[b]

Value	Log K_{ow}	K_{oc}	Coefficient of Diffusion (25°C)		Enthalpy of Vapourisation (454 K)	Critical temp
			Air	Water		
	-	-	M^2 s^{-1}	m^2 s^{-1}	cal mol^{-1}	K
Recommended	1.47[h]	28.8[b]	8.20E-06[e]	9.10E-10[e]	10920[f]	694.2[f]

[^] Conversion factor from mmHg to Pa = multiply by 133.3

[#] Conversion factor from atm-m^3 mol^{-1} to Pa-m^3 mol^{-1} = multiply by 101325; atm-m^3 mol^{-1} to dimensionless = multiply by 41

[a] WHO reported value (WHO 1994a)

[b] USEPA reported value (USEPA 1996a)

[e] data from the ChemDAT8 model database, cited by USEPA (USEPA 1996a)

[f] data from (CRC Handbook 2000-2001)

[h] data from European Chemicals Bureau (ECB 2002)

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7. ABBREVIATIONS

AEAT	AEA Technology
ATSDR	Agency for Toxic Substances and Disease Registry
BaP	Benzo(a)pyrene
BCF	Bioconcentration Factor
BRE	Building Research Establishment
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTX	Benzene, Toluene, Xylene
BUA	Beratergremium für Umweltrelevante Altstoffe (GDCh Advisory Committee on Existing Chemicals of Environmental Relevance
CAS	Chemical Abstracts Service
CLEA	Contaminated LandExposure Assessment model
CLR	Contaminated Land Report
CONCAWE	Conservation of Clean Air and Water in Europe
DAF	Dermal Absorption Factor
DCA	Dichloroethane
DCM	Dichloromethane
DEFRA	Department for Environment, Food and Rural Affairs
DETR	Department of the Environment, Transport, and the Regions (superseded by DEFRA and the Department of Transport, Local Government and the Regions)
Dia	Diffusion in air
Diw	Diffusion in water
DNAPL	Dense Non-Aqueous Phase Liquid
DQRA	Detailed Quantitative Risk Assessment
ECB	European Chemicals Bureau
ECD	Electron Capture Detector
ECSA	European Chlorinated Solvents Association
EHC	Environmental Health Criteria

EPA	Environment Protection Agency (USEPA)
EU	European Union
EUSES	European Union System for the Evaluation of Substances
FDA	(US) Food and Drug Administration
Foc	Fractional soil organic carbon content
FSA	Food Standard Agency
GC	Gas Chromatography
GCMS	Gas Chromatography/Mass Spectrometry
GCS	German Chemical Society
HCFC	Hydrochlorofluorocarbon
HMIP	Her Majesty Inspectorate of Pollution
HPLC	High Performance Liquid Chromatography
HSDB	Hazardous Substances Data Bank
ICRCL	Interdepartmental Committee on Reclamation of Contaminated Land
IEH	Institute for Environment and Health
IUCLID	International Uniform Chemical Information Database
IUPAC	International Union of Pure and Applied Chemistry
K_h	Henry's Law Constant
K_{oc}	Octanol water partition coefficient normalised for the organic carbon content of the soil
K_{ow}	Octanol Water Partition Coefficient
LSC	Liquid Solid Chromatography
MAFF	Ministry of Agriculture, Fisheries and Food (now superseded by DEFRA
MTBE	Methyl tertiary-butyl ether
OC	Organic Carbon
OSW	Office of Solid Waste (U.S.)
PAH	Polyaromatic Hydrocarbon
PCB	Polychlorinated Biphenyl

PCE	Tetrachloroethene
PID	Photoionisation Detector
POP	Persistent Organic Pollutant
QSAR	Quantitative Structure-Activity Relationship
QSPR	Quantitative Structure Property Relationship
RIVM	(Dutch) National Institute for Public Health and the Environment
RMM	Relative Molecular Mass
RPLC	Reversed Phase Liquid Chromatography
RSP	Risk Science Programme
RTI	Research Triangle Institute
SCDM	Superfund Chemical Data Matrix
SGV	Soil Guideline Values
SI (units)	Système International d'unités
SOM	Soil Organic Matter
SRC	Syracuse Research Corporation
SSL	Soil Screening Levels
SVOC	Semi Volatile Organic Compounds
TCA	Trichloroethane
TCE	Trichloroethene
TDS	Total Diet Studies
TGD	Technical Guidance Document
TNO	Netherlands Organisation for Applied Scientific Research
TPHCWG	Total Petroleum Hydrocarbon Working Group
UMN	University of Minnesota
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WHO	World Health Organisation

8. GLOSSARY

Abiotic	Non-living. Usually the physical and chemical components of an organism's environment.
Absorption	The process where a component (for example a chemical) is transferred from the bulk state of one phase into the bulk state of another phase.
Adsorption	The process where constituents are concentrated at the interface of two phases, such as the solid-liquid or gas-liquid boundary.
Advection	A process by which solutes or gaseous constituents are transported, which is caused by the concurrent bulk movement of the solution or gas volume within which they exist.
Ageing of pollutant	As the soil-chemical contact time increases, the bioavailable fraction decreases and the recalcitrant fraction increases. The process is referred to as ‘ageing’ of the pollutant
Aqueous medium	Water-based environment.
Aqueous solubility	The mass of a substance that will dissolve completely in a given volume of water at a specified temperature.
Bioaccumulation	The ability of a chemical to persist in an organism and so be transferred to the next trophic level in the foodchain.
Bioavailability	The fraction of a substance that is accessible to biological processes. Such processes may include degradation by microorganisms or uptake through the skin.
Bioconcentration factor	The ratio of the concentration of a chemical in an organism to the concentration of the chemical in its surrounding environment.
Biodegradation	The breakdown of a chemical by biological processes.
Biomagnification	Increasing concentration of a chemical per unit body weight through the foodchain.
Biosurfactants	Biological compounds able to increase the aqueous solubility of a chemical.
Biota	Collective term to describe living organisms

Biotic	Alive or living.
Boiling point	The temperature at which the saturated vapour pressure of a liquid is equal to the external atmospheric pressure.
Chemical oxidation	The transformation of a substance into a new chemical form, involving combination with oxygen or alternative electron acceptor.
Coefficient of diffusion	A measure of the diffusion of a molecule in a gaseous medium as a result of intermolecular collisions, or in an aqueous medium.
Critical temperature	The temperature below which a gas can be liquefied by applying pressure and above which no amount of pressure is sufficient to bring about liquefaction.
Degradation	The breakdown of a chemical by either biological or non-biological processes.
Diffusion/Diffusive transport	The process by which particles move from an area of higher concentration to an area of lower concentration along a concentration gradient.
Enrichment factors	A factor included in the derivation of SGVs to account for the fact that certain contaminants bind preferentially to the finer fraction of soils, the fraction which is most likely to be inhaled and adhere to skin.
Enthalpy of vapourisation	The energy required to convert 1 mole of a liquid into 1 mole of a gas at a specified temperature and pressure (also called the latent heat of vapourisation).
Generic assessment criteria	Criteria derived and published by an authoritative body which take into account generic assumptions about the characteristics of contaminants, pathways and receptors and which are designed to be protective in a range of defined conditions.
Health Criteria Values	A summary term for benchmark criteria that represent an assessment of levels of exposure that pose a risk to human health, for example tolerable daily intake (TDI) and Index Dose.
Henry's Law Constant	The ratio of the partial pressure of a gas above a liquid to its solubility in that liquid at constant temperature and pressure; a measure of its partition between the gas phase and the solute phase.

Hydrolysis	A chemical reaction in which water is used to break down a compound.
Hydrophilic	Literally 'water-loving'. Describes the character of a molecule which has an affinity for water and therefore high aqueous solubility.
Hydrophobic	Literally 'water-hating', hydrophobic describes compounds with a low aqueous solubility that are more fat soluble.
Index dose	The dose that can be considered to present a minimal risk from exposure to soil contaminants. However, and in addition, efforts are still needed to reduce exposures from all routes to as low as reasonably practicable (ALARP), so that even this minimal risk is further diminished.
Lipophilicity	Literally 'fat-loving', lipophilicity describes compounds with a high solubility in fat and low aqueous solubility.
Molecular weight	The sum of the relative atomic masses of the constituent atoms of a molecule.
Organic carbon partition coefficient (K_{oc})	The tendency of a compound to be adsorbed onto the organic carbon within the soil i.e. the partitioning of the solute between soil water (l) and organic carbon (kg)
Octanol water partition coefficient (K_{ow})	The ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. Octanol is an organic solvent that is used as a surrogate for natural organic matter
Octanol-air partition coefficient (K_{oa})	The ratio of the concentration of a chemical in octanol and in air at equilibrium and at a specified temperature. This is sometimes used as surrogate for the partitioning between atmosphere and leaf surfaces.
Partial pressure	The pressure that a component, X, of a gas mixture would exhibit if X alone occupied the total volume of the mixture, at the temperature of the mixture.
Pathway	The means by which a hazardous substance or agent comes into contact with, or otherwise affects a receptor.
Photolysis	The decomposition of a substance into simpler units as a result of its absorbing light of the appropriate wavelength.

Photo-oxidation	Oxidation of a substance as a result of its exposure to light of the appropriate wavelength.
Recalcitrant	Used to describe a compound that is resistant to degradation processes.
Receptor	The entity (human, animal, water, vegetation, building services etc.) that is vulnerable to the adverse effects of the hazardous substance or agent. May also be called the “target”.
Rhizosphere	The area of soil around a plant’s roots characterised by high numbers of microorganisms.
Saturated vapour concentration	The concentration of a substance at its (saturated) vapour pressure.
Screening	A general process by which generic approaches with a range of broad assumptions are used to generate approximate values in order to ‘screen out’ non-significant issues.
Soil Guideline Values	The concentration of a substance in soil where predicted exposure for each standard land-use is less than or equals the Health Criteria Value.
Soil Organic Matter	Fraction of the soil composed of organic matter. Consists of plant and animal remains in variable stages of decomposition, root and microbial exudates and humus (well-decomposed organic material).
Solute	A substance that is dissolved in a solvent. One of the two parts (along with solvent) which make up a solution.
Sorption	Describes either an absorptive or adsorptive process. Term may be used where the exact process is not known.
Source	The hazardous substance/agent or activity/process that releases that substance.
Tolerable Daily Intake	An estimate of the average daily intake of a contaminant, expressed in terms of µg per day, that can be ingested over a lifetime without appreciable heath risk.

Toxicity	Adverse effects of a substance on a living organism defined with reference to the quantity of substance administered or absorbed, the way in which the substance is administered (inhalation, ingestion, dermal) and distributed in time (single or repeated doses), the type and severity of injury, the time needed to produce the injury, the nature of the organism(s) affected, and other relevant conditions. A toxic substance is defined as material causing injury to living organisms as a result of physicochemical interactions.
Vapour pressure	The pressure exerted by a saturated vapour in equilibrium with its condensed phase at a specified temperature.