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Evaluation of models for predicting plant uptake of chemicals from soil

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Executive summary

The Contaminated Land Exposure Assessment (CLEA) model is used by the Environment Agency to derive Soil Guideline Values for the protection of human health from chronic exposure to chemicals in soil. One potentially important route of human exposure is from the consumption of homegrown produce such as fruit and vegetables. Critical to assessing exposure via this pathway is the estimation of the amount of chemical taken up by the plant from soil during growth and prior to harvesting.

As part of an ongoing evaluation of the science that underpins the CLEA model, the Environment Agency decided to review research on screening approaches to plant uptake of organic chemicals from soil. Several researchers have proposed uptake models including Briggs et al. (1982, 1983), Chiou et al. (2001), Hung and Mackay (1997), Ryan et al. (1988), Topp et al. (1986), Trapp and Matthies (1995), and Travis and Arms (1988). The aim of this review was to evaluate the performance of these models in assessing the risks posed by contaminated land, and compare these against experimental data for vegetables and pollutants from the scientific literature.

The study was divided into several phases of work. An initial literature review was carried out to identify case studies and numerical modelling approaches, and to establish our current understanding of the processes of plant uptake and translocation, along with key influencing factors. Based on the available literature, six models were chosen for comparison with five different sets of experimental data. The case studies included common garden vegetables such as cabbage, carrot and lettuce and a range of chemical pollutants including chlorobenzenes and polycyclic aromatic hydrocarbons (PAHs).

Of the six models tested, the majority over-predicted root concentrations by at least one order of magnitude. This is consistent with the findings of a review sponsored by the Danish Environmental Protection Agency (Samsøe-Petersen et al., 2003). The trend was more confused for predictions of shoot concentration, with some models tending to over-predict, some to under-predict, while others gave mixed results depending on circumstances. Performance was not related to model complexity, where the simple empirical models were as effective as the multiple compartment models.

While the results of this study provide a useful insight into the modelling of plant uptake processes for organic chemicals, it is clear that the exercise should be undertaken more widely with a far greater number of case studies. Many plant uptake models have been poorly validated, with limited supporting studies under a range of different soil and plant conditions. More complex models often require careful parameterisation, but there is little data to support such choices beyond the original scientific paper cited in their derivation. This may be one reason why the simple regression models perform as well as the dynamic and multiple-compartment models, because they are based on a broader range of chemical data. In general, the literature is limited by the availability of good quality experimental data for a broad range of organic industrial chemicals.

The existing approach in the CLEA model is a contaminant-specific approach, where the available literature on uptake is reviewed in order to estimate the soil-to-plant concentration factor. According to Briggs et al. (1982, 1983) and Ryan et al. (1988), it gives reasonable estimates of shoot concentration but performs poorly for root concentrations. While supporting the continued use of a chemical-specific approach, this review recommends that the Environment Agency evaluate several plant-specific models including those for carrots, potatoes and tree fruits, because of their importance to consumers of homegrown produce (Samsøe-Petersen et al., 2003; Trapp et al. 2003; Trapp 2002).
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1 Introduction

1.1 Background

The Contaminated Land Exposure Assessment (CLEA) model assesses the risks to health from exposure to contaminated soil by adults and children living, working and playing on different types of land (Defra and Environment Agency 2002). It is used by the Environment Agency in the derivation of Soil Guideline Values (SGV), that is, generic assessment criteria used for the protection of human health from chronic exposure to chemicals in soil. One potentially important route of human exposure is from consumption of homegrown produce such as fruit and vegetables\(^1\) that are cultivated in contaminated soils.

A critical part of predicting human exposure via this pathway is the estimation of the amount of chemical taken up by the plant from soil during its growth and prior to harvesting. The CLEA model currently uses the approach of Briggs et al. (1982 and 1983) to predict the root and shoot plant concentrations from polluted soils (Defra and Environment Agency, 2002). This model has only been validated against chemicals with log \(K_{OW}\) values between -1 and 5, where key industrial chemicals lie outside this range (including dioxins and four- and five-ring polycyclic aromatic hydrocarbons or PAHs). It is also limited conceptually to chemical uptake through the root system as part of passive transpiration (Briggs et al., 1982, 1983). Recent studies have highlighted the need to consider other more direct routes to contamination of above-ground plant parts such as leaves and fruits, for example from soil splash or air exchange.

As part of an ongoing evaluation of the science that underpins the CLEA model, the Environment Agency considered it timely to review research on screening approaches to plant uptake from soil. Since the mid-1990s, several researchers have proposed alternative uptake models including Trapp and Matthies (1995), Dowdy and McKone (1997), Hung and Mackay (1997), and Chiou et al. (2001). The aim of this review was therefore to re-evaluate whether the Briggs et al. approach remains the most appropriate algorithm to use for the derivation of Soil Guideline Values, in the light of more recent work.

1.2 Methodology and report overview

The project was divided into several phases of work. Initially, an extensive literature review was carried out to identify case studies and numerical modelling approaches, and to establish general scientific understanding of the process of plant uptake and translocation, along with key influencing factors. This review focused primarily on the literature published in scientific journals, particularly for research areas where there have been advances since Briggs et al. (1982, 1983) and Ryan et al. (1988), such as aerial deposition.

Based on the available literature and the project aims, several modelling approaches were selected for more detailed consideration. These models included Briggs et al.

\(^1\) Currently, the CLEA model is limited to the following common vegetables: Brussels sprouts, cabbage, carrot, leafy salads, onions, leeks, shallots, and potatoes.
(1982, 1983), Chiou et al. (2001), Hung and Mackay (1997), Ryan et al. (1988), Topp et al. (1986), Trapp and Matthies (1995), and Travis and Arms (1988). Several of these models have been used in contaminated land risk assessment and in wider risk screening of chemicals in the environment. These models were translated on to an Excel worksheet and compared with experimental case studies from the scientific literature. Five case studies were chosen based on research quality, relevance of crops and chemicals to CLEA, and consideration of a range of soil organic carbon content, which is known to influence uptake.

The report consists of the following chapters:

Chapter 1 Provides an overview of this study

Chapter 2 Introduces the science of soil-plant interactions and the factors that influence plant uptake and accumulation of organic chemicals

Chapter 3 Summarises the six generic models chosen for comparative analysis within this study and provides an overview of the selection process itself

Chapter 4 Summarises the five experimental studies used to evaluate the performance of the generic models and includes a discussion of the case studies found in the wider literature

Chapter 5 Describes the results of the model comparison study

Chapter 6 Provides conclusions and makes recommendations for further work and the approach to modelling uptake in the CLEA model
2 Uptake processes

This chapter provides an introduction to soil-plant interactions and the factors that influence plant uptake and accumulation of organic chemicals. There are four principal uptake pathways, as illustrated in Figure 2-1. These pathways include passive and active uptake through the root system, gaseous and particulate deposition to above-ground shoots, and direct contact between soil and plant tissues. In addition to describing each pathway, this chapter also considers the controlling factors for uptake and the ways these can be used to model such uptake processes.

Figure 2-1: Principal pathways for plant uptake of organic chemicals

2.1 Root uptake

2.1.1 Soil-root interactions

In general, plant roots are the most important site for uptake of chemicals from soil (Bell, 1992). Root systems have been shown to take up organic chemicals from both water and air. In general, this uptake process has been shown to involve passive and diffusive transport, with chemicals carried into the plant during the natural transpiration cycle. Active uptake has been shown for a few organic chemicals including the phenoxy acid herbicides (Bromilow and Chamberlain, 1995).

Experiments on the uptake of non-ionised chemicals from a hydroponic solution showed that uptake consisted of two stages (Briggs et al., 1983). Firstly, equilibration between the chemical concentration in the aqueous phase within the plant root and the external solution, and secondly, chemical sorption on to lipophilic root solids. These
solids include lipids in membranes and cell walls (Mackay, 2001). Briggs et al. (1983) adopted the earlier definition of Shone and Wood (1977) in defining the root concentration factor (RCF) as the ratio of chemical concentration in the root to the concentration found in an external solution.

Lipophilic organic chemicals possess a greater tendency to partition into plant root lipids than hydrophilic chemicals. Polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes, polychlorinated biphenyl (PCBs), and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) have all been found at elevated levels in plant roots (Duarte-Davidson and Jones, 1996; Wild and Jones, 1992).

Briggs et al. (1983) found a linear relationship between the octanol-water partition coefficient ($K_{\text{OW}}$) of non-ionised chemicals and the observed root concentration factor, based on experiments using O-methylcarbamoyloximes and substituted phenylureas and their uptake by barley plants (Figure 2-2).\(^2\) Wild et al. (1992) categorised non-ionised organic chemicals with $\log K_{\text{OW}} > 4$ as having a high potential for retention in plant roots. Conversely, Cousins and Mackay (2001) suggested that for organic chemicals with $\log K_{\text{OW}} < 2$ and a Henry’s Law constant ($H$) of less than 100 cm\(^3\) cm\(^{-3}\), the plant aqueous phase was the most important storage compartment.

Although chemical properties are important predictors of uptake potential, the physiology and composition of the plant root itself is also a significant influence. Trapp and Pussemier (1991) found that the relationship derived by Briggs et al. (1983) appeared to overestimate uptake of organic carbamates by the common bean plant. One explanation for such differences in uptake potential is the varying types and amounts of lipids in root cells (Bromilow and Chamberlain, 1995). However, the available data across a range of plant species is limited.

Figure 2-2: Relationship between the octanol-water partition coefficient ($K_{\text{OW}}$) and the root concentration factor in studies by Briggs et al. (1983)

Environmental scientists often use the octanol-water partition coefficient ($K_{\text{OW}}$) as a surrogate for chemical lipophilic tendency (see also Section 3.8.1).
Chemical transfers from the soil into the root are primarily mediated by the uptake of soil porewater during plant transpiration. Therefore, the factors that influence the chemical concentration in porewater also exert control over the passive uptake process. Organic chemicals can be sorbed or bound to several components in soil including clays, iron oxides, and organic matter, although it is the latter that usually exerts the strongest influence on the porewater concentration. Several researchers including Karickhoff (1981) have found empirical relationships between a chemical’s lipophilicity and its affinity to sorb to soil organic matter.

In principle, as the organic matter content of a soil increases (typically measured using the weight fraction of organic carbon present), so the proportion of the chemical in the porewater decreases. This impact on plant uptake is illustrated in Figure 2-3 using the modelling approach of Ryan et al. (1988). As the weight fraction of soil organic carbon increases, so the total amount of chemical taken up by the root decreases. In addition, the optimum chemical lipophilicity for root uptake decreases, reflecting the increase in competitive sorption between plant lipids and soil organic carbon. Several models described in Chapter 3 use the fraction of organic carbon as a key variable in the prediction of the uptake of contaminants by plants.

Figure 2-3: Influence of the weight fraction of organic carbon in soil ($f_{oc}$) on the predicted root concentration factor using the model of Ryan et al. (1988)

![Figure 2-3: Influence of the weight fraction of organic carbon in soil ($f_{oc}$) on the predicted root concentration factor using the model of Ryan et al. (1988)](image)

2.1.2 Transfer from roots to other plant parts

Although the root is the most important site for chemical entry from soil, the edible fractions for many plants are the stems, leaves, tubers and fruits, and only if a chemical accumulates in these parts is there a potential risk to human health.³ The transport of water within the plant, which is also the major mechanism for movement of nutrients and energy-rich photosynthate, is known as translocation (Bell, 1992). It is also the principle route by which contaminants move from the root system to stems, leaves, and

³ Tubers, such as potatoes, are morphologically stems, and although they reside underground and are often exposed to direct contact with soil, they function as stems (McFarlane, 1995).
storage organs (McFarlane, 1995). The plant vascular system includes the xylem and the phloem.

Water and solutes are transported upward from the root into other plant parts through the xylem by mass flow resulting from a pressure gradient. This driving force is created during transpiration, where water is drawn in through the root system to replace evaporative losses from stomata within the leaves, and is supplemented by capillary action (McFarlane, 1995). In order for chemicals taken up into plant roots to reach the xylem, they must penetrate a number of plant tissues: the epidermis, cortex, endodermis and pericycle (see Figure 2-4). At the endodermis the chemical must pass through at least one cell membrane, and it is the combination of their aqueous solubility and their solubility in the lipid-rich cell membrane that determines their potential movement into roots and subsequent transport to other plant parts.

Briggs et al. (1983) derived an empirical relationship for predicting chemical concentration in the xylem transpiration stream from its concentration in external aqueous solution, based on experiments investigating the uptake of non-ionised chemicals into barley plants. They adopted the earlier definition of Shone and Wood (1977) in defining the transpiration stream concentration factor (TSCF) as the ratio of chemical concentration in the transpiration stream to the concentration found in an external solution. Briggs et al. (1983) found that the TSCF could be predicted from knowledge of a chemical’s lipophilicity, with maximum uptake at a log $K_{ow}$ of about 1.8. In a study of plant uptake of chlorophenols, Duarte-Davidson and Jones (1996) observed a similar effect, with those compounds with a log $K_{ow}$ values between 2.15 and 3.62 having the highest potential for root uptake and translocation. Further studies by Hsu et al. (1990) and Burken and Schnoor (1998) reported similar relationships for soybean plants and hybrid poplar respectively with a range of industrial chemicals. These relationships between the transpiration stream concentration and chemical lipophilicity are summarised in Figure 2-5.

Figure 2-4: Root structure showing the plant tissues controlling uptake of organic chemicals (after Salisbury and Ross, 1985)
Figure 2-5: Variation in predicted TSCF with chemical octanol-water partition coefficient (Briggs et al., 1982; Burken and Schnoor, 1998; Hsu et al., 1990)

Figure 2-5 shows that these TSCF relationships all suggest an uptake maximum between high and low log K<sub>OW</sub> values (in the range two to four depending on the individual relationship). Bromilow and Chamberlain (1995) suggested that uptake potential was a balance between on the one side, reduced potential for the less lipophilic or polar chemicals to cross cell membranes and on the other, by the more lipophilic chemicals being retained by lipids in the endodermis. However, the exact reasons are not fully understood.

While the direction of flow within the xylem is generally from the root to the shoot, movement within the phloem can be up or down. The primary role of the phloem is to carry sucrose formed by photosynthesis in the leaves to storage areas including fruits and tubers, where it is converted to starches and complex sugars. Although there are several theories on what drives this flow, McFarlane (1995) suggests it is a result of osmotic potential along the phloem between the sugar source and sink regions. In mature plants, the phloem flows away from the leaves where photosynthesis results in a build-up of sugars. However, when the plant is under stress the direction may be reversed and materials stored in fruits, tubers and other plant tissues may be needed, changing the direction of phloem flow.

Bromilow and Chamberlain (1995) noted that the xylem has a much greater flow volume compared to the phloem (between 50 and 100-fold). Non-ionised chemicals of intermediate cell permeability such as the pesticides oxamyl and aldoxycarb (with log K<sub>ow</sub> values of −0.47 and −0.57 respectively) show some degree of phloem movement. This is because they enter at areas of high chemical concentration but are too polar to move out of the phloem readily (Bromilow and Chamberlain, 1995). The phloem may also be an important transport mechanism for ionisable organic chemicals because of the ion-trapping effect (see Section 2.1.3).

After vascular transport, water and solutes diffuse laterally into adjacent tissues and may become concentrated in plant shoots, tubers and fruits (McFarlane, 1995). This is a two-step process beginning with equilibrium partitioning between water in the vascular system and the aqueous solution in cell tissues, followed by sorption to cell walls. Briggs et al. (1983) and Barak et al. (1983) showed that partitioning to plant stems is linearly proportional to chemical lipophilicity for non-ionised organic chemicals.
Therefore, the lipid composition of above-ground plant tissues is likely to be an important factor determining chemical retention and accumulation.

As noted in Section 2.1.1, chemical transfers from the soil into plants are strongly influenced by chemical concentration in the soil porewater. As the organic matter content of a soil increases (typically measured using the weight fraction of organic carbon present), so the proportion of the chemical in the porewater decreases. This impact on the shoot concentration factor is illustrated in Figure 2-6 using the modelling approach of Ryan et al. (1988). As the weight fraction of soil organic carbon increases, so the total amount of chemical taken up by the shoot decreases. In addition, the optimum chemical lipophilicity for uptake decreases, reflecting the increase in competitive sorption between plant lipids and soil organic carbon.

Figure 2-6: Influence of the weight fraction of organic carbon in soil ($f_{oc}$) on the shoot concentration factor modelled by Ryan et al. (1988)

![Graph showing the influence of $f_{oc}$ on shoot concentration factor](image)

2.1.3 Soil-root interactions for ionic chemicals

The previous discussion has focused on neutral organic chemicals, that is, compounds that do not appreciably ionise under ambient soil and plant solution conditions. Most industrial chemicals do not ionise readily in the subsurface. However, chemicals such as amines, carboxylic acids, phenols (including chloro- and nitrophenols), and some pesticides may appreciably ionise under ambient soil conditions (US EPA, 1996). Although uptake of electrolytes into plants has been extensively studied, there are few predictive models available because of the additional complexity required to understand such systems (Trapp, 2000 and 2003).

Most ionisable organic chemicals are described as weak acids or weak bases by their potential to dissociate into ions in aqueous solution (McFarlane, 1995). The extent of ionisation of a weak acid can be estimated using Equation 2-1, where both the solution pH and the acid dissociation constant ($pK_a$) of the chemical are known (US EPA, 1996). For example, at a solution pH of 7, phenol ($pK_a$ of 9.9) is only 0.2 per cent ionised while pentachlorophenol ($pK_a$ of 4.7) is over 99 per cent ionised.
Equation 2-1

\[
\Phi_{n,\text{acid}} = \frac{[HA]}{[A^-]} = \left(1 + 10^{pH - pK_a}\right)^{-1}
\]

where

- \(\Phi_{n,\text{acid}}\) is the fraction of neutral species present for organic acids (dimensionless)
- \([HA]\) is the equilibrium concentration of organic acid (mol L\(^{-1}\))
- \([A^-]\) is the equilibrium concentration of the organic anion (mol L\(^{-1}\))
- \(pH\) is the acidity of the aqueous solution (unitless)
- \(pK_a\) is the acid dissociation constant of the chemical (unitless)

As noted previously, the xylem is the principal plant structure for the transport of water and chemicals to the shoot (see Section 2.1.2). Chemicals penetrating into the plant root system and the xylem must pass through one or more cell membranes. These membranes and cellular compartments are illustrated in Figure 2-7. Cell membranes contain proteins known as “proton pumps” that regulate the flow of charged ions from inside to outside the cell (and \textit{vice versa}). This creates an electrochemical gradient that acts as a kind of battery or reservoir of stored energy for the cell.

The movement of ions across an electrically charged membrane is driven by chemical and electrical potential and is generally described by the Nernst-Planck equation (Trapp, 2003). Since the chemical environment within a cell may vary from the external solution, the degree of dissociation may increase or decrease within plant compartments. For example, a compound that is predominantly in a neutral form in a slightly acidic soil solution may dissociate in the mildly alkaline conditions of the cell cytoplasm (Bromilow and Chamberlain, 1995; Trapp, 2003). These ionised molecules may subsequently be unable to pass through the charged cell membrane and become trapped within the cell (the “ion trap effect”). This can lead to the strong phloem transport of weak acids (Trapp, 2003).

Figure 2-7: Soil-plant systems and uptake processes for a weak organic base (from Trapp, 2003)
It is therefore critical that in assessing uptake of weak organic acids and bases that models consider not only the partitioning behaviour of lipophilic compounds between water and cellular lipids, but also the degree to which they are partitioned into ionic and non-ionic forms within cell compartments (Trapp, 2003). Bromilow and Chamberlain (1995) attempted to classify uptake potential for organic chemicals based on both their ionisation potential (as defined by $pK_a$) and their lipophilic tendency (as defined by $K_{ow}$). This is illustrated in Figure 2-8. Most industrial chemicals have a $log K_{ow}$ between two and six and according to Figure 2-8, would only be xylem mobile. Phloem mobility is unlikely to be significant for root uptake of most industrial chemicals, but will be important for the foliar uptake of hydrophilic and readily ionised chemicals such as certain amines, phenols, pesticides and herbicides.

There is a big difference between our understanding of plant uptake of neutral organic compounds and that of weak electrolytes (Trapp, 2003). All of the models described in Chapter 3 apply only to neutral organic chemicals. Trapp (2003) concluded that there remain considerable gaps in our knowledge about the uptake of ionic organic compounds, including the measurement and prediction of their cell membrane permeabilities and the effect of ionic complexation processes.

Figure 2-8: Relationship between the acid dissociation coefficient ($pK_a$), lipophilicity ($log K_{ow}$) and phloem and xylem mobility (after Bromilow and Chamberlain, 1995)
2.2 Leaf uptake

2.2.1 Vapour or gas uptake from ambient air

In addition to the root system, another potential pathway for plant uptake is the absorption of chemical vapour from ambient air by shoots during respiration (Bell, 1992). This pathway differs from root uptake because it is mediated via gaseous exchange rather than through aqueous solution. As a result, this pathway is likely to be important not just for highly volatile pollutants but those with a strong preference to partition to air rather than water (Bell, 1992). This has been shown to be the main uptake pathway into above ground plant parts for a variety of organic chemicals, including PAHs (Simonich and Hites, 1994; Nakajima et al., 1995), PCBs (Bohme et al., 1999) and tetra- and hexa-chlorinated PCDD/Fs (Welsch-Pausch et al., 1995; Meneses et al., 2002).

Leaf physiology is illustrated in Figure 2-9. Chemicals enter the leaf by either crossing the cuticle (a waxy coating that covers the outer leaf) or by entering directly through the stomata, which regulate the exchange of carbon dioxide and oxygen (McCready, 1994; Bacci et al., 1992). It is also the principal route by which water vapour from the transpiration stream is lost by the plant.

After entering the leaf, chemicals diffuse into intercellular air spaces and partition to the aqueous and lipophilic phases of adjacent plant tissues. Lipophilic leaf tissues include interior lipids, such as membrane and storage lipids, resins and essential oils, and surface lipids, such as cutin and cuticular waxes (Riederer, 1995). Topp et al. (1986) concluded that since substances absorbed by leaves must have passed through a cell wall covered by a cuticle, the process of penetration may be somewhat different from that of absorption by root cells. For cuticle penetration, cutin and wax composition are probably more important than thickness, with surface wax concentration correlated with resistance to foliar absorption (Topp et al., 1986).

Figure 2-9: Schematic cross-section of leaf structure
Tolls and McLachlan (1994) and Hauk et al. (1994) have suggested that, in terms of the storage of organic chemicals, plant leaves can be divided into two compartments: a relatively small surface compartment with rapid uptake and clearance kinetics, and a larger reservoir compartment with relatively slow chemical migration. The composition of the larger reservoir is believed to influence the retention of organic chemicals, but the physiological relationship between the two compartments has not been established.

Air-to-plant concentration factors for a variety of organic chemicals have been estimated by empirical studies (Bacci and Gaggi, 1986 and 1987; Bacci et al., 1990a and 1990b). Various studies have reported a good correlation between shoot uptake and chemical properties including the octanol-water partition coefficient ($K_{ow}$), Henry’s Law constant, molecular weight and the octanol-air partition coefficient (Paterson et al., 1991; Ryan et al., 1988; Tolls and McLachlan, 1994; Topp et al., 1986; and Komp and McLachlan, 1997).

Riederer (1990) developed a fugacity-based model to describe the partitioning of organic gases between the atmosphere and leaf. In this theoretical approach, the leaf was viewed as consisting of four well-mixed phases: an air phase, a water phase, a lipid phase, and a non-lipid phase that does not participate in the partitioning process (Polder et al., 1997). In the steady-state condition, Riederer (1990) defined the partitioning of a chemical between leaf and air ($K_{la}$) as a function of chemical lipophilicity and its partitioning between air and water. Trapp and Matthies (1995) built on the steady-state approach by accounting for the kinetics of uptake, including the impact of elimination processes and dilution by growth.

McLachlan (1999) used knowledge of the partitioning behaviour of organic chemicals to build an interpretative framework to identify those compounds most likely to be dominated by foliar uptake (see Figure 2-10). Gaseous uptake will be the primary pathway for chemicals with an octanol-air partition coefficient ($\log K_{oa}$) less than 11, although between $\log K_{oa}$ of 8.5 to 11 this process will be kinetically limited.4

Figure 2-10: Relationship between the octanol-air partition coefficient and uptake process for organic chemicals in the atmosphere (McLachlan, 1999).

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4 The plant will not come into contact with enough air for it to become saturated with the chemical and will not approach equilibrium.
2.2.2 Particulate deposition on plant surfaces

Organic chemicals bound to soil particles may be deposited on above-ground leaves and shoots as a result of wind resuspension or rain splash, and is a well-recognised phenomenon for metals and radionuclides (Smith and Jones, 2000; Thorne et al., 2004). Kao and Venkatarana (1995) found that after taking into account the relatively high deposition velocity of soil particles, local soils accounted for 70 to 90 per cent and 20 to 40 per cent of total PCDD/F deposition in urban and rural areas respectively.

Hulster and Marschner (1993) found that direct contact between soil particles and plant surfaces was a significant uptake pathway for PCDD/Fs in hay. Nakajima et al. (1995) investigated the uptake of PAHs from the atmosphere into Azalea leaves and suggested that for benzo(a)pyrene and perylene, dry deposition of suspended particles with subsequent permeation into the cuticle represents the major pathway of contamination. Welsch-Paulsch et al. (1995) also determined that the dry deposition of large particles represented an important uptake pathway for hepta- and octo-chlorinated PCDDs into grass leaves.

Although the processes of wet and dry deposition of dust particles are similar for both organic and inorganic contaminants, there are also likely to be important differences (McLachlan, 1999); for example, the size and type of particles on which inorganic and organic chemicals are preferentially sorbed.

Wet deposition is the process of gravitational coagulation of solid particles with water droplets. It is thought to be the dominant deposition mechanism for organic chemicals with Henry’s Law constant of less than $1 \times 10^{-6}$, although the majority of particles will not be intercepted by vegetation and will return directly to the soil (Cousins and Mackay, 2001). Relatively little information is available on the wet deposition of particle-bound and gaseous phase organic chemicals to plant surfaces, and this pathway is seldom considered when looking at the contamination of vegetation (Smith and Jones, 2000). Dry deposition of particles to plant surfaces involves diffusion, interception, impaction and sedimentation processes (Chamberlain, 1991). Once particles have been deposited on plant foliage they are subject to removal and degradation.

Above-ground plant parts may become contaminated with organic chemicals via pathways involving direct contact between soil particles and plant surfaces, and chemicals retained on plant surfaces may subsequently be taken up into or through the plant cuticle (Riederer, 1995). Small particle-bound compounds may be taken up via the stomata, but the stomatal entry route will generally only be significant for chemicals present in air in the gaseous phase (Smith and Jones, 2000). The most likely transfer pathway is through physical contact between the particle and the waxy leaf surface, where chemical transfer occurs via diffusion. Organic chemicals entering the plant cuticle become adsorbed to lipophilic tissues or permeate into the leaf interior (Riederer, 1995).

There is currently insufficient understanding of this process and in particular, of how the physicochemical properties of organic compounds influence transfer from particles into the leaf. Dreicer et al. (1984) investigated the rain splash pathway for tomato plants and found that only finer soil particles were retained on plant surfaces. The octanol-air partition coefficient ($K_{oa}$) has been suggested as a suitable indicator of the significance of the dry deposition contamination pathway for semi-volatile organic chemicals (McLachlan, 1999). Cousins and Mackay (2001) suggested that for chemicals with a log $K_{oa}$ greater than nine, particle-bound deposition becomes relatively more important than gaseous deposition. Rikken et al. (2001) observed that differences between predicted uptake using the Trapp and Matthies (1995) model and experimental data were reduced when soil resuspension was accounted for in the comparison.
Particulate deposition may also represent a source of chemical contamination of plants through inadvertent soil ingestion, where the soil material may not completely washed from the surface of leaves, fruits and tubers before cooking and consumption (Defra and Environment Agency, 2002). In reviewing the limited literature, NRPB (1995) commented that only in exceptional circumstances would soil loading be as much as 0.1 per cent on a dry weight basis.

2.3 Plant species and its influence on uptake

Not surprisingly, plant uptake varies considerably between types of plant and individual species (Bell, 1992). Factors likely to influence uptake include root growth and depth, transpiration rate, active uptake mechanisms, growth period, location of fruits and tubers, and the size and shape of leafy foliage (Buckley, 1982).

2.3.1 Active uptake

Hulster et al. (1994) found that courgette and pumpkin plants accumulated and translocated higher concentrations of PCDD/Fs from contaminated soil than other fruits and vegetables, and that this was the main contamination pathway for these species. Higher accumulation in the courgette and pumpkin family has been reported by other workers (Mattina et al., 2002; White, 2002). The authors postulated that this was due to root exudates, unique to these species, which actively mobilise PCDD/Fs from the soil and make these compounds available for uptake and translocation.

2.3.2 Lipid composition

Certain plant species, including carrots, are assumed to have high lipid contents along with the presence of oil channels (Bell, 1992; Topp et al., 1986). Experimental results have shown that carrots possess a greater potential to take up non-ionised chemicals than other crop species (Smelt et al., 1974; O’Connor et al., 1990; Schroll and Scheunert, 1992). Since lipophilic chemicals will tend to partition to leaf lipids, differences in the lipid content of plant foliage would seem to explain interspecies variability in organic chemical concentrations in plant foliage (Buckley, 1982). Simonich and Hites (1994) found that interspecies variability was reduced in an experimental study of PAH uptake by normalising data to leaf lipid contents. In contrast, Bohme et al. (1999) found that interspecies variability in leaf/air bioconcentration factors could not be explained by variability in extractable lipid contents, and that lipid quality was also an important factor. For foliar uptake models, such as that of Muller et al. (1994), the leaf lipid content represents the most sensitive plant characteristic for lipophilic chemicals.

2.3.3 Foliage

Several researchers have also found that the exposed surface area of the plant foliage influences the foliar uptake rate for a variety of species (McCrady and Maggard, 1993; Schreiber and Schönherr, 1992). Simonich and Hites (1995) suggested that this plant characteristic would be particularly significant if chemical partitioning to foliage did not approach equilibrium. Riederer (1995) reported two orders of magnitude difference in the permeability of plant cuticles for different species. For chemicals that penetrate the
cuticle to the leaf interior, the leaf lipid content and quality will also affect the extent of accumulation.

Significant differences between plant species have been observed in mass loadings of soil-to-plant surfaces, as a result of contact with soil particles (Smith and Jones, 2000). Plant characteristics that affect the rate of particle deposition and retention include the exposed surface area of the foliage and the presence or absence of leaf hairs. Little and Wiffen (1977) observed that rough or hairy leaf surfaces were more efficient at collecting aerosols than smooth surfaces, explained by the increased surface area and projection of roughness elements through the leaf-air boundary layer. Pinder et al. (1991) found that the largest soil loadings occurred on broad-leaved species growing close to the ground.

Plant transpiration will move some chemicals to sub-stomatal tissues within leaves, from which they will subsequently be lost by volatilisation (McFarlane and Fleeger, 1990). Volatilisation is likely to be a significant transport pathway for chemicals with high water solubility and vapour pressure. This pathway was found to be significant for benzene by Collins et al. (2000), but has not been widely reported.

Leaf loss and senescence can lead to the transfer of chemicals from plant foliage to the surrounding soil, thus reducing the chemical concentration in foliage. However, edible plant parts are likely to be harvested before leaf loss and senescence become significant chemical transport pathways.

### 2.3.4 Plant metabolism

Chemicals accumulated in plants may be metabolised, thus reducing their concentration within the plant's tissues. Although considerable research has been carried out on the metabolism of pesticides, only in recent years has there been any interest in industrial chemicals (Bell, 1992). Plant metabolism has been reported for a small number of such chemicals, including benzo[a]pyrene, trichloroethylene and benzene (Brady et al., 2003; Shang and Gordon, 2002; Ugrekhelidze et al., 1997). Metabolic processes and rates will be specific to particular chemicals and possibly plant species.

### 2.3.5 Growth dilution

Plant growth has been recognised as an important variable in the plant uptake of radionuclides by root uptake and aerial deposition (Thorne et al., 2004). Over the growing season the biomass of plant increases, diluting the chemical concentration within plant tissues relative to the flux of chemical uptake, and increasing the above-ground canopy for interception of aerial deposition. Plant growth has been simulated using models based on simple first-order exponential increases (assuming a time to doubling of biomass), and through more complex functions based on a power law estimated from observed behaviour (Samsøe-Petersen et al., 2003; Thorne et al., 2004).

The importance of growth dilution has been recognised in several dynamic plant uptake models (Samsøe-Petersen et al., 2003; Trapp and Matthies, 1995; Hung and Mackay, 1997). However, these models tend to assume that plants are in the middle stage of exponential growth and do not describe biomass accumulation over a season.

Collins and Finnegan (in preparation) noted the importance of growth dilution in predicting foliar uptake of organic chemicals. Using growth dilution, the Trapp and Matthies (1995) model predicted a plateau region in uptake above octanol-air partition.
coefficients of greater than seven, in the region predicted by McLachlan (1999) to be kinetically limited. This is consistent with a scenario where the uptake of chemical per unit mass is slower than the accumulation of dry matter per unit mass, an effect observed by Schwab et al. (1998) for uptake of naphthalene by older roots of tall fescue and alfalfa.
3 Generic uptake models

This chapter summarises the six generic models chosen for comparative analysis within this study. It begins with an overview of the selection process itself, followed by a description of each model. It concludes with an initial evaluation of model performance by showing the effect of varying common parameters, including simple chemical properties, on predicted uptake in leafy and root vegetables.

Each model description includes its background and basis, input requirements, and the main advantages and limitations of the model. Where mathematical equations are included, the original nomenclature used by the authors of each approach has been reproduced to enable easier comparison with the source references.

3.1 Selection methodology

In a review of literature up to 2003, this study identified a large number of predictive models for plant uptake of organic chemicals, with many considering the application of pesticides and herbicides. In order to select a subset of approaches for the study, a simple and largely subjective screening procedure was adopted, which included a consideration of the models' scientific basis and applicability.

The models selected in Section 3.2 to 3.7 have been described in peer reviewed journals and have a clearly set out empirical or semi-mechanistic basis, which relates to one or more of the uptake processes set out in Chapter 2. Models were selected to represent as wide a theoretical basis as possible, ranging from the simple empirical studies by Travis and Arms (1988) and Topp et al. (1986), to the fugacity-based approach of Hung and Mackay (1997) and the dynamic model of Trapp and Matthies (1995). Several of the models including Travis and Arms (1988), Trapp and Matthies (1995), and Briggs et al. (1982, 1983) have been adopted by regulatory agencies in other countries for screening the impact of soil contamination.

Models such as Trapp (2002), Samsøe-Petersen et al. (2003), and Trapp et al. (2003) were excluded from this study because of their specificity to certain plant types or limitation to specific chemical compounds. Since the case study data covered a wide range of plants and chemical contaminants, models were chosen that took into account a wide range of plant and chemical types, either on an empirical basis or in their theoretical considerations. Although a more simplistic model would be preferable for screening level assessments, more compartmentally-based models such as Hung and Mackay (1997) and Trapp and Matthies (1995) were not excluded from this study, despite recognised limitations in the available input data.

Models included in this study are similar to those selected by other authoritative reviews, no doubt reflecting limitations in the scientific literature (Bell, 1992; Collins and Fryer, 2003; Rikken et al., 2001; Samsøe-Petersen et al., 2003).

3.2 Chiou et al. (2001)

3.2.1 Overview

Chiou et al. (2001) proposed a simple and mechanistic partition-limited model for the passive root uptake of contaminants from soil, taking into account the chemical
concentration in soil and plant composition. Chiou et al. (2001) commented that most screening models rely on, and are sensitive to, the use of transfer factors between one compartment and another. Their approach involved establishing the upper (equilibrium) limit for the level of contaminant in a plant compared to that in soil, against which the actual approach to equilibrium at the time of analysis could then be estimated.

### 3.2.2 Technical basis

Chiou et al. (2001) assumed that passive root uptake is the dominant process for chemical accumulation by plants from soil. The organic chemical is dissolved in water, carried into the plant during transpiration, and partitions from the water to plant tissue in contact with the solution. The chemical concentration in external solution is assumed to drive chemical uptake through a series of partitioning processes that may or may not come to equilibrium with the external solution (Chiou et al., 2001).

Initial chemical partitioning into the soil porewater is estimated from the soil-water partition coefficient, which for non-ionic organic contaminants is proportional to the soil organic matter content (Chiou et al. 2001). The concentration in the plant is estimated from the contaminant concentration in the porewater (which is assumed to be equal to the concentration in the transpiration stream) via the plant organic matter to water partition coefficient. This coefficient is expressed as the sum of contributions from all plant organic components, weighted according to their mass fraction of the whole plant (Chiou et al., 2001). This calculation is summarised in Equation 3-1.

**Equation 3-1**

\[
C_{pt} = \alpha_{pt} \left( \frac{C_{som}}{K_{som}} \right) \left[ f_{pom} K_{pom} + f_{pw} \right]
\]

where \( f_{pom} + f_{pw} = 1 \) and \( f_{pom} K_{pom} = \sum f_{pom}^i K_{pom}^i, \ i = 1, 2, 3, ... n \)

where

- \( C_{pt} \) is the calculated mass of chemical per unit mass of plant (µg kg\(^{-1}\) FW plant)
- \( \alpha_{pt} \) is the quasi-equilibrium factor, which describes the approach to equilibrium of any absorbed contaminant in the plant (or in a part of it) with respect to the same chemical in the external water phase (dimensionless)
- \( C_{som} \) is the soil organic matter normalised chemical concentration in soil (µg kg\(^{-1}\) DW soil)
- \( K_{som} \) is the chemical partition coefficient between soil organic matter and water (dimensionless)
- \( f_{pom} \) is the total weight fraction of the organic matter in the plant (g.g\(^{-1}\))
- \( K_{pom} \) is the chemical partition coefficient between plant organic matter and water (dimensionless)
- \( f_{pw} \) is the weight fraction of water in the plant (g.g\(^{-1}\))

The term \( \alpha_{pt} \) is the ratio of the concentration in plant tissue to that in the soil porewater (Chiou et al., 2001). It is a quasi-equilibrium factor that reflects the extent to which equilibrium is actually established. Assuming passive uptake from the soil, at equilibrium the concentration in the plant tissues will equal the concentration in the porewater (that is, \( \alpha_{pt} \) equals one). A value of less than one indicates that equilibrium has not yet been achieved (and either progress is slow or may never be achieved), and a value greater than one indicates active plant uptake (Chiou et al., 2001). This factor can be calculated for existing experimental studies and field observations and can be...
used to indicate the degree to which a system has achieved equilibrium. In generic
modelling $\alpha_{pt}$ would be set to one, indicating a worst-case scenario for passive uptake,
unless there was strong evidence to the contrary from other experimental studies.

Chiou et al. (2001) compared the results of their model to the output of several other
published studies including the work of Briggs et al. (1982, 1983), for a range of
chemicals (mainly pesticides) and plant types including carrots and radishes. They
concluded that the estimated $\alpha_{pt}$ values calculated from these studies showed a
consistent trend with relatively water-soluble compounds achieving a value close to
one (that is, near equilibrium) and more hydrophobic compounds a value much less
than one.

3.2.3 Input requirements

Chiou et al. (2001) is a deceptively simple model and has limited input requirements.
The user is required to specify the octanol-water coefficient for the chemical of interest,
the weighted average plant fractions for lipid, water and carbohydrate content, and the
fraction of soil organic carbon.

3.2.4 Advantages and limitations

Chiou et al. (2001) is a mechanistic model and has a similar underlying rationale to the
approaches of Ryan et al. (1988) and Briggs et al. (1982, 1983). The quasi-equilibrium
adjustment factor is an important feature, and is useful for interpreting the results of
experimental studies. If applied carefully, it can provide a useful insight into the factors
controlling uptake in a variety of different circumstances.

However, the model considers only passive root uptake and does not account for
processes such as leaf-air exchange, metabolism, or growth dilution. The assumption
of equilibrium may be highly conservative for compounds that have a low aqueous
solubility or high lipid affinity, since they may never approach equilibrium in critical plant
tissues such as tubers or leaves. The model is clearly sensitive to $\alpha_{pt}$ and therefore
further studies are probably required in order to calibrate it for various combinations of
vegetables and organic chemicals.

3.3 Hung and Mackay (1997)

3.3.1 Overview

Hung and Mackay (1997) is a relatively complex and mechanistic model to estimate the
equilibrium concentration of an organic chemical in herbaceous agricultural plants over
time. It is also a dynamic model and can be used to evaluate the kinetics of uptake into
three plant compartments, namely the leaf, stem (including fruits and seeds) and roots.

The model was developed to achieve a balance between simple screening models
such as Travis and Arms (1988) and more complex approaches that often require
extensive plant physiological data. The aim of this approach was to generate
reasonable estimates of the bioaccumulation of organic chemicals by herbaceous
plants, based on an understanding of chemical behaviour.
3.3.2 Technical basis

Hung and Mackay (1997) based their model on the concept of chemical fugacity. Fugacity is a measure of the tendency of a chemical to partition from one phase into another (Mackay, 2001). According to Mackay (2001), the fugacity concept in environmental chemistry enables scientists to better understand the thermodynamic ‘driving force’ behind chemical partitioning.

In the model, the plant is treated as three homogenous compartments consisting of leaves, stem and roots, with surrounding compartments of air and soil (Hung and Mackay, 1997). Chemical concentrations are modelled using flows into and out of each compartment by processes including transport in the xylem and phloem, air-leaf exchange, passive root uptake, growth dilution, and metabolism. Steady-state conditions are established by using partition coefficients derived for all compartments with respect to water, for example the root-water partition coefficient, and solving simultaneously for each compartment using a mass-balance approach (Hung and Mackay, 1997). In the literature, individual partition coefficients are based on experimental measurements or derived from correlation with other physical chemical properties.

The model makes four major assumptions about soil-plant-chemical interactions (Hung and Mackay, 1997):

- chemical transport processes are unidirectional;
- air and soil concentrations are constant over the growth period;
- all model parameters (including chemical properties) are constant with time;
- aerosol deposition is not taken into account.

Hung and Mackay (1997) compared the outputs of the model to an experimental study on the uptake of radiolabelled bromacil by soybean plants from hydroponic solution.

3.3.3 Input requirements

Hung and Mackay (1997) judged the model to be the simplest available plant uptake model that includes all relevant processes. Nonetheless, it requires a number of input parameters, many of which are plant, soil and chemical-specific including three compartment volumes, seven partition coefficients, three half-lives for growth and three for metabolism. Eight further transport parameters must also be considered including air-leaf exchange, xylem flow rate, phloem flow rate, and diffusive and bulk flow rate from soil to root. Although default flow rates are provided for several transport parameters and others are simplified to chemical properties, many of the variables required for this model are intended to come from detailed experimental data.

3.3.4 Advantages and limitations

Hung and Mackay (1997) proposed a comprehensive uptake model incorporating many of the processes absent in other screening approaches. Although the structure is complex, the system can potentially be solved for steady-state conditions using a simplified set of equations that could be accommodated within the CLEA model. The adoption of a fugacity approach is unique amongst the other approaches considered by

5 Because of its complexity, the underlying equations have not been reproduced in this report.
this review, but has been adopted as the primary mechanism of transport analysis in tools such as CALTOX and HAZCHEM (California EPA, 1993; ECETOC, 1994).

It is questionable whether the model can be applied to the development of generic assessment criteria, and whether the data exist to parameterise the model for common garden vegetables such as potato and carrots. As with all models, the quality of the output will be strongly influenced by the quality of the input parameters and the greater their number, the greater the potential for error.

3.4 Ryan et al. (1988)

3.4.1 Overview

Ryan et al. (1988) sets out a screening model for assessing the uptake of non-ionic chemicals from soil. It was intended to provide a simple approach to identifying those chemicals for which plant uptake may be an important pathway for human exposure. The model built on the experimental work of Briggs et al. (1982, 1983) by applying a correction for the reduced availability of chemicals from soil compared to an aqueous nutrient solution.

Ryan et al. (1988) was the default approach used by the CLEA model (the model currently uses the approach of Briggs et al. (1982 and 1983)) and is described in R&D Publication CLR10 (Defra and Environment Agency, 2002).

3.4.2 Technical basis

The basis for the Ryan et al. (1988) approach is the work of Briggs et al. (1982, 1983), who undertook an experimental study on the uptake of two series of non-ionised chemicals, o-methylcarbamoyloximes and substituted phenylureas, by barley roots and shoots from hydroponic solution. Briggs et al. measured the passive uptake of each chemical during transpiration over a period of up to 96 hours, and observed that the root and stem concentration factors were proportional to the lipophilicity of the chemical as estimated by its octanol-water partition coefficient.

Ryan et al. (1988) combined the empirical relationships of Briggs et al. (1982, 1983) which related to plant uptake from hydroponic solution, with a simple partitioning model that related the total concentration of a chemical in soil with its concentration in soil solution. It was assumed that soil adsorption of a chemical was proportional to the organic matter content of the soil and that adsorption tendency could be predicted from the organic carbon-water partition coefficient.

Ryan et al. proposed two equations based on the Briggs et al. work to estimate plant root and shoot concentrations. These are shown in Equation 3-2 and Equation 3-3.
**Equation 3-2**

\[
RCF = \left(10^{0.77 \log K_{ow} - 1.52} + 0.82\right) \times \left(\frac{\delta}{\theta + \delta K_{oc} f_{oc}}\right)
\]

where
- \( RCF \) is the calculated soil-to-plant root concentration factor (\( \mu g \) g\(^{-1}\) FW plant over \( \mu g \) g\(^{-1}\) DW soil)
- \( K_{ow} \) is the octanol-water partition coefficient for the chemical (dimensionless)
- \( \delta \) is the soil bulk density (g DW cm\(^{-3}\))
- \( \theta \) is the soil-water content by volume (cm\(^3\) cm\(^{-3}\))
- \( K_{oc} \) is the organic carbon-water partition coefficient for the contaminant (cm\(^3\) g\(^{-1}\) DW)
- \( f_{oc} \) is the fraction of organic carbon in the soil (dimensionless)

**Equation 3-3**

\[
SCF = \left(10^{0.95 \log K_{ow} - 2.05} + 0.82\right) (0.784 \times 10^{-0.434(\log K_{ow} - 1.78)^2 / 2.44}) \left(\frac{\delta}{\theta + \delta K_{oc} f_{oc}}\right)
\]

where
- \( SCF \) is the calculated soil-to-plant stem concentration factor (\( \mu g \) g\(^{-1}\) FW plant over \( \mu g \) g\(^{-1}\) DW soil)
- \( K_{ow} \) is the octanol-water partition coefficient for the chemical (dimensionless)
- \( \delta \) is the soil bulk density (g DW cm\(^{-3}\))
- \( \theta \) is the soil-water content by volume (cm\(^3\) cm\(^{-3}\))
- \( K_{oc} \) is the organic carbon-water partition coefficient for the contaminant (cm\(^3\) g\(^{-1}\) DW)
- \( f_{oc} \) is the fraction of organic carbon in the soil (dimensionless)

### 3.4.3 Input requirements

Ryan *et al.* (1988) is a screening model and therefore only a few parameters are required. Chemical properties are limited to the octanol-water partition coefficient (\( K_{ow} \)) and the organic carbon-water partition coefficient (\( K_{oc} \)), although in the absence of relevant data the latter can be estimated from the former. Soil parameters include the soil bulk density, water-filled soil porosity and the fraction of organic carbon. These parameters are commonly collected for soils and are used in a wide range of fate and transport models, including estimates of vapour intrusion into buildings.

### 3.4.4 Advantages and limitations

As a screening approach, Ryan *et al.* (1988) is simple to use. It is based on a semi-mechanistic understanding of plant uptake from soil into plants and uses empirical evidence from the studies of Briggs *et al.* (1982, 1983), which are well-respected and widely used experimental observations. The model estimates equilibrium soil-to-plant concentration factors and therefore can be used within the CLEA model to predict exposure from consumption, without adjusting exposure and averaging periods.
This is a screening approach intended to indicate the potential for plant uptake, and caution must therefore be used in applying its results to quantitative estimates of plant uptake. The approach assumes that passive root uptake is the dominant process and takes no account of potential variations arising from plant biology or from uptake via other routes including active root uptake, surface soil contact, particle deposition, or leaf-air exchange. It does not take account of any loss mechanisms such as leaf-air exchange, metabolism or growth dilution. The empirical studies on which the relationship between plant and soil concentrations is based are limited to two chemical families and a single plant species. Care should be taken when applying this approach to garden vegetables and chemicals outside of a working range of log $K_{ow}$ from nought to four. It should not be used for chemicals that may ionise appreciably in soil.

3.5  Topp et al. (1986)

3.5.1  Overview

Topp et al. (1986) proposed a simple regression model. Topp et al. (1986) studied the uptake of radioactively labelled organic chemicals by barley and cress seedlings from soil and separately from air after volatilisation. They found that uptake could be correlated to some physicochemical and structural properties of the soil contaminant. The Topp et al. (1986) approach is noteworthy for its conclusion that molecular weight is a more appropriate property than octanol-water partition coefficient ($K_{ow}$) for predicting plant uptake of organic chemicals.

3.5.2  Technical basis

Topp et al. (1986) studied root and foliar uptake of sixteen different chemicals by barley and cress seedlings. Short-term laboratory studies over a period of seven days were undertaken using a closed aerated apparatus. Outdoor experiments to simulate field conditions were also carried out in small-scale lysimeters. The chemicals studied included benzene, atrazine, pentachlorophenol, a selection of chlorobenzenes, and DDT (Topp et al., 1986). All chemicals were radioactively labelled.

In the field studies, observed uptake was shown to reach equilibrium for only two chemicals over a period of one hundred days and no correlation was possible. In the laboratory studies, Topp et al. (1986) found a correlation in barley between soil porewater concentration and plant concentration, and foliar uptake and air concentration. However, the strongest correlation was shown by combined uptake in barley with molecular weight. This is shown in Equation 3-4. Topp et al. (1986) found only two chemicals, benzene and pentachlorophenol, which did not fit this curve. They concluded that this was due to their degradation to carbon dioxide (and loss from the system) over the duration of the experiments.
Equation 3-4

\[
\log CF = 5.943 - (2.385 \log MW)
\]

where \( CF \) is the calculated bioconcentration factor for above-ground plant parts (mg kg\(^{-1}\) FW plant over mg kg\(^{-1}\) DW soil)

\( MW \) is the molecular weight of the chemical of concern (g mol\(^{-1}\))

### 3.5.3 Input requirements

Topp et al. (1986) is a simple regression model that requires only the molecular weight of the contaminant of concern.

### 3.5.4 Advantages and limitations

Topp et al. (1986) based their approach on a wide range of chemicals including neutral and ionic compounds (where molecular weights varied from 75 to 600 g mol\(^{-1}\)). It explicitly considered both root and foliar uptake.

Topp et al. (1986) concluded that the relationship in Equation 3-4 was not valid for plants with higher lipid concentrations than barley, such as carrot and parsnip. In the same study, no relationship could be found for cress, a plant that also contains oil channels. The authors were unable to define a relationship between the chemical itself in plant and soil, only the radioactively labelled carbon concentration (Topp et al., 1986). Therefore, the degree to which the carbon has been fixed by the plant in a metabolised form or degraded/ixed in soil remains unknown.

### 3.6 Trapp and Matthies (1995)

#### 3.6.1 Overview

Trapp and Matthies (1995) proposed a mechanistic, generic one-compartment model for uptake of organic chemicals by leafy vegetation, designed for use in multimedia models. This approach has been adopted under the European Union System for the Evaluation of New and Existing Substances (EUSES) for screening risks from plant uptake (EU, 2003). Rikken et al. (2001) proposed that it be used for the derivation of Serious Risk Concentrations in the Netherlands as a direct replacement for Briggs et al. (1982, 1983) in their CSOIL model. Rikken et al. (2001) carried out a comparative study between the two approaches.

#### 3.6.2 Technical basis

Trapp and Matthies (1995) is a mechanistic model that considers passive uptake from soil through the root system, translocation to shoots, air-leaf exchange, metabolism,
and dilution by plant growth. It establishes as a key property of the uptake process a partition coefficient between the plant tissue and water, this being based on the lipid concentration in various parts of the plant including the roots and leaves. Flow into and out of the plant compartment from both the surrounding soil and air are then solved simultaneously using a mass-balance approach (Trapp and Matthies, 1995). Dilution and metabolism within the plant compartment can be accounted for using first-order half-lives from the available literature.

Passive root uptake is calculated from the equilibrium porewater concentration using a root/water partition coefficient based on the chemical’s octanol-water partition coefficient, and the lipid/water content of the fine root system (Trapp and Matthies, 1995). An experimental correction factor is used to account for differences in chemical partitioning between plant lipids and water. Rikken et al. (2001) noted that the model outputs are sensitive to this coefficient, particularly for chemicals with high lipophilicity.

A more complex calculation is used to estimate concentrations in the plant shoots, because of the number of competing processes including inflows from the root and leaves, and losses to the air and through metabolism, along with growth dilution. Chemical concentrations in the transpiration stream are estimated using the relationship of Briggs et al. (1982) and Hsu et al. (1990). Transpiration stream flow rates are then used to calculate the flux into plant shoots via root uptake (Trapp and Matthies, 1995).

Leaf-air exchange is modelled as a diffusive gaseous flux across a concentration gradient from the shoot to air. Rikken et al. (2001) noted that the air concentration adjacent to the leaf system should take account of releases directly from the soil, but this is not included in the standard model. Trapp and Matthies (1995) determined the net flux between air and leaf using a leaf-air partition coefficient, leaf area and a leaf conductance constant. The leaf-to-air partition coefficient is based on the ratio of the partition coefficient for plant tissue to water and the coefficient for air to water (itself based on the octanol-water partition coefficient and Henry’s Law constant of a chemical).

Trapp and Matthies (1995) estimated loss mechanisms using first order rate constants. Once uptake and loss fluxes have been calculated, an analytical solution is applied to find a steady-state concentration in plant shoots. Model validation is limited to experimental studies on uptake of bromacil by soybean plants and uptake of 2,3,7,8-TCDD by meadow grass (Trapp and Matthies, 1995).

### 3.6.3 Input requirements

Rikken et al. (2001) identified twelve plant parameters required to use the Trapp and Matthies (1995) approach including water, lipid and air content of the plant, plant tissue density, transpiration stream flow rate, leaf conductance, leaf area and volume, harvest time, and growth constant. Many of these parameters have default values in the EUSES model (EU, 2003).

Chemical properties are limited to the octanol-water partition coefficient ($K_{ow}$) and dimensionless form of Henry’s Law constant. Soil parameters include the soil bulk density, water-filled soil porosity, and the fraction of organic carbon (Trapp and Matthies, 1995). These parameters are commonly collected for soils and are used in a wide range of fate and transport models, including estimates of vapour intrusion into buildings.

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6因为在其复杂性，其背后的方程尚未在本报告中复制。
Rikken *et al.* (2001) concluded from a sensitivity analysis that the most influential input parameters were the plant lipid content, the correction factor for plant lipid to octanol, the transpiration stream rate, leaf conductance, and the growth rate constant. The most uncertain parameters were the transpiration stream and leaf conductance because they depended on growth conditions, weather, and even the time of day (Rikken *et al.*, 2001).

### 3.6.4 Advantages and limitations

The Trapp and Matthies (1995) approach to modelling plant uptake is mechanistic and incorporates a number of different uptake processes and potentially significant loss mechanisms, including metabolism and growth dilution. It is relatively complex but can be solved analytically for steady-state conditions.

The model is applicable only to non-dissociating organic compounds (Rikken *et al.*, 2001; Trapp and Matthies, 1995). The approach assumes continuous exponential plant growth, which means that it can only be used for plants that are eaten before they stop growing (Rikken *et al.*, 2001). This may be an issue for plants where the fruits and berries are consumed, because there is a substantial reduction in growth at the end of the season.

The approach requires a number of plant-specific parameters and the model is particularly sensitive to several of the more uncertain values, such as plant lipid content, degradation and growth dilution (Rikken *et al.*, 2001). As with all models, the quality of the output will be strongly influenced by the quality of the input parameters and the greater their number, the greater the potential for error.

### 3.7 Travis and Arms (1988)

#### 3.7.1 Overview

Travis and Arms (1988) proposed an empirical relationship between soil concentration and the amount of chemical found in above-ground plant parts, based on a review of data in more than twenty experimental and observational studies. The empirical relationship was to be used by risk assessors in deriving biotransfer factors (BTF) to evaluate the accumulation potential of chemicals in the human food chain.

#### 3.7.2 Technical basis

Travis and Arms (1988) reviewed more than twenty studies where researchers had reported either a biotransfer factor, or the concentration of a chemical in soil and correspondingly in above-ground vegetation from which a BTF could be calculated. Data from twenty-nine different chemicals were collected and the resulting BTF values plotted against the octanol-water partition coefficient ($K_{ow}$). A geometric mean functional regression method was used to determine an empirical relationship between BTF and $K_{ow}$. This is shown in Equation 3-5.
Equation 3-5

$$\log B_v = 1.588 - (0.578 \log K_{ow})$$

Where $B_v$ is the calculated soil-to-plant biotransfer factor for above-ground plant parts ($\mu$g g$^{-1}$ DW plant over $\mu$g g$^{-1}$ DW soil)

$k_{ow}$ is the octanol-water partition coefficient for the chemical (dimensionless)

3.7.3 Input requirements

Travis and Arms (1988) is a screening model that requires only the octanol-water partition coefficient ($k_{ow}$) of the chemical of interest. This parameter is commonly measured for most organic chemicals and is used in a wide range of fate and transport models.

3.7.4 Advantages and limitations

As a screening approach, Travis and Arms (1988) is simple to use. It is empirically based, taking into account a wide range of different chemicals and plant types. Therefore, it does not assume any one single plant uptake mechanism and is potentially more robust than other, more mechanistic, approaches. The model has been calibrated with chemical data over a wide range of lipophilicity ($\log k_{ow}$ range from one to ten) and has potentially a broad chemical applicability.

The empirical relationship on which Travis and Arms (1988) depends is strongly dependent on only a few data points, most notably the value reported at a $\log k_{ow}$ of nine, and variability in the region $\log k_{ow}$ three to seven is high. It is a wholly empirical method and tells us little about the most likely uptake mechanisms or the considerable variations likely to exist between plant species and soil type.

Travis and Arms (1988) was derived only for above-ground plant parts although it has been used in risk assessment for both leafy and root vegetables (Birak et al., 2001). Kulhánek et al. (2005) observed that differences between a crop-specific root model and the Travis and Arms regression were ‘surprisingly small’ in a study of PAH uptake. It has therefore been used to assess both leafy and root vegetable uptake in this study.

3.8 Preliminary review of model performance

The models described in this chapter vary in complexity from simple regressions involving a single parameter such as Topp et al. (1986) and Travis and Arms (1988), to more complex multiple compartment systems such as Hung and Mackay (1997) and Trapp and Matthies (1995). One objective of this study was to evaluate how the results of these different models varied with changing key chemical and soil properties. The properties chosen were the chemical octanol-water partition coefficient ($k_{ow}$), the chemical Henry’s Law constant (H), and the soil organic carbon content ($f_{oc}$). These parameters were chosen because of their importance in describing the fate and transport of chemicals in the soil environment, and their widespread use in quantitative risk assessments.
3.8.1 Octanol-water partition coefficients ($K_{ow}$)

The octanol-water partition coefficient ($K_{ow}$) is a measure of the degree to which a chemical dissolves in an organic solvent. It is used widely in modelling as a surrogate measure for the tendency of a chemical to adsorb or accumulate in natural soil organic matter and in biological lipids, such as those found in plant and animal tissues (Environment Agency, 2003). Chemicals with a high $K_{ow}$ are more likely to dissolve in organic solvents, potentially bind more strongly to soil organic matter, and bioaccumulate in fat-rich plant and animal tissues.

Of the models described in this chapter, all with the exception of Topp et al. (1986) depend on the octanol-water partition coefficient to predict plant uptake. It is the key regression parameter in Briggs et al. (1982, 1983), Ryan et al. (1988), Trapp and Matthies (1995), and Travis and Arms (1988). See Chapter 2 for further discussion.

Figure 3-1 presents a comparison of predicted plant uptake by shoots and roots by the models over a wide range of log $K_{ow}$ values. All other chemical properties were fixed, including a Henry’s Law Constant of $1 \times 10^{-4}$ (cm$^3$ cm$^{-3}$).$^7$

The general trend in predicted shoot concentrations (see Figure 3-1a) across all models is one of reduced uptake with increasing octanol-water partition coefficient ($K_{ow}$). This is consistent with our understanding of transport processes from the root to the shoots via passive transpiration within the xylem (see Chapter 2). In addition, lipophilic chemicals are more likely to be sorbed to soil organic matter and less available for uptake via the soil solution. Most models reported a similar trend over the range log $K_{ow}$ zero to four; however, there were significant deviations outside this region. Hung and Mackay (1997) showed a sharp decline in uptake above a log $K_{ow}$ of five, where in contrast Chiou et al. (2001) showed a slight increase over the same range.

The relationship for root concentrations (see Figure 3-1b) is more complicated, with only Travis and Arms (1988) showing a constant decrease in uptake with increasing $K_{ow}$. Briggs et al. (1982, 1983), Chiou et al. (2001), and Trapp and Matthies (1995) reported a decrease in uptake with increasing $K_{ow}$ until around a log $K_{ow}$ of three, where root uptake starts to rise again. These results are consistent with a competitive effect between soil organic carbon and plant lipids. Initially, soil sorption is the dominating process as $K_{ow}$ increases. However, Briggs et al. (1982, 1983) observed an exponential increase in root sorption for chemicals above log $K_{ow}$ of three (see Chapter 2), and it is this effect that eventually overcomes any increased absorption to soil. Along with Travis and Arms (1988), the approach of Hung and Mackay (1997) shows a decrease in root uptake for chemicals with a log $K_{ow}$ value above four. This is consistent with the available literature.

$^7$ A sandy soil as described in Environment Agency (2004) was assumed with 2.5% SOM. Cabbage and carrot plants were used for shoot and root estimates respectively.
Figure 3-1: Comparison of predicted plant uptake by (a) cabbage and (b) carrot by varying only the octanol-water partition coefficient ($K_{ow}$) of the contaminant.

Key: Briggs (Briggs et al., 1982, 1983), Chiou (Chiou et al., 2001), H + M (Hung and Mackay, 1997), T + M (Trapp and Matthies, 1995), and T + A (Travis and Arms, 1988)
3.8.2 Henry’s Law constant (H)

The Henry’s Law constant (H) of a chemical is a commonly used measure of its partitioning potential between the air and water compartments in environmental systems (Environment Agency, 2003). Bromilow and Chamberlain (1995) suggested that H could be used as an indicator of the preferential pathway by which chemicals enter plants (either aqueous uptake through the roots or from air-leaf interactions). Ryan et al. (1988) proposed that chemicals could be categorised according to their Henry’s Law constant:

- chemicals with H greater than $2.5 \times 10^{-3}$ cm$^3$ cm$^{-3}$ are likely to volatilise easily;
- chemicals with H greater than $2.5 \times 10^{-5}$ cm$^3$ cm$^{-3}$ have a moderate tendency to volatilise;
- chemicals with H less than $2.5 \times 10^{-7}$ cm$^3$ cm$^{-3}$ are unlikely to volatilise.

Of the models described in this chapter, Hung and Mackay (1997), Trapp and Matthies (1995), and Briggs et al. (1982, 1983) take the air-water partitioning behaviour of chemicals into account. In the case of Briggs et al., air-water partitioning is included in the calculation of the soil porewater concentration of the chemical and not directly used in the algorithms presented in Section 3.4.

**Figure 3-2: Comparison of predicted plant uptake for cabbage shoots by varying only the Henry’s Law constant (H) of the contaminant**

Key: Briggs (Briggs et al., 1982, 1983), H + M (Hung and Mackay, 1997), and T + M (Trapp and Matthies, 1995)
3.8.3 Soil organic carbon content ($f_{oc}$)

It is widely recognised that for most soils, the retention of organic chemicals is controlled primarily by sorption to soil organic matter (Bell, 1992; Defra and Environment Agency, 2002; Rikken et al., 2001; Samsøe-Petersen et al., 2003; Trapp and Matthies, 1995). Passive uptake of chemicals through the transpiration stream and chemical volatilisation from soil to air depends on its aqueous concentration in soil porewaters. As noted in Chapter 2, the amount and type of organic matter present in soil influences the overall amount of organic chemicals available for uptake, and shifts the tendency for peak uptake towards less lipophilic compounds.

Of the models described in this chapter, Briggs et al. (1982, 1983), Chiou et al. (2001), Hung and Mackay (1997) and Trapp and Matthies (1995) take the organic matter content of soil into account. In the case of Briggs et al., the fraction of organic carbon (on a weight basis) is included in the calculation of the soil porewater concentration of the chemical and not directly used in the algorithms presented in Section 3.4.

Figure 3-3 presents a comparison of predicted plant uptake by roots and shoots for these four models over a wide range of soil organic carbon contents, with an assumed log $K_{ow}$ of two and an $H$ of $1 \times 10^{-4}$. All other chemical, soil and plant properties were fixed. All models behave similarly, with significant decreases in chemical plant concentrations as the organic matter content increases from zero to five per cent.

**Figure 3-3: Comparison of predicted plant uptake for (a) cabbage shoots and (b) carrot roots by varying only the organic matter content of the soil**

![Graph showing predicted plant uptake vs. soil organic matter content](image)

**Key:** Briggs (Briggs et al., 1982, 1983), Chiou (Chiou et al., 2001), H + M (Hung and Mackay, 1997), and T + M (Trapp and Matthies, 1995)
Key: Briggs (Briggs et al., 1982, 1983), Chiou (Chiou et al., 2001), H + M (Hung and Mackay, 1997), and T + M (Trapp and Matthies, 1995)
4 Case studies

This chapter summarises the five experimental studies used to evaluate the performance of the generic models described in Chapter 3. An overview of the selection method explains the criteria used to identify the studies that were taken forward into the comparative analysis. The discussion also provides more general advice on evaluating the scientific literature on plant uptake, to consider the suitability of information for use as input data in risk assessment.

Each case study is outlined with an extended description, which includes the study objectives and context, the methodology including chemical, plant and soil types used, and a summary of the main findings along with the uptake data used subsequently.

4.1 Selection of case studies

In a review of the scientific literature up to 2003, this study found a large number of references to plant uptake of chemicals, although most considered either inorganic contaminants or the application of pesticides and herbicides. After filtering these references for relevance to industrial organic chemicals and key homegrown vegetable crops such as cabbage, carrot and potato, the number of studies available dropped significantly. Further, many of these studies were limited to persistent chemicals such as PAHs, PCBs, and dioxins/furans. There was little data available on industrial chemicals including petroleum hydrocarbons (such as benzene and xylene), and low molecular weight chlorinated compounds (such as trichloroethene and tetrachloroethene). This study was therefore unable to compare model performance with as wide a range of industrial chemicals as had been originally envisaged.

Several characteristics were evaluated for short-listed case studies, including:

- research quality and track record;
- method description and detail;
- limitations of scope and scale.

Studies were preferred from respected peer-reviewed journals such as Environmental Science and Technology, and from researchers and research groups with recognised national and international expertise. This was used as a subjective indicator of experimental quality.

Surprisingly, many studies were rejected because the experimental method was not fully described or critical aspects were ambiguous. For example, several studies did not make clear whether the results were reported on a fresh weight or dry weight basis, nor whether the shoots, roots, fruits or tubers of the plant were sampled. Soil-to-plant concentration factors should relate to the edible portions of a plant, since the concentrations in each fraction can differ considerably. In addition, it is important to distinguish between studies that directly measure the concentration of a chemical in plant tissues from those that analyse for the carbon-14 tracer. Although it is often a complex analytical procedure, direct measurement of chemical concentration reports

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8 Potato is the vegetable with the highest production worldwide and is the dominant vegetable by weight in the basket of produce included in the CLEA model (Defra and Environment Agency, 2002; Samsøe-Petersen et al., 2003)
the amount of intact (that is, non-metabolised) chemical in the plant tissues. Using a tracer method can over-predict chemical uptake because it measures the concentration of metabolised and sequestrated carbon, some of which may no longer be toxicologically active.

Several studies did not report the relevant soil concentrations, only the levels found in the plants. This was primarily because the objective of these studies was to examine the role of more ambient contamination associated with diffuse sources, including aerial deposition. Also, the methodology often failed to describe key soil properties including texture and organic matter content, important parameters in several of the models outlined in Chapter 3. Several studies were rejected because of insufficient sample sizes, where sample variability could not be adequately taken into account when assessing the results; for example, in several experiments only a single plant was sampled under a range of conditions. Some studies were rejected because results were generally below the detection limits of older analytical methods.

Plant uptake studies have been carried out on a range of scales, from bench-scale hydroponics through pot and chamber experiments to field-scale investigations. This is a trade-off between realism and reproducible controlled conditions. Field-scale studies are likely to be more realistic of the home or allotment gardener, but many factors such as weather conditions, contaminant profiles and soil properties are difficult to measure, control and reproduce. Pot experiments, in a growth chamber or indoor greenhouse, are often seen as a compromise between control and realism. However, pot experiments also have known limitations, including:

- Restricted soil volume for root growth may mean that uptake is under-predicted for deep rooting plants and over-predicted for shallow rooting plants.
- Managed watering, feeding and temperature control may increase leaching, vaporisation or soil degradation of contaminants under optimised conditions.
- Closely spaced pots in an enclosed area may result in cross-contamination.

In addition, there is a tendency for laboratory experiments to use homogenised soils, often with the chemical added as a soluble solution (with and without a subsequent period of acclimatisation). As a result, these experiments may over-predict plant uptake and other fate processes compared to more naturally weathered soils, where the contamination becomes more strongly bound to soil particles over time. Studies where the chemical is added in sewage sludge may underestimate domestic plant uptake, because the amount of organic carbon added is artificially high.

Where possible, case studies were chosen to reflect a range of chemical properties and take into account different uptake pathways. The studies selected were by Goodin and Webber (1995), Groom et al. (2002), Kipopoulou et al. (1999), Wang and Jones (1994a), and Berry-Spark et al. (2003). They are described in the remainder of this chapter.
4.2 Goodin and Webber (1995)

4.2.1 Overview

Goodin and Webber (1995) investigated the persistence, fate and plant uptake of anthracene in a series of pot and microcosm experiments. The aim of the study was to provide further evidence on the risks associated with trace organic chemicals in municipal sludge applied to agricultural land.

Surface samples of a sandy loam soil (‘Caledon’) were collected from arable fields, ground to pass a two-mm sieve, and wetted to 60 per cent of its field capacity (Goodin and Webber, 1995). The soil’s properties are summarised in Table 4.1.

Table 4.1: Properties of Caledon soil (after Goodin and Webber, 1995)

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Fraction of organic carbon</th>
<th>Texture (per cent weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caledon</td>
<td>7.2</td>
<td>0.013</td>
<td>Sand 73 Silt 20 Clay 7</td>
</tr>
</tbody>
</table>

Notes: 1Measured using 0.01 M CaCl₂

The soil was amended with anaerobically digested municipal sludge (with no detectable PAH content) to produce a treated soil with one per cent dry weight of sludge solids. Anthracene was then added to the sludge-amended soil as a radiolabelled (¹⁴C) solution to give a final soil concentration of approximately 10 mg kg⁻¹ dry weight.

Greenhouse experiments were carried out using a stainless steel microcosm, with airflow and moisture content carefully controlled and monitored (Goodin and Webber, 1995). Plants were inserted into soil within glass tubes, thereby minimising soil-air-plant transfer. Ryegrass (Lolium multiflorum) and soybean (Glycine max) were each grown for seven weeks and then harvested for chemical analysis (both ¹⁴C-labelled content and intact anthracene). The experiment was carried out in quadruplicate.

4.2.2 Selection criteria

The study is relevant to the development of the CLEA model and the SGV work programme. Anthracene is a commonly encountered soil contaminant and a typical member of a PAH analytical suite.

The methodology of the study is clear and detailed, and the Journal of Environmental Quality is an internationally respected and peer-reviewed publication. This, combined with the carefully controlled conditions and number of experimental replicates, gives a degree of confidence in the data obtained. Goodin and Webber (1995) reported good reproducibility of results, with coefficients of variation less than five per cent for anthracene. Calculated mass balances indicated more than 85 per cent of the radiolabelled carbon added to the soil was accounted for in the soil air, soil and plant materials (Goodin and Webber, 1995).

9 Goodin and Webber (1995) also considered benzo[a]pyrene but this data has not been included in this study.
The study measured both the radiolabelled component and the intact chemical concentration in soil and plant, allowing considerations of metabolism and degradation to be taken into account.

A disadvantage of the study was that it was a pot experiment and that the anthracene was added as an aqueous solution, with little opportunity for soil acclimatisation or weathering before the plants were introduced. Goodin and Webber (1995) conceded that this was likely to be representative of “worst case conditions”.

The experimental design prevented any soil-air-plant transfer, including the potential for soil particles to be deposited on above-ground leaves and shoots (Goodin and Webber, 1995). Since this is known to be an important transfer route for the higher molecular weight PAH compounds, the experimental results might be expected to under-predict uptake.

4.2.3 Results

Goodin and Webber (1995) reported the results of their study as a bioconcentration factor (BCF) calculated from the ratio of radioactivity in above-ground plant material to the original soil concentration (that is, 10 mg kg\(^{-1}\)) on a dry weight basis. The results are presented in Table 4.2.

Approximately 90 per cent of the anthracene was lost from the soil over the duration of the microcosm experiments (about 15 weeks). Although radiolabelled carbon was measured in small amounts in the plant materials, extraction and chemical analysis found no evidence of intact anthracene being present (Goodin and Webber, 1995).

Goodin and Webber (1995) concluded that although “worst case” experimental conditions had been used, uptake of [intact] anthracene was not observed in the study.

Table 4.2: Results of anthracene uptake from soil by rye grass and soybean plants in greenhouse microcosm study (Goodin and Webber, 1995)

<table>
<thead>
<tr>
<th>BCF (on a dry weight basis)(^1)</th>
<th>Plant concentration (mg kg(^{-1}) fresh weight)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ryegrass</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>Soybean</td>
<td>0.41 ± 0.16</td>
</tr>
</tbody>
</table>

Notes:  
\(^1\)Bioconcentration factor based on measured \(^{14}\)C activity in plant over soil on a dry weight basis  
\(^2\)Based on assumed plant tissue water content of 65 per cent (EU, 2003) and an initial soil concentration of 10 mg kg\(^{-1}\) dry weight

4.3 Groom \textit{et al.} (2002)

4.3.1 Overview

Groom \textit{et al.} (2002) investigated the uptake and transformation of the explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) by plants as part of a work programme to assess the feasibility of phytoremediation at a firing-range site in Alberta, Canada. HMX is a chemical component of anti-tank missiles and surface soils across the site had been contaminated with levels in the range 25 – 50 mg kg\(^{-1}\) dry weight.
Soil samples were collected from the site, homogenised in a cement mixer, and shipped frozen to the laboratory in polyethylene bags (Groom et al., 2002). The firing-range soil was described as a ‘sandy loam’ with a limited ion exchange capacity. Its properties are summarised in Table 4.3.

Table 4.3: Properties of firing-range soil (after Groom et al., 2002)

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Fraction of organic carbon</th>
<th>Texture (per cent weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sand</td>
</tr>
<tr>
<td>Firing-range</td>
<td>7.8</td>
<td>0.02</td>
<td>60</td>
</tr>
</tbody>
</table>

Notes: ¹Estimated by subtracting sand and silt content from 100 per cent

Several plants including rape (*Brassica rapa*) and bush bean (*Phaseolus vulgaris*) were grown in pots containing 2.5 kg of contaminated soil collected from the firing-range (Groom et al., 2002). Greenhouse conditions were carefully controlled including temperature, relative humidity and light. Watering was undertaken as required to ensure adequate soil moisture content throughout the growing period of 77 days. At the end of the experiment, plant tissue samples were collected to represent aerial and root tissues and HMX extracted and analysed (Groom et al., 2002). Leaves were washed to remove any fine soil particles that might have adhered to the surfaces.

4.3.2 Selection criteria

The study is relevant to the development of the CLEA model since HMX is a chemical explosive identified within the SGV work programme. However, the plants grown are not directly representative of the vegetables considered by the CLEA model, although rape (*Brassica rapa*) is in the same family as spinach and bush bean (*Phaseolus vulgaris*) is in the same family as French bean.

HMX will likely persist in the soil environment and will be mobile in aqueous solution, with a low sorption potential for organic matter and a very low volatility (Groom et al., 2002). It is a highly mobile compound in the xylem (readily transferable from root to shoots) with a cyclic nitramine structure similar to that found in atrazine.

The methodology of the study is clear and detailed, and the journal *Environmental Science and Technology* is an internationally respected and peer-reviewed publication. This, combined with the carefully controlled conditions and number of experimental replicates, gives a degree of confidence in the data obtained. Groom et al. (2002) reported good reproducibility of results with relative standard deviation for soils and plants of less than 11 per cent. The study measured the intact chemical concentration in soil and plant.

The experiments were conducted in pots under carefully controlled conditions and are therefore not especially representative of what might happen in the field. In particular, constant watering and the prevention of any leaching from the base of the pots may have artificially elevated likely aqueous concentrations of HMX for root uptake. The study used contaminated soil taken from the site and therefore chemical availability was likely to be realistic.
4.3.3 Results

Groom et al. (2002) concluded that passive root uptake and translocation during plant transpiration was the most important accumulation mechanism in this study. Most plant species investigated had leaf concentrations of HMX significantly above the soil concentration and there was no direct evidence of plant-mediated HMX chemical transformation. The results used in the comparison study are presented in Table 4.4.

Table 4.4: Results of HMX uptake from soil by bush bean and rape plants in greenhouse pot study (Groom et al., 2002)

<table>
<thead>
<tr>
<th></th>
<th>BCF (on a dry weight basis)</th>
<th>Plant concentration (mg kg(^{-1}) fresh weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rape</td>
<td>7.0 ± 1.0</td>
<td>49.2 ± 5.4</td>
</tr>
<tr>
<td>Bush bean</td>
<td>3.9 ± 0.5</td>
<td>28.4 ± 2.4</td>
</tr>
</tbody>
</table>

Notes:  
1 Bioconcentration factor based on average measured HMX concentration in plant over soil on a dry weight basis and an initial median value soil concentration of 31.8 mg kg\(^{-1}\) dry weight with a relative standard deviation of 3.3 per cent  
2 Based on experimental plant tissue water content of 78 per cent for rape and 77 per cent for bush bean (Groom et al., 2002)

4.4 Kipopoulou et al. (1999)

4.4.1 Overview

Kipopoulou et al. (1999) investigated the relationship between PAHs accumulated within the inner tissues of leaf and root vegetables and their concentration in the surrounding air and soil. Samples of soil, particulate dust, and plants were collected from four sites spread geographically over an area of 6 km\(^2\) within an industrial area of northern Greece. The sampling took place over two growing periods in autumn and the following spring.

Soil data was not reported by individual site (Kipopoulou et al., 1999). Soils across the sampling area were generally described as being 'light to moderately light-textured, alluvial sandy loam and silt loam' with pHs in the range 6.7 to 8.8 and organic carbon contents in the range 0.6 to 1.2 per cent by weight. After collection soil samples were homogenised and sieved, with the fraction less than 2 mm used for chemical analysis.

Samples of atmospheric suspended dust were collected in filters positioned at the centre of two local residential communities over a twelve-month period (Kipopoulou et al., 1999). Dust samples were therefore collected at different locations from soil and plant samples.

Composite samples of vegetables, including cabbage (Brassica oleracea capitata), carrot (Daucus carota), and lettuce (Lactuca sativa), were collected from each site (Kipopoulou et al., 1999). All vegetables were washed with fresh running water to remove any surface dust, the carrots were peeled, and the dead/yellow outer leaves were removed from cabbage and lettuce. Plant material for each vegetable was then homogenised in a stainless steel mixer and freeze-dried.

Soil, dust and plant materials were analysed using HPLC with fluorescence detection after soxhlet extraction. Recoveries of all PAHs were in the 71 to 92 per cent range for the entire procedure, although naphthalene results were highly variable (Kipopoulou et al., 1999).
Analysis was checked using a Certified Reference Material (CRM), with replicates found to give an error the range ± 5 to 15 per cent for individual PAHs.

4.4.2 Selection criteria

The study is relevant to the development of the CLEA model since PAH compounds are found on many contaminated sites and are priority chemicals within the SGV work programme. Also, three of the plants considered, namely cabbage (*Brassica oleracea* capitata), carrot (*Daucus carota*) and lettuce (*Lactuca sativa*), are specifically identified within the CLEA model as being common homegrown vegetables in the UK (Defra and Environment Agency, 2002).

The methodology of the study is clear and detailed, and the journal *Environmental Pollution* is an internationally respected and peer-reviewed publication. Sampling and analysis were undertaken using recognised international protocols and errors within extraction and measurement quantified (Kipopoulou *et al*., 1999). The study measured the intact chemical concentration in soil and plant.

Vegetables were sampled from agricultural soils in the field and therefore were representative of realistic field conditions. However, using composites samples from all four locations lost considerable data resolution. Dust measurements suggested there was a significant background PAH signal in ambient air from regional industrial pollution. The relative contribution of ambient and local air sources to gaseous plant uptake cannot be readily determined from the study because soil/plant and dust samples were collected from different locations (Kipopoulou *et al*., 1999).

4.4.3 Results

Table 4.5 presents summary soil and vegetable data for five PAH compounds representative of two, three, four, five and six-ring structures. Kipopoulou *et al.* (1999) observed that all sixteen US Environment Protection Agency (US EPA) PAHs were detected in vegetable samples across all four sites, with the lower molecular weight compounds being in greater abundance than the heavier compounds.

The most important pathway for plant uptake was considered to be gaseous phase transfer from air to plant leaves, with concentration qualitatively proportional to surface leaf area for above-ground vegetables.\(^{10}\) It was also observed that the profile of PAHs in air vapour was consistent with the profile found in the plants, although a regional ambient or local soil air source could not be distinguished (Kipopoulou *et al*., 1999).

\(^{10}\) Cabbage was noted as being an exception to this trend, with the lower than expected uptake being attributed to a tighter and more compact internal leaf structure that restricted gaseous penetration (Kipopoulou *et al*., 1999)
Table 4.5: Summary soil and plant data for five PAH compounds (Kipopoulou et al., 1999)

<table>
<thead>
<tr>
<th>PAH</th>
<th>Soil concentration (µg kg(^{-1}) dry weight)(^1)</th>
<th>BCF (dry weight)(^2)</th>
<th>Plant concentration (µg kg(^{-1}) fresh weight)(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cabbage Carrot Lettuce</td>
<td>Cabbage Carrot Lettuce</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>17</td>
<td>0.3</td>
<td>1.2 2.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>8.6</td>
<td>2.1</td>
<td>3.1 6.7</td>
</tr>
<tr>
<td>Chrysene</td>
<td>3.7</td>
<td>0.2</td>
<td>0.1 1.1</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>2.4</td>
<td>0.04</td>
<td>0.05 0.12</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>3.6</td>
<td>0.09</td>
<td>0.08 0.05</td>
</tr>
</tbody>
</table>

Notes:
1 Median value of all soil samples
2 Bioconcentration factor based on median concentration in plant divided by median concentration in soil on a dry weight basis
3 Converted to fresh weight plant concentrations from median dry weight concentrations by assuming moisture content of 92%, 88%, and 95% for cabbage, carrot, and lettuce respectively (Gebhardt and Thomas, 2002)

A non-parametric analysis of variants in the study identified only plant species as an important factor in plant concentration, with no significant effect of season or sampling site (Kipopoulou et al., 1999). Soil-to-plant concentration factors were found to correlate well with chemical water solubility and the octanol-water coefficient (K\(_{ow}\)). Overall, Kipopoulou et al. (1999) concluded that vegetables grown in polluted areas [such as the one used in this study] did not make a significant contribution to the total PAH dietary intake if they were washed and peeled.

4.5 Wang and Jones (1994a)

4.5.1 Overview

Wang and Jones (1994a) investigated the uptake of chlorobenzenes by carrots from sewage sludge amendments to agricultural soil. This study was part of a larger project assessing the significance of organic chemicals in sewage sludges applied to land.

Chlorobenzenes are ubiquitous in sludges and as a chemical family, possess a range of physicochemical properties and possible plant uptake mechanisms. This series of pot experiments was set up to represent a worst-case situation.

A sandy loam soil with a low organic matter content was collected from a site adjacent to the Woburn Market Garden Experiment managed by the Rothamsted Experimental Station (Wang and Jones, 1994a and 1994b). After collection, the soil was air-dried, sieved through 2-mm mesh size, and thoroughly mixed. Sewage sludge was collected from a municipal and industrial treatment works, containing about 11 per cent dry matter solids by weight after centrifuging (Wang and Jones, 1994a). The properties of the soil only and soil-sludge mixtures are presented in Table 4.6 (Wang and Jones, 1994b).
Chlorobenzenes were added to the soil in two ways (Wang and Jones, 1994a). Firstly, the soil was amended with sewage sludge at two different application rates: a low rate (19.4 t ha\(^{-1}\), dry weight) and a high rate (165 t ha\(^{-1}\), dry weight). Secondly, the soil was spiked with an aqueous solution of chlorobenzenes (previously diluted with hexane and acetone) to levels equivalent to the high rate sludge application. The aim was to assess differences in uptake behaviour attributable to experimental methods of adding chlorobenzenes to the soil.

Pots of each soil were prepared in triplicate, watered and fertilised in a glasshouse with temperatures in the range 20 to 30°C. Pots were arranged so that no pot was next to a pot with the same soil treatment (Wang and Jones, 1994a). Carrot seeds (\(Daucus carota\)) were planted in each pot and the seedlings thinned to about twenty plants per pot.

The carrots were harvested after 100 days and plant yields and wet weights were measured (Wang and Jones, 1994a). Plants were separated into top foliage/stems and roots, and cleaned with deionised water to remove soil particles. Carrot roots were subsequently peeled and the core and peel analysed separately. All plant materials were bagged and stored at 4°C before chemical analysis.

### 4.5.2 Selection criteria

The study is relevant to the development of the CLEA model since chlorobenzenes are a group of priority chemicals within the SGV work programme. These chemicals have a range of physicochemical properties, many of which are comparable with other semi-volatile organics within the programme and may be indicative of their uptake behaviour. Also, carrot (\(Daucus carota\)) is specifically identified within the CLEA model as being a common homegrown vegetable in the UK (Defra and Environment Agency, 2002). Carrots are a key root vegetable with a high lipid content, and are thus one of the most likely crops to accumulate organic contaminants from polluted soils.

The methodology of the study is clear and detailed, and the journal *Environmental Science and Technology* is an internationally respected and peer-reviewed publication. Sample sizes were good and analytical recoveries of chlorobenzenes were in the range 82 to 97 per cent for soils and 66 to 93 per cent for plant materials (Wang and Jones, 1994a). In both cases, the coefficients of variation were less than ten per cent.

Vegetables were grown in pots within a greenhouse and experimental conditions were therefore reasonably controlled. Chlorobenzenes were added to the soil in two forms, enabling comparison of results using different experimental methods. One problem with pot experiments is that plant growth can become restricted, but in this study the vessels were of a reasonable size (20 litres) and plants were harvested after only 100 days.
4.5.3 Results

Table 4.7 presents summary soil and carrot data for 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene.

Wang and Jones (1994a) observed that during soil preparation (that is, air drying, sieving and mixing with sludge), the greatest proportions of chlorobenzenes were lost from high rate and spiked soils. They concluded that this was important because the low rate application was similar to the real situation and chlorobenzenes might therefore persist longer in soil under field conditions.

Carrot yields were highest in pots with low rate applications of sewage sludge and lowest for high rate applications, the latter being indicative of excessive amounts of nitrogen addition (Wang and Jones, 1994a). In the spiked soil pots, carrot roots were 40 per cent less than the control soils and some were observed to be mouldy at the time of harvest. It was suggested that the spiked soil was “harder” than the control soil and that this adversely affected growth.

In the above-ground foliage, the concentrations of 1,4-dichlorobenzene and 1,2-dichlorobenzene were higher than the other chlorobenzenes in all soils, irrespective of treatment (Wang and Jones, 1994a). Hexachlorobenzene levels were observed to be much lower than those found under field conditions, where it occurs as an impurity in some pesticide formulations. Foliage concentrations of the dichlorobenzenes and trichlorobenzenes correlated well with soil concentration, but the others did not (Wang and Jones, 1994a). However, for all chlorobenzenes the amount found in foliage correlated well with foliage yield. The authors suggested that foliar uptake from ambient air, possibly after volatilisation from soil, was an important uptake pathway.

In the roots, the concentration of chlorobenzenes was highest in the peel (Wang and Jones, 1994a). Levels of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene were higher than the other chlorobenzenes. The concentrations of all chlorobenzenes in the carrot root, with the exception of 1,4-dichlorobenzene, increased with increasing soil concentration. Better root growth in sludge-amended pots resulted in lower concentrations of chlorobenzenes, possibly as a result of increased root diameters reducing chemical penetration (a “dilution effect”).

Wang and Jones (1994a) concluded that the translocation of chlorobenzenes from root to shoot appeared to be seriously restricted, and that plant uptake to the two different plant compartments should be viewed as separate pathways and mechanisms. Root uptake was assumed to occur firstly by sorption to the peel and then diffusion into the core, while foliar uptake assumed evaporation from soil and sorption by leaves from the air (Wang and Jones, 1994).
Table 4.7: Summary results of soil and carrot data for selected chlorobenzenes (Wang and Jones, 1994a)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Soil concentration (µg kg⁻¹ dry weight)²</th>
<th>BCF (dry weight basis)³</th>
<th>Carrot foliage concentrations (µg kg⁻¹ fresh weight)⁴</th>
<th>Carrot root core concentrations (µg kg⁻¹ fresh weight)⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DB¹</td>
<td>TCB¹</td>
<td>TeCB¹</td>
<td>PCB¹</td>
</tr>
<tr>
<td>Soil – spiked</td>
<td>16 ± 0.51</td>
<td>12 ± 0.41</td>
<td>1.4 ± 0.019</td>
<td>2.1 ± 0.021</td>
</tr>
<tr>
<td>Soil – sludge (low rate)</td>
<td>10 ± 1.2</td>
<td>4.6 ± 0.89</td>
<td>0.16 ± 0.004</td>
<td>0.3 ± 0.035</td>
</tr>
<tr>
<td>Soil – sludge (high rate)</td>
<td>38 ± 0.58</td>
<td>17 ± 0.41</td>
<td>1.1 ± 0.054</td>
<td>2.0 ± 0.009</td>
</tr>
</tbody>
</table>

Notes: ¹ Abbreviation for chlorobenzenes used in this table are: 1,4-dichlorobenzene (DB), 1,2,4-trichlorobenzene (TCB), 1,2,4,5-tetrachlorobenzene (TeCB), pentachlorobenzene (PCB) and hexachlorobenzene (HCB)

² Based on soil concentrations before seeds were sown

³ Bioconcentration factor based on concentration in plant divided by concentration in soil before seeds were sown, on a dry weight basis

⁴ Converted to fresh weight plant concentrations from dry weight concentrations by measured dry matter contents of 18.6%, 19.2%, and 16.9% for spiked soil, low rate-amended soil, and high rate-amended soil respectively

⁵ Converted to fresh weight plant concentrations from dry weight concentrations by measured dry matter contents of 10.8%, 12.1%, and 12.1% for spiked soil, low rate-amended soil, and high rate-amended soil respectively
4.6 Berry-Spark et al. (2003)

4.6.1 Overview

Berry-Spark et al. (2003) investigated the plant uptake of hexachloro-1,3-butadiene (HCBD) by carrot and lettuce under laboratory conditions. The study was part of a programme of work to understand the potential for human exposure to HCBD from garden soils at the village of Weston, Cheshire.

The experimental work originally planned was based on the use of radiolabelled HCBD to establish uptake, distribution and fate of the contaminant in soil (Berry-Spark et al., 2003). However, problems in synthesising the radiolabelled compound necessitated a revised study based on direct chemical analysis of HCBD using GC-MS.

Samples of two agricultural soils were obtained for the study: a sandy-silt soil and clay loam soil containing respectively, 10.1 per cent and 9.5 per cent organic carbon on a dry weight basis (Berry-Spark et al., 2003). Each soil was air-dried for 48 hours before spiking with reagent grade HCBD dissolved in acetone and distilled water. The low concentration HCBD spike produced soils containing between 122 and 399 µg kg⁻¹ dry weight, and the high concentration spike produced soils containing between 11,160 and 17,130 µg kg⁻¹ dry weight (Berry-Spark et al., 2003).

Lettuce and carrot were selected because they are both common garden vegetables and may both be eaten raw (Berry-Spark et al., 2003). After germination (about seven to ten days), seedlings were transferred to experimental plastic pots containing 1.5 kg of spiked soil. Pots were placed inside glass growth chambers within a greenhouse under controlled heat, light and watering conditions. Humidified air was passed through the chambers and the exhaust gas sampled regularly to measure the loss of any volatile HCBD. After growing for a period of seven to twelve weeks, samples of lettuce and carrot were obtained and stored at -20°C prior to analysis. Samples of carrot were washed with tap water to remove adhered soil (Berry-Spark et al., 2003).

4.6.2 Selection criteria

The study is relevant to the development of the CLEA model since hexachloro-1,3-butadiene (HCBD) is a priority chemical within the SGV work programme. Also, lettuce (Lactuca sativa) and carrot (Daucus carota) are specifically identified within the CLEA model as being common homegrown vegetables in the UK (Defra and Environment Agency, 2002).

The methodology of the study is clear and detailed. Although not reported in a peer-reviewed journal, plant scientists from Lancaster University carried out this study with a very high level of QA/QC quality assurance (Berry-Spark et al., 2003). Sample sizes were good and analysis was often carried out in triplicate. Evaluation of QA/QC data and the inherent variability of biological systems suggested that the relative uncertainty in the soil-to-plant concentration factors calculated by this experiment would be in the region of one order of magnitude. Berry-Spark et al. (2003) commented that this was likely to be “significantly better than the accuracy reported (two orders of magnitude or more) in most papers deriving numerical models of plant uptake.”

Vegetables were grown in pots within glass chambers and experimental conditions were controlled, although problems were reported with the moisture content of the soil and overall temperature and humidity (Berry-Spark et al., 2003). In particular, the latter
resulted in “emergency” sampling of the lettuce plants from several pots because of wilting and for stunted carrot growth. One further issue with the pot experiments was that HCBD was added to the soil as a spiked solution and therefore uptake was unlikely to be representative of weathered contamination.

4.6.3 Results

Table 4.8 presents a summary of the results from this study. There was limited uptake of HCBD by lettuce from both soil types at the low application rate and for the clay loam at the high application rate. Levels of HCBD were measured in plant tissues at the high application rate in the sandy-silt soil, which because of its soil texture was “less prone to clumping” than the clay-loam soil (Berry-Spark et al., 2003). However, uptake in this soil may also have been skewed by the existence of chemical hot spots formed by incomplete mixing after spiking.

The authors observed uptake of HCBD by carrot (core and peel) from both soils at the higher application rates, with plant concentrations proportional to soil concentrations (Berry-Spark et al., 2003). Concentrations were typically ten times higher in the peel than in the core, indicative of direct absorption of HCBD in the lipid-rich outer surface of the carrot root and limited penetration into the edible interior.

The study found no chlorinated substances in any of the soil or air samples, suggesting that no breakdown products from HCBD were formed during this experiment (Berry-Spark et al., 2003). There was, however, a significant loss of HCBD from the soil over the duration of the experiment, which was not balanced by the measured plant uptake. One likely sink for HCBD appeared to be the silicone sealant used in constructing the glass chambers, highlighting the practical difficulties of undertaking such studies.

Table 4.8: Mean soil and plant concentrations of HCBD for each growth chamber (Berry-Spark et al., 2003)

<table>
<thead>
<tr>
<th></th>
<th>Soil concentration¹ (µg kg⁻¹ dw)</th>
<th>Plant concentration (µg kg⁻¹ fresh weight)²</th>
<th>BCF (on a dry weight basis)³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carrot</td>
<td>Lettuce</td>
<td>Carrot</td>
</tr>
<tr>
<td>Sandy-silt (low rate)</td>
<td>87</td>
<td>46</td>
<td>5.01</td>
</tr>
<tr>
<td>Clay loam (low rate)</td>
<td>29</td>
<td>28</td>
<td>9.31</td>
</tr>
<tr>
<td>Sandy-silt (high rate)</td>
<td>5,085</td>
<td>632*</td>
<td>1.18</td>
</tr>
<tr>
<td>Clay loam (high rate)</td>
<td>10,118</td>
<td>2,111</td>
<td>1.98</td>
</tr>
<tr>
<td>Sandy-silt (low rate)</td>
<td>73</td>
<td>&lt;10</td>
<td>1.75</td>
</tr>
<tr>
<td>Clay loam (low rate)</td>
<td>68</td>
<td>&lt;10</td>
<td>1.90</td>
</tr>
<tr>
<td>Sandy-silt (high rate)</td>
<td>9,127</td>
<td>338</td>
<td>0.47</td>
</tr>
<tr>
<td>Clay loam (high rate)</td>
<td>6,569</td>
<td>&lt;10</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Notes: ¹ Post-harvest soil concentrations corrected from fresh weight to dry weight using Lancaster University data and experimental correction factors for each chamber (Berry-Spark et al., 2003)
² Reported mean concentrations for whole carrot (except * where carrot core only) using Central Science Laboratory (CSL) data, and lettuce leaves using Lancaster University data. Limit of quantification was 10 µg kg⁻¹
³ Soil-to-plant concentration factors on a dry weight basis obtained by correcting soil and plant data to dry weight using experimental correction factors for each chamber (Berry-Spark et al., 2003). As a worst-case estimate, plant concentrations below detection limits have been assumed to be at the limit of quantification.
5 Model comparison

This chapter summarises the results of the model comparison study. It gives an overview of the methodology including the selection of model parameters, followed by a comparison of model predictions with the selected results from the five experimental studies described in Chapter 4. It concludes with an evaluation of overall model performance.

5.1 Methodology

5.1.1 Model construction and parameter selection

Each of the models identified in Chapter 3 was coded into a Microsoft Excel 97 workbook and the cell outputs independently verified. Subsequently, the models were combined into a single workbook to enable them to use a common parameter data set and to more easily report comparison data across all seven models studied. Where necessary, model outputs were corrected to report the predicted plant concentrations in either shoots or roots in common units of mg kg\(^{-1}\) fresh weight.

Several of the models used, including Briggs et al. (1982, 1983), Hung and Mackay (1997) and Trapp and Matthies (1995), depend on media concentrations not reported in the original experimental studies. These values were therefore estimated using the media partitioning and transport equations from the CLEA model, which were coded into the workbook (Defra and Environment Agency, 2002; Environment Agency, 2004). Theoretical limits of aqueous solubility and vapour saturation were applied.

An important factor in the variation between different model outputs can be traced to inconsistencies in the parameters chosen for the properties of the chemical, soil or plant. In order to reduce this effect within the comparative study, common data was selected from the case study itself (in the case of soil and plant properties) and from the wider reference literature.

Chemical data

The chemical data used in this study came from a number of sources including Environment Agency (2000, 2003), Mackay et al. (2000), Pennsylvania Department of Environmental Protection (2006), and US EPA (2003). The organic-carbon partition coefficient (K\(_{oc}\)) was estimated from the octanol-water partition coefficient (K\(_{ow}\)) using the QSAR relationship for non-hydrophobic contaminants (cited by Environment Agency, 2003). This is shown in Equation 5-1.

There is very little reliable data on the environmental degradation and plant metabolism of organic chemicals, and very few generic values were found in the literature. Such rates were therefore assumed to be zero in the comparison study. The data used for each chemical can be found in Appendix 1.

\[\text{Chemical data} \]

11 The workbook containing these models is available for download from the Environment Agency’s web site at www.environment-agency.gov.uk
Equation 5-1

\[ \log K_{oc} = 0.52 \log K_{ow} + 1.02 \]

Where \( K_{oc} \) is the calculated partition coefficient between organic carbon and water (cm\(^3\) g\(^{-1}\))
\( K_{ow} \) is the octanol-water partition coefficient for the chemical (dimensionless)

**Soil data**

Most of the case studies in Chapter 4 provide rudimentary soil data including the fraction of organic carbon, soil pH, and a qualitative description of soil texture such as sandy loam. Where necessary, the soil organic matter content has been converted to the fraction of organic carbon using Equation 5-2 (Rowell, 1994).

Equation 5-2

\[ f_{oc} = f_{som} \times 0.58 \]

Where \( f_{oc} \) is the fraction of organic carbon by weight (g g\(^{-1}\))
\( f_{som} \) is the fraction of soil organic matter by weight (g g\(^{-1}\))

Several of the uptake models and the air and porewater calculations taken from the CLEA model require a more detailed set of parameters than reported by the case studies. These properties have therefore been estimated by comparing the qualitative descriptions of soil texture with the soil types included in the CLEA model, and adopting the data for the closest match (Environment Agency, 2004).

**Plant data**

Plant composition is reported to be a significant factor affecting the passive uptake of organic chemicals and, in particular, the lipid content of shoots and roots (Bromilow and Chamberlain, 1995; Muller et al., 1994; Simonich and Hites, 1994). However, a review of the available literature suggests that such information is not readily accessible for the majority of plants, including fruits and vegetables. It was not reported for any of the plants in the experimental cases used by this study.

Some generic data was obtained from sources including the US Department of Agriculture (Gebhardt and Thomas, 2002), Danish Environmental Protection Agency (2003), and European Union (EU, 2003). The major differences between important food crops were the higher water content and lower carbohydrate levels in leafy crops and the higher lipid concentrations in root and fruit crops. Specific plant data for a few species such as soy bean (Glycine max) was obtained from other detailed experimental or modelling studies (Trapp and MacFarlane, 1995; Trapp 2002). Where a plant parameter was used only in a single model and generic values were not available, the default value reported by the authors in the original model exposition has been adopted in this study. The data used for each plant species is summarised in Appendix 2.
5.1.2 Results presentation

All the models used by this study were corrected to predict the plant concentration of a chemical in mg kg\(^{-1}\) on a fresh weight basis. With the exception of the models of Topp et al. (1986) and Travis and Arms (1988), all outputs distinguished between shoot (including leaves and stems) and root concentrations. Topp et al. (1986) and Travis and Arms (1988) estimated shoot concentrations only.

The predicted concentration from each model was compared with the observed experimental concentration from the relevant case study. Since outputs varied by several orders of magnitude, this was difficult to present graphically and so the output graphs show the logged values either for plant concentrations directly (see Section 5.2) or the ratio of the predicted value to the experimental value (see Section 5.2). Equation 5-3 has been used to calculate the ratio of the modelled plant concentration to experimental plant concentration in each case study.

**Equation 5-3**

\[
CR = \frac{C_{mod}}{C_{exp}}
\]

Where
- \(CR\) is the ratio of the predicted plant concentration to observed plant concentration (dimensionless)
- \(C_{mod}\) is the modelled plant concentration in either shoots or roots (mg kg\(^{-1}\) fresh weight)
- \(C_{exp}\) is the measured experimental plant concentration in either shoots or roots (mg kg\(^{-1}\) fresh weight)

The graphs in Section 5.2 show the calculated log values (base 10) of \(CR\) for each model compared with the relevant experimental data as tabulated in Chapter 4. The following general points are intended to assist interpretation of these results:

- A value of zero indicates that the predicted and experimental plant concentrations are the same (that is, the model appears to have accurately predicted observed uptake).
- A value of greater than zero indicates that the modelled plant concentration exceeds the experimental concentration (that is, the model appears to have over-predicted uptake).
- A value of less than zero indicates that the modelled plant concentration is lower than the experimental concentration (that is, the model appears to have under-predicted uptake).
- Each step away from zero (that is, 0 to 1, 1 to 2, 0 to –1) represents a ten-fold difference or one order of magnitude.
5.2 Model comparison with case studies

5.2.1 Goodin and Webber (1995)

Overall, model performance was highly variable in comparison with the experimental data for uptake of anthracene by either soya plant or ryegrass (see Figure 5-1). Fifty per cent of the predicted concentrations were out by more than one order of magnitude. The closest predictions were those of Ryan et al. (1988), Briggs et al. (1982, 1983) and Hung and Mackay (1997). The difference between Ryan et al. and Briggs et al. is attributed to the latter model taking into account the maximum aqueous solubility of anthracene, which would be exceeded based on the experimental soil concentration used by Goodin and Webber (1995).

Figure 5-1: Comparison of predicted and measured uptake of anthracene by soya plant and ryegrass (Goodin and Webber, 1995)

5.2.2 Groom et al. (2002)

Several models were very good predictors of the uptake of HMX by rape and bush bean (see Figure 5-2). Ryan et al. (1988), Topp et al. (1986), Trapp and Matthies (1995) and Travis and Arms (1988) all predicted the experimentally observed concentrations within about a factor of five. The very large under-prediction by Briggs et al. (1982, 1983) is attributed to the very low maximum aqueous solubility of HMX used to predict the porewater concentration. This suggests that either the aqueous solubility of HMX was significantly increased by the presence of other compounds in the field samples, or that factors other than passive root uptake were important in its plant accumulation.
5.2.3 Kipopoulou et al. (1999)

All the models, with the exception of Travis and Arms (1988), over-predicted the uptake of PAH compounds by carrot roots in this study (see Figure 5-3b). The difference between modelled and observed plant concentrations increased with molecular weight and chemical lipophilicity (as indicated by the octanol-water partition coefficient).

In the case of cabbage and lettuce, the predictions were much more varied although the models of Briggs et al. (1982, 1983) and Ryan et al. (1988) were typically within an order of magnitude of the experimental data (see Figure 5-3a and 5-3c). The approaches of Hung and Mackay (1997), Trapp and Matthies (1995) and Travis and Arms (1988) generally under-predicted PAH uptake in leafy vegetables, while the shoot concentrations were significantly overestimated by Chiou et al. (2001) and Topp et al. (1986). In most cases, naphthalene uptake was particularly poorly estimated. Similar to the root data and with the exception of naphthalene, most models appeared to better predict plant concentration of the lower molecular weight PAHs compared to the high-end PAHs. However, Trapp and Matthies (1995) appeared to reverse this trend.

Kipopoulou et al. (1999) suggested that there was a significant atmospheric component to the PAH contamination in the study area. Most models might therefore be assumed to underestimate plant uptake, especially to above-ground shoots and leaves; however, only three models consistently under-predicted the shoot concentrations (namely Hung and Mackay 1997, Trapp and Matthies 1995 and Travis and Arms 1988).
Figure 5-3: Comparison of predicted and measured uptake of five PAHs by (a) cabbage, (b) carrot, and (c) lettuce (Kipopoulou et al., 1999)

(a)  

(b)  

(c)  

Key: Briggs (Briggs et al., 1982, 1983), Chiou (Chiou et al., 2001), H + M (Hung and Mackay, 1997), Ryan (Ryan et al., 1988), Topp (Topp et al., 1986), T + M (Trapp and Matthies, 1995), and T + A (Travis and Arms, 1988)
5.2.4 Wang and Jones (1994)

With the exception of Travis and Arms (1988), all models over-predicted the uptake of chlorobenzenes by carrot root in the experimental studies (see Figure 5-4). The initial concentration and the method of chemical addition as a spiked solution or solid sludge appeared to have little effect on this pattern.

Travis and Arms (1988) gave the prediction nearest to the observed value although it significantly under predicted uptake. Trapp and Matthies (1995) was the best performer across all chlorobenzenes amongst the models that over predicted uptake, with the outputs for di-, tri-, and tetrachlorobenzene generally better than for penta- and hexachlorobenzene.

Figure 5-4: Comparison of predicted and measured uptake of chlorobenzenes by carrot roots in (a) spiked soil, (b) low rate sludge amended, and (c) high rate sludge amended (Wang and Jones, 1994)
5.2.5 Berry-Spark *et al.* (2003)

The results of this study need to be viewed with some caution because of the problems in growing healthy vegetables in the pot chambers. However, most models appeared to under-predict uptake of hexachlorobutadiene by both lettuce and carrots (see Figure 5-5). This is consistent with the findings of Berry-Spark *et al.* (2003). The worst performer was Trapp and Matthies (1995) which appeared to under-predict uptake by up to four orders of magnitude. There was a noticeable difference between the results for the low and high level spiked soils, with most models moving from under-prediction at lower soil concentrations to over-prediction at higher values.

Figure 5-5: Comparison of predicted and measured uptake of hexachloro-1,3-butadiene by lettuce and carrot grown in (a) low level spiked soils and (b) high level spiked soils (Berry-Spark *et al*., 2003)

![Graph showing predicted and measured uptake of hexachloro-1,3-butadiene](image)

The **Key** for the graph is as follows:
- Briggs (Briggs *et al*., 1982, 1983)
- Chiou (Chiou *et al*., 2001)
- H + M (Hung and Mackay, 1997)
- Ryan (Ryan *et al*., 1988)
- Topp (Topp *et al*., 1986)
- T + M (Trapp and Matthies, 1995)
- T + A (Travis and Arms, 1988)
Model predictions were considerably better for uptake by carrots than for lettuce, although in the latter case many of the results were close to or below detection limits (Berry-Spark et al., 2003). Briggs et al. (1982, 1983), Chiou et al. (2001), Hung and Mackay (1997) and Ryan et al. (1988) provided very good estimates of uptake for carrot across a wide range of soil concentrations.

### 5.3 Overall model evaluation

Table 5.1 summarises the results of the comparison between predicted and observed root and shoot concentrations in Section 5.2 using log CR as an indicator (see Equation 5-3). Results are presented as the average of all comparisons, which are 24 data points for root concentrations and 18 data points for shoot concentrations. Relative difference distinguishes between over-prediction (positive log CR values) and under-prediction (negative log CR values), while absolute difference looks only at the log CR value without any numerical sign. Relative difference therefore gives an indication of whether the model tends to over or under-predict uptake, while absolute difference gives a better indication of the variation between predicted and measured values.

<table>
<thead>
<tr>
<th>Model</th>
<th>Average relative difference (log CR)</th>
<th>Average absolute difference (log CR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Root</td>
<td>Shoot</td>
</tr>
<tr>
<td>Briggs et al.</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Chiou et al.</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Hung and Mackay</td>
<td>1.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ryan et al.</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Topp et al.</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Trapp and Matthies</td>
<td>0.8</td>
<td>-1.7</td>
</tr>
<tr>
<td>Travis and Arms</td>
<td>-0.9</td>
<td>-0.7</td>
</tr>
</tbody>
</table>

Notes:  \(^1\)Log CR is the ratio of the predicted plant concentration to observed plant concentration and is defined in Equation 5-3. A value of zero indicates that the predicted and experimental plant concentrations are the same, that is, the underlying CR value is one.

Figure 5-6 shows a graph of log CR against log Kow for each model and case study. With the exception of Travis and Arms (1988)\(^1\), most models consistently over-

\(^12\) The average log CR value for each model has been calculated by dividing the sum of all the individual study log CR values for roots and shoots by the number of observations in each category (that is, 24 and 18 respectively).

\(^13\) Relative difference includes both positive and negative numbers in the original summation, while absolute difference assumes that all log CR values are positive.

\(^14\) Travis and Arms (1988) state that the empirical relationship applies only to above-ground plant concentrations.
predicted the root concentration, with the greatest differences observed for chemicals with high octanol-water coefficients. There was no observed pattern for the relationship between log CR and the octanol-water partition coefficients for shoot concentrations. The models of Chiou et al. (2001) and Topp et al. (1986) tended to over-predict shoot concentrations, whilst that of Trapp and Matthies tended to under-predict the uptake. Based on absolute difference, Travis and Arms (1988) and Trapp and Matthies (1995) were the best performing models for predicting root concentrations, and Ryan et al. (1988) and Briggs et al. (1982, 1983) were best for shoot concentrations.

Figure 5-6: Comparison of log CR versus log Kow for (a) root concentrations and (b) shoot concentrations for the studied models

Key: Briggs (Briggs et al., 1982, 1983), Chiou (Chiou et al., 2001), H + M (Hung and Mackay, 1997), Topp (Topp et al., 1986), T + M (Trapp and Matthies, 1995), and T + A (Travis and Arms, 1988)
6 Conclusions

6.1 Results

This review compared several plant uptake models used in contaminated land risk assessment with five case studies. Model performance was highly variable, with predicted concentrations up to five orders of magnitude different from observed concentrations. None of the models tested were considered suitable as a general screening tool for all chemicals and vegetable types of relevance to contaminated land risk assessment.

Performance was not related to model complexity, with the more simple empirical models such as Travis and Arms (1988) as effective as the multiple compartment models such as Trapp and Matthies (1995) and Hung and Mackay (1997). This may be due to the regression models being based on a wide range of chemical data and the fact that they represent an aggregation of all uptake pathways. However, the more complex models were at a disadvantage in this study, because much of the data required to parameterise these models was not available and calculations relied on default values provided by the authors. The absence of authoritative and complete data sets for these complex models therefore represents a challenging barrier to their routine application as screening tools.

Of the six models tested, all over-predicted root concentrations by at least one order of magnitude with the exception of Travis and Arms (1988), a finding consistent with a review sponsored by the Danish Environmental Protection Agency (Samsøe-Petersen et al., 2003). The trend was more confused for predictions of shoot concentration, with most models over-predicting in some circumstances and under-predicting in others. Topp et al. (1986) and Chiou et al. (2001) tended to over-predict shoot uptake while Trapp and Matthies (1995) tended to under-predict uptake.

For shoot concentrations, the Ryan et al. (1988) and the Briggs et al. (1982, 1983) models performed the best, with an average absolute variation much less than one order of magnitude. Both models use the same relationship for shoot concentration based on the Briggs et al. work, and differ only in their approach to the soil-water relationship. While the Ryan et al. equations are self-contained, Briggs et al. is coupled to the partitioning approach used in the CLEA model (Defra and Environment Agency, 2002), which takes into account air-water partitioning and theoretical saturation limits. It is the use of saturation limits that appears to reduce the effectiveness of the Briggs et al. approach in this study and suggests that equilibrium partitioning does not limit uptake in all cases.

The under-prediction of shoot concentrations in several of the models tested might well arise from the importance of the soil-air-leaf pathway, which is generally not represented in the models tested. Ryan et al. (1988) stated that this pathway was potentially significant for all chemicals with a Henry’s Law constant greater than $1 \times 10^{-4}$. However, Muller et al. (1994) and Kipopoulou et al. (1999) both found that off-site migration and subsequent gaseous uptake may well be more important. Particulate deposition may also have influenced the shoot concentrations of the experimental data, although there is little separation between them, Ryan et al. (1988) performed marginally better than the Briggs et al. (1982, 1983) approach on the basis of a smaller absolute difference in Table 5.1.
but this was not accounted for in any of the models tested, although it is included as a separate pathway in the CLEA model (Defra and Environment Agency, 2002).

For root concentrations, Trapp and Matthies (1995) and Travis and Arms (1988) were the best performing models, although results were on average about one order of magnitude out. Trapp and Matthies (1995) tended to over-predict uptake, while Travis and Arms (1988) under-predicted uptake. An important limitation of this study was the lack of data on contaminant uptake by potatoes, a key vegetable crop that dominates the diet in the UK and across Europe (Defra and Environment Agency, 2002; Samsøe-Petersen et al., 2003). Potatoes are often incorrectly described as root vegetables, but the tuber is a storage organ and receives nutrients via the phloem and not the xylem.

The performance of the best models in this study, that is, Ryan et al. (1988) for shoot concentrations and Trapp and Matthies (1995) for root concentrations, are summarised in Figure 6-1 against chemical lipophilicity.

Throughout this study, the pattern of empirical data suggested that chemicals behave in a predictable pattern with respect to plant uptake. For example, Figure 6-2 shows the relationship between the empirical soil-to-plant concentration data and the chemical lipophilicity for all the studies detailed in Chapter 4. Similar behaviour was noted with individual contaminants between studies such as anthracene (Goodin and Webber, 1995; Kipopoulou et al., 1999). This suggests that realistic predictive modelling of the fate and behaviour of a wide range of chemicals could potentially be achieved.

**Figure 6-1: Comparison of log CR versus log Kow for the two best performing models in this study**

![Graph showing log CR versus log Kow](image)

**Key:** Ryan (Ryan et al., 1988) and T + M (Trapp and Matthies, 1995)
Figure 6-2: Comparison of experimental BCF versus log Kow for all case study data introduced in Chapter 4

Key: BCF is the soil-to-plant concentration factor reported on a dry weight basis (regression $r^2 = 0.32$)

6.2 Recommendations

**Recommendation 1:** The Environment Agency and other organisations with an interest in assessing plant uptake of organic chemicals should support further research in this area, specifically targeted at industrial chemical releases to land.

This study compared generic models with five case studies. While the results have provided a useful insight into the modelling of plant uptake processes for organic chemicals, it is clear that the exercise should be undertaken more widely with a far greater number of case studies and results. Many plant uptake models have been poorly validated, with limited supporting studies under a range of different soil and plant conditions. More complex models often require careful parameterisation, but there is little data to support such choices beyond the original scientific paper cited in their derivation. This may be one reason why the simple regression models perform as well as the dynamic and multiple-compartment models in this study, because they are based on a broader range of chemical data. The scientific literature is limited by the availability of good quality experimental data for a broad range of organic industrial chemicals. The more persistent and highly lipophilic substances, including PAHs, therefore dominated the data set used here.

**Recommendation 2:** The approach of reviewing existing literature for plant uptake data on each chemical is clearly prudent, given the wide range of results reported here. The Environment Agency should consider using Briggs et al. (1982, 1983) only for predicting shoot concentrations and remove the artificial limitation on aqueous solubility applied in the model.

The existing approach in the CLEA model is a contaminant specific approach, where the available literature on uptake is reviewed in order to estimate the soil-to-plant concentration factor (Defra and Environment Agency, 2002). As noted above, there are limited studies on a wide range of important industrial chemicals and in the absence of
such data, the CLEA model defaults to the approach of Briggs et al. (1982, 1983) model. This study suggests that although Briggs et al. (1982, 1983) gives a reasonable estimate of shoot concentrations (without applying theoretical solubility limits), it performed poorly for root concentrations.

**Recommendation 3:** None of the models included in this study can confidently be recommended for use as a screening tool for root concentrations. However, it is reassuring that the general trend is to over- rather than under-predict uptake. It is recommended that the Environment Agency evaluate the suitability of other crop-specific approaches for the CLEA model, accepting that they have been developed for specific vegetables.

Prediction of root concentrations was generally poor across all the models reviewed and although Trapp and Matthies (1995) was the best performer, it still significantly over-predicted uptake for chemicals with a high lipophilicity. Several models have been developed that deal with specific root and tuber vegetables including carrot and potato (Samsøe-Petersen et al., 2003; Trapp et al., 2003; Trapp 2002; Trapp et al., unpublished).

**Recommendation 4:** The Environment Agency and other organisations should support collaborative research on the mechanisms that control plant uptake by key food crops, including the development and parameterisation of predictive models for fruits, seeds and tubers.

None of the models assessed in this survey are suitable for predicting the concentration of chemicals in fruits and seeds. Several models have been developed for specific crops such as fruit trees, but these were not included in this study. This is probably the strength of a compartment-based approach such as that of Hung and Mackay (1997) or Paterson et al. (1994). Further work needs to be undertaken to improve our understanding of transport from external plant surfaces to internal organs.
References


List of abbreviations

BaP   Benzo(a)pyrene
BCF   Bioconcentration factor
CF    Concentration factor
CLEA  Contaminated Land Exposure Assessment model
DCB   Dichlorobenzene
Defra Department for Environment, Food and Rural Affairs
f_o.c. Fraction organic carbon
f_o.m. Fraction organic matter
H_C   Henry’s Law constant
HCB   Hexachlorobenzene
H     Henry’s Law constant
HMX   High Melting eXplosive
K_{AW} Air-to-water partition coefficient
      = Concentration_{Air} / Concentration_{Water}
K_d   Soil-to-water partition coefficient
      = Concentration_{Soil} / Concentration_{Water}
K_{LA} Leaf-to-air partition coefficient
       = Concentration_{Leaf} / Concentration_{Air}
K_{OA} Octanol-to-air-partition coefficient
       = Concentration_{Octanol} / Concentration_{Air}
K_{OC} Organic carbon-to-water partition coefficient
       = Concentration_{Soil Organic Carbon} / Concentration_{Water}
K_{OW} Octanol-to-water partition coefficient
       = Concentration_{Octanol} / Concentration_{Water}
K_{RW} Root-to-water partition coefficient
       = Concentration_{Root} / Concentration_{Water}
MCI   Molecular Connectivity Index
OM    Organic matter
PAH   Polycyclic aromatic hydrocarbon
PCB   Polychlorinated biphenyl
PCDD/F Polychlorinated dibenzo dioxin/furan
RCF   Root concentration factor
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>Royal Demolition Explosive. The chemical name for RDX is 1,3,5-trinitro-1,3,5-triazine.</td>
</tr>
<tr>
<td>SCF</td>
<td>Stem concentration factor</td>
</tr>
<tr>
<td>TCB</td>
<td>Trichlorobenzene</td>
</tr>
<tr>
<td>TCDD</td>
<td>2,3,7,8-tetrachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>TSCF</td>
<td>Transpiration stream concentration factor</td>
</tr>
<tr>
<td>Glossary</td>
<td>Definition</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
</tr>
<tr>
<td>Active transpiration</td>
<td>The active loss of water from a plant, mainly through the stomata of leaves.</td>
</tr>
<tr>
<td>Active uptake</td>
<td>The uptake of substances across biological membranes into cells by means other than through diffusion or passive uptake and often occurring against concentration gradients.</td>
</tr>
<tr>
<td>Cortex</td>
<td>The typically parenchymatous layer of tissue external to the vascular tissue and internal to the corky or epidermal tissues of a green plant; <em>broadly</em>: all tissues external to the xylem.</td>
</tr>
<tr>
<td>Cuticle</td>
<td>A thin continuous fatty or waxy film on the external surface of many higher plants that consists chiefly of cutin.</td>
</tr>
<tr>
<td>Cutin</td>
<td>An insoluble mixture containing waxes, fatty acids, soaps, and resinous material that forms a continuous layer on the outer epidermal wall of a plant.</td>
</tr>
<tr>
<td>Endodermis</td>
<td>The innermost tissue of the cortex in many roots and stems.</td>
</tr>
<tr>
<td>Epidermis</td>
<td>A thin surface layer of tissue in higher plants formed by growth of a primary meristem.</td>
</tr>
<tr>
<td>Exponential growth</td>
<td>The phase of development of maximum growth.</td>
</tr>
<tr>
<td>$f_{o.c.}$</td>
<td>Fraction organic carbon, The amount of natural organic material in the form of carbon in a soil. The greater the fraction by weight of organic carbon ($f_{o.c.}$), the greater the adsorption of organic chemicals.</td>
</tr>
<tr>
<td>$f_{o.m.}$</td>
<td>Fraction organic matter</td>
</tr>
<tr>
<td>Fugacity</td>
<td>The tendency of a substance to exist in one environmental compartment rather than another. Some risk assessment tools use partition coefficients to calculate fugacity capacity constants for soil water, soil air, and soil. These describe the capacity of each compartment to contain the contaminant, assuming an equilibrium between the three phases.</td>
</tr>
<tr>
<td>Fugacity capacity ($Z$)</td>
<td>A proportionality constant that indicates the ability of the solute for a solvating phase. Using the fugacity concept in environmental calculations tells us the thermodynamic driving force behind chemical partitioning.</td>
</tr>
<tr>
<td>Henry’s Law constant</td>
<td>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.</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>Literally ‘water-hating’, hydrophobic describes compounds with a low aqueous solubility that are more fat soluble.</td>
</tr>
<tr>
<td>Hydroponic solutions</td>
<td>Nutrient solutions used to grow plants with or without an inert medium (such as sand and gravel) to provide mechanical support.</td>
</tr>
<tr>
<td>$K_{OC}$</td>
<td>Organic carbon-to-water partition coefficient. 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 ($kg$).</td>
</tr>
</tbody>
</table>
\[ K_{OC} = \frac{\text{Concentration Soil Organic Carbon}}{\text{Concentration Water}} \]

\[ K_{OW} \]
Octanol-to-water partition coefficient. 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.

\[ K_{OW} = \frac{\text{Concentration Octanol}}{\text{Concentration Water}} \]

Lipophilic
Literally ‘fat-loving’, lipophilicity describes compounds with a high solubility in fat and low aqueous solubility.

Molecular Connectivity Index (MCI)
An index system based on the size and shape of a molecule that is calculated from the groupings of skeletal atoms, weighted by the degree of skeletal branching.

OM
Organic matter. The decayed/partially decayed plant and animal material in the soil. Soil organic carbon is a proportion of this material.

Passive transpiration
Simple diffusive loss of water or small uncharged molecules in the direction of a concentration gradient and which does not require energy.

Passive uptake
The uptake of substances across biological membranes into cells by means of diffusion along concentration gradients.

Pericycle
A thin layer of parenchymatous or sclerenchymatous cells that surrounds the stele in most vascular plants.

Phloem
A complex tissue in the vascular system of higher plants that consists mainly of sieve tubes and elongated parenchyma cells usually with fibres and that functions in translocation and in support and storage.

Photolytic degradation
A chemical reaction in which the breaking of a chemical bond within a molecule of a substance is brought about by exposure to light or ultraviolet radiation.

Photodegradation
The process of decomposition of the material upon exposure to radiant energy such as the action of light.

PCDD/F
Polychlorinated dibenzo dioxin/furan

pK\text{a}
Acid dissociation constant

Quasi-equilibrium factor (\(\alpha_{pt}\))
An empirical factor that represents the ratio of the concentration in plant tissue to that in the soil porewater. The factor can be used to measure the extent to which equilibrium has been achieved in experimental studies.

Root concentration factor

\[ \text{RCF} = \frac{\text{root concentration of compound X}}{\text{soil concentration of compound X}} \]

Senescence
The growth phase in a plant or plant part (as a leaf) from full maturity to death.

SCF
Stem concentration factor. A concentration factor which relates the concentration in soil to that in the stem of the plant.

Stele
The usually cylindrical central vascular portion of the axis of a vascular plant.
Soil bulk density Soil bulk density is defined as the ratio of the mass of dry solids to the bulk volume of the soil occupied by those dry solids. Bulk density of the soil is an important site characterisation parameter since it changes for a given soil. It varies with structural condition of the soil, particularly that related to packing.

Translocation The conduction of soluble material (as metabolic products) from one part of a plant to another.

Transpiration stream concentration factor

**TSCF**

\[
\text{concentration of compound } X \text{ in xylem sap} = \frac{\text{concentration of compound } X \text{ in external solution}}{\text{concentration of compound } X}
\]

Xylem A complex tissue in the vascular system of higher plants that consists of vessels, tracheids, or both usually together with wood fibres and parenchyma cells; functions chiefly in conduction of water and dissolved minerals but also in support and food storage, and typically constitutes the woody element (as of a plant stem). Plant tissue that conducts water and minerals from roots to other plant parts.
### Physical-chemical data used in the model comparison study

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Log $K_{ow}$</th>
<th>Vapour pressure (Pa)</th>
<th>Solubility (g m$^{-3}$)</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>Diffusion coefficient in air (cm$^2$ s$^{-1}$)</th>
<th>Diffusion coefficient in water (cm$^2$ s$^{-1}$)</th>
<th>Henry’s Law constant (cm$^3$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>4.54E+00</td>
<td>1.00E-03</td>
<td>4.50E-02</td>
<td>1.78E+02</td>
<td>3.20E-02</td>
<td>7.74E-06</td>
<td>3.28E-04</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>6.04E+00</td>
<td>7.00E-07</td>
<td>3.80E-03</td>
<td>2.52E+02</td>
<td>4.30E-02</td>
<td>9.00E-06</td>
<td>1.17E-06</td>
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<tr>
<td>Benzo[g,h,i]perylene</td>
<td>6.50E+00</td>
<td>NA</td>
<td>2.60E-04</td>
<td>2.68E+02</td>
<td>4.70E-02</td>
<td>5.50E-06</td>
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<tr>
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<td>3.40E+00</td>
<td>1.30E+02</td>
<td>8.00E+01</td>
<td>1.47E+02</td>
<td>6.90E-02</td>
<td>7.90E-06</td>
<td>2.49E-02</td>
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<tr>
<td>Chrysene</td>
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<td>5.70E-07</td>
<td>2.00E-03</td>
<td>2.28E+02</td>
<td>2.48E-02</td>
<td>6.21E-06</td>
<td>3.08E-06</td>
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<td>5.50E+00</td>
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<td>5.00E-03</td>
<td>2.85E+02</td>
<td>5.42E-02</td>
<td>5.91E-06</td>
<td>9.31E-03</td>
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<tr>
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<td>2.00E+01</td>
<td>3.20E+00</td>
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<td>6.16E-06</td>
<td>2.10E-01</td>
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<td>HMX</td>
<td>1.76E-01</td>
<td>1.40E-12</td>
<td>2.60E+00</td>
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<td>6.30E-02</td>
<td>5.30E-06</td>
<td>6.60E-14</td>
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<tr>
<td>Naphthalene</td>
<td>3.37E+00</td>
<td>1.04E+01</td>
<td>3.10E+01</td>
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<td>5.90E-02</td>
<td>7.50E-06</td>
<td>5.74E-03</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>5.00E+00</td>
<td>2.20E-01</td>
<td>6.50E-01</td>
<td>2.50E+02</td>
<td>5.70E-02</td>
<td>6.30E-06</td>
<td>3.44E-02</td>
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<tr>
<td>Phenanthrene</td>
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<td>2.00E-02</td>
<td>1.10E+00</td>
<td>1.78E+02</td>
<td>3.30E-02</td>
<td>7.47E-06</td>
<td>1.31E-03</td>
</tr>
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<td>1,2,4,5-Tetrachlorobenzene</td>
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<td>7.20E-01</td>
<td>1.27E+00</td>
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<td>2.11E-02</td>
<td>8.80E-06</td>
<td>4.94E-02</td>
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<td>1,2,4-Trichlorobenzene</td>
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<td>4.00E+01</td>
<td>4.00E+01</td>
<td>1.81E+02</td>
<td>3.00E-02</td>
<td>8.23E-06</td>
<td>5.82E-02</td>
</tr>
</tbody>
</table>

Notes:  
1. Unless noted otherwise, all physical chemical data from Mackay *et al.* (2000).  
2. Unless noted otherwise, calculated by the CLEA model as described in Environment Agency (2004).  
5. Chemical and Physical Properties Database of the Pennsylvania Department of Environmental Protection Land Recycling Program
## Appendix 2

### Plant physiological parameters

<table>
<thead>
<tr>
<th>Plant</th>
<th>Root lipids</th>
<th>Root water</th>
<th>Shoot lipids</th>
<th>Shoot water</th>
<th>Root density</th>
<th>Shoot density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g g⁻¹</td>
<td>m³ m⁻³</td>
<td>g g⁻¹</td>
<td>m³ m⁻³</td>
<td>g g⁻¹</td>
<td>m³ m⁻³</td>
</tr>
<tr>
<td>Bush bean (Phaseolus vulgaris)</td>
<td>2.50E-02²</td>
<td>3.02E-02</td>
<td>9.42E-01</td>
<td>9.42E-01</td>
<td>3.54E-02</td>
<td>3.51E-02</td>
</tr>
<tr>
<td>Cabbage (Brassica oleracea capitata)</td>
<td>2.50E-02²</td>
<td>3.02E-02</td>
<td>9.42E-01</td>
<td>9.42E-01</td>
<td>1.00E-03³</td>
<td>9.92E-04</td>
</tr>
<tr>
<td>Carrot (Daucus carota)</td>
<td>4.00E-03³</td>
<td>4.84E-03</td>
<td>8.90E-01³</td>
<td>8.90E-01³</td>
<td>3.54E-02</td>
<td>3.51E-02</td>
</tr>
<tr>
<td>Lettuce (Lactuca sativa)</td>
<td>2.50E-02²</td>
<td>3.02E-02</td>
<td>9.42E-01</td>
<td>9.42E-01</td>
<td>4.00E-03³</td>
<td>3.97E-03</td>
</tr>
<tr>
<td>Rape (Brassica rapa)</td>
<td>1.00E-03³</td>
<td>1.21E-03</td>
<td>9.20E-01³</td>
<td>9.20E-01³</td>
<td>2.00E-03</td>
<td>1.98E-03</td>
</tr>
<tr>
<td>Ryegrass (Lolium perenne)</td>
<td>2.50E-02²</td>
<td>3.02E-02</td>
<td>9.42E-01</td>
<td>9.42E-01</td>
<td>2.00E-03</td>
<td>1.69E-03</td>
</tr>
<tr>
<td>Soybean (Glycine max)</td>
<td>8.27E-03⁴</td>
<td>1.00E-02</td>
<td>9.42E-01⁴</td>
<td>9.42E-01⁴</td>
<td>3.03E-02⁴</td>
<td>3.00E-02⁴</td>
</tr>
</tbody>
</table>

Notes:  
1. All physiological parameters not listed here based on default model values.  
We are The Environment Agency. It's our job to look after your environment and make it a better place – for you, and for future generations.

Your environment is the air you breathe, the water you drink and the ground you walk on. Working with business, Government and society as a whole, we are making your environment cleaner and healthier.

The Environment Agency. Out there, making your environment a better place.