Mass Transport within Soils

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Chapter 8

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8.1 Introduction

Contaminants in soil can impact human health and the environment through a complex web of interactions. Soils exist where the atmosphere, hydrosphere, geosphere, and biosphere converge. Soil is the thin outer zone of the earth's crust that supports rooted plants and is the product of climate and living organisms acting on rock. A true soil is a mixture of air, water, mineral, and organic components. The relative proportions of these components determine the value of the soil for agricultural and for other human uses. These proportions also determine, to a large extent, how a substance added to soil is transported and/or transformed within the soil (Spositio, 2004). In mass-balance models, soil compartments play a major role, functioning both as reservoirs and as the principal media for transport among air, vegetation, surface water, deeper soil, and ground water (Mackay, 2001). Quantifying the mass transport of chemicals within soil and between soil and atmosphere is important for understanding the role soil plays in controlling fate, transport, and exposure to multimedia pollutants.

Soils are characteristically heterogeneous. A trench dug into soil typically reveals several horizontal layers having different colors and textures. As illustrated in Figure 1, these multiple layers are often divided into three major horizons:

(1) the *A* horizon, which encompasses the root zone and contains a high concentration of organic matter;
(2) the *B* horizon, which is unsaturated, lies below the roots of most plants, and contains a much lower organic carbon content; and
(3) the *C* horizon, which is the unsaturated zone of weathered parent rock consisting of bedrock, alluvial material, glacial material, and/or soil of an earlier geological period.

Below these three horizons lies the saturated zone--a zone that encompasses the area below ground surface in which all interconnected openings within the geologic media are completely filled with water. Similarly to the unsaturated zone with three major horizons, the saturated zone can be further divided into other zones based on hydraulic and geologic conditions. Wetland soils are a special and important class in which near-saturation conditions exist most of the time.

When a contaminant is added to or formed in a soil column, there are several mechanisms by which it can be dispersed, transported out of the soil column to other parts of the environment, destroyed, or transformed into some other species. Thus, to evaluate or manage any contaminant introduced to the soil column, one must determine whether and how that substance will (1) remain or accumulate within the soil column, (2) be transported by dispersion or advection within the soil column, (3) be physically, chemically, or biologically transformed within the soil (i.e., by hydrolysis, oxidation, etc.), or (4) be transported out of the soil column to another part of the environment through a cross-media transfer (i.e., volatilization, runoff, ground water infiltration, etc.). These competing processes impact the fate of physical, chemical, or biological contaminants found in soils. In order to capture these mechanisms in mass transfer models, we must develop

mass-transfer coefficients (MTCs) specific to soil layers. That is the goal of this chapter. The reader is referred to other chapters in this Handbook that address related transport processes, namely Chapter 13 on bioturbation, Chapter 15 on transport in near-surface geological formations, and Chapter 17 on soil resuspention.

This chapter addresses the following issues: the nature of soil pollution, composition of soil, transport processes and transport parameters in soil, transformation processes in soil, mass-balance models, and MTCs in soils. We show that to address vertical heterogeneity in soils in is necessary to define a characteristic scaling depth and use this to establish process-based expressions for soil MTCs. The scaling depth in soil and the corresponding MTCs depend strongly on (1) the composition of the soil and physical state of the soil, (2) the chemical and physical properties of the substance of interest, and (3) transformation rates in soil. Our particular focus is on approaches for constructing soil-transport algorithms and soil-transport parameters for incorporation within multimedia fate models. We show how MTC's can be developed to construct a simple two-compartment air-soil system. We then demonstrate how a multi-layer-box-model approach for soil-mass balance converges to the exact analytical solution for concentration and mass balance. Finally, we demonstrate and evaluate the performance of the algorithms in a model with applications to the specimen chemicals benzene, hexachlorobenzene, lindane (gamma-hexachlorocyclohexane, benzo(a)pyrene, nickel, and copper.

8.2 Sources of Contamination in Soils

Soil contamination is found throughout the world and can be traced to local, regional, and global pollution sources. This pollution is often the result of human and natural activities that involve the direct emission of contaminants to soil through waste disposal practices, pesticide

applications, leaking tanks and pipelines, irrigation with contaminated water, and disposal of sewage and industrial sludge. Soil contamination also results from the deposition and exchange of contaminants from the atmosphere. Metal species and radionuclides released from combustion processes or from volcanoes, and persistent organic pollutants (POPs) migrate globally in the atmosphere and result in low-levels of soil contamination through deposition from the atmosphere. Some sources of contamination, such as local high concentrations of toxic elements, the natural production of radon in soils, and the growth of toxic organisms are not external but internal to the soil. Pesticide use and the disposal of radioactive, biological, and chemical wastes can lead to much higher but localized levels of soil contamination.

Contaminant releases to soil are normally quantified in terms of the mass of substance per unit area per unit time or per release episode. For example, pesticide applications to agricultural fields can range from under 1 kg/ha to over 20 kg/ha per application. Organic contaminants with low water solubility, when introduced to the soil, will migrate to the organic carbon-phase of the soil where they can be retained for relatively long periods. Some metal species can also accumulate and persist in soil if their soil chemistry favors the binding of these contaminants into the mineral phase. A large fraction of the sewage sludge produced in many regions of the world is used as soil amendments often after treatment to reduce the content of harmful microorganisms. Sewage sludge contains contaminants and pathogens that are discharged to the sewer system from homes, businesses, industries and streets (National Research Council, 2002).

As is discussed in more detail in Chapters 6 and 7, contaminants in the atmosphere can be transferred to soil either directly through dry deposition, wet deposition, and vapor partitioning or indirectly through deposition to plants with subsequent transfer to soil. Dry deposition is the

process by which particulate matter settles out of the atmosphere and onto soil and plant surfaces. Contaminants that are attached to these particles will be transferred to soil through this deposition process. Atmospheric contaminants on particles are also washed out of the air to soil with rain or snow in the wet deposition of the particles. Contaminants dissolved in the gas phase of air and not bound to particles can also be transferred to soil through a combination of wet deposition and chemical partitioning. Gaseous contaminants with low air-water or K_{AW} partition coefficients are readily washed out during rain and snow by wet deposition. In addition, contaminants with high octanol-air ($K_{OA)}$ and low K_{AW} partition coefficients are transferred preferentially from air to soil through partitioning that involves chemical diffusion from "solution" in air to solution in the soil water. Similarly, hydrophobic contaminants that are sparingly soluble in water but highly lipid soluble can be carried from air to soil through partitioning into the organic phases of soil. In this process, the contaminants diffuse from solution in air directly to the organic phase of soil. Finally, as discussed in Chapter 7, contaminants in air can be transferred from air to vegetation surfaces by dry deposition, wet deposition, and by partitioning into the lipid and water phases of plants. When the plants decay, lose leaves, or are mowed; residual contamination is transferred to soil. This litterfall is a primary source of the organic matter in soil.

8.3 Composition of Soils

Soils are composed of three major phases—gases, liquids, and solids. The volume fraction of soil that is gas (air) ranges from 10%, in clay soils, to 25% in sandy soils and typically decreases with increasing depth (Jury et al., 1983; Brady and Weil, 2004). The soil solution is mostly water but also includes dissolved minerals, nutrients, and organic matter such as fulvic acid. The volume fraction of soil that is liquid ranges from 10% typical for sandy soils to 40%

typical for clay soils (Jury et al., 1983; Brady and Weil, 2004). The fraction of solid material in soil accounts for some 50 to 80% by volume and 75 to 90% by mass (Brady and Weil, 2004). Soil solids include both mineral (i.e. the parent rock) and organic components, including humic acids and decaying matter. The organic phase of soil is often characterized by its organic-carbon content. While the mineral component of soil is in the range of 70 to 90% by mass, the organic-carbon content of soil ranges from a fraction of 1% by mass for desert and/or sandy soils to as much as 5% by mass for clay soils and even as high as 10% by mass for peat bogs (Jury et al., 1983; Brady and Weil, 2004).

8.4 Transport Processes in the Soil Column

Chemicals move through soil by advection in the liquid phase by water transport, diffusion in the gas phase and to some extent in the liquid phase, bioturbation caused by soil-dwelling organisms such as worms, and erosion near the soil surface (Roth and Jury, 1993; Anderson et al., 1991; Thibodeaux, 1996; Mullerlemans and Vandorp, 1996). The partitioning of chemicals among the components of soils (gas, liquid, mineral, and organic) strongly impacts the rates of transport and transformation in and among soil compartments. The key conceptual issue for multimedia models is how soils function as systems to store, destroy, and transport substances within the soil column. Of particular interest is the way these factors combine to determine the structure and performance of MTCs for soil in environmental mass-balance models. Table 1 summarizes processes by which contaminants are transferred to, from, and within soils.

Studies of radioactive fallout in agricultural land-management units reveal that, in the absence of tilling, particles deposited from the atmosphere accumulate in and are resuspended from a thin ground- or surface-soil layer with a thickness in the range 0.1 to 1 cm at the top of the

A soil horizon (Whicker and Kirchner, 1987). The ground-surface-soil layer has a lower water content and higher gas content than underlying layers. Contaminants in this surface-soil layer are transported horizontally by mechanical runoff and soil-solution runoff to nearby surface waters. Surface-soil contaminants are susceptible to wind erosion (as discussed in detail in Chapter 16), volatilization, photolysis, biodegradation, and transfer to plant surfaces by rainsplash. These contaminants are transferred to and from the root-zone soil by diffusion and leaching.

The roots of most plants are confined within the first meter of soil depth. In agricultural lands, the depth of plowing is 15 to 25 cm. Contaminants in the *A* horizon below the surface layer, that is, in the root-zone soil, are transported upward by diffusion, volatilization, root uptake, and capillary motion of water; transported downward by diffusion and leaching; and transformed chemically primarily by biodegradation or hydrolysis. The presence of clay and organic matter in the root-zone layer serves to retain water, resulting in a higher water content. In addition, the diffusion depth, which is the depth below which a contaminant is unlikely to escape by diffusion, is on the order of a meter or less for all but the most volatile contaminants (Jury et al., 1990).

The deeper unsaturated soil (generally below 1 meter depth) includes the soil layers below the root zone and above the saturated zone, where all pore spaces are filled with water. The soil in this layer typically has a lower organic carbon content and lower porosity than the root-zone soil. Contaminants in this layer move downward to the ground-water zone primarily by capillary motion of water and leaching.

The partitioning of chemicals among the components of soils (gas, liquid, mineral, and organic) strongly impacts the rates of transport and transformation in and among soil compartments. This is illustrated in Figure 2. Also affecting the rate of transport and

transformation are climate and landform properties, which include temperatures of air and soil, rainfall rates, soil properties (bulk density, porosity), and variability of these properties within soil. Finally as discussed in Chapter 13, there is bioturbation—the mixing of mass within the soil column by detritivores such as worms and burrowing animals such as shrews, moles, and mice.

8.5 Transformation Processes in Soil

The transformation of toxic substances in soil can have a profound effect on their potential for transport and accumulation at different soil depths. The rate of transformation processes impact the effective penetration depth of contaminants in soil, which in turn determines the length scale needed to define the soil compartment dimensions in mass transfer models. Transformation processes in soil include chemical conversions such as photolysis, hydrolysis, and oxidation/reduction; biological processes such as microbial transformations; and physical processes such as radioactive decay.

Most organic contaminants are capable of undergoing photolytic decomposition. Although the atmosphere attenuates solar radiation before it reaches the earth's surface, the solar radiation generally sufficient to break bonds in many compounds at this surface. Photo-transformation in soil impacts only those contaminants on the soil surface. However, in agricultural lands that are tilled, contaminants in the tilling horizon, (~15-20 cm) can be brought to the surface where photo-transformation can occur. Photo-transformations can result in relatively short half-lives (e.g., hours to days) for contaminants such as pesticides that are applied directly to crops or soil surfaces.

Hydrolytic transformation of organic chemicals can be a significant destructive process for compounds that are present in the aqueous phase of soils. Hydrolysis is most important for

chemicals that have functional groups (e.g., amides, esters, carbamates, organophosphates), which can be rapidly altered (e.g., minutes to days) in the presence of water. Conversely, hydrolytic degradation of compounds that contain stable constituents (e.g., halogenated compounds such as carbon tetrachloride) can have half-lives of several thousand years. Because hydrolytic reactions are driven by the availability of hydrogen and hydroxide ions, the pH of the soil can dramatically affect the rate of hydrolysis for any given compound.

Many inorganic and organic chemicals can undergo oxidation or reduction reactions in soil. An indicator of a compound's ability to be oxidized or reduced is provided by its oxidation potential (EO), which is the voltage at which it is transformed to its reduced state. A similar measure of a soil’s ability to reduce a compound is provided by the redox potential (pE), which is a measure of electron activity. Redox potentials are relatively high and positive in oxidized environments (e.g., surface waters), and low and negative in reduced environments (e.g., aquatic sediments and the subsurface soil layers). These environmental conditions are especially important for inorganic chemicals that are rarely present in their elemental form in the environment. Arsenic, for example, exists primarily in its oxidized form (arsenate) in the atmosphere and in surface waters and in its reduced form (arsenite) in sediments.

Because of their broad range of enzymatic capabilities, microorganisms are capable of destroying other microorganisms and transforming many inorganic and organic compounds. The chemical transformations can result in the partial degradation of a compound (e.g., conversion of trinitro-toluene to dinitro-toluene), mineralization (i.e., complete transformation to carbon dioxide and water), or synthesis of a stable product (e.g., formation of methyl arsenicals from arsenate). While these processes generally result in the detoxification of the parent compound, toxic products

may also be formed. For example, the microbial metabolism of aromatic amines can result in the formation of toxic byproducts.

Radioactive decay applies only to radioactive elements, which have unstable nuclei and emit atomic radiation as part of a process of attaining stability resulting in the formation of another chemical element, which may be stable or may be radioactive resulting in further decay.

8.6 Soil Mass Transfer: Theory and Equations

In this section, we describe and illustrate an approach for constructing soil-transport parameters, algorithms, and MTCs. The resulting MTCs account for diffusion in gas and liquid components; advection in gas, liquid, or solid phases; and multiple transformation processes. They also provide an explicit quantification of the characteristic soil penetration depth. We apply transport algorithms to and develop MTCs for both a simple one-layer soil model and more detailed and presumably more realistic multi-layer models.

8.6.1 Background

There are significant variations in both the complexity and structure of transport models applied to the soil compartment. Among the differences are the types of soils considered, the number of layers used for each soil type, and how the depth of the soil compartment is selected. Models developed for assessing the behavior of contaminants in soils can be categorized in terms of the transport/transformation processes being modeled. Partitioning models such as the fugacity models of Mackay (1979, 2001) and Mackay and Paterson (1981, 1982) describe the distribution of a contaminant among the liquid, solid, and organic phases of soils. Jury et al. (1983) have developed an analytical screening model that can be used to calculate the extent to which contaminants buried in soil evaporate to the atmosphere or infiltrate down to deeper soil layers.

For radioactive-fallout deposition on agricultural lands, Whicker and Kirchner (1987) have developed a model that includes three soil layers, surface soil (0 to 0.1 cm), intermediate soil (0.1 to 25 cm), and deep soil (>25 cm).

Because experimental and theoretical evidence shows a large variation in the depth to which different chemicals penetrate, multimedia-model developers have acknowledged that each specific chemical substance requires a different soil depth to scale its transport into soil (Cowan et al., 1995; McKone and Bennett, 2003). When a model is used for groundwater or soil protection or when the source resides below the soil-atmosphere interface, detailed soil concentration profiles are vitally important. This often requires detailed numerical simulation models. But when the modeler's primary goal is to assess multimedia transport, then capturing the magnitude of chemical transport between air and soil is as important or (in some cases) more important than capturing the concentration profile within the soil. Examples include efforts to address the role of air/soil exchange in assessments of persistence and long-range transport in the atmosphere. Multimedia models require simple but reliable mass-exchange algorithms between the air compartment and soil.

8.6.2 Conceptual Model

Contaminant penetration in soil and the gaseous exchange between surface soil and the atmosphere are influenced by chemical-specific rates of dispersion/diffusion, advection, and transformation. The relative magnitude of these processes depend strongly on the relative partitioning among the mobile (liquid and gas) and sorbed phases of the soil. The partitioning of a chemical between the three soil phases is defined by any two among the three primary partition properties: the octanol-water partition coefficient (K_{OW}), the octanol-air partition coefficient

(K_{OA}), and the air-water partition coefficient (K_{AW}). We focus on K_{OW} and K_{AW} and note that to a first approximation, K_{OA} equals K_{OW}/K_{AW}. Dispersion/diffusion processes are driven by concentrations gradients in gas and liquid phases of soil. Advection rates are determined by the processes that drive liquids and gases through soil. The link between partitioning and transport by different mechanisms is illustrated in Figure 2. In addition to liquid and gas-phase advection, it should be noted that the solid phases of soil are not necessarily stagnant. Vertical transport of the solid phase transport in surface soils occurs by many processes such as bioturbation, cryoturbation, and erosion into cracks formed by soil drying as well as tilling in agricultural lands (McLachlan et al., 2002).

Most models that handle the transport of organic contaminants within soil are based on the landmark publication of Jury et al. (1983). This model treats soil as a mixture of air, water, and soil particles with the assumption of uniform soil properties, linear sorption isotherms, and equilibrium partitioning between the solid, gas, and liquid phases of soil.

Our approach here is essentially that of McKone and Benett (2003), which is based on the Jury et al (1983) model. It is incorporated within the latest version of the CalTOX model (McKone, 1993) and the original version of the TRIM (US EPA, 2003) model, but also used in other models such as BETR (MacLeod et al., 2001). This approach uses one or more soil compartment layers while maintaining a structure that links easily to other compartments such as air and vegetation in multimedia models. This approach begins by setting up the differential equations describing the mass-balance in soil and accounting for diffusion in air and water phases, advection via water, bioturbation, and chemical transformation. From the steady-state analytical

solution to these equations, which can be applied stepwise to different layers, one develops an equivalent compartment model that uses compartment-based inventories and transfer factors.

These transfer factors are obtained by matching the fugacity and flux at the boundary between each pair of soil compartments with those obtained from an analytical solution. We consider the appropriate scaling depth for selecting compartment depth and generalize this approach to layers of different composition.

8.6.3 Mass Balance Equations

In any defined horizontal layer of soil, the rate in mol d^{-1} at which the dilute chemical mass inventory in that layer is changing is defined by balancing three processes. First there is dispersion due to both physical (diffusion) and biological (bioturbation) processes. Second is advection in soil fluids—primarily the downward (or upward) movement of water. Third is removal by physical, biological, or chemical reactions. Based on these three processes, Jury et al. (1983) have defined the governing equation for mass balance concentration within any specified region of the soil column in the following form

$$\frac{\partial C}{\partial t} = \frac{\partial}{z}\left[D_e \frac{\partial C}{\partial z}\right] - v_e \frac{\partial C}{\partial z} - kC \qquad (1)$$

Concentration Change in time = Dispersion _ Advection loss _ Removal reactions

where C represents the bulk chemical concentration in soil, mol(chemical) m^{-3} (soil); t is time, d; z is depth in a soil column measured from the top surface, m; k is a removal rate constant, d^{-1}, that accounts for first-order losses by chemical transformation, root uptake, etc; D_e is

the bulk dispersion coefficient in the soil, $m^2\ d^{-1}$; and v_e is the bulk advection velocity of the chemical in the soil, $m\ d^{-1}$.

We can easily convert concentration as the state variable in Equation 1 to fugacity-based equations using the relationship $C = fZ$, where f is the chemical fugacity in soil, Pa, and Z is the bulk-soil fugacity capacity, mol/(m^3Pa). More detail on fugacity capacities is given in Chapter 5.

In the case where the soil is being contaminated by the atmosphere such that the soil surface is maintained at constant concentration, C_0, the solution to Equation 1 yields a rather complex expression for C as a function of both depth and time.

$$C(z,t) = C_0 \left\{ \frac{1}{2} \exp\left[\frac{(v_e - u)z}{2D_e} \right] erfc\left[\frac{(z - ut)}{2\sqrt{D_e t}} \right] + \frac{1}{2} \exp\left[\frac{(v_e + u)z}{2D_e} \right] erfc\left[\frac{(z + ut)}{2\sqrt{D_e t}} \right] \right\} \tag{2}$$

where $u = \sqrt{v_e^2 + 4kD_e}$ and $erfc$ is the complimentary error function, and

C_0 is the bulk concentration in soil at the soil surface (assumed to be at the same fugacity as the air), mol m^{-3}

Equation 2 is somewhat intimidating and can be difficult to program into simple programs such as spreadsheets. Fortunately this equation takes on a much simpler form as the soil concentration profile approaches steady-state, a situation that often applies and is most often of interest. In this case the soil concentration dependence on depth becomes

$$C(z) = C(0)e^{-\gamma z} \tag{3}$$

where γ is a function of D_e, v_e, and k and is obtained from Equation 1 in the limit as t goes to infinity.

$$\gamma = \sqrt{\left[\left(\frac{v_e}{2D_e}\right)^2 + \frac{k}{D_e}\right]} - \frac{v_e}{2D_e} \quad \text{or, if } v_e = 0, \quad \gamma = \sqrt{\frac{k}{D_e}} \quad . \tag{4}$$

The γ parameter is developed in more detail in the following section. In order to apply Equations 1 through 4 to soil layers, we must consider how D_e, v_e, and k depend on both soil and chemical properties.

8.6.4 Normalized Gradient of Soil Concentration

As shown above, Equation 2 reduces to a very simple form (Equation 3) under steady-state conditions and with a fixed concentration at its upper boundary and uniform soil properties. Indeed, Equation 3 reveals that concentration in any soil layer at a depth z, describes the vertical gradient of concentration in a soil layer when we know the long-term concentration that applies at its surface, $C(0)$. The γ term has units of m^{-1} and tells us how steep the concentration gradient is in a soil layer. It can be viewed as the reciprocal of a characteristic depth of concentration change as discussed below.

At any depth z of a soil layer, there is competition between reaction processes and dispersion/diffusion and advection processes. The ratio of these competing processes is expressed by the Damkoehler number (N_{DA}), which is the ratio of the rate of loss by chemical transformation to the rate of loss by diffusion/dispersion and advection (Cowan et al., 1995) and is defined as

$$N_{\mathrm{DA}} = \frac{\text{transformation loss rate}}{\text{advection \& diffusion/dispersion loss rate}} = \frac{C \times k \times z}{C\left(v_e + D_e / z\right)} = \frac{k \times z}{\left(v_e + D_e / z\right)} \quad . \qquad (5)$$

When the Damkoehler Number is 1, rates of transformation losses and diffusion/advection transport are equal. This happens when *z* is the characteristic depth or the average depth of penetration for chemical molecules moving into a soil layer from its surface (Cowan et al., 1995). When N_{DA} is 1, Equation 5 can be rearranged to find the *z* corresponding to the characteristic penetration depth, a parameter we label z*,

$$k\,(z^*)^2 + v_e\, z^* + D_e = 0 \qquad (6)$$

Using the quadratic formula to solve Equation 6 gives

$$\frac{1}{z^*} = \sqrt{\left[\left(\frac{v_e}{2D_e}\right)^2 + \frac{k}{D_e}\right]} - \frac{v_e}{2D_e} \quad \text{or, if } v_e = 0, \quad \frac{1}{z^*} = \sqrt{\frac{k}{D_e}} \quad . \qquad (7)$$

Comparing Equation 7 to Equation 4 leads to the realization that

$$\gamma = \frac{1}{z^*} \qquad \text{and} \qquad C(z) = C(0)e^{-(z/z^*)} \qquad (8)$$

In a vertical soil profile with a fixed surface concentration, a unit value of N_{DA} corresponds to the depth, *z*, at which soil concentration (or fugacity) decreases by 1/e relative to the surface concentration (fugacity). So *z** is a “characteristic” depth for mass transport and can be interpreted as the average penetration depth of a molecule in vertical cross section of a soil layer. A large value of *z** indicates a soil with a steep gradient of concentration and reflects a substance that

penetrates deeply into soil. A small value of z^* indicates a shallow concentration gradient and a substance that penetrates only to a small depth within soil. We refer to z* as the "penetration depth" and use it to normalize the scale for mass transfer in soils. This corresponds to the characteristic depth derived from the Jury et. al (1983) steady-state solution to Equation 1.

Just as there is a characteristic penetration depth that characterizes the steady-state penetration depth, there is a characteristic time, t^*, that that tells how long it takes for the soil compartment to reach steady state. McKone and Bennett (2003) have shown that evaluating Equation 2 provides an analytical estimate of t^*.

$$t^* = \frac{4D_e}{(v_e^2 + 4D_e k)} \tag{9}$$

This expression provides us with a parameter to normalize time for any specific chemical and soil system. It is when the normalized time t/t^* approaches infinity that Equation 2 simplifies to Equation 3. But it is of interest that this simplification effectively applies when $t > 2t^*$. This is illustrated in Figure 3, which shows how the concentration profile (concentration versus depth) evolves as t/t^* increases.

8.7 Soil Transport Parameters

As demonstrated in the previous section, the key soil transport parameters are the bulk diffusion coefficient, D_e, and the advection velocity, v_e, and their values relative to the reaction rate constant, k, which is a function of the chemical and its reactive environment. We determine the effective bulk diffusion coefficient resulting from vapor and water-phase tortuous diffusion following the approach of Jury et al. (1983). This approach has been widely used by

environmental models for more than two decades. We make one adjustment to the Jury et al. (1983) approach by adding a bulk diffusion coefficient, D_{bio}, as a term that represents the bioturbation dispersion, accounting for worms and other detritivores that consume soil as well as burrowing creatures such as ants whose tunneling moves soil and increases the spread of chemicals in soil (Mullerlemans and Vandorp, 1996). Chapter 13 suggests values for D_{bio}.The resulting bulk-soil effective diffusivity, $D_{\text{e,i}}$ in $\text{m}^2\ \text{d}^{-1}$, for any soil layer, i, takes the form:

$$D_{\text{e},i} = \frac{Z_{air}}{Z_i}(\alpha_i^{10/3}/\phi_i^2)D_{\text{a}} + \frac{Z_{water}}{Z_i}(\beta_i^{10/3}/\phi_i^2)D_{\text{w}} + D_{\text{bio,i}} \tag{10}$$

where the ratios Z_{air}/Z_i and Z_{water}/Z_i are, respectively, the dimensionless air/soil and water/soil bulk partition coefficients; Z_{air}, Z_{water}, and Z_i represent, respectively, the fugacity capacities of pure-phase air, pure-phase water, and a bulk phase soil (*i* refers to the *i*th soil layer in multi-layered system), mol/(m^3-Pa); and D_{x} is the diffusion coefficient of the chemical in a pure fluid (x = a for air and w for water), $\text{m}^2\ \text{d}^{-1}$. Other parameters used in Equation 3 are described in Table 2. Table 3 provides definitions of the fugacity capacities expressions used throughout this chapter.

When we consider multiple soil layers, there is an effective bulk advection velocity, $v_{\text{e,i}}$ in m d^{-1}, for each soil layer characterizing contaminant transport by the flux of water induced by net rain-fall or irrigation infiltration. The value of this bulk property is derived from an assumed equilibrium partitioning of a chemical to the mobile phase relative to the bulk inventory,

$$v_{\text{e,i}} = v_{\text{water}}\ \frac{Z_{water}}{Z_i} \tag{11}$$

where v_{water} is the flux of water through the soil, m d^{-1}.

In order to demonstrate the use of chemical and environmental properties to determine MTCs in soil compartments, we use the set of six specimen chemicals that have been used in other chapters. These chemicals and there properties are listed in Table 4. Also listed in Table 4 are values obtained for the derived estimates of K_D, Z_{air}, k, z^* and t^*. Notable among these parameters is K_D, the steady-state concentration ratio between soil liquid and soil solids and used to characterize the bulk water/soil partition coefficient. Among the six substances listed in Table 4, K_D spans some four orders of magnitude—from 0.93 to 7600 L/kg. Z_{water} also spans some 4 orders of magnitude—from 0.0018 to 22 Pa-m^3/mol. In contrast, the penetration depth z^* varies by only a little over one order of magnitude among the six substances—from 0.09 to 4 m. But the characteristic time (time to steady state) varies over six orders of magnitude. This indicates that, because of the narrow range of z^*, it is not difficult to scale the depth of a soil compartment to capture variability in penetration depth. But determining whether and when steady-state is achieved can be more challenging.

8.8 Soil-Air Mass-Transfer Rates

We now exploit the theoretical foundation provided above to calculate mass transfer rates from soils to the overlying atmosphere and vice-versa. Parameter values required in these calculations are suggested. Three models are presented that vary in the detail with which vertical concentration profiles in the soil are treated:

Single soil compartment, well mixed. The first and simplest approach assumes that the soil is a single well-mixed "box" with a constant concentration vertically. This situation is most likely to apply when the rate of vertical transport of the chemical in the soil layer is fast relative to the rate of mass transfer through the soil-air interface.

Single soil compartment with a gradient in concentration. The second approach also assumes a single soil layer of constant properties, but there is allowance for concentration gradients within the layer. This situation likely applies when the soil is homogeneous and the rate of vertical transfer of chemical in the soil is equal to, or slower than the rate of mass transfer through the interface.

Multiple soil layers with gradients in concentration. Finally, and most detailed and demanding of parameters, is a soil that varies in properties vertically. In principle any number of layers can be treated, but for illustrative purposes we describe a three-layer soil.

The models are presented in both concentration and fugacity formats. The fugacity format is convenient because at the interface between layers a common fugacity applies whereas there can be differences in concentration, especially at the air-soil interface. This is illustrated in Figure 4.

In all cases we assume that the air phase is well mixed vertically, except in the boundary layer immediately above the soil surface in which there is a resistance to mass transfer. The rate of transfer from air to soil influences the chemical levels in the soil and is included in these models, but the reader is referred to Chapter 6 for a more detailed treatment of atmospheric deposition and absorption processes and to Chapter 7 for treatment of absorption to vegetation and subsequent transport to the soil surface.

The equations presented here have been derived in more detail by McKone and Bennett (2003). Readers can refer to this publication for further information. Some changes in nomenclature have been made, especially "*T* factors" in that paper have been designated here as rate constants with symbol *k*.

Regardless of the model used there is a single average concentration of chemical in the soil defined as the total chemical quantity in the soil, M mol, divided by the soil volume, i.e. M/V mol/m^3. The average fugacity is M/(VZ). The models differ in their characterization of vertical spatial differences in concentration or fugacity. An obvious approach is to apply the simplest model first then increase the resolution, and demands for parameter values in the light of experience.

8.8.1 Two-compartment (air-soil) model assuming a well-mixed soil.

Mass transfer between soil and air involves diffusion, dry deposition, washout by rain. With one well-mixed soil compartment, the rate of net mass transfer from soil to air is given by Equation 12, which contains terms for *net* gaseous diffusion, dry particle deposition, and transfer in precipitation (rain) to obtain the *net* flow ($Flow_{sa}$, mol d^{-1}) across the air-soil interface.

$$Flow_{sa} = Area\left[\left(\frac{Z_{air}}{Z_s}C_s - C_a\right)\left(\frac{Z_{air}}{Z_s U_s} + \frac{1}{U_a}\right)^{-1} - \left(V_d \frac{PC \times Z_{ap}}{\rho_{ap} Z_a} + rain\frac{Z_{water}}{Z_a}\right)C_a\right] \quad (12)$$

In this expression, *Area* is the horizontal area of contact between two compartments, m^2; C_a is the bulk contaminant concentration in the air compartment, mol/m^3; and C_s is the bulk contaminant concentration in the surface soil compartment, mol/m^3. Table 3 provides definitions of the fugacity capacities Z_{air}, Z_s, Z_a, and Z_{ap}. Table 2 provides suggested values for V_d, PC, ρ_{ap}, and *rain.* Chapter 6 gives more details on obtaining values for these deposition parameters. But the key parameters in this expression are the air-side mass-transfer coefficient (MTC) U_a and the soil-side MTC U_s (m/d) as given below.

$$U_a = \frac{D_{air}}{\delta_{as}} \tag{13}$$

$$U_s = \frac{D_{e,s}}{\delta_s} \tag{14}$$

where D_{air} as the contaminant diffusion coefficient in pure air, $m^2\ d^{-1}$, δ_{as} is the thickness of equivalent diffusion boundary layer in the air above the soil (illustrated in Figure 4), and estimated as 0.005 m; $D_{e,s}$ is the equivalent bulk diffusion coefficient in the ground-surface soil layer, $m^2\ d^{-1}$; and δ_s is the diffusion path length in soil (sometimes estimated as 0.5 times d_s, the thickness of soil layer). Whereas the molecular diffusivities in pure phases (air, water) are well established, values of diffusion path lengths and the equivalent bulk diffusion coefficient in the soil can be in doubt and judgment is required for selection of parameters used to establish MTC values.

If particle and rain deposition are ignored and only diffusion applies, the equation for net soil to air transfer becomes

$$Flow_{sa} = Area\left(\frac{C_s}{K_{sa}} - C_a\right)\left(\frac{1}{U_a} + \frac{1}{K_{sa}U_s}\right)^{-1} \tag{15}$$

where K_{sa} is the soil-air partition coefficient equal to Z_s/Z_{air}. Clearly, when C_s equals $K_{sa}C_a$, there is no net transfer and chemical equilibrium applies to the concentration ratio between these two compartments.

We can also present Equations 12 and 15 by defining the fugacity-based mass-transfer coefficient at the soil-air interface, Y_{sa}, mol/(m^2-Pa-s),

$$Y_{sa} = \left[\frac{1}{Z_s U_s} + \frac{1}{Z_{air} U_a} \right]^{-1} \tag{16}$$

and substituting f_a and f_s (fugacities in Pa) for C_a/Z_a and C_s/Z_g to obtain

$$Flow_{sa} = Area \left[Y_{sa} \left(f_s - f_a \right) - \left(V_d \frac{PC \times Z_{ap}}{\rho_{ap}} + rain \times Z_{water} \right) f_a \right] . \tag{17}$$

Consider the application of the expressions above to mass transfer factors for the situation illustrated in Figure 4, which shows two compartments—air and soil—exchanging chemical mass. In this case, the source of contamination, S_a (mol d^{-1}), is in the air so that the fugacity in air is higher than soil, a situation that causes the chemical contaminant to penetrate into the soil layer. In this case, each compartment is represented by a single fugacity or concentration with no spatial variation of concentration. In this system, the concentration of a compartment is simply M_i/V_i and the fugacity is $M_i/(Z_i V_i)$ where M_i is the total mass inventory of the compartment (mol), V_i is the volume of the compartment (m^3), and Z_i is its fugacity capacity [mol/(m^3-Pa)].

In order to illustrate the use of mass transfer coefficients for the two compartment model, we apply mass balance to the chemical inventory of a single vertical soil compartment designated by the subscript *s* below an air compartment above soil designated by the subscript *a*. We consider the case where chemical emissions to the air compartment of volume V_a maintains it at a bulk concentration of C_a (mol/m^3) and bulk inventory of $M_a = C_a V_a$ (mol). We assume no emissions to

soil, but these could be added as a bulk input of mol d^{-1}. The mass inventory in the soil layer is designated M_s (mol). In setting up the mass balance, we account for losses due to chemical and biological transformation processes with the removal rate constant k_a (d^{-1}) . We use the mass transfer factors, k_{as} and k_{sa} (d^{-1}) to account for the rate of chemical mass transfer at the surface between air and soil compartments. We use the parameter $k_{a\text{-}out}$ (d^{-1}) to account for losses due to leaching and dispersion below the soil layer. Under steady-state conditions the mass balance in the soil compartment is described by the following equation:

$$\left(k_s + k_{sa} + k_{s-out}\right)M_s = k_{as} M_a \tag{18}$$

The parameter k_a is obtained from the compartment-specific half-life or residence times that apply to bulk removal by processes such as photolysis, hydrolysis, oxidation/reduction, microbial transformations, and radioactive decay (see section 8.5). This parameter is estimated as $0.693/T_{1/2}$, where $T_{1/2}$ is the half-time for a given removal process.

By matching the net flow across the air-soil boundary from Equation 18, $Flow_{as} = k_{as}M_a - k_{sa}M_s$, with the flow expressed in Equation 17, and substituting $M_i = f_i Z_i V_i$ we obtain the following expressions for the mass transfer factors k_{as} and k_{sa}.

$$k_{as} = \frac{1}{Z_a \times d_a}\left(Y_{as} + V_d \frac{PC}{\rho_p} Z_{ap} + rain \times Z_{water}\right) \tag{19}$$

$$k_{sa} = \frac{Y_{as}}{Z_s d_s}. \tag{20}$$

The parameter $k_{s\text{-out}}$ must account for diffusion/dispersion and advection losses at the lower boundary of a soil compartment. Advection with water that infiltrates through the soil is typically a unidirectional process, which removes chemicals with the effective velocity obtained in Equation 11. However, dispersion and diffusion processes such as molecular diffusion and bioturbation move chemicals both up and down within the soil, making it difficult to define a net loss factor applicable to the bulk soil. However, with a single well mixed compartment receiving chemical input at is surface, we can assume that the net diffusion is in the downward direction and proportional to the concentration gradient in the penetration depth z^*. In this case the parameter $k_{a\text{-out}}$ is obtained from a simple model for mass loss at the lower boundary of the soil compartment:

$$\textit{Mass loss (mol/d)} = k_{s\text{-out}}M_s = Area \times \left(v_{e,s}C_s - D_{e,s}\frac{dC_s}{dz} \right). \tag{21}$$

Where C_s is the bulk concentration in the soil layer in mol/m^3, equal to M_s/V_s, and, as defined above, $v_{e,s}$ is the effective velocity in m/d of the trace chemical carried through soil by water infiltrating at velocity v_{water}, m/d, and $D_{e,s}$ is the effective bulk diffusion coefficient is soil, m^2/d. We have found that in well mixed soil layers the concentration gradient at the lower boundary of a single soil layer, dC_s/dz, is approximated reasonably well by C_s/z^*. With these substitutions and the substitution of M_s/V_s for C_s, Equation 21 becomes

$$\textit{Mass loss (mol/h)} = k_{s\text{-out}}M_s = \frac{1}{d_s}\left(v_{e,s} + \frac{D_{e,s}}{z^*} \right) M_s. \tag{22}$$

From this we determine that

$$k_{s\text{-out}}\ (\text{no gradient}) = \frac{1}{d_s}\left(v_{e,s} + \frac{D_{e,s}}{z^*} \right). \tag{23}$$

This expression is obtained under the assumption of uniform mixing in a soil layer, with an only an implicit gradient used to estimate diffusion and bioturbation losses. Because we expect a concentration gradient that makes $C_s(z)$ at $z = d_s$ lower than the bulk concentration C_s, we expect this approach can overestimate losses at the lower boundary of the single soil layer. But setting $k_{s\text{-out}}$ to zero can cause our mass balance to ignore a potentially important loss process and underestimate loss from soil. So the absence of an explicit gradient (uniform concentration) simplifies the mass-transfer calculation but introduces uncertainty. In the next section, we provide an approach that is more accurate in capturing both advection and dispersion processes at the lower soil boundary. It should be noted that comparisons of this uniform concentration approach to an approach with an explicit concentration gradient, reveals that the advection/dispersion estimates obtained from uniform-concentration approach are typically no more than a factor of two larger than the estimates obtained with a concentration gradient. Moreover, advection/dispersion losses are not typically the dominant losses from a single soil layer, such that this simple approach will not result in large errors for estimating surface-soil mass inventories. But this simple approach becomes problematic when it is necessary to estimate the transfer of contaminants to deeper soil layers or to groundwater. Table 5 provides a summary of values obtained for the parameters k_{as}, k_{sa}, k_s and $k_{s\text{-out}}$ for a 15-cm deep soil layer based on chemical properties for the substances in listed in Table 4 and based on default values for the parameters V_d, PC, ρ_{ap}, and *rain* listed in Table 2. This table compares the alternate (gradient/no gradient) approaches. The derivation of $k_{s\text{-out}}$ for a single soil layer with a concentration gradient is provided in the next section.

8.8.2 Two-compartment (air-soil) model with a concentration gradient in the soil

We now illustrate the mass balance derivation for $k_{\text{s-out}}$ using a gradient of concentration in a single soil layer. When there is a concentration gradient in a single soil layer, the concentration $C(d_s)$ at the lower boundary of the soil layer is $C(d_s) = C(0)e^{-\gamma d_s}$. So with a concentration gradient, Equation 22 becomes

$$\begin{aligned} \textit{Mass loss (mol/h)} = k_{\text{s-out}}M_s &= Area \times \left(v_{e,s}C(d_s) - D_{e,s}\frac{dC(d_s)}{dz} \right) \\ &= Area \times C(0)e^{-\gamma d_s}\left(v_{e,s} + \gamma D_{e,s}\right). \end{aligned} \tag{24}$$

We also note that, with a concentration gradient, the total mass M_s in this compartment must be determined as

$$M_s = Area \times C(0)\int_0^{d_s} e^{-\gamma x}dx = Area \times C(0)\frac{1-e^{-\gamma d_s}}{\gamma} \tag{25}$$

Combining Equations 24 and 25 results in the following expression for $k_{\text{s-out}}$, which is presented both in terms of the γ parameter and in terms of z*.

$$k_{\text{s-out}}(\text{with a gradient}) = \frac{v_{e,s}\gamma + D_{e,s}\gamma^2}{\left(e^{\gamma d_s} - 1\right)} = \frac{1}{z^*\left(e^{[d_s/z^*]} - 1\right)} \times \left(v_{e,s} + \frac{D_{e,s}}{z^*} \right) \tag{26}$$

This expression can be compared to Equation 23 in order to see how the $k_{\text{s-out}}$ format changes with the addition of a concentration gradient.

8.8.3 Discussion of the two approaches to a single soil compartment

An exercise considering MTCs for different specimen chemicals in a two-compartment (air and soil) model provides a number of insights. In order illustrate the application of the expressions in the previous sections, Table 5 provides for each of the six specimen chemicals listed in Table 4 values for the mass transfer parameters U_a, U_s, Y_{as}, $Y_{s\text{-out}}$, $v_{e,s}$, k_{as}, k_{sa}, and $k_{s\text{-out}}$. In reviewing parameter values in Table 5, we note that in this system the only mass-transfer parameter that depends on z* is $k_{s\text{-out}}$. But $k_{s\text{-out}}$ varies significantly among the specimen chemicals. This variation is important for cases in which this transfer from the lower boundary of the soil compartment is a major loss mechanism or when it is a key process by which deeper soil layers are contaminated. Other issues to consider in looking at these results and at Figure 4 are that concentration falls by almost an order of magnitude within a depth of 2*z** and that more than 90% of the mass transferred to and retained in the top soil layer is contained above a depth of 2z*. From this we see the potential importance of z* for scaling the system and selecting an appropriate value of soil thickness, d_s for use in evaluative models.

In order to further explore the impact of MTC values on model performance, we employ a numerical experiment with 300 chemicals reflecting a range of K_{OW}, K_{AW}, and soil half-life values. In this set, K_{OW} varies from 0.01 to 10^8, K_{AW} varies from 10^{-14} to 100, and the chemical half-life in soil varies from 3 hr to 10,000 d. The results of this exercise are shown in Figure 5, which shows how the a key model output, overall persistence Tov (days), varies among these 300 chemicals between a two-compartment model using a fixed depth in the range of 0.1 to 0.15 m and the same model using a chemical-specific depth, which is d_s = z*. The use of a chemical-specific depth provides a basis for selecting the depth parameter. But this exercise with overall persistence

as a measure of model performance, reveals that that a single soil compartment of roughly 0.10 to 0.15 m provides a reliable approximation of the more complex model for most chemicals. The exception is chemicals with a high mobility in soil and low reaction rates where the single compartment model can overestimate residence time by a factor of as much as five. But in considering overall reliability it is important to recognize that uncertainty in parameters such as the bioturbation factor is more important than the uncertainty introduced by the use of a single soil layer with a fix depth. Nevertheless, this exercise does not negate the need for using the scaling factors z* and γ in setting chemical-specific MTC values. There also remains the problem of setting up the appropriate soil depth and MTC values in soils having multiple layers with different composition and properties. This is taken up in the next section.

8.8.4 Multiple soil layers with concentration gradients

As noted above, there are cases where we need more accurate representations of how chemical concentration varies with depth. For example we may be interested in transfers of chemicals from air to shallow ground water or want to consider how long-term applications of pesticides to the soil surface can impact terrestrial ecosystems—including burrowing creatures. However, we also wish to maintain a simple mathematical mass-balance structure of the multimedia model. To illustrate how we can set up a multi-layer model that accurately captures soil mass transport processes, we next derive a vertical compartment structure with an air and three soil compartments, but any number of environmental compartments and soil layers can be employed in this scheme. Figure 6 provides a schematic of three soil layers linked to an air compartment and carrying pollutants downward to a saturated zone. We represent the inventory in

each vertical compartment i, as M_i (mol), transformation rate constants as k_i, and transfer factors as k_{ij} (d^{-1}). The latter account for the rate of transfer between each i and j compartment pair.

The set of steady-state mass-balance equations describing losses from the air compartment by degradation and net transfer to the ground-surface compartment, the time-dependent mass balance for the air and three soil-layer compartments is described by:

$$\left(k_{ag} + k_a\right)M_a = S_a + k_{ga}M_g \qquad \text{\{AIR\}} \qquad (27)$$

$$\left(k_{ga} + k_{gs} + k_g\right)M_g = k_{ag}M_a + k_{sg}M_s \qquad \text{\{Ground-surface SOIL\}} \qquad (28)$$

$$\left(k_{sg} + k_{sv} + k_s\right)M_s = k_{gs}M_g + k_{vs}M_v \qquad \text{\{Root-zone SOIL\}} \qquad (29)$$

$$\left(k_{vs} + k_{v-out} + k_v\right)M_v = k_{sv}M_s \qquad \text{\{Deeper vadose SOIL\}} \qquad (30)$$

where the compartment subscripts used are a for air, g for ground-surface soil, s for root-zone zone soil and v for deeper vadose-zone soil. S_a represents the source term to air, mol d^{-1}. This set of four equations can be solved to find the inventories M_i, in terms of k's and S_a. The resulting M_i, can be converted to either an equivalent fugacity or bulk concentration. But to do this requires that we define the k_{ij} factors in terms of know chemical and compartment properties.

McKone and Bennett (2003) have demonstrated how one can use Equation 3 to develop analytical expressions for inventories M_i and MTCs for each soil layer among a set of multiple linked layers and then match these to expressions obtained from Equations 27-30 for the mass

flow and fugacity at the boundary between compartments. To define "*k*" factors in Equations 27 through 30, McKone and Bennett (2003) show that, when Equation 1 is applied to soil layers in which soil properties (distribution coefficient, reaction half-life, etc.) change with depth, Equation 1 can be solved stepwise in each layer to obtain the steady-state results

$$C_i(z) = C_i^* e^{-\gamma_i (z - h_{i-1})} \tag{31}$$

$$C_i^* = \frac{\left[D_{e,1}\gamma_1 + v_{e,1}\right]}{\left[D_{e,i}\gamma_i + v_{e,i}\right]} C(0) e^{-(\gamma_1 d_1 + \gamma_2 d_2 + \ldots + \gamma_{i-1} d_{i-1})} \tag{32}$$

where i refers to the ith layer in a sequence of different soil layers; h_i is the depth to the lower boundary of the ith soil layer, m; and d_i is the thickness of the ith soil layer, m. Equations 31 and 32 produce concentrations that can be discontinuous at layer interfaces, but produce fugacities and fluxes that are continuous at layer interfaces.

McKone and Bennett (2003) obtain analytical expressions for the k_{ij} factors between adjacent soil compartments by matching the mass flow obtained from the solution of the compartment mass balance (Equations 27-30) to the mass flow obtained from the exact analytical solution, Equation 31. This requires that each soil layer is homogeneous such that Equation 31 is continuous with depth in each soil layer, but allows for differences in properties among soil layers i. Table 6 provides a summary of the general and specific definitions of k_{ij} factors that are obtained by McKone and Bennett (2003) from the mass-balance matching of the exact and discrete soil layer approach. Figure 7 illustrates how the general multi-layer approach compares with the mass distribution of the exact analytical model solution for cases with three and four soil compartments.

Summary

Quantifying the mass transport of chemicals in soil and between soil and atmosphere is a key step in understanding the role soil plays in controlling fate, transport, and exposure to multimedia pollutants. In existing multimedia mass-balance models there have been significant variations in both the complexity and structure applied to the soil compartment. Here we have described the conceptual issues involved in the transport and transformation of pollutants in soils. We then describe and evaluate novel approaches for constructing soil transport algorithms and the corresponding MTCs for multimedia fate models. We focus on those algorithms that provide an explicit quantification of the characteristic soil penetration depth in soil layers of different composition. We consider in detail a recently published approach constructed as a compartment model using one or more soil layers. This approach can replicate with high reliability the flux and mass distribution obtained from the exact analytical solution describing the transient diffusion/dispersion, advection, and transformation of chemicals in soil layers with different properties but a fixed boundary condition at the air-soil surface. We demonstrate and evaluate the performance of the various soil algorithms using specimen chemicals benzene, hexachlorobenzene, lindane (gamma-hexachlorocyclohexane, benzo(a)pyrene, nickel, and copper. We consider the relative advantages of generic versus chemical-specific soil compartment modeling in multimedia models. This example offers important insight into the trade-offs between model complexity and reliability, and provides a case study of quantitative evaluation of model performance. We have learned that this problem can be limited by selecting a shallow (0.1 to 0.15 m) compartment depth when building regional mass balance models.

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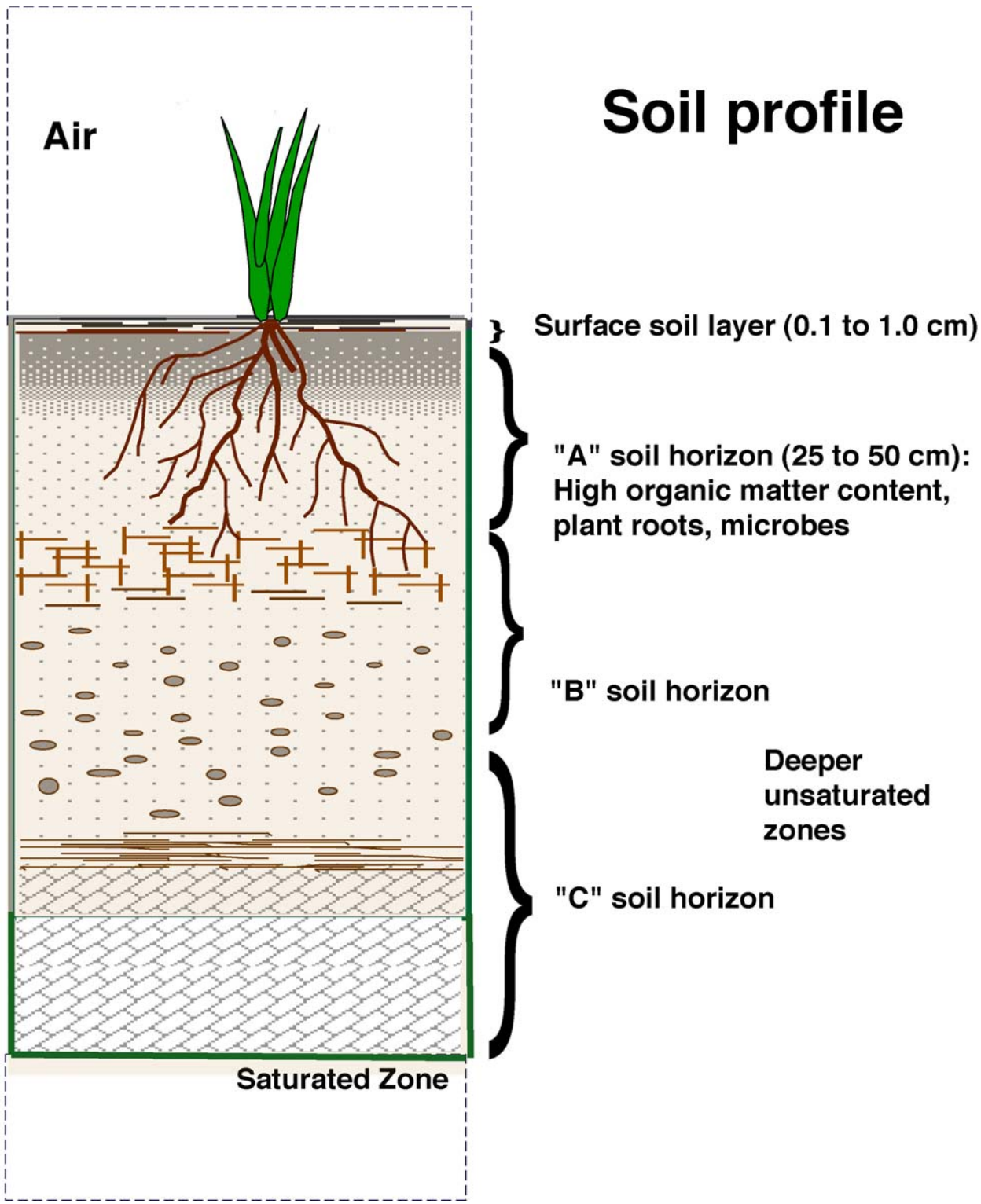

Figure 1. An illustration of the "horizons" in a typical soil column [this diagram is reproduced from McKone (2005)]

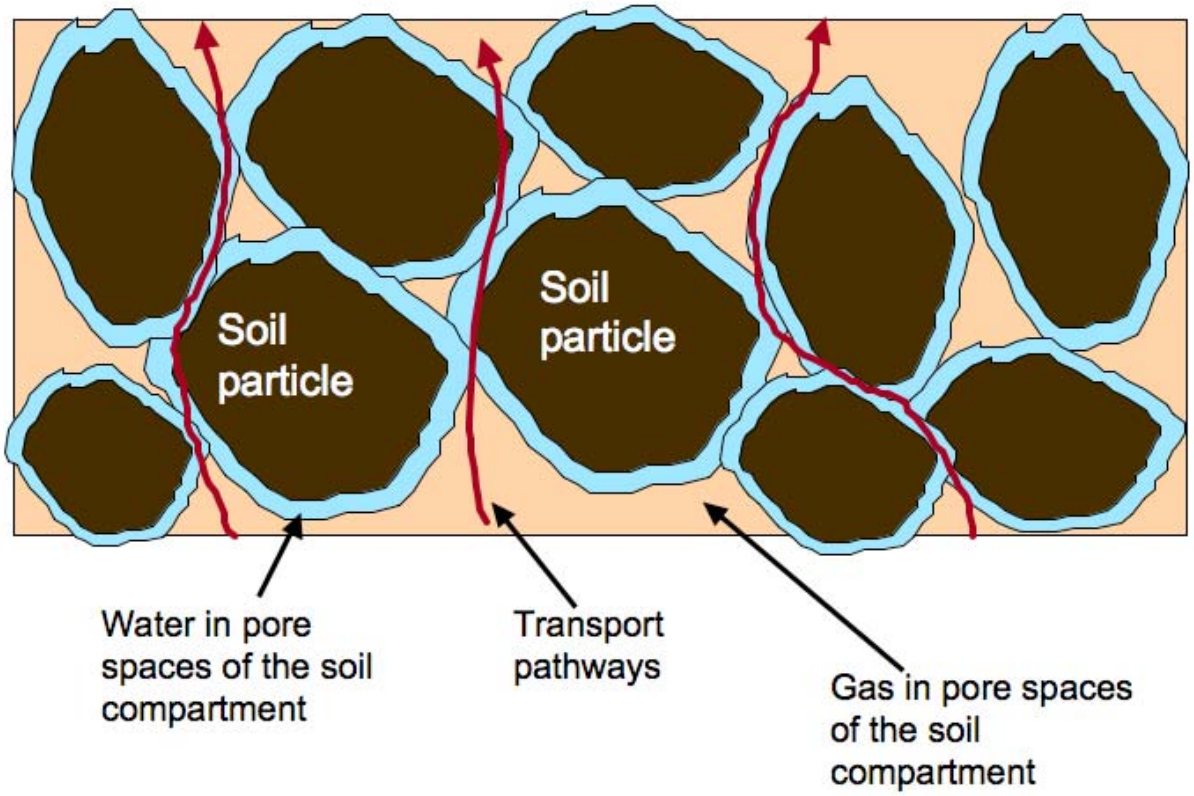

Figure 2. Microscopic view of partitioning and transport in soil layers.

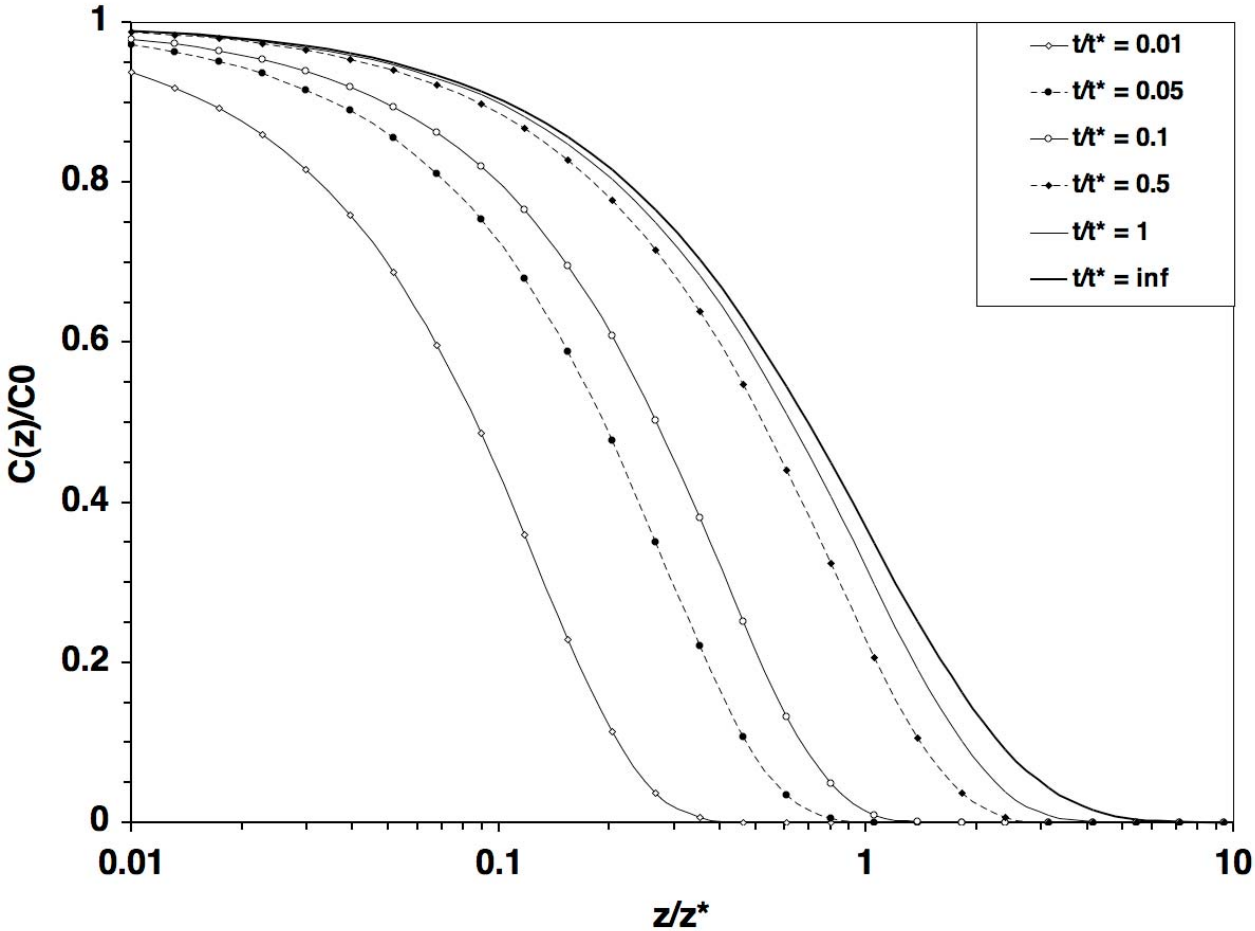

Figure 3. Concentration curves at various normalized times, t/t*, plotted against a normalized, z/z* depth scale.

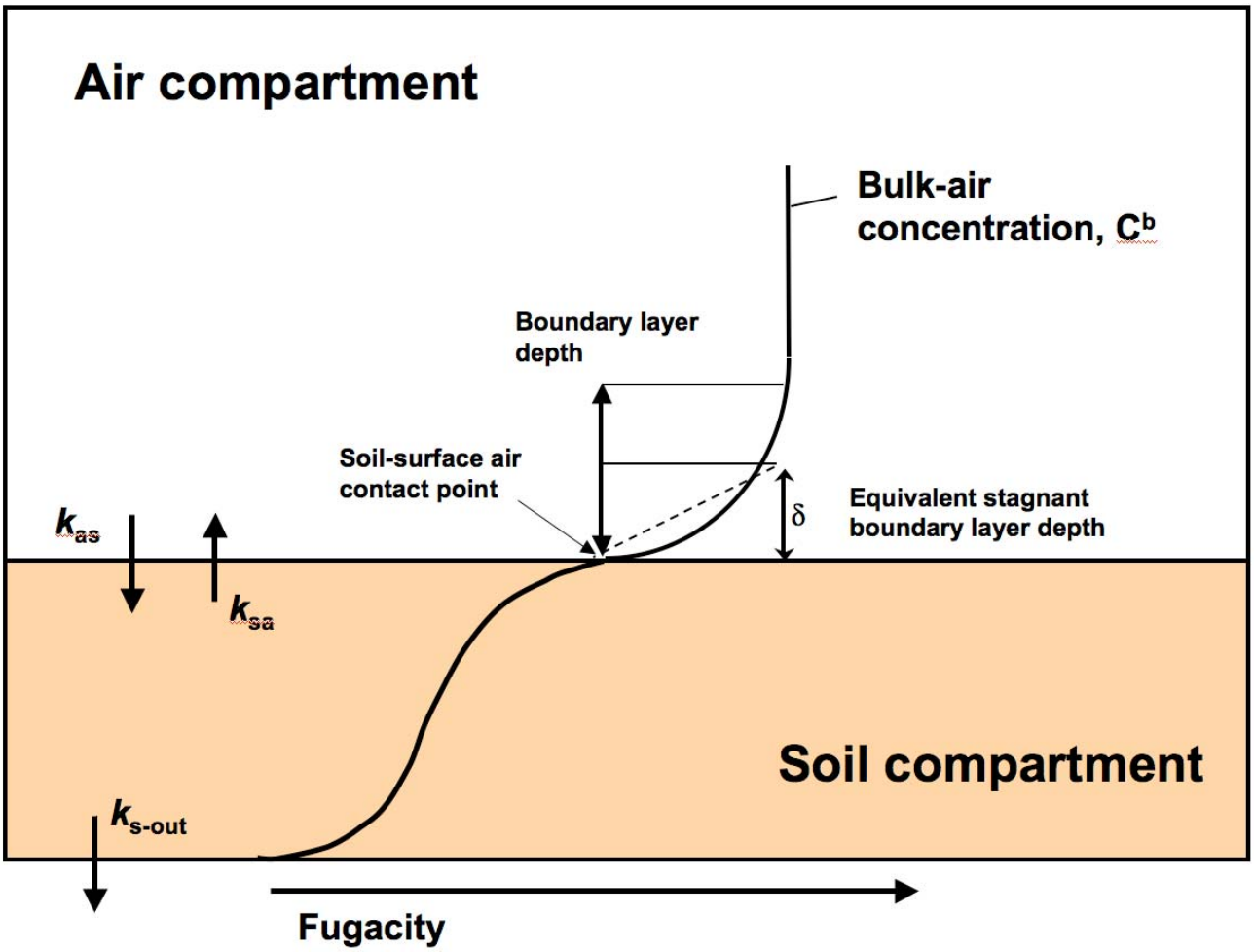

Figure 4. An illustration of the role of mass transfer coefficients in establishing mass balance in a two-compartment system consisting of soil and air.

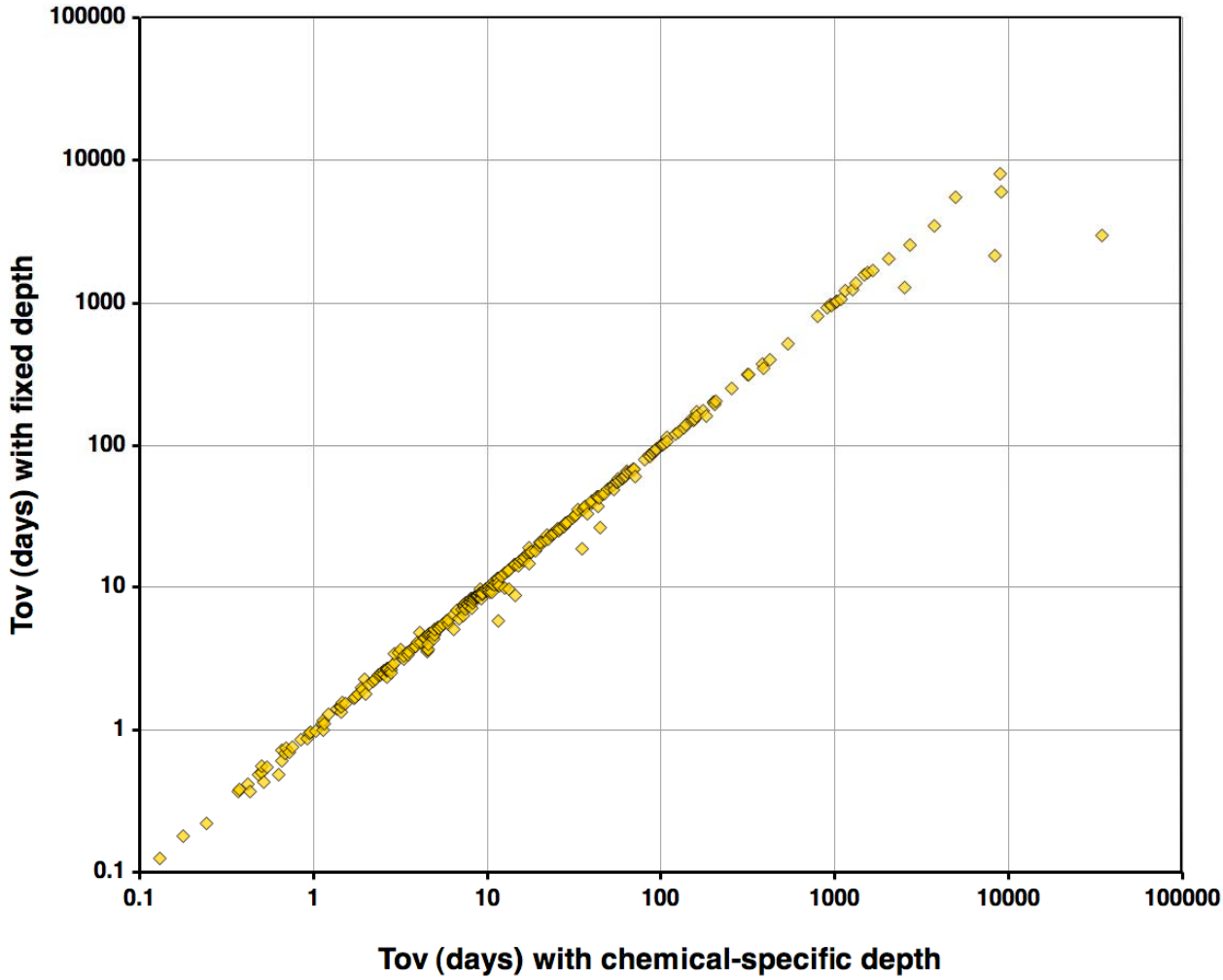

Figure 5. An illustration of how the model output overall persistence (Tov in days) varies among 300 chemicals between a two-compartment model using a fixed depth in the range of 0.1 to 0.15 m and the same model using a chemical-specific depth, which is ds = z*.

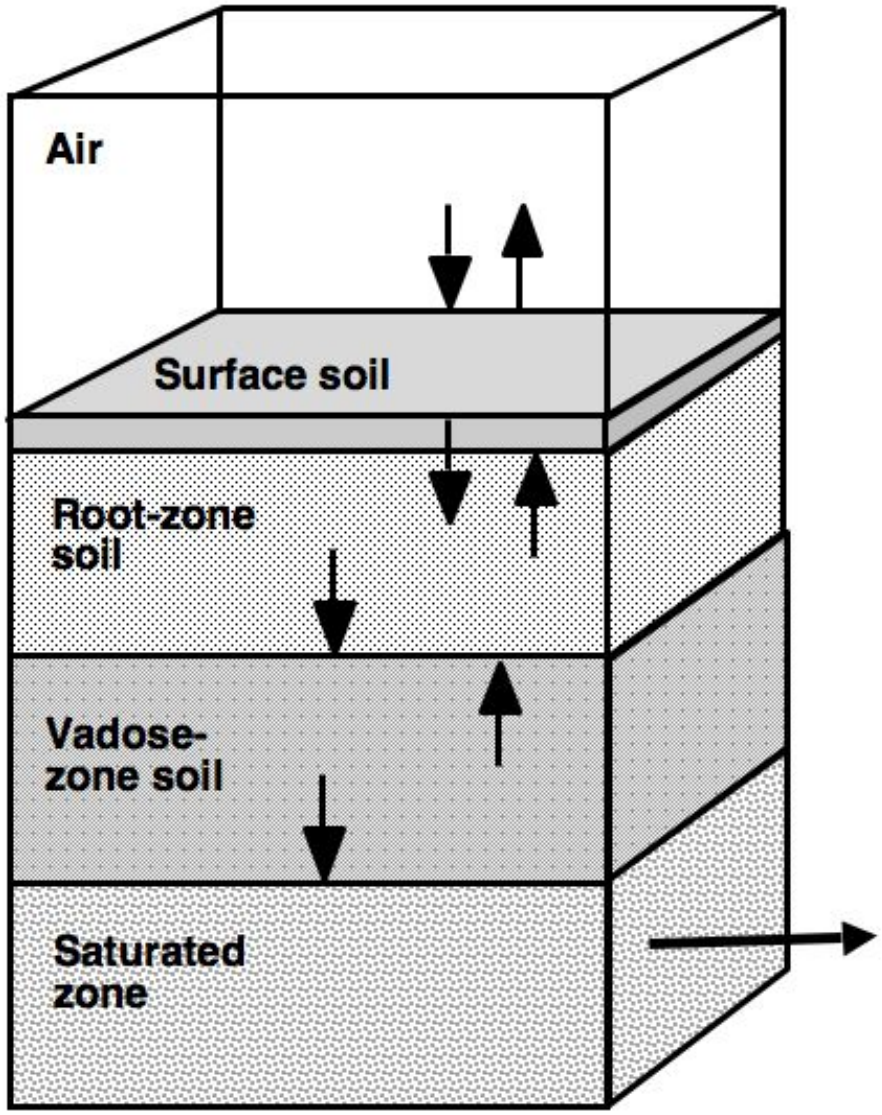

Figure 6. A schematic of three soil layers linked to an air compartment and carrying pollutants downward to a saturated zone.

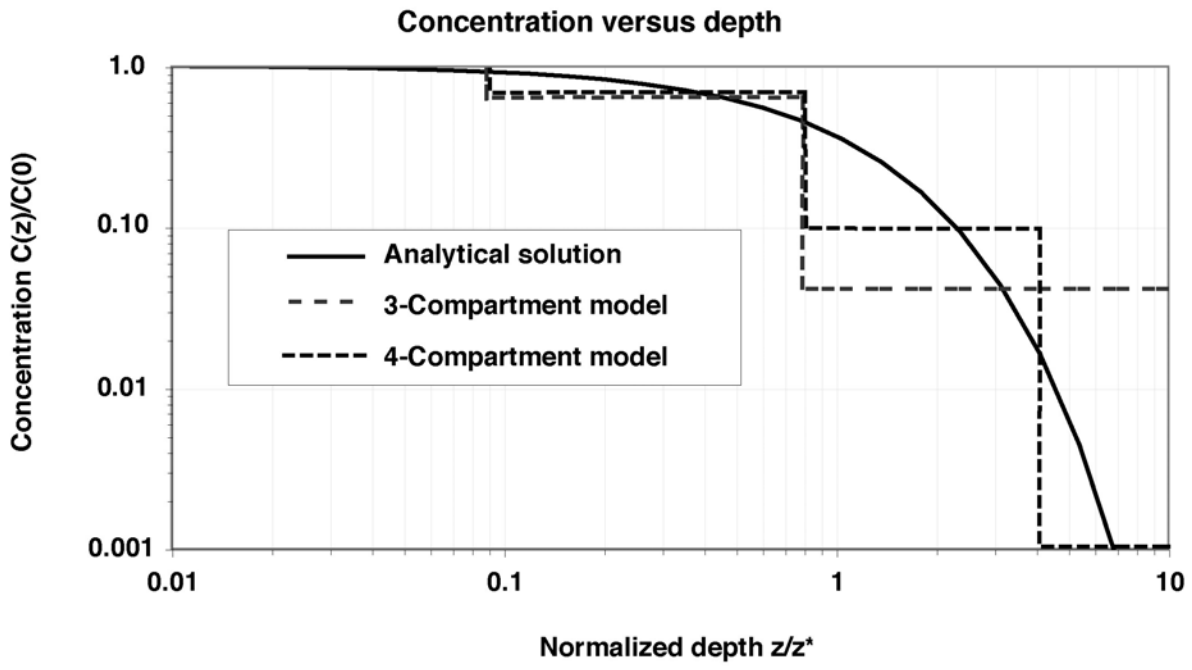

Figure 7. This graph compares the concentration change (where C(0) is the concentration at thw soil surface) versus normalized depth z/z* of the compartment-model solution and analytical solution for the case where soil properties are assumed uniform. (from McKone and Bennett, 2003).

Table 1. Processes by which contaminants are transferred to and from soils layers

Gains	Losses
direct application	volatilization to air
deposition from air	resuspension of soil particles
washout from air by rainfall	mass transfer (diffusion and advection) downward to deeper soil layers and to ground water
dry deposition of air particles	transfers to vegetation
mass transfer (diffusion and advection) upward from deeper soil layers and from ground water	soil solution runoff
	erosion (mineral runoff) to surface water
	chemical, physical, and biological transformation

Table 2. Definitions, symbols, units and values of compartment properties[a]

Property name	Symbol	Units	Value
Density of air particles[b]	ρ_{ap}	kg m^{-3}	1000
Concentration of particles in air	C_a	kg m^{-3}	5.0 x 10^{-8}
Fraction organic matter associated with particulate matter in air	f_{om}	no units	0.4
Long-term average deposition velocity (wet and dry) of air particles to soil	V_d	m d^{-1}	400
Long-term average rainfall	*rain*	m d^{-1} (m y^{-1})	0.0027 (1.0)
Flux of water through the soil	v_{water}	m d^{-1} (m y^{-1})	0.00082 (0.3)
Thickness of equivalent diffusion boundary layer in air above the surface soil	δ_{ag}	m	0.05
Density of soil particles	ρ_{sp}	kg m^{-3}	2600
Volume fraction of soil that is gas	α_i	no units	0.2
Volume fraction of soil that is liquid	β_i	no units	0.3
Volume fraction of soil that is void	$\phi_i = \alpha_i+\beta_i$	no units	0.5
Volume fraction of soil that is solid	$(1-\alpha_i-\beta_i)$	no units	0.5
Fraction of organic carbon in soil	f_{oc}	no units	0.02
Equivalent diffusion coefficient for bioturbation	D_{bio}	m^2 d^{-1}	1.7x10^{-5} (2.6x10^{-6} to 8.6x10^{-4})

[a] Descriptions and values in this Table come from McKone and Bennett (2003)

Table 3. Definitions of fugacity capacities and partition coefficients used in the soil compartment model.[a]

Name	Symbol	Formula or value	Units
Fugacity capacity of gas phase	Z_{air}	= 1/(RT)	mol/(m^3-Pa)
Fugacity capacity of substances dissolved in water	Z_{water}	= 1/H	mol/(m^3-Pa)
Fugacity capacity of air particles[b]	Z_{ap}	$= 0.00123\, K_{oa} f_{om} Z_{air} \rho_{ap}$	mol/(m^3-Pa)
Fugacity capacity of soil solids	Z_{ss}	$= 0.001\, K_D \rho_{sp} Z_{water}$	mol/(m^3-Pa)
Fugacity capacity of bulk air (gases and particles)	Z_a	$= Z_{air} + (PC/\rho_{ap}) Z_{ap}$	mol/(m^3-Pa)
Fugacity capacity of soil compartment i, for the three-compartment example: i = g for ground surface i = s for root zone i = v for vadose etc.	Z_i	$= \alpha_i Z_{air} + \beta_i Z_{water} + (1-\alpha_i-\beta_i) Z_{sp}$	mol/(m^3-Pa)
Octanol/water partition coefficient	K_{ow}	Literature citations	L(water)/ L(octanol)
Octanol/air partition coefficient	K_{oa}	$= RTK_{ow}/H$	m^3(air)/ m^3(octanol)
Organic carbon partition ratio	K_{oc}	Measure values or estimated as $0.35K_{ow}$	L(water)/ kg(organic carbon)
Soil distribution coefficient (solid/water concentration ratio)	K_D	$= K_{oc}\, f_{oc}$	L(water)/ kg(soil solids)

[a]See Table 2 for definitions of parameters other than Z values and partition coefficients

[b]Harner et al. (1995)

Table 4. Properties used for the specimen chemicals and the resulting estimates of K_D, Z values, k_s, v_e, D_e, z* and t*. Lindane is gamma hexachlorocyclohexane, B(a)P is benzo(a)pyrene.

Chemical	Benzene	Hexachloro-benzene	Lindane	B(a)P	Nickel	Copper
Molecular formula	C_6H_6	C_6Cl6	$C_6H_6Cl_6$	$C_{20}H_{12}$	Ni	Cu
Molar mass (kg)	78.1	284.8	290.8	252.3	58.71	63.54
Henry's law constant (Pa m^3/mol)	557	131	0.149	0.0465	0	0
log K_{AW}	-0.65	-1.28	-4.22	-4.73	-	-
log K_{OW}	2.13	5.50	3.70	6.04	-	-
log K_{OA}	2.78	6.78	7.92	10.77	-	-
log K_{OC}	1.67	5.04	3.24	5.58	~2	~5
Transformation half life (d)	100	1000	300	500	-	-
K_D [L(water)/ kg(soil solids)]	0.93	2190	34.8	7600	2	2000
Z_{air} (Pa m^3/mol)	0.000425	0.000425	0.000425	0.000425	0.000425	0.000425
Z_{water} (Pa m^3/mol)	0.0018	0.0076	6.71	21.9	1.0	1.0
Z_{ss} (Pa m^3/mol)	0.00435	10.2	0.163	35.6	5.20	5,200
Z_{ap} (Pa m^3/mol)	0.252	2,520	34,800	2.46×10^7	5.20	5,200
k_s, the reaction rate constant d^{-1}	0.00693	0.000693	0.00231	0.00139	0	0
v_e	5.28×10^{-4}	2.89×10^{-7}	1.80×10^{-5}	8.32×10^{-8}	2.83×10^{-4}	3.16×10^{-7}
D_e	0.00146	1.78×10^{-5}	6.63×10^{-5}	1.73×10^{-5}	2.95×10^{-5}	1.70×10^{-5}
Penetration depth *z** (m)	0.49	0.16	0.09	0.11	4	0.7
Characteristic time *t** (d)	140	1440	423	721	1500	4×10^8

Table 5. Mass-transfer parameters for the six specimen chemicals

Chemical: / Parameter	Benzene	Hexachloro -benzene	Lindane	B(a)P	Nickel	Copper
U_a (m d^{-1})	100	100	100	100	100	100
U_s (m d^{-1})	0.0195	0.000237	0.000883	0.000230	0.000393	0.000227
Y_{as} [mol/(m^2-Pa-d)]	5.40 x10^{-5}	0.00118	7.20 x10^{-5}	0.00373	0	0
$v_{e,s}$ (m d^{-1})	5.28 x 10^{-4}	2.89 x 10^{-7}	1.80 x 10^{-5}	8.32 x 10^{-8}	2.83 x 10^{-4}	3.16 x 10^{-7}
$D_{e,s}$ (m d^{-1})	0.00146	1.78 x 10^{-5}	6.63 x 10^{-5}	1.73 x 10^{-5}	2.95 x 10^{-5}	1.70 x 10^{-5}
k_{as} (d^{-1})	0.000140	0.00285	0.000936	0.233	22,800	23
k_{sa} (d^{-1})	0.130	0.00154	0.00588	0.00140	0	0
k_s (d^{-1})	0.00693	0.000693	0.00231	0.00139	0	0
$k_{s\text{-}out}$ (d^{-1}) [no gradient]	0.0234	0.000743	0.00503	0.00105	0.00194	0.00016
$k_{s\text{-}out}$ (d^{-1}) [with gradient	0.0200	0.000448	0.00195	0.000489	0.00190	0.00015

Table 6. Summary of the mass-inventory and fugacity-based transfer factors for the multi-layer soil compartment model (McKone and Bennett, 2003).

Transfer	**Mass-Inventory Based Transfer Factor, d^{-1}**	**Fugacity-Based Transfer Factors [Mackay "D" values] in mol $d^{-1}Pa^{-1}$**
Air to ground-surface soil	$\boldsymbol{k_{ag}} = \frac{1}{Z_a \times d_a}\left(Y_{ag} + V_d \frac{PC}{\rho_p} Z_{ap} + rain \times Z_{water}\right)$	$\boldsymbol{D_{ag}} = \boldsymbol{Z_a V_a k_{ag}} = Area \times \left(Y_{ag} + V_d \frac{PC}{\rho_p} Z_{ap} + rain \times Z_{water}\right)$
Ground-surface soil to air	$\boldsymbol{k_{ga}} = \frac{Y_{ag}}{Z_g d_g}$, $Y_{ag} = \left[\frac{1}{Z_{air} U_a} + \frac{1}{Z_g U_g}\right]^{-1}$	$\boldsymbol{D_{ga}} = \boldsymbol{Z_g V_g k_{ga}} = Area \times Y_{ag}$
Fugacity-based diffusive-transfer coefficient from g to s		$\boldsymbol{Y_{sg}}$ (mol $m^{-2}s^{-1}$) = $\left[\frac{e^{\gamma_g d_g} - 1}{D_{e,g}\gamma_g^2 Z_g d_g} - \frac{1 - e^{-\gamma_s d_s}}{D_{e,s}\gamma_s^2 Z_s d_s}\right]^{-1}$
Transfer from surface soil to root soil	$\boldsymbol{k_{gs}} = \frac{Y_{gs}}{Z_g d_g} + \frac{v_{e,g}\gamma_g}{\left(e^{\gamma_g d_g} - 1\right)}$	$\boldsymbol{Z_g V_g k_{gs}} = Area \times \left[Y_{gs} + \frac{v_{e,g}\gamma_g Z_g d_g}{\left(e^{\gamma_g d_g} - 1\right)}\right]$
Transfer from root soil to surface soil	$\boldsymbol{k_{sg}} = \frac{Y_{gs}}{Z_s d_s}$	$\boldsymbol{Z_s V_s k_{sg}} = Area \times Y_{gs}$
Generalized Relationship between any two upper (u) and lower (l) soil layers		
Fugacity-based diffusive-transfer coefficient from *u* to *l*		$\boldsymbol{Y_{ul}} = \left[\frac{e^{\gamma_u d_u} - 1}{D_{e,u}\gamma_u^2 Z_u d_u} - \frac{1 - e^{-\gamma_l d_l}}{D_{e,l}\gamma_l^2 Z_l d_l}\right]^{-1}$ $\boldsymbol{Y_{u\text{-}out}} = \left[\frac{D_{e,u}\gamma_u^2 Z_u d_u}{e^{\gamma_u d_u} - 1}\right]$ (last layer)
Transfer from *u* to *l*	$\boldsymbol{k_{ul}} = \frac{Y_{ul}}{Z_u d_u} + \frac{v_{e,u}\gamma_u}{\left(e^{\gamma_u d_u} - 1\right)}$	$\boldsymbol{Z_u V_u k_{ul}} = Area \times \left[Y_{ul} + \frac{v_{e,u}\gamma_u Z_u d_u}{\left(e^{\gamma_u d_u} - 1\right)}\right]$
Transfer from *l* to *u*	$\boldsymbol{k_{lu}} = \frac{Y_{ul}}{Z_l d_l}$	$\boldsymbol{Z_l V_l k_{lu}} = Area \times Y_{ul}$