CalTOX, A Multimedia Total-Exposure Model for Hazardous-Waste Sites

Part II: The Dynamic Multimedia Transport and Transformation Model

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FOREWORD

This is the second of a series of three reports describing the technical and scientific basis of the CalTOX risk assessment model. The major objective of CalTOX is to improve the accuracy of risk assessment information presented to risk managers. In the development of CalTOX, the Department of Toxic Substance Control (DTSC) has given great weight to scientific credibility. A recognized international expert in the field of environmental chemical transport and risk assessment developed the model based on publications in the peer-reviewed scientific literature. These CalTOX reports have undergone three review and revision cycles focusing exclusively on the technical and scientific issues.

The reader will note that every page has a disclaimer regarding the use of these documents for regulatory action. The Department of Toxic Substances Control has intentionally avoided issues relating to the application of the model to assess risk for regulatory action in this document. Every effort has been made to prevent non-scientific regulatory considerations from jeopardizing the scientific credibility of the model. However, these regulatory considerations must be addressed before the model can be used for regulatory action. CalTOX differs from current regulatory risk assessment practices in a number of areas. These differences include a stochastic method of estimating risk and a description of chemical transport in the environment that allows for source depletion. Existing risk assessment policy will not be adequate to guide the use of CalTOX in regulatory applications. Therefore, additional policy will have to be developed before the model can be implemented to assess risk for regulatory decision making. These technical reports should be viewed as describing the technical basis around which future policy will be developed. These reports do not contain that policy context and are insufficient for applying the model to assess risk as a basis for regulatory action. Therefore, **do not cite, quote or use these documents to support any regulatory action**.

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CalTOX, A Multimedia Total Exposure Model for Hazardous-Waste Sites

Part II: The Dynamic Multimedia Transport and Transformation Model

ABSTRACT

Environmental scientists recognize that the environment functions as a complex, interconnected system. A scientifically based risk-management strategy for many contaminants requires a comprehensive and integrated assessment of local and regional transport and transformation processes. In response to this need, environmental scientists have developed multimedia models that simulate the movement and transformation of chemicals as they spread through air, water, plants, soils, sediments, surface water, and ground water. In these models, each component of the environment is treated as a homogeneous subsystem or compartment that can exchange water, nutrients, and chemical contaminants with other adjacent compartments. In this report, we describe the development of a dynamic multimedia model that can be used to assess time-varying concentrations of contaminants released continuously to air, the soil surface, or surface water or introduced initially to subsurface soil layers. We examine how chemical properties affect the distribution of contaminants among multiple environmental media. This distribution determines both the ultimate route and quantity of human and biotic contact.

INTRODUCTION

In 1985, the Council on Environmental Quality (CEQ, 1985) recommended that long-term environmental research focus on (1) contaminant-transfer rates among environmental media (i.e., soil, water, and air); (2) geohydrological processes at soil/water/air interfaces; (3) the role of biological, physical, and chemical processes in biogeochemical transport; and (4) the scientific basis for quantitative risk assessment (CEQ, 1985). The nature of these processes requires a multimedia approach. In contrast to the single-medium paradigm for assessing exposure, in a multimedia approach, we locate all points of release to the environment; characterize mass-balance relationships (e.g., between sources and sinks in the environment); trace contaminants through the entire environmental system, observing and recording changes in form as they occur; and identify where in this chain of events control efforts would be most appropriate. This type of information has focused attention on the behavior of chemicals released from modern industrial economies into the environment. Organic-chemical, inorganic-chemical, and radionuclide contamination of soils as well as the release of volatile organic compounds to air and to soil and toxic-chemical runoff to surface water are all multimedia problems.

In this report, we describe the development of a dynamic multimedia model that can be used to assess time-varying concentrations of contaminants introduced initially to subsurface soil layers or for contaminants released continuously to air, to the ground surface, or to surface water. We examine how chemical properties affect both the ultimate route and quantity of human and biotic contact. We are particularly interested in those components of the environment with which humans are most likely to have contact. In order to carry out this characterization, we view the environment as a series of interacting compartments. In this framework, one must determine whether a substance will (a) remain or accumulate within the compartment of its origin, (b) be physically, chemically, or biologically transformed within the compartment of its origin (i.e., by hydrolysis, oxidation, etc.), or (c) be transported to another compartment by cross-media transfer that involves dispersion or advection (i.e., volatilization, precipitation, etc.).

The purpose of this report is to provide an overview of methods that can be used to determine how the competition among these processes results in temporal and spatial variations of the concentrations of contaminants in the environment. In the sections below, we describe methods and models that are incorporated into the CalTOX spreadsheet. We begin by providing a background discussion on

multimedia modeling and some of the underlying science and policy issues that have given rise to this approach. We next provide an overview of the CalTOX multimedia transport and transformation model including identification of its seven compartments and the nature of the mathematical models describing chemical transport and fate in this seven-compartment system. Also in this section, we consider for each compartment transport processes that lead to the dispersion of substances within a single environmental medium. In the next section, we define the physical composition and fugacity capacities of each compartment. This is followed by a section that addresses transport processes in CalTOX with an emphasis on cross-media transfers by which contaminants move among two or more compartments. The next section deals with transformation processes. We then describe the landscape and chemical-property data needed to carry out a multimedia analysis. This is followed by a section in which we develop explicit mathematical descriptions for transformation processes, loss rate constants, and all inter-compartment rate constants in the CalTOX model. We then show how these rate constants are used to develop the gain-loss equations for a contaminated landscape unit and develop a dynamic solution to this set of equations. The use of the CalTOX model is illustrated with several example calculations. The contaminants considered include the volatile organic compounds trichloroethylene (TCE) and tetrachloroethylene (PCE), the semi-volatile organic compound benzo(a)pyrene, and the radionuclides tritium and uranium-238. We conclude the report with a summary of the model and a discussion of its strengths, weaknesses, and uncertainties.

BACKGROUND

In response to the need for multimedia models in risk assessment, a number of multimedia transport and transformation models have appeared. These models use the partitioning, reaction, and intermedia-transport properties of a chemical in a representative or generic environment to assess impacts such as health risk. Each compartment of the environment is treated as a homogeneous subsystem that can exchange water, nutrients, and chemical contaminants with other adjacent compartments. There are two basic features that make compartment models suitable for an integrated model of transport and transformation in air, water, and soil environments. First, each compartment forms a unit in which one can balance gains and losses attributable to sources, transfers to and from other compartments,

and physicochemical transformations. Second, each compartment forms a unit in which we can evaluate chemical partitioning according to chemical equilibria.

Efforts to assess human exposure from multiple media date back to the 1950's when the need to assess human exposure to global fallout led rapidly to a framework that included transport both through and among air, soil, surface water, vegetation, and food chains (Whicker and Kirchner, 1987). Efforts to apply such a framework to nonradioactive organic and inorganic toxic chemicals have been more recent and have not as yet achieved the level of sophistication extant in the radioecology field. In an early book on multimedia transport, Thibodeaux (1979) proposed the term “chemodynamics” to describe a set of integrated methods for assessing the cross-media transfers of organic chemicals. The first widely used multimedia compartment models for organic chemicals were the "fugacity" models proposed by Mackay (1979) and Mackay and Paterson (1981, 1982). Fugacity models have been used extensively for modeling the transport and transformation of chemical contaminants in complex environmental systems (see Mackay, 1991). Fugacity is a way of representing chemical activity at low concentrations. Cohen and his co-workers introduced the concept of the multimedia compartment model as a screening tool with the MCM model (Cohen and Ryan, 1985) and more recently with the spatial multimedia compartment model (SMCM) model (Cohen et al., 1990), which allows for nonuniformity in some compartments. Another multimedia screening model, called GEOTOX (McKone and Layton, 1986; McKone, et al., 1987), was one of the earliest multimedia models to explicitly address human exposure. The proceedings of two recent workshops (Cohen, 1986; Allen et al., 1989), both held at the National Center for Intermedia Transport at the University of California, Los Angeles (UCLA), provide an overview of current research on multimedia transport, transformation, and human exposure.

Sources, Transport, and Transformation

Three dynamic processes must be balanced in a multimedia model—sources, transport, and transformation.

Knowledge of source-term characteristics is an important first step in the multimedia analysis. Pertinent information includes the physical and chemical properties of the substance(s) released and attributes of the source (e.g., emission rates or depth of and method of incorporation for soil contaminants). Sources can be categorized in terms of space (e.g., area source vs. point source), time (e.g., transient vs. chronic release), and mode of formation.

In a multimedia model, major components of the environment are lumped into homogeneous subsystems or compartments that can exchange mass with other adjacent compartments. Quantities or concentrations within compartments are described by a set of linear, coupled, first-order differential equations. A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and/or gas-phase mass. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface runoff and ground-water recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. Each chemical species is assumed to reach chemical equilibria among the phases within a single compartment. However, there is no requirement for equilibrium between adjacent compartments. Decay and transformation processes (such as radioactive decay, photolysis, biodegradation, etc.) are typically treated as first-order, irreversible removals.

Fugacity Models

Fugacity models have been used extensively for modeling the transport and transformation of nonionic organic chemicals in complex environmental systems. Modified fugacity and fugacity-type models have also been used for ionic-organic and inorganic species, including metals. Fugacity is a way of representing chemical activity at low concentrations. Fugacity has units of pressure (pascal [Pa]) and can be regarded physically as the partial pressure or escaping potential exerted by a chemical in one physical phase or compartment on another (Mackay, 1979, 1991; Mackay and Paterson, 1981, 1982). When two or more media are in equilibrium, the escaping tendency (the fugacity) of a chemical is the same in all phases. This characteristic of fugacity-based modeling often simplifies the mathematics involved in calculating partitioning. Fugacity models can also be used to represent a dynamic system in which the fugacities in two adjacent media are changing in time due to an imbalance of sources and losses or a dynamic system that has achieved steady state by balancing gains and losses even though fugacities are not equal.

At low concentrations, like those typical of environmental interest, fugacity, f (Pa), is linearly related to concentration C (mol/m^3) through the fugacity capacity, Z (mol/m^3-Pa),

$$C = fZ \quad . \qquad [1]$$

Z depends on the physical and chemical properties of the chemical and on various characteristics of phase, such as temperature and density. The property that fugacities are equal at equilibrium allows for simple determination of Z values from partition coefficients. For example for two phases in equilibrium (phase 1 and 2):

$$C_1 / C_2 = f Z_1 / f Z_2 = Z_1 / Z_2 = K_{12} \ , \qquad [2]$$

where C_1 and C_2 are the concentrations in each phase, Z_1 and Z_2 are the fugacity capacities of each phase, and K_{12} is a dimensionless partition coefficient, such as K_{ow}, the octanol-water partition coefficient.

One of the major advantages of fugacity models is their ability to represent diffusive and advective intermedia-transport processes. In a fugacity model, the net diffusive flux, in mol/m^2-d, across an interface is given by

$$flux = Y_{12} \, (f_1 - f_2) \ , \qquad [3]$$

where Y_{12} is the fugacity mass-transfer coefficient across the boundary between medium 1 and medium 2 with units mol/(m^2-Pa-d) and f_1 and f_2 are the fugacities of medium 1 and medium 2. Equation [3] is analogous to the flow of electrons in a circuit, in which (f_1-f_2) acts as a voltage difference, Y_{12} acts as a conductance, and the mass flux serves as the equivalent of electrical current. The fugacity mass-transfer coefficient depends only on the mass transfer coefficient on either side of the interface.

$$Y_{12} = \left(\frac{1}{Z_1 U_1} + \frac{1}{Z_2 U_2} \right)^{-1} , \qquad [4]$$

where U_1 and U_2 are the mass-transfer coefficients (m/d) in the boundary layers in medium 1 and medium 2 and Z_1 and Z_2 are the fugacity capacities of medium 1 and medium 2. The net advective flux between medium 1 and medium 2 is given by

$$flux = Z_{water} \, [F_{12}^{w} \ f_1 - F_{21}^{w} \ f_2] + Z_{1p} \, F_{12}^{p} \ f_1 - Z_{2p} \, F_{21}^{p} \ f_2 \ , \qquad [5]$$

where Z_{water} is the fugacity capacity of water, mol/m^3-Pa; F_{12}^{w} is the flux of water from medium 1 to 2, m^3/m^2-d; F_{21}^{w} is the flux of water from medium 2 to 1,

m^3/m^2-d; Z_{1p} and Z_{2p} are, respectively, the fugacity capacities of the solid phases of media 1 and 2, mol/m^3-Pa; F_{12}^p is the flux of solids from medium 1 to 2, m^3/m^2-d; and F_{21}^p is the flux of solids from medium 2 to 1, m^3/m^2-d.

OVERVIEW OF THE CalTOX MULTIMEDIA MODEL

CalTOX is a seven-compartment regional and dynamic multimedia fugacity model that was developed for assessing the spread of contamination among the environmental media at a landscape unit that represents a toxic-substances-release site. It is designed to model a landscape on the order of 1,000 to 10^7 m^2. Smaller landscape areas can be treated with the model, but in such cases the model has greater uncertainty associated with model predictions and the persistence of contamination. CalTOX is a spreadsheet model and has been developed with the EXCEL application on Macintosh and IBM-type personal computers.

In this section, we describe the objectives of the model, critical sensitivities and uncertainties, the chemical classes for which it is appropriate, and situations for which the model should not be used. We also describe the general structure of the CalTOX model and its compartments; the form of the differential equations describing the balance of contaminant gains and losses in each compartment; the structure, mass, volume, and phase composition of the compartments; and the fugacity capacities of organic and inorganic chemicals in each CalTOX compartment.

Objectives, Capabilities, and Limitations

The precision of environmental models is most often limited by the precision of the inputs. Under these conditions increasing the complexity of models does not necessarily increase the precision of model predictions and might often decrease it. The most simple view of the environment that could be posed in an environmental model is that of a world composed of a number of phases, each homogenous, well-mixed and static. Our goal in developing the CalTOX model was to start with this view and then add compartments, heterogeneity, and time dependence reluctantly but as necessary. There are two components to the CalTOX model, the multimedia transport and transformation model and the exposure pathways model. The objectives, capabilities, and limitations of the multimedia transport and transformation model are discussed here.

The CalTOX model relies on fugacity as a means of describing the mass potential of organic and inorganic chemical species among a set of connected environmental compartments. The fugacity approach is best suited to nonionic organic chemicals for which partitioning is related strongly to chemical properties, such as vapor pressure, solubility, and the octanol-water partition coefficient. CalTOX has been designed to also handle ionic organic and inorganic contaminants such as radionuclides and metals, based on a modified fugacity-type approach. For all species, fugacity and fugacity capacities are used to represent mass potential and mass storage within compartments. Mathematically, CalTOX addresses the inventory of a chemical in each compartment and the likelihood that, over a given period of time, that chemical will remain in the compartment, be transported to some other compartment, or be transformed into some other chemical species.

CalTOX is a lumped systems, zero-(spatial)-dimension model. This means that it includes compartments to represent various components of the environment, but that there are no explicit vertical or horizontal dimensions in these compartments. However, because of the nature of these compartments, and the way mass exchange is modeled among these compartments, there are implicit transport vectors within the model. Transport in the soil column is implicitly vertical within CalTOX, chemicals move up toward the atmosphere and/or down to ground water. Once in the atmosphere contaminants either move vertically back to the ground-surface soil or to surface water or are blown by wind horizontally out of the landscape. Transport from soil to surface water is implicitly horizontal and at the surface. Implicit in CalTOX is the assumption that, in the unsaturated soil layers, vertical transport is much greater than horizontal. In level terrain, we estimate that this assumption holds for landscapes on the order of 1,000 m^2 or greater. CalTOX has more resolution of chemical transport in soils than in surface waters and is intended for landscapes in which there is a large ratio of land area to surface-water area. CalTOX was designed to be applied over long time periods, months to years, when seasonally and yearly averaged partition factors apply.

Model Objectives

The major objective of CalTOX is to provide risk decision makers with an representation of both how potential human exposure comes about and how precisely it can be quantified for soil-bound contaminants. In order to meet this goal, the objectives of the multimedia transport and transformation components of CalTOX are to (1) provide realistic (although) uncertain ranges of contaminant

concentrations available in environmental media at a contaminated site, (2) provide a relatively simple and accessible model, (3) conserve contaminant mass and comply with laws of chemical equilibrium, (4) address both transport and transformation processes, (5) allow for a distinction between environmental concentrations and exposure concentrations, (6) be compatible with uncertainty and sensitivity analyses, (7) provide time-varying chemical inventories, and (8) be capable of addressing both continuous inputs and initial concentrations.

Chemical Classes

The are many classes of chemicals that must be addressed in environmental transport/transformation models, including organic chemicals, metals, inorganic chemicals, and radionuclides. These chemicals species can also be categorized according to the physical state in which they are introduced to the environment (gas, liquid, or solid), according to whether they dissociate in solution (ionic or nonionic) and according to the charge distribution on the molecule (polar or nonpolar). The traditional fugacity approach is most appropriate for nonionic, organic chemicals in a liquid or gaseous state. However, with modifications for condensation of solids on air particles, this approach can be made appropriate for solid-phase organic chemicals. Additional adjustments make possible the treatment of inorganic species, metals, and fully ionized organic species. Metals (such as mercury) and inorganic chemicals with a relatively large vapor pressure pose special problems, which are not addressed here. Special modeling problems also occur with mixed polarity, dissociating organic species, such as surfactants. The CalTOX model, in descending order of reliability, is capable of handling nonionic organic chemicals, radionuclides, fully dissociating organic and inorganic chemicals, and solid-phase metal species. With careful attention to inputs, the model can be used for partially dissociated organic and inorganic species. The model has not been designed to work with surfactants, inorganic chemicals species with high vapor-pressure-to-solubility ratios, and volatile metals such as mercury.

Critical Sensitivities and Uncertainties

Sensitivity analysis as applied to mathematical models involves the determination of the changes in model response as a result of changes in individual model parameters, whereas uncertainty analysis involves the determination of the variation or imprecision in an output function based on the collective variance of model inputs. There are five factors that determine the precision or reliability of an

environmental transfer model. These are (1) specification of the problem (scenario development), (2) formulation of the conceptual model (the influence diagram), (3) formulation of the computational model, (4) estimation of parameter values, and (5) calculation and documentation of results including uncertainties (IAEA, 1989). Parameter uncertainties and sensitivities are addressed in a supplemental report on model inputs (including ranges and coefficients of variability). However, it should be recognized at the outset that there are some important inherent sensitivities and uncertainties in the CalTOX approach.

Many of the model sensitivities are highly dependent on the chemical properties of the chemical species being modeled. Nonetheless, in all cases the model is very sensitive source terms. All model predictions are directly proportional to the initial inventory or input rates used. For many applications of a model such as CalTOX source data has large variability and/or uncertainty. This is particularly the case for contaminant measurements in soils. For most chemicals, another important model sensitivity is to the magnitude of the transformation rates in soils, air, surface water, and/or sediments. These rate constants can have a large impact on the predicted persistence of any chemical species and are often the most uncertain inputs to the model. For volatile chemicals, the model is sensitive to the magnitude of the air-water partition coefficient. For semi-volatile chemicals and inorganic species the model is more sensitive to the soil-water partition coefficients. It is assumed that these partition coefficients are linear and reversible. When this is not the case, the reliability of the model is reduced because of the uncertainties about how far soil partition processes are from this ideal behavior.

What the CalTOX Transport Model Should Not Be Used For

As is the case with any model, CalTOX was designed for use in a limited range of spatial scales, time scales, geographic conditions, and chemical classes. As has been noted above it is not for surfactants or volatile metals. It should be used for partially ionized organic chemicals only when great care is exercised to adjust the partition coefficients to make sure they are appropriate for the pH of the landscape under consideration. CalTOX is intended for application over long time scales, several months to decades. It should be used cautiously for time periods less than one year and then only when properly time-averaged landscape properties are employed. It should not be used for landscapes in which water occupies more than 10% of the land surface area. CalTOX is designed for modeling very low concentrations of contamination. When contaminant concentration exceeds the

solubility limit in any phase, the results of the model are no longer valid. There is a warning in the spreadsheet model to warn the user when this happens.

CalTOX should not be used as substitute for measured data, where it is available.

Model Structure

In the CalTOX multimedia model, major components of the environment are lumped into homogeneous subsystems or compartments that can exchange mass with other adjacent compartments. The seven-compartment structure used in CalTOX is illustrated in Figure 1. Quantities or concentrations within compartments are described by a set of linear, coupled, first-order differential equations. A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and gas-phase mass. Contaminants are moved among and lost from each compartment through a series of transport and transformation processes that can be represented mathematically as first-order losses. Thus, the transport and transformation equations solved in CalTOX have the form:

$$\frac{d}{dt} N_i(t) = - R_i N_i(t) - \sum_{\substack{j=1 \\ j \neq i}}^{m} T_{ij} N_i(t) + \sum_{\substack{j=1 \\ j \neq i}}^{m} T_{ji} N_j(t) + S_i(t) - T_{io} N_i(t) \qquad [6]$$

where, $N_i(t)$ is the time-varying inventory of a chemical species in compartment i, mol; R_i is the first-order rate constant for removal of the species from compartment i by transformation, 1/d; T_{ij} is the rate constant for the transfer of the species from compartment i to compartment j; and, similarly, T_{ji} is the rate constant for the transfer of the species from compartment j to compartment i, both in 1/d; T_{io} is the rate constant for the transfer of the species from compartment i to a point outside of the defined landscape system, 1/d; S_i is the source term for the species into compartment i, mole/d; and m is the total number of compartments within the landscape system. Equation [6] is solved for the seven compartments shown in Figure 1. The air, surface water, ground-surface-soil, plants, and sediment compartments are assumed to be in quasi-steady state with the root-zone-soil, and vadose-zone-soil compartments. Contaminant inventories in the root-zone soil and vadose-soil zone are treated as time-varying state variables. Contaminant concentrations in ground water are based on the leachate from the vadose-zone soil.

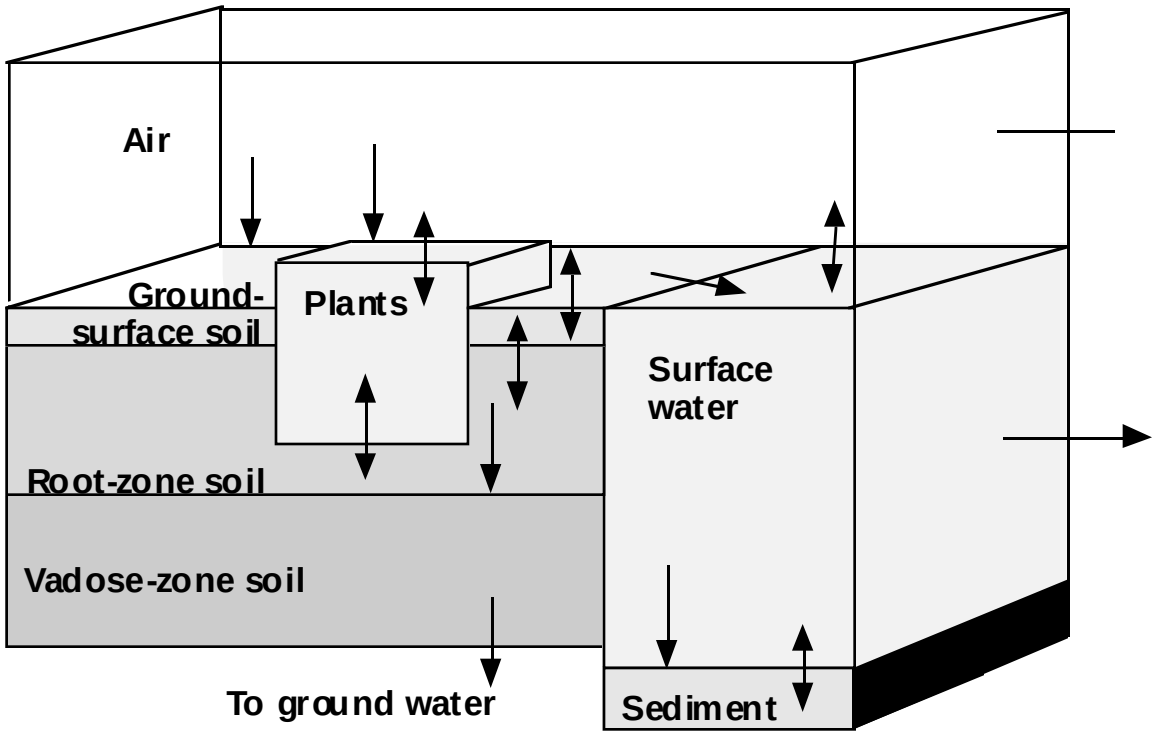


Figure 1. An illustration of mass-exchange processes modeled in the CalTOX seven-compartment environmental transport and transformation model. (Ground water is not explicitly modeled in the system of equations but is used in the exposure calculations.)

Gains and Losses

Predicting the movement of a toxic substance in the environment involves the use of models that describe the partitioning of chemical species among the various environmental media, including air, water, soils, and sediments. One approach to this problem is the use of compartment models. As noted above, models of this type have been developed over the last decade for studying the global fate of toxic elements and radionuclides and for studying the transport and transformation of organic chemicals. There are two basic features that make compartment models suitable for modeling transport and transformation in air, water, or soil. First, each compartment forms a unit in which one can balance gains and losses attributable to sources, transfers from other compartments, transfers to other compartments, and physical/chemical transformations. Second, each compartment forms a unit in which we can evaluate chemical partitioning according to thermodynamic principles. Also, in combination, these two features

allow us to model not only the distribution within a compartment but how this *intra*-compartment distribution impacts *inter*-compartment transfers.

Illustrated in Figure 2 are the types of gains and losses that are considered in defining the inventory of each compartment in the CalTOX model. Listed in Table I are the specific gains and losses that are represented in each of the seven CalTOX compartments for which mass inventory is explicitly modeled. CalTOX simulates all decay and transformation processes (such as radioactive decay, photolysis, biodegradation, etc.) as first-order, irreversible removals.

Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface run-off and ground-water recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. Each chemical species is assumed to achieve chemical equilibrium among the phases within a single compartment. However, there is no requirement for equilibrium between adjacent compartments. As an example, consider the root-zone soil layer, which contains solids, liquids, and gases. An organic chemical added to the soil distributes itself among these three phases such that it achieves chemical and physical equilibrium. Among the potential transport pathways from the root-zone soil compartment are liquid advection (soil water runoff), solid-phase

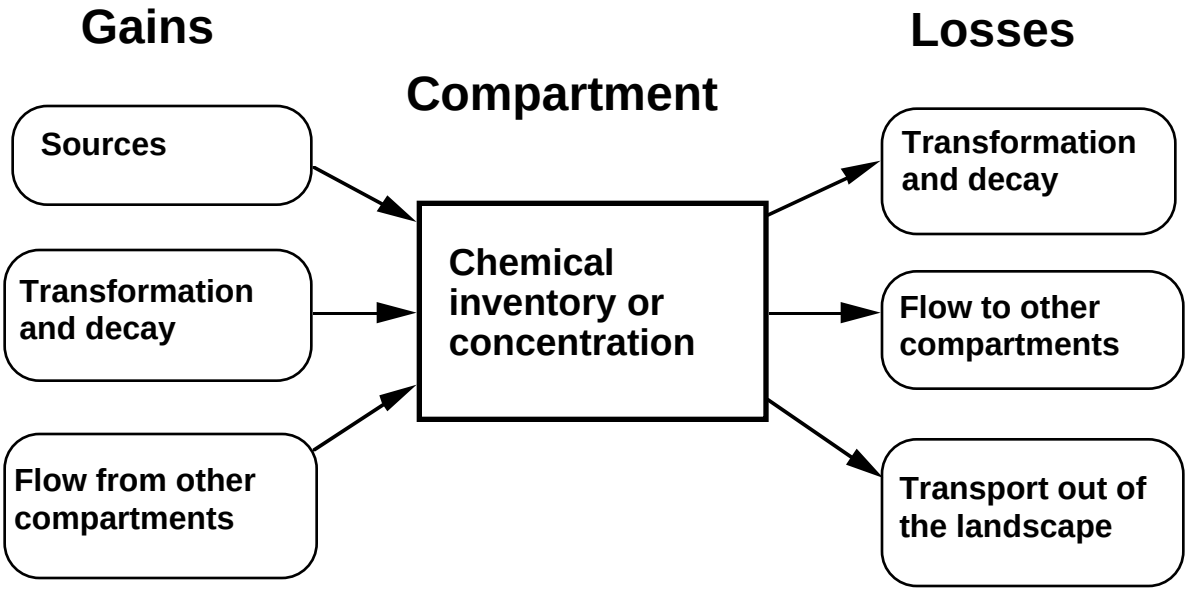


Figure 2. An illustration of the balancing of gains and losses in an environmental transport and transformation model, such as CalTOX.

Table I. Summary of the processes by which contaminants are exchanged and lost among seven CalTOX compartments.

Compartment	Gains	Losses
(1) Air (both the gas phase and particles of the troposphere)	diffusion from soil diffusion from plants diffusion from surface water resuspension of deposited soil particles ***contaminant sources***	diffusion to ground-surface soil diffusion to surface water diffusion to plants washout by rainfall convection losses deposition to soil deposition to plants deposition to surface water chemical / physical transformation
(2) Plants (land vegetation)	deposition of particles from air foliar uptake root-uptake from root-zone soil	diffusion from leaf surfaces washoff from leaf surfaces chemical / physical transformation
(3) Ground-surface soil	diffusion from air diffusion from root-zone soil washout from air by rainfall dry deposition of air particles ***contaminant sources***	diffusion to air diffusion to root-zone soil advection to root-zone soil soil solution runoff erosion (mineral runoff) to surface water resuspension of soil particles chemical / physical transformation
(4) Root-zone soil	diffusion from ground-surface soil advection from ground-surface soil ***contaminant sources***	diffusion to ground-surface soil infiltration (leaching) to vadose-zone soil chemical / physical transformation
(5) Vadose-zone soil	infiltration from root-zone soil ***contaminant sources***	infiltration to ground-water zone
(6) Surface water	diffusion from air washout by rainfall deposition of atmospheric particles soil solution runoff erosion (mineral runoff) diffusion from sediment sediment resuspension ***contaminant sources***	sediment deposition diffusion of vapors to air diffusion to sediment surface-water outflow chemical / physical transformation
(7) Sediment layer	diffusion from surface water sediment deposition (from surface water)	diffusion to surface water sediment resuspension chemical / physical transformation

advection (erosion to surface water or dust stirred up and blown about), and diffusion from both the soil gas phase and soil water into the lower atmosphere. Figure 3 illustrates how the combination of partitioning among the liquid, solid, and/or gas phases of individual compartments determines not only the contaminant fate within that compartment but also the rate and pathway (i.e., diffusion, solid-phase advection, or liquid-phase advection) by which a contaminant flows among the seven CalTOX compartments. In this diagram, C_S refers to contaminant concentration within the soil phase of a compartment, C_L refers to the contaminant concentration within the liquid phase of a compartment, and C_G refers to the contaminant concentration within the gas phase of compartment.

Source Terms

As is noted in Table I, contaminant sources can be introduced to five of the CalTOX compartments—air, ground-surface soil, root-zone soil, vadose-zone soil, and surface water. In root-zone soil and vadose-zone soil the source must be specified as an initial concentration. This type of source is used to represent the burial of toxic chemicals in soils. In these cases, the CalTOX model is used to assess how the slow decay and migration of these soil-layer deposits determine both concentrations in the soil layers and the concentrations in adjacent environmental media. In air, ground-surface soil, and surface water, the source must be specified as a continuous input. This type of source is used to represent such things as atmospheric emissions, pesticide applications, surface-water discharges, and other types of regional and continuous nonpoint pollution.

The Seven CalTOX Compartments

In this section, we describe the seven CalTOX compartments in terms of their mass, volume, and the characteristics that influence advection and diffusion at the boundaries of each compartment. We put particular emphasis on those factors that determine whether a substance will (a) remain or accumulate within the compartment, (b) be physically, chemically, or biologically transformed within the compartment, or (c) be transported to another compartment by cross-media transfer that involves diffusion or advection. The seven CalTOX compartments are (1) air, (2) ground-surface soil, (3) plants, (4) root-zone soil, (5) the vadose-zone soil below

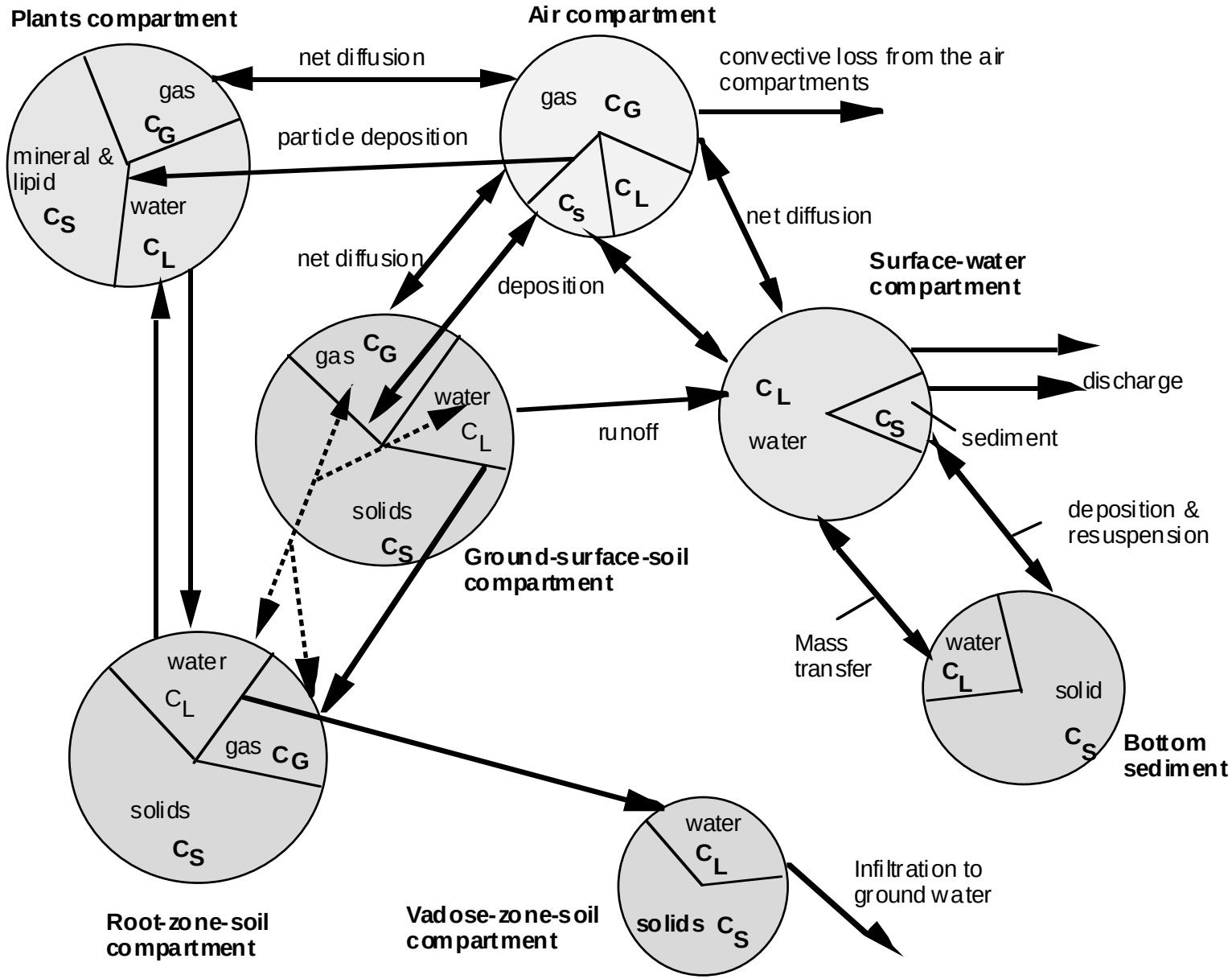


Figure 3. Partitioning among the liquid, solid, and/or gas phases of individual compartments determines not only the contaminant fate within that compartment but also the rate and pathway (i.e., diffusion, solid-phase advection, or liquid-phase advection) by which contaminants flow among the seven CalTOX compartments.

the root zone, (6) surface water, and (7) sediments. In the remaining sections of this report, we often refer to these compartments using single-letter representations as follows: air (a), ground-surface soil (g), plants (p), root-zone soil (s), vadose-zone soil (v), surface water (w), and sediments (d).

The Lower-Atmosphere or Air Compartment (a)

Substances in outdoor (or ambient) air are dispersed by atmospheric advection and diffusion. The volume and mass of the air compartment is defined by the area of the contaminated landscape and the mixing height of the lower atmosphere. Meteorological parameters have an overwhelming influence on the behavior of contaminants in the lower atmosphere. Among them, wind parameters (direction, velocity, and turbulence) and thermal properties (stability) are the most important. The standard models for estimating the time and spatial distribution of point sources of contamination in the atmosphere are the Gaussian statistical solutions of the atmospheric diffusion equation. These models are obtained from solution of the classical differential equation for time-dependent diffusion in three dimensions. Pasquill (1961) has discussed the physical basis, analytical solutions, and the use of these equations. Turner (1970) and Hanna et al. (1982) have compiled workbooks on applications of these solutions to air pollution problems, including the application of the Gaussian models to area and line sources. There are numerous computer programs available and many papers describing algorithms for assessing the dispersion of point, line, and volume air pollution sources.

Another approach to the dispersion of substances in the atmosphere is based on the application of a mass balance to a volume element, parcel or box of air. This gives rise to the “box” models. In this approach, the region to be studied is divided into cells or boxes. The concentration in each box is assumed to be uniform and is a function of the box volume, the rate at which material is being imported, emission rates within the box, and the rate at which material is exported from the box. Gifford and Hanna (1973) have shown that in a simple box model, the yearly average concentration of contaminant within the box is proportional to the source strength in mass per unit area divided by the wind speed. Based on data from U.S. cities, they have developed for both gases and particles proportionality coefficients that can be used to estimate long-term contaminant concentrations. Dispersion in the air-compartment of CalTOX is based on the box-model approach. Based on the work of Hanna et al. (1982), it can be shown that ratio of concentration to source

predicted by the Gaussian plume model is similar in form to that predicted by the box model when this ratio is averaged over long time periods (on the order of one year) and over an area of 10 km^2 or greater. This derivation is provided in Appendix B.

The Plants Compartment (p)

The dominant component of the terrestrial plants compartment is land plants. Plants generally have contact with two environmental media—air and soil. Plant interactions with these media are not understood well enough to define an accurate method of predicting chemical uptake. The translocation of chemicals from soils appears to be a relatively minor pathway for the accumulation of these compounds in plants (Fiedler *et al.*, 1991). In the absence of experimental studies, there has been a reliance on simple bioconcentration factors (BCFs) that relate either a soil or air concentration to a plant concentration. The earliest use of vegetation BCFs was for assessing the effects of global fallout by relating concentrations of radionuclides in plants to concentrations in soil (Ng, 1982). More recently, vegetation BCFs have been proposed for organic chemicals (Travis and Arms, 1988). What is meant by the "concentration in a plant" is difficult to define in large plants where roots, stems, and leaves each may have different chemical concentrations. Recent studies on the bioconcentration of nonionic-organic chemicals have focused on correlations between BCFs and known chemical properties such as Henry's law constant and octanol-water partition coefficients (Bacci et al., 1990; Briggs et al., 1982; Briggs et al., 1983; Travis and Hattemer-Frey, 1988; Travis and Arms, 1988). However, McFarlane et al. (1987) have demonstrated experimentally that chemicals with similar values of K_{ow} can have drastically different long-term partitioning, pointing out a lack of understanding for the mechanisms determining plant uptake and partitioning. The failure of simple BCF correlation models to predict reliably plant uptake has resulted in the publication of several more-detailed models of chemical uptake from soil or air by plants. For radioactive fallout studies, Whicker and Kirchner (1987) developed a model called PATHWAY, which is a dynamic model that includes air-plant and soil-plant uptake and includes treatment of plant growth and senescence. Calamari et al. (1987) proposed two fugacity-based equilibrium models of plant uptake. Riederer (1990) has proposed a fugacity-based equilibrium model that treats only the leaf-air interface, but includes much detail on the composition of leaves. Based on azalea-leaf experiments with five chemicals, Bacci et al. (1990) have developed a correlation of leaf-air bioconcentration factors

with air-water and octanol-water partition coefficients. Trapp et al. (1990) have used barley plants in growth chambers to develop a four compartment—air, soil, roots, and shoots—steady-state fugacity model and found that, in most cases, chemicals in the roots of the barley plants reach equilibrium with the soil, whereas chemicals in the shoots are in equilibrium with the air. Paterson and Mackay (1989) have proposed a seven-compartment fugacity model for plants that, in addition to the leaves, stem, and roots included in the models described above, includes compartments for xylem, phloem, and cuticle. This model was validated against experimental results obtained by Bacci and Gaggi (1986), who found that foliage concentrations were not directly dependent on chemical concentration in soil, but on concentration in air.

In the CalTOX model, vegetation is modeled as a single compartment consisting of air, water, plant lipids and other materials. The fugacity capacity of this compartment is based on a simplified version of the model proposed by Paterson and Mackay (1989). From the literature noted above, it can be concluded that, for nonionic organic chemicals, the fugacity in the total plant mass (that is, both roots and above-ground biomass) is somewhere between that of the root-zone soil and the air. Thus, we assume that the fugacity in the plants is the average of the root-zone soil and air fugacities. It can also be determined that, for ionic organic chemicals and inorganic species, the fugacity in the plant tissues will approach that of the soil when equilibrium is attained.

The Three Soil Compartments

Soil, the thin outer zone of the earth's crust that supports rooted plants, is the product of climate and living organisms acting on rock. A true soil is a mixture of air, water, mineral, and organic components (Horne, 1978). The relative mix of these components determines to a large extent how a chemical will be transported and/or transformed within the soil. The movement of water and contaminants in soil is typically vertical as compared to horizontal transport in the ground-water (i.e., saturated) zone. A chemical in soil partitions among soil water, soil solids (mineral and organic phases), and soil air. For example, the rate of volatilization of an organic compound from soil depends on the partitioning of the compound into the soil air and on the porosity and permeability of the soil.

Soils are characteristically heterogeneous. A trench dug into the soil zone reveals typically several horizontal layers having different colors and textures. These multiple layers are often divided into three major horizons: the *A* horizon,

which encompasses the root zone and contains a high concentration of organic matter; the *B* horizon, which is unsaturated, is below the roots of most plants, and contains a much lower organic carbon content; and 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 (Bowen, 1979).

Models developed for assessing the behavior of contaminants in soils can be categorized in terms of the transport/transformation processes being modeled. Partition models such as the fugacity models of Mackay (1979, 1991) 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 lower soil layers. The multimedia model GEOTOX (McKone and Layton, 1986) has been used to determine the inventory of chemical elements and organic compounds in soil layers following various contamination events. This model addresses volatilization to atmosphere, runoff to surface water, leaching to ground water, and first-order chemical transformation processes. 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).

The Ground-Surface-Soil Compartment (g). 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 (Whicker and Kirchner, 1987). The ground-surface-soil layer is at the top of the *A* soil horizon. 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, 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 Root-Zone-Soil Compartment (s). 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. Soil-water content in the root zone is somewhat higher than that in surface soils. The presence of clay in this layer serves to retain water. 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. 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 Vadose-Zone-Soil Compartment (v). This compartment is used to represent the soil layers below both the root zone and the diffusion depth and above the saturated layer. This compartment can encompass both the *B* and the *C* soil horizons. The soil in this layer typically has a lower organic carbon content and lower porosity than the root-zone soil. Contaminants in this layer are assumed to move downward to the ground-water zone primarily by capillary motion of water and leaching. Chemical transformation in this layer is primarily by biodegradation.

The Surface-Water Compartment (w)

The behavior of chemicals in surface waters is determined by two factors—the rate of physical transport in the water system and chemical reactivity. Chemical reactions in surface waters are discussed below in the section on transformation. Physical transport process are dependent to a large extent of the type of water body under consideration—oceans, seas, estuaries, lakes, rivers, or wetlands. Schnoor (1981) and Schnoor and MacAvoy (1981) have summarized important issues relating to surface-water transport. Fugacity models have been develop by Mackay et al. (1983a) for lakes and also by Mackay et al. (1983b) for rivers.

At low concentration, contaminants in natural waters exist in both a dissolved and a sorbed phase. In slow-moving surface waters, both advection and dispersion are important. In rapidly moving water systems, advection controls mass transport and dissolved substances move at essentially the same velocity as the bulk water in the water system. Contaminants that are sorbed to colloidal material and fine suspended solids can also be entrained in water currents, but they may undergo additional transport processes that alter their effective residence time in surface waters. Such processes include sedimentation and deposition and scouring and resuspension. Thus, determining the transport of contaminants in surface waters requires that we follow both water movement and deposition and resuspension from sediment.

A water balance is the first step in assessing surface-water transport. A water balance is established by equating gains and losses in a water system with storage. Water can be stored within estuaries, lakes, rivers, and wetlands by a change in elevation or stage. Water gains include inflows (both runoff and stream input) and direct precipitation. Water losses include outflows and evaporation.

In CalTOX the surface-water compartment is used to represent the surface-water body nearest to a contamination site and receiving runoff and/or airborne deposition from that site. The surface-water compartment is composed of two phases, pure water and suspended sediment material that contains the sorbed contaminants. Surface waters are assumed to be well-mixed systems. The surface-water velocity relative to area, depth, and volume determines the residence time of the pure-water phase. The effective residence time of suspended sediments is determined by both the residence time of the water phase and the deposition and resuspension rates of the sediments. Contaminants in surface water are transported into this compartment by deposition from air, by runoff from soil, and by diffusion and resuspension from sediments. Contaminants in surface water are transported out of this compartment by advection in both the liquid and sediment phases, by diffusion to air at the upper surface of the water body and by diffusion and deposition to sediments.

Contaminants in surface water are also taken up by aquatic organisms and this can also impact the distribution of these contaminants. In CalTOX, the modeling of contaminant transport in surface water is based on the assumption that essentially all the contaminant mass is in either liquid or suspended-solid phases. This assumption implies that a very small fraction of the total compartment inventory is distributed among aquatic species. However, this does not imply that there are low concentrations in these organisms. Quite the contrary is often the case.

The Sediment-Zone Compartment (d)

This compartment represents the porous, active layer of water and solid material that forms at the bottom of the surface-water compartment primarily as a result of sediment and organic-matter deposition from the surface water above. Reuber et al. (1987) note that the bottom sediments of surface-water bodies have at least two distinct layers—an active layer characterized by a high degree of chemical and biological activity and a deeper inactive layer in which chemicals are essentially isolated from the water column. In lakes, the active layer can be further divided

into a fluffy or "nepheloid" layer at the water-sediment interface and a more consolidated lower layer below. The nepheloid layer consists of about 95% water and 5% solids and is highly organic in nature; it consists of deposited particles and fecal material from the water column and is stirred by currents and by burrowing animals (Mackay, 1991). The consolidated layer is on the order of several centimeters thick and has lower water content, on the order of 50%, but can still have an abundance of organic material and mixing due to the activities of aquatic organisms. The bottom sediments of rivers can be much more turbulent than those of lakes and tend to have less organic matter and a more rapid mixing due to resuspension and deposition.

Deposition, resuspension, burial, diffusion, oxidation, and biotransformation are continuous processes that impact the inventory of contaminants in bottom sediments. Deposition of mineral matter and organic matter from surface water to sediments is a continuous process in any water body and an important mechanism for transferring particle-bound contaminants to the sediment layer. In any water system, some of the deposited material is resuspended by water currents, which depend on the hydrology of the system. In lakes, deposition is typically greater than resuspension and, in rivers, resuspension can equal or exceed deposition. Burial refers to the rate at which contaminants move from the active to the inactive layer. The pore water of the sediment layer together with the colloidal organic matter in this pore water provide vehicles for diffusion. Contaminants dissolved in the pore water or sorbed to the colloids can diffuse or migrate from sediments up to the water column or down to deeper sediment layers. Oxidation can play an important role in the chemical transformation of inorganic and (to a lesser extent) organic chemicals in the sediment layer. Biotransformation is also an important transformation process in the sediment layer. However, the rate at which these processes can remove contaminants from sediments depends on the availability of oxygen in the water column (Mackay, 1991).

Ground-Water Contamination

In the current version of CalTOX, we do not explicitly model the flow and dilution of contaminants in ground water. Instead, we consider the concentration of a contaminant in the water leaching from the vadose-zone soil as an input to the ground-water zone. This concentration is used to make calculations of potential doses to contaminants in ground water. There is also an option for the user to enter

a contaminant concentration in ground water and this concentration is used in the potential dose calculations described in the Part-III report.

In ground water, the dilution of contaminants occurs at much slower rate than it does in air and surface water. After water from precipitation infiltrates the ground surface, it travels vertically down through the unsaturated zone to where it contacts the water table and then flows approximately horizontally. This horizontal movement is driven by the hydraulic gradient, which is the difference in hydraulic head at two points divided by the distance (along the flow path) between the points. Bear and Verruijt (1987) and Freeze and Cherry (1979) have compiled extensive reviews on the theory and modeling of ground-water flow and on the transport of contaminants in ground water. The movement of contaminants in ground water is described by two principal mechanisms—(1) gross fluid movement (advective flow) and (2) dispersion. Dispersion depends on both fluid mixing and molecular diffusion. The transport of many chemical species in ground water is often slowed or "retarded" relative to the flow of the bulk fluid by sorption of the contaminant material to organic material, soil particles, and rock. Any transport of ground water away from the contaminated landscape unit should result in reduction in contaminant concentration.

PARTITION COEFFICIENTS AND FUGACITY CAPACITIES

For each model compartment, we determine the fugacity capacity of the total compartment from the sum of the volume-fraction-weighted fugacity capacities of the constituent phases—air, water, particles, and lipids.

Fugacity Capacities in Pure Air, Pure Water, Particles, and Lipids

The fugacity capacity in units of mol/m^3-Pa for a nonionic organic chemical in *pure* air, Z_{air}, is given by

$$Z_{air} = 1/RT \ , \qquad [7]$$

where R is the universal gas constant, 8.314 Pa-m^3/mol-°K, and T is temperature in kelvins (°K).

The fugacity capacity in units of mol/m^3-Pa for a nonionic organic chemical in *pure* water, Z_{water}, is given by

$$Z_{water} = 1/H \quad , \qquad [8]$$

where H is the Henry's law constant, Pa-m^3/mol, which expresses the ratio of equilibrium activities of a chemical in air (expressed as vapor pressure, Pa) and in water (mol/m^3) when the two phases are well mixed. Instead of being measured directly, the Henry's law constant can be estimated as the ratio of measured vapor pressure, VP, in Pa to water solubility, *S*, in mol/m^3 (Mackay, 1991),

$$H = VP/S \quad . \qquad [9]$$

However, when the Henry's law value is calculated in this way, both the solubility and the vapor pressure should be determined for the same state—either liquid or solid.

Soil and Sediment Particles

A chemical in the solid or particle phase of soils, sediments, and surface waters has a fugacity capacity given by

$$Z_{ip} = K_{Di} \times \rho s_i \times Z_{water} \times \frac{1 \text{ m}^3 \text{ water}}{1000 \text{ L water}} \quad , \qquad [10]$$

where Z_{ip} is the fugacity capacity of the pure solid phase, mol/m^3-Pa; i refers to the compartment name (i.e., *a, g, b, s,* etc.); K_{Di} represents, for compartment *i*, the sorption coefficient, which is the ratio at equilibrium of chemical concentration attached to particles (mol/kg) to chemical concentration in the solution, mol/L; and ρs_i is the density of the actual particles in kg/m^3 (not the bulk density of the particles when mixed in solution). For inorganic chemicals, values of K_{Di} must be derived either from experiments or implied from geochemical data. For nonionic organic chemicals, Karickhoff (1981) has shown that the sorption coefficient, K_{Di}, can be related to the product of the organic-carbon partition coefficient, K_{oc}, and the fraction of organic carbon, f_{oci}, in a specific compartment, i,

$$K_{Di} = K_{oc} \times f_{oci} \quad . \qquad [11]$$

For example, for the root-zone-soil compartment (s), K_{Ds} (with units of L/kg) is the product of f_{ocs}, the fraction organic carbon in this soil compartment, and K_{oc}, the organic carbon partition coefficient. The organic-carbon partition coefficient provides a measure of chemical partitioning between organic carbon (in soils and sediments) and water. The higher the K_{oc}, the more likely a chemical is to bind to the solid phase of soil or sediment than to the liquid phase. Karickhoff (1985) has described several empirical estimation methods for obtaining K_{oc} from K_{ow}.

$$\log K_{oc} = 0.72 \log K_{ow} + 0.49 \quad \text{(methylated and halogenated benzenes)} \qquad [12]$$

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18 \quad \text{(13 pesticides)} \qquad [13]$$

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad \text{(5 poly-nuclear aromatics [PNAs])} \qquad [14]$$

$$\log K_{oc} = \log K_{ow} - 0.317 \quad \text{(22 PNAs and substituted PNAs)} \qquad [15]$$

The most general of these, equation [15], represents K_{oc} as equal to 0.48 times K_{ow}, and is the correlation incorporated into the CalTOX model as a default. However, the user has the option of entering K_{oc} as an input. When a value of K_{oc} is entered, the default correlation is not used.

Particles in Air

In the air compartment contaminants bound to aerosol particles achieve equilibrium with gas-phase contaminants. Our derivation of the fugacity capacity of aerosol particles is based on a model originally developed by Junge (1977) but used frequently by others (for example, Cohen and Ryan, 1985; Mackay et al., 1986; Pankow, 1987; Ryan and Cohen, 1986; Taylor, 1992). In this model the fraction of contaminant bound to aerosol particles, φ, is given by

$$\varphi = \frac{c\theta}{(VP + c\theta)} \quad , \qquad [16]$$

where, θ is the total suspended particle surface area concentration in m^2/m^3, VP is the vapor pressure of the pure contaminant in Pa, and c is an approximate constant that Junge sets equal to 0.173 m-Pa. Although the model is widely used in this form,

there remains uncertainty about how the various parameters are evaluated (Bidleman and Foreman, 1987; Ligocki and Pankow, 1989; Mackay et al., 1986; Pankow, 1987; Taylor, 1992;). Whitby (1978) reports values for θ ranging from 4.2×10^{-5} m^2/m^3 for a clean continental site to 1.1×10^{-3} m^2/m^3 for urban sites. Much of the variation in this parameter can be accounted for by the variation in particle concentrations in clean, rural versus urban sites, 10 $\mu g/m^3$ versus 100 $\mu g/m^3$, respectively (Hinds, 1982). A more difficult question involves the vapor pressure to be used in the model. For contaminants that exist as solids at ambient temperatures, it is not clear whether the vapor pressure of the sub-cooled liquid, VP_l° or the vapor pressure of the solid, VP_s, should be used (Mackay et al. 1986; Mackay, 1991; Taylor, 1992). The relationship between these two vapor pressures is given by Prausnitz (1969) as

$$\ln\left(\frac{VP_l^\circ}{VP_s}\right) = \Delta S_f \frac{(T_m - T)}{RT} \quad , \qquad [17]$$

where ΔS_f is the entropy of fusion at the melting point, J/mole/°K; T_m is the melting point of the compound, and T is the ambient temperature. As shown by Mackay and Shiu (1981), equation [17] can be written with substitutions as

$$\frac{VP_l^\circ}{VP_s} = \exp\left[6.79\,(T_m/T - 1)\right] \quad . \qquad [18]$$

For compounds such as dioxins and polycyclic aromatic hydrocarbons, this ratio can be as large as 1000, so the selection of sub-cooled liquid versus solid vapor pressure can lead to uncertainty. Following the recommendation of Mackay et al. (1986), we use the sub-cooled liquid vapor pressure to estimate the fugacity capacity of air particles. The fugacity capacity for air particles, Z_{ap} in mol/m^3-Pa, is derived from equation [16] by noting that

$$f_{vap} \times Z_{ap}/Z_{air} = \frac{c\theta}{VP} \quad , \qquad [19]$$

where f_{vap} is the volume fraction of the air that is occupied by air particles. Under the assumption that the particle load in the air is 100 $\mu g/m^3$ and that particle density

is 1500 kg/m^3, this fraction is 6.7×10^{-11}. Substituting this with θ equal to 1.1×10^{-3} m^2/m^3, c equal to 0.173 m-Pa, and Z_{air} equal to 1/RT into equation [19] gives

$$Z_{ap} = \frac{3 \times 10^6}{VP_l^\circ \, RT} \quad . \qquad [20]$$

This expression is similar to one derived by Mackay et al. (1986) using a somewhat different approach.

Lipids

A lipid is any substance that is soluble in nonpolar organic solvents and together with proteins and carbohydrates constitute the principal structural components of living cells. Lipids include fats, waxes, phosphatides, cerebrosides, and related derived compounds. Lipid fugacity capacities form the basis of estimating partitioning of organic contaminants from air and water into terrestrial and aquatic biota. Mackay (1991) has shown the general form of the fugacity capacity, Z_{lipid} in mol/m^3-Pa, for nonionic organic chemicals in biological species has the form

$$Z_{lipid} = aK_{ow}^{b} \times Z_{water} \ , \qquad [21]$$

where *a* and *b* are empirical constants that vary with both the organism involved and the type of lipid tissue. The *a* constant represents the fraction of a lipid tissue that behaves as an organic solvent. In lipid tissues that reach chemical equilibrium with their environment, we expect *b* to be close to 1. For tissues that do not attain equilibrium or for tissues that attain steady-state that is not at chemical equilibrium (due to processes such as metabolism), we expect *b* to be different from and, most likely, less than 1. For species, such as fish, the bioconcentration factor (BCF) is ratio of tissue concentration to water concentration, mol/kg(fish) per mol/L(water). For these species, the BCF is explained primarily by partitioning into lipid tissues and we expect BCF to be proportional to Z_{lipid}/Z_{water}, and the proportionality constant reflects the lipid fraction of the fish, which means

$$Z_{fish} \propto Z_{lipid} = \text{BCF} \times Z_{water} \ . \qquad [22]$$

Modifications to Fugacity Capacities for Inorganic and Ionic-Organic Chemicals

The traditional fugacity approach was developed for nonionic organic chemicals. The modifications described here make possible the treatment of inorganic species (including radionuclides), metals, and fully ionized organic species. In order to make these adjustments, it should be recognized that the basic premise of the fugacity approach is that the mass potential of any compartment can be scaled to a single phase through a series of partition coefficients. In the traditional fugacity approach this scaling is 1/RT. However, for chemicals that have extremely low vapor pressure and relatively high water solubility this leads to the problem of having extremely large fugacity capacities in water. To avoid this problem for chemicals with very low vapor pressure, such as inorganic chemicals and speciated or ionized organic chemicals, we assume that these chemicals can be described by zero fugacity in air, that is, $Z_{air} = 0$. We then set the fugacity capacity of water, Z_{water}, equal to 1 mol/m^3-Pa. This approach has been used by Mackay and Diamond (1989) and Diamond et al. (1992) for inorganic species in lakes. They refer to this modification as "aquivalence." This leads to a scaling of other phases and compartment fugacity capacities based on the fugacity capacity of the water phase. Thus, as above, the fugacity capacity of the particles of compartments (i=g, s, v, w, d) is of the form

$$Z_{ip} = K_{Di} \times \rho s_i \times Z_{water} \times \frac{1\ m^3\ water}{1000\ L\ water} \quad , \qquad [23]$$

and, since Z_{air} is now assumed equal to zero, the fugacity capacity of air particles becomes the same as that of the ground-surface-soil particles,

$$Z_{ap} = Z_{gp} = K_{Dg} \times \rho s_g \times Z_{water} \times \frac{1\ m^3\ water}{1000\ L\ water} \quad . \qquad [24]$$

Physical Composition of Model Compartments and Fugacity Capacities

The fugacity capacity of the total compartment is calculated from the sum of the volume-fraction-weighted fugacity capacities of the constituent phases.

Air Compartment

In the air compartment, the total fugacity capacity, Z_a in mol/m^3-Pa, is composed of the volume-weighted average of the fugacity capacities of its two constituent phases, air and air particles,

$$Z_a = Z_{air} + f_{vap} \times Z_{ap} \quad , \qquad [25]$$

where f_{vap} is the volume fraction of particles in air. The volume fraction of the gas phase is essentially unity.

Plants

Because of the difficulty of modeling terrestrial vegetation using fugacity-type models, it has largely been ignored in multimedia models (Mackay, 1991). Riederer (1990) reports that a full description of steady-state partitioning within plant foliage requires a model that includes rates of uptake from and loss to aqueous and solid phases at the surface of the cuticle and the rates of translocation, metabolism, and dilution due to growth. Riederer (1990) has shown that, for foliar uptake of gas-phase organic contaminants, the most general form of a steady-state plant-air partition model is

$$K_{pa} = f_{pa} + (f_{pw} + f_{pl} \times K_{ow}) \times \frac{RT}{H} \quad , \qquad [26]$$

where K_{pa} is the ratio of contaminant concentration in plant tissue to that in air, mol/m^3 per mol/m^3; f_{pa} is the volume fraction of plant tissue that is air; f_{pw} is the volume fraction of plant tissue that is water; f_{pl} is the volume fraction of the plant tissue that is lipid; R is the universal gas constant, 8.31 Pa-m^3/mol-k; T is the temperature in kelvins (293 K); and H is the Henry's law constant of the contaminant in Pa-m^3/mol. Based on azalea-leaf experiments with five chemicals, Bacci et al. (1990) have developed a correlation of leaf-air bioconcentration factors with air-water and octanol-water partition coefficients and have shown that f_{pl} is on the order of 0.01. Paterson and Mackay (1989) have estimated that f_{pa} is 0.5. This implies that the remainder of the plant volume fraction, 0.49, is either water or non-

lipid solids. Based on our assumption that 80% of total plant mass is water, we set f_{pw} equal to 0.4. These assumptions together with the recognition that K_{pa} is the ratio of plant fugacity capacity to air fugacity capacity—that is, Z_p / Z_{air} or $Z_p \times RT$—leads to the following expression to estimate the plant fugacity capacity Z_p for organic chemicals in plant tissue relative to air,

$$Z_p = \frac{0.5}{RT} + (0.4 + 0.01 \times K_{ow}) \times Z_{water} \quad . \qquad [27]$$

The fugacity capacity of plant tissues relative to soil can be related to the plant-soil partition coefficient, K_{ps}, which expresses the ratio of contaminant concentration, mol/kg, in the fresh mass of vegetation to the contaminant concentration in the root-zone soil, mol/kg. This means K_{ps} is equal to $(Z_p \rho b_s)/(Z_s \rho_p)$, where ρb_s is the soil bulk density in kg/m^3 and ρ_p is the plant density, assumed to be 1000 kg/m^3. For nonionic organic chemicals, there are methods for estimating K_{ps} or Z_p from chemical solubility in the absence of measured data. Briggs et al. (1982, 1983) have developed an equation to estimate uptake of contaminants by roots from soil solution. They refer to this partition coefficient as the root concentration factor, RCF. It represents the ratio of contaminant concentration in root tissue, mol/kg(fresh mass), to contaminant concentration in soil solution, mol/kg, and it takes the form

$$RCF = 0.82 + 0.03\, K_{ow}^{0.77} \quad . \qquad [28]$$

We note that RCF is the ratio of plant fugacity capacity to soil-solution fugacity capacity, that is, Z_p / Z_{water} (or $Z_p \times H$). This means that equation [28] leads to the following expression for estimating the plant fugacity capacity Z_p,

$$Z_p = (0.82 + 0.03 \times K_{ow}^{0.77}) \times Z_{water} \quad . \qquad [29]$$

It is of interest that, based on experiments that measured chemical uptake from air to leaves and experiments that measured chemical uptake from soil solution to roots, the implied fugacity capacity of plants in both cases as expressed by, respectively, equations [27] and [29], are quite similar. Equation [27], because it

includes all three phases of the plants compartment, is used to represent the fugacity capacity in plants in the CalTOX model for nonionic organic chemicals.

For inorganic species and ionic organic compounds, we estimated Z_p as

$$Z_p = K_{ps} \times Z_{soil} / \rho b_s \ . \qquad [30]$$

As a rule, for inorganic species and ionizing organic compounds, K_{ps} should be obtained from measured data. In the absence of measured data, we obtain K_{ps} by assuming that the contaminant concentration is plant water is equal to that in soil water so that K_{ps} is equal to $(1\text{-bio}_{dm}) / K_{Ds}$, where bio_{dm} is the dry-mass fraction of plants and (1-bio_{dm}) is the water-mass fraction of the plants.

Soil Compartments

For the soil compartments, which have air, water, and solid components all at the same fugacity, the total compartment fugacity capacities are the volume-weighted average of the fugacity capacities of three component phases. For ground-surface-, root-zone, and vadose-zone soil; these compartment fugacities are, respectively, Z_g, Z_s, and Z_v in mol/m^3-Pa. As an example, for the root-zone soil compartment (s), the equation describing the overall fugacity capacity of this compartment is

$$Z_s = \alpha_s Z_{air} + \beta_s Z_{water} + (1- \phi_s) Z_{sp} \ , \qquad [31]$$

where α_s is the volume fraction of air in the soil compartment, β_s is the volume fraction of water in the compartment, $(1 - \phi_s)$ is the volume fraction of solid in the compartment, ϕ_s $(= \alpha_s + \beta_s)$ is the total void fraction in soil, and Z_{sp} is the fugacity capacity of the soil particles, mol/m^3-Pa.

Surface Water

In the surface-water compartment the total fugacity capacity, Z_w in mol/m^3-Pa, is composed of the volume-weighted average of the fugacity capacities of its two constituent phases, water and suspended particles,

$$Z_w = Z_{water} + (\rho b_w / \rho s_w) \times Z_{wp} \qquad [32]$$

where ρb_w is the suspended particle load in surface water, kg/m^3, ρs_w is density of the suspended-particle material, kg/m^3, and Z_{wp} is the fugacity capacity of the particles and given by

$$Z_{wp} = K_{Dw} \times \rho s_w \times Z_{water} \times \frac{1\ m^3\ water}{1000\ L\ water} \quad , \qquad [33]$$

in which K_{Dw} represents the sorption coefficient of suspended particles, L/kg. The volume fraction of suspended particles in water is assumed to be so small that the volume fraction of the water phase is essentially unity.

Sediment

In the sediment compartment the total fugacity capacity, Z_d in mol/m^3-Pa, is composed of the volume-weighted average of the fugacity capacities of its two constituent phases, sediment particles and water,

$$Z_d = \beta_d \times Z_{water} + (1-\beta_d) \times Z_{dp} \quad , \qquad [34]$$

where β_d is the void fraction of the sediment compartment, $1-\beta_d$ is the volume fraction of sediment particles in the sediment compartment, and Z_{dp} is the fugacity capacity of the sediment layer particles and given by

$$Z_{dp} = K_{Dd} \times \rho s_d \times \frac{1\ m^3\ water}{1000\ L\ water} \quad , \qquad [35]$$

in which K_{Dd} represents the sorption coefficient of sediment layer particles, L/kg.

TRANSPORT PROCESSES IN THE CalTOX MODEL

In a multimedia model, major components of the environment are lumped into homogeneous subsystems or compartments that can exchange mass with other adjacent compartments. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface runoff and ground-water recharge. In the previous section, we considered the use of fugacity to describe how each chemical species is partitioned among the phases within a single compartment. The nature of this partitioning in combination with

mass flows at compartment boundaries defines the overall rate of cross-media transfer of contaminants between any two adjacent compartments. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. The modeling of these two processes is described in this section.

Molecular Diffusion Coefficients

Molecular diffusion is the net transport of a molecule in a liquid or gas phase and is the result of intermolecular collisions rather than turbulence or bulk transport. Mass transport via molecular diffusion is driven by concentration (or fugacity) gradients. A diffusion coefficient depends on properties of both the chemical species being transported and the phase or phases through which it is transported.

Diffusion in Air

Analytical methods for estimating the diffusion coefficient of a binary gas system have been reviewed by Reid et al. (1987) and Lyman et al. (1982). These methods have their foundations in a theoretical relationship referred to as the Chapman-Enskog model for dilute gases at low pressures (Chapman and Cowling, 1939; Reid et al., 1987). Based on accuracy and ease of use, Lyman et al. (1982) recommend two methods for use under ambient environmental conditions. When applied at atmospheric pressure, the most straightforward of these two methods, which is used in CalTOX, relates diffusion in air to the molecular weight of the compound as

$$D_{air} = 8.6 \times 10^{-3}\, T^{1.75} \frac{\sqrt{\dfrac{(29 + M_x)}{29\, M_x}}}{\left[2.7 + (V_x)^{1/3}\right]^2} \quad , \qquad [36]$$

where D_{air} is the diffusion coefficient in air for compound *x* in m^2/d, T is the air temperature in K, M_x is the molecular weight of compound *x* in g/mol, and V_x is the molecular volume of the compound *x* in cm^3/mol. The values 29 and 2.7 represent the molecular weight and cubic root of molecular volume, respectively, for air. Methods for estimating molecular volumes are reviewed in Lyman et al. (1985). For many organic compounds, D_{air} is in the range of 0.1 to 1 m^2/d.

Diffusion in Water

Reid et al. (1987) and Lyman et al. (1982) have also reviewed several methods for estimating liquid diffusion coefficients and found these methods are all based on the Stokes-Einstein equation relating diffusivity to the temperature and viscosity of the solvent and the molecular radius of the solute. As noted by Reid et al. (1987), one of the oldest but still widely used empirical estimation methods for binary diffusion in liquids is that of Wilke and Chang (1955). This method of estimating water diffusion coefficients in CalTOX and has the form

$$D_{xy} = \frac{6.5 \times 10^{-7} \, (\phi \, M_y)^{1/2} \, T}{\eta_y \, V_x^{0.6}} \quad , \qquad [37]$$

where D_{xy} is the diffusion coefficient in of solute *x* in solvent *y*, m^2/d; ϕ is the association factor of solvent *y*, no units; M_y is the molecular weight of the solvent, g/mol; T is the temperature of the solute-solvent system, K; η_y is the viscosity of the solvent *y* , cP; and V_x is molecular volume of the solute at its normal boiling temperature, cm^3/mol. Wilke and Chang (1955) report an average estimation error of 10 per cent in predicting diffusion coefficients for 251 solute-solvent systems. They recommend an association factor of 2.6 when the solvent is water. The viscosity of water is 0.79 cP at 30 °C. Molecular volume can be estimated by the LeBas incremental method as described in Lyman et al. (1982). For many organic compounds, D_{water} is in the range of 10^{-5} to 10^{-4} m^2/d.

Diffusion in Tortuous, Multi-Phase Systems, Such as Soils and Sediments

Compartments such as soils and sediments are neither homogeneous nor single phase. When air and water occupy the tortuous pathways between stationary particles in a porous medium such as a soil or sediment, Millington and Quirk (1961) have shown that the effective diffusivity, D_{eff}, of a chemical in each fluid of the mixture is given by

$$D_{eff} = (\omega^{10/3} / \phi^2) \, D_{pure} \quad , \qquad [38]$$

where ω is the volume fraction occupied by this fluid, ϕ is the total void fraction in the medium (the volume occupied by all fluids) , and D_{pure} is the diffusion coefficient of the chemical in the pure fluid. Jury et al. (1983) have shown that the

effective tortuous diffusivity in the water and air of a soil compartment, such as the root-zone soil (s), is given by

$$D_s = \frac{Z_{air}}{Z_s}(\alpha_s^{10/3}/\phi_{soil}^2)\ D_{air} + \frac{Z_{water}}{Z_s}(\beta_s^{10/3}/\phi_{soil}^2)\ D_{water}\ , \qquad [39]$$

where D_s is the effective tortuous, mixed phase diffusion coefficient in the root-zone soil compartment, the Z's are the fugacity capacities derived previously, and other parameters are as defined previously. We use an equation of this form to describe the effective diffusion coefficient in ground-surface soil (g), vadose-zone soil (v), and sediments (d).

Diffusion and Boundary-Layer Models

The exchange of contaminants at the boundary between two environmental compartments that are made up in part of fluids in motion (i.e., air or water) involves two modes of diffusion—molecular diffusion within a thin boundary layer and turbulent diffusion within the bulk of the compartment. In a compartment, such as the atmosphere, in which turbulent mixing is rapid and continuous, molecular diffusion will only be significant at boundaries with other less turbulent compartments, such as soil and surface water. At these boundaries, the air makes a transition from a well-mixed turbulent fluid to an essentially zero-velocity boundary. The nature of this transition zone defines the rate of diffusion mass transport from one compartment to another. In a multimedia model, such as CalTOX, it is assumed that turbulent diffusion within a compartment, such as the lower atmosphere, is so efficient that the bulk concentration, C^b in mol/m^3, is simply the compartment inventory divided by the compartment mass. However, at the boundary between two compartments, the modeling of diffusive mass transfer must include both turbulent and molecular processes at these transition zones that can not be lumped or neglected.

Diffusive mass transfer at compartment boundaries is modeled using a boundary-layer model. In order to derive this model, we consider as an example the turbulent air mass over a well-mixed but stagnant layer of air that is in contact with a surface, such as soil or water. The contaminant concentration in the bulk air above the stagnant layer is $C^b\ mol/m^3$. The contaminant concentration at the boundary with the surface is $C^* mol/m^3$. This is shown in Figure 4. The concentration in the air above the stagnant layer makes a transition from the surface

concentration to the bulk concentration in a distance that is referred to as the mass-transfer boundary layer. The flux in mol/m^2-d of contaminant from the surface to the bulk fluid is proportional to the difference in concentration between the surface and the bulk air mass and is given by

$$Flux = U_a(C^b - C^*) \ , \qquad [40]$$

where U_a is the mass-transfer coefficient for combined turbulent and molecular diffusion and has units of m/d. The mass-transfer coefficient, U_a, can be evaluated by replacing it with the mass-transfer coefficient corresponding to molecular diffusion of a contaminant with diffusion coefficient, D_{air} (m^2/d), through a layer of still air having a depth δ, such that the same flux is obtained for this concentration gradient,

$$Flux = \frac{D_{air}}{\delta}(C^b - C^*) \ . \qquad [41]$$

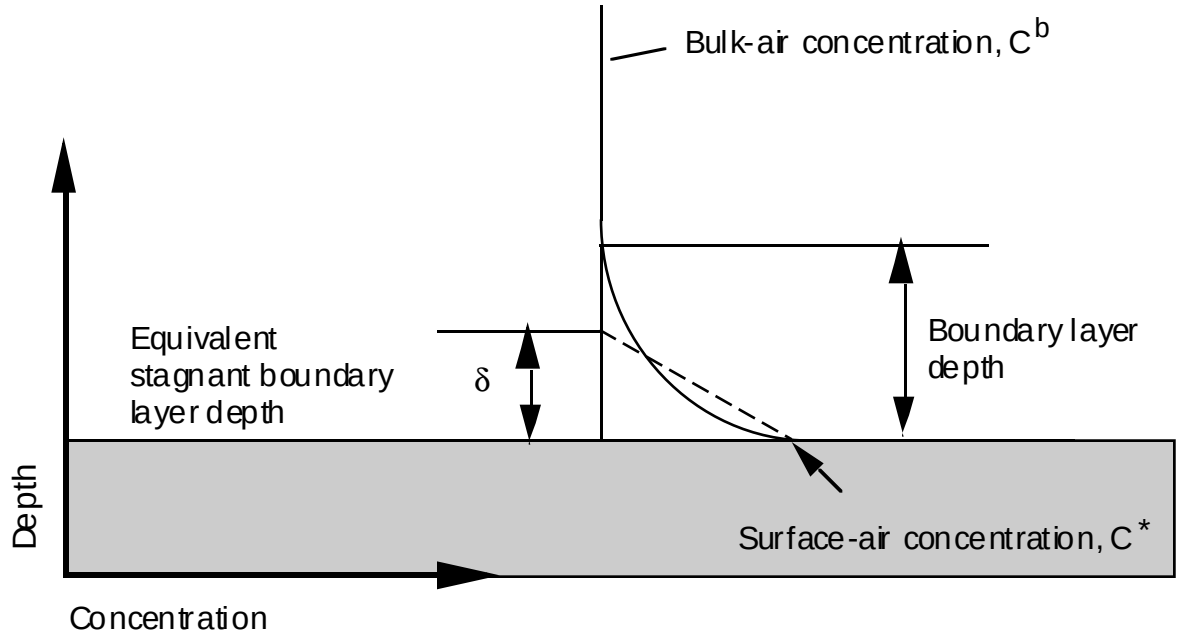


Figure 4. The concept of the stagnant boundary layer versus the true boundary layer thickness in the transition between the contaminant concentration at the surface of soil or water and the concentration in the bulk air.

The depth, δ, is the equivalent stagnant-layer boundary depth and is given by

$$\delta = D_{air} / U_a \ . \qquad [42]$$

The mass transfer coefficient, U_a, depends on the diffusion coefficient, D_{air}, the Nusselt number, Nu, and a characteristic length, L_a, measured along the surface,

$$U_a = D_{air}\ \mathrm{Nu} / L_a \ . \qquad [43]$$

The Nusselt number is a dimensionless mass-transfer coefficient that depends on the diffusion coefficient, fluid viscosity of the transport medium (air), and other properties of the fluid, which are the same for all contaminants. The characteristic length is a property that depends on the nature of the mass-transfer surface and the velocity of the fluid across that surface and is also almost independent of the contaminant being considered. Combining equations [42] and [43] gives,

$$\delta = L_a / \mathrm{Nu} \ . \qquad [44]$$

Nu has weak dependence on the diffusion coefficient in the medium. Because this dependence is weak, it is often possible to approximate a δ for a large set of chemicals with similar diffusion coefficients.

Equations [40] to [44] illustrated the calculation of intermedia transfers on the air side of air-soil and air-water interfaces. This approach applies also to intermedia transfer in the water compartment at water-air and water-sediment interfaces.

The Two-Resistance Diffusion Model at Compartment Boundaries

When two compartments, such as surface water and air, are in contact, the mass transfer from air to water (or from water to air) depends on mass transfer through both the air-side and water-side boundary layers. This is illustrated in Figure 5. The overall resistance to mass transfer through the two boundary layers is the sum of the two resistances through the air and water boundary layers. The mass-transfer resistance is proportional to the inverse of the mass transfer coefficient. In order to derive the combined mass-transfer coefficient through water and air, we note that the flux to the air / water surface from the air side must be equal to the flux out of this surface on the water side,

$$\textit{net flux at the surface} = U_a \left(C_a^b - C_a^*\right) \text{ and} \qquad [45]$$

$$\textit{net flux at the surface} = U_w \left(C_w^* - C_w^b\right) . \qquad [46]$$

We note that at the surface, $C_a^* / C_w^* = Z_a / Z_w$. Thus, if we multiply equation [45] by Z_w and equation [46] by Z_a and combine the two expressions, we obtain

$$\text{net flux at the surface} = \left(C_a^b - \frac{Z_a}{Z_w} C_w^b\right)\left(\frac{1}{U_a} + \frac{Z_a}{U_w Z_w}\right)^{-1} . \qquad [47]$$

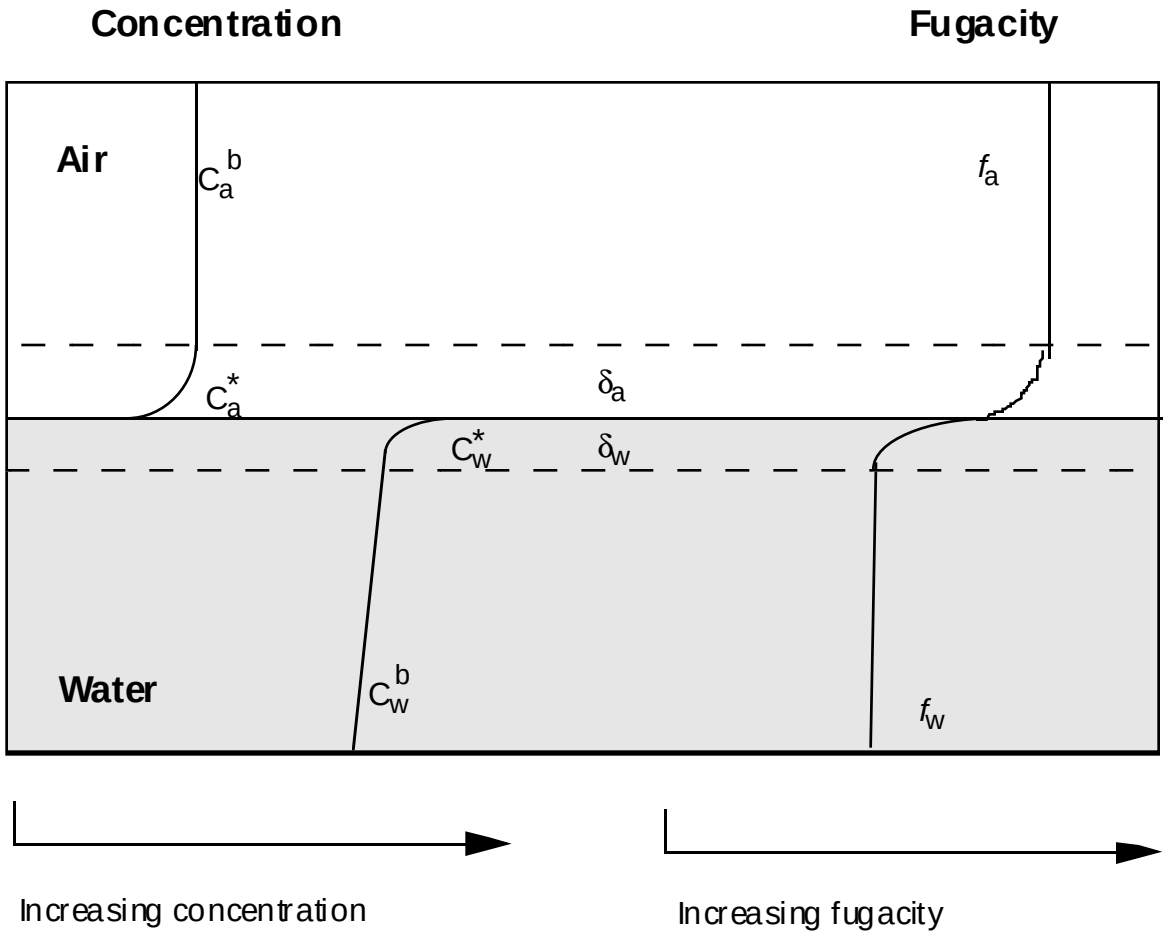


Figure 5. An illustration of mass transfer through two boundary layers at the interface between air and water compartments. There is a step discontinuity in concentration at this boundary because the concentration at the interface reflects the equilibrium partitioning of contaminant concentration in the different phases. In contrast, the fugacity is continuous across this interface.

The second term in equation [47] is the overall mass-transfer coefficient through the combined air-water boundary system.

As was noted earlier in this report, one of the major advantages of fugacity models is their ability to more easily represent diffusive transfer. In a fugacity model, the net diffusive flux, in mol/m^2-d, across the interface described above is

$$\textit{net flux at the surface} = Y_{aw} (f_a - f_w) \ , \qquad [48]$$

where Y_{aw} is the fugacity mass-transfer coefficient across the boundary between air and water with units mol/(m^2-Pa-d) and f_a and f_w are the fugacities of air and water. Y_{aw} acts as a conductance, and the difference in fugacities is the mass potential driving mass transfer across this boundary. The overall fugacity mass-transfer coefficient depends only on the mass-transfer coefficient on either side of the interface.

$$Y_{aw} = [1/(Z_a U_{a)} + 1/(Z_w U_w)]^{-1} \ . \qquad [49]$$

If we substitute equation [49] together with f_a equal to C_a/Z_a and f_w equal to C_w/Z_w into equation [48], we obtain equation [47]. It should be noted that the overall fugacity mass transfer coefficient, Y_{aw}, is related to the air-side fugacity mass-transfer coefficient for this interface, Y^a_{aw}, and the water-side fugacity mass-transfer coefficient for this interface, Y^w_{aw}. These mass-transfer coefficients have units of mol/(m^2-Pa-d) and are given by

$$Y^a_{aw} = Z_a U_a = Z_a \frac{D_{air}}{\delta_{aw}} \qquad [50]$$

and

$$Y^w_{aw} = Z_w U_w = Z_w \frac{D_w}{\delta_{wa}} \ , \qquad [51]$$

where D_{air} is the diffusivity in the air compartment, m^2/d; δ_{aw} is the boundary-layer thickness in the air above water, m; where D_w is the effective diffusivity in the water compartment, m^2/d; and δ_{wa} is the boundary-layer thickness in the water below the air, m. The relationships derived in this section for mass transfer at the

air-water interface can be generalized to mass transfer at air-soil, soil-soil, and water-sediment interfaces.

Diffusive Mass-Transfer Coefficients at Compartment Interfaces

In the subsections below, we develop expressions for fugacity mass-transfer coefficients on each side of the compartment interfaces associated with air-water, air-soil, and sediment-water transfers. The emphasis is on developing the effective boundary-layer thickness, which, when combined with the compartment diffusion coefficient, gives a mass-transfer coefficient.

Diffusive Mass Transfer at the Air and Surface-Water Interface

The exchange by diffusion of organic chemicals between the lower atmosphere and surface-water bodies is an important component of the overall rate constant defining transport between air and water. The exchange of chemicals between air and water bodies depends on both the physicochemical properties of the contaminant and the physical properties of the air and water compartments involved. Important physicochemical properties include solubility, molecular weight, vapor pressure, and diffusion coefficients in air and water. The important landscape properties include temperatures of air and water, wind speed, water-flow velocity, water depth, and water turbulence.

The air-side fugacity mass transfer coefficient, Y_{aw}^{a}, and the water-side fugacity mass-transfer coefficient, Y_{aw}^{w}, for the air-water interface are given by equations [49] and [50]. These mass-transfer coefficients have units of $mol/(m^2\text{-Pa-d})$. Lyman et al. (1982) have reviewed several methods for estimating water-side and gas-side mass transfer coefficients for atmosphere-surface water exchange of organic chemicals. In CalTOX, the estimation of the water-side boundary mass-transfer coefficient, D_{water}/δ_{wa}, is based on methods developed by Southworth (1979) from laboratory data for chemicals with H in the range 1 to 100 $Pa\text{-}m^3/mol$. When the surface-water current, $current_w$ in m/s, is less than 0.04 times the wind velocity, v_w in m/s, to the 0.67 power, then D_{water}/δ_{wa} is 0.24 m/d. For larger surface-water currents and for land units in which the yearly average wind velocity, v_w, is less than 1.9 m/s,

$$D_{water}/\delta_{wa} = 5.64\left(\frac{current_w^{0.969}}{d_w^{0.673}}\right)\sqrt{\frac{32}{MW_x}} \quad m/d \ , \qquad [52]$$

where d_w is the average depth of the surface-water body in m. For land units in which the yearly average wind velocity, v_w, is larger than 1.9 m/s,

$$D_{water}/\delta_{wa} = 5.64\left(\frac{current_w^{0.969}}{d_w^{0.673}}\right)\sqrt{\frac{32}{MW_x}}\ e^{0.526\,(v_w-1.9)}\ \ m/d\ . \qquad [53]$$

For estimating the air-side mass-transfer coefficient, D_{air}/δ_{aw}, we also used methods developed by Southworth (1979), based on laboratory data for chemicals with H in the range 1 to 100 Pa-m^3/mol. In this case the mass-transfer coefficient, D_a/δ_{aw}, in m/d, is given by

$$D_{air}/\delta_{aw} = 273\left(v_w + current_w\right)\sqrt{\frac{18}{MW_x}}\ \ m/d\ , \qquad [54]$$

when the sum, $v_{wind} + current_w$, is greater than 0.5 m/s, and by

$$D_{air}/\delta_{aw} = 140\sqrt{\frac{18}{MW_x}}\ \ m/d\ , \qquad [55]$$

when the sum, $v_{wind} + current_w$, is less than 0.5 m/s.

Diffusive Mass Transfer in Air at the Air and Ground-Surface Soil Interface

Diffusive mass transfer at the soil-air interface accounts for both net volatilization of contaminants from soil and deposition of gas-phase contaminants to the ground-surface-soil layer. Once again, net mass transfer depends on mass transfer through both the air-side and ground-soil-side boundary layers. The fugacity mass transfer coefficient on the air side of the air-ground-soil interface is given by

$$Y_{ag}^{a} = Z_a\frac{D_{air}}{\delta_{ag}}\ , \qquad [56]$$

where δ_{ag} is the boundary layer thickness in the air above the ground-soil layer. This thickness is assumed to be on the order of 0.005 m. On smooth surfaces the boundary layer thickness varies from about 1 cm in still air to 1 mm when the air moves over the surface at 1 m/s (Hanna et al., 1982).

Diffusive Mass Transfer in the Ground-Surface and Root-Zone Soil Layers

Because soil is not a well-mixed compartment such as air or surface water, the boundary-layer approach described above is not readily applicable to soil. The concentration gradient of contaminants may not level off for several meters. In well-mixed air and water compartments, the boundary layer thickness is on the order of centimeters. Cohen et al. (1990) have noted that the soil compartment in a multimedia model should use a spatial diffusion model. Jury et al. (1990) have shown that the "limiting soil-cover depth" varies from 0.001 m (for chrysene) to 160 m (for dichlorodifluoromethane) in sandy soil and from <0.001 to 61 m for the same compounds in clay soil. The limiting soil depth is the thickness of soil that is required to limit volatilization loss over an infinite time to less than 1% of the initial concentration. This is the depth at which volatilization at the surface has essential no impact on concentration. Above this depth, there is a gradient of concentration that will be controlled by the rate of evaporation at the surface of the soil.

There have been several approaches to the problem of devising a simple but accurate model of soil transport. In one of the more simple approaches, Mackay and Paterson (1991) use a diffusion-path length that is half the depth of the soil compartment as the boundary-layer thickness in their regional fugacity model. This value is independent of chemical species. However, this model has a relatively thin soil layer (0.1 m) and is not designed to handle contaminants that have been incorporated into soil at depths of several meters as is the case at hazardous waste sites. Mackay (1991) notes that using a single soil layer and a half-depth boundary layer can significantly underestimate volatilization at the soil surface. He suggests two potential remedies for this situation, (1) use more than one soil-layer compartment in the multimedia model and (2) use the geometric-mean value of the soil-layer depth as an approximation for boundary layer.

Jury et al (1983) have developed a comprehensive closed-form analytical expression for estimating the flux and concentration of a contaminant at any point at or above the initial depth of contaminant incorporation. Jury et al. (1991) have also developed a version of this model that can be applied to contaminants buried at some depth below the surface. These models have the advantage of being analytical solutions and validated against field experiments with pesticides. The main disadvantage of these analytical solutions is that they are complex. The solutions involve expressions that include numerous terms and the error function and

complimentary error function, which must be looked up or estimated using series approximations. Also the solutions include products of error functions and exponentials that must be combined and analyzed using limit approximations to avoid getting results that go to infinity. It is difficult to incorporate such analytical models into a simple and flexible multimedia model. Cohen et al. (1990) addressed the problem of nonuniform concentration in soils by numerically solving a one-dimensional diffusion equation in the soil layer. This approach also tends to substantially increase the complexity of the resulting model and, by adding numerical algorithms, makes it difficult to trace calculations through the model.

In CalTOX we deal with the problem of nonuniform concentration in soils by (1) using three soil layers to represent the region between the soil surface and the top of the saturated zone, (2) applying the model of Jury et al (1983) to this model system with multiple simulations that allowed for a range of chemical properties (K_D and H) and effective soil diffusivities, and then (3) developing a regression model that uses effective soil diffusion coefficients to estimate boundary layer thicknesses in each of these three soil layers by an optimized fit against these simulations. The optimization goal was to minimize the estimation error in the surface flux and compartment inventories predicted for the surface and root-zone soil layers relative to values obtained from the Jury et al. (1983) analytical solution. In effect, this procedure allows us to mimic the Jury et al (1983) model with a more simple regression model based on effective diffusivity. The price we pay for this increased simplicity is less precision. However, we can calculate this loss of precision and note that so long as it is comparable to the variability or uncertainty in characterizing the initial soil concentrations, it should not lead to significant degradation of the model reliability relative to the Jury et al. (1983) model from which it is derived. The following expressions were used to estimate the boundary layer thickness or diffusion length in CalTOX,

$$\delta_g = 0.108 \times D_g^{0.229} \quad \text{and} \qquad [57]$$

$$\delta_s = 318 \times D_s^{0.683} \quad . \qquad [58]$$

In these expressions, δ_g and δ_s are the diffusion lengths (in m) in the ground-surface and root-zone-soil compartments and D_g and D_s are the effective diffusivities in these compartments (in m^2/d) as obtained from equations [38] and [39]. We have

compared the mass inventory in the two upper soil compartments and the surface flux predicted using this regression model to values for these factors obtained from the Jury et al. (1983) model and found that, for predictions over a period of 30 y and for D_s and D_g spanning eight orders of magnitude, the geometric standard deviation of the residual error associated with the approximation is on the order of 3. This means that for roughly 68% of the compounds for which the approximation is used, the estimated inventory and flux are within a factor of 3 of the Jury et al (1983) predictions. This residual error increases as the effective water velocity becomes a significant fraction (>0.1) of the diffusion velocity, that is D/δ. Other restrictions that apply to the use of this approximation are (a) that the depth of the ground-surface-soil compartment can not exceed 0.02 m, (b) that the depth of the root-zone-soil compartment must be at least 0.4 times the boundary layer depth, δ, and (c) that the vadose-zone soil is sufficiently thick that there is a negligible probability that a contaminant molecule in this zone will escape from the soil surface by diffusion.

The use of this approximation for estimating the time-dependent concentration of trichloroethylene (TCE) and hexachlorobenzene (HCB) are illustrated, respectively in Figures 6 and 7. In each case, contaminant is initially incorporated uniformly within a soil column at a concentration of 100 $\mu mol/cm^3$ to a depth 10 meters. Concentrations in ground-surface soil, root-zone, and vadose-zone soil calculated by CalTOX using a boundary layer model are compared at one, five, and ten years after placement to the concentrations obtained from the analytical solution of Jury et al. (1983). For time periods greater than one year, the CalTOX approximation is accurate in reproducing the time history of average compartment inventory of TCE and HCB in the surface, root-zone, and vadose-zone soil compartments.

Figure 8 compares the surface flux of TCE and HCB calculated by CalTOX over a 10-y period using a boundary layer model to the surface flux obtained from the analytical solution of Jury et al. (1983). The flux calculation is also based on the assumption of the initial placement of 100 $mmol/cm^3$ of a chemical uniformly from the surface to a depth of 1000 cm (10 m).

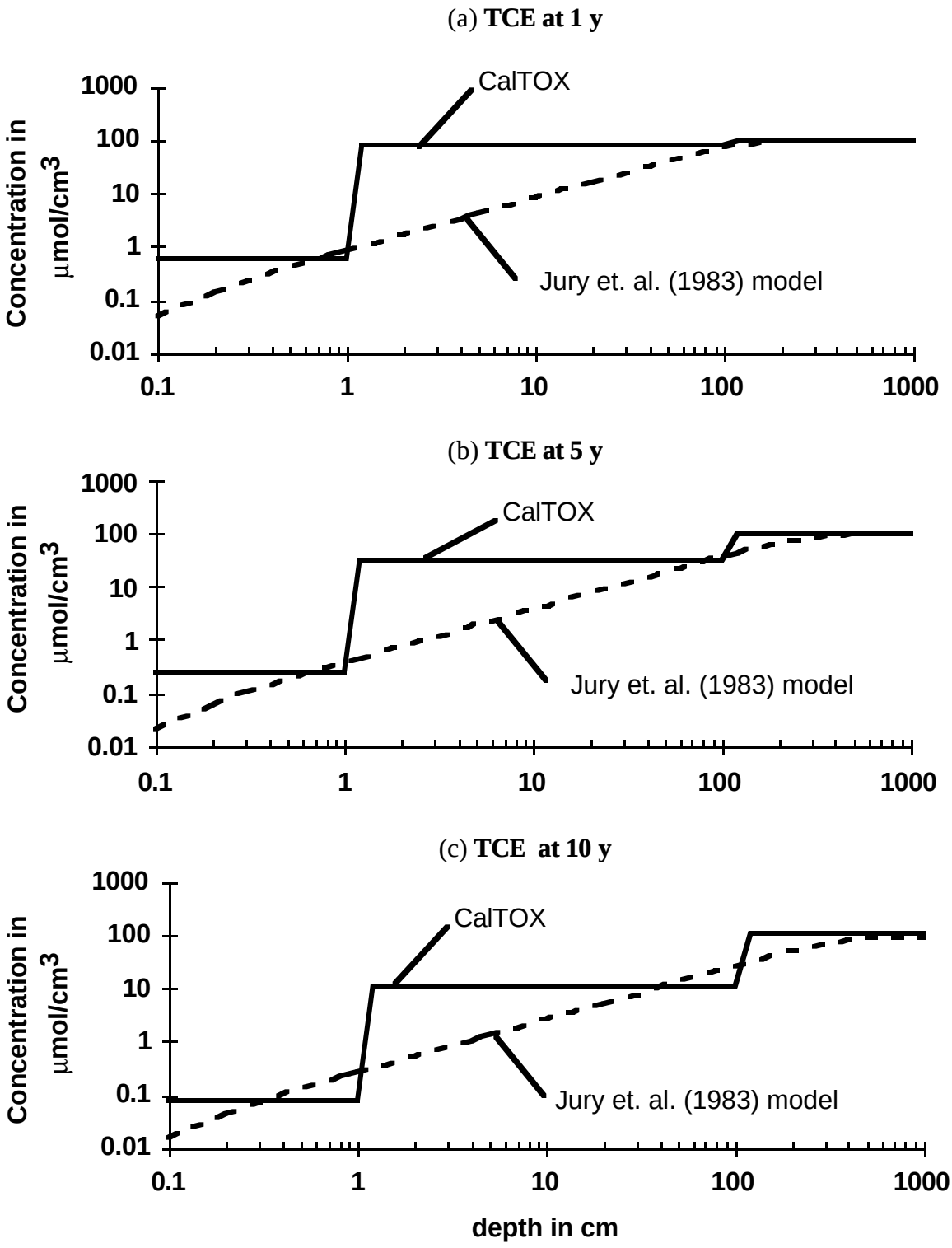


Figure 6. Concentrations in ground-surface (<1 cm depth) root-zone (1 to 100 cm depth) and vadose-zone soil (>100 cm depth) for trichloroethylene (TCE) as calculated by CalTOX using a boundary layer model at (a) 1 y, (b) 5 y, and (c) 10 y after placement and compared to the analytical solution based on the model of Jury et al. (1983).

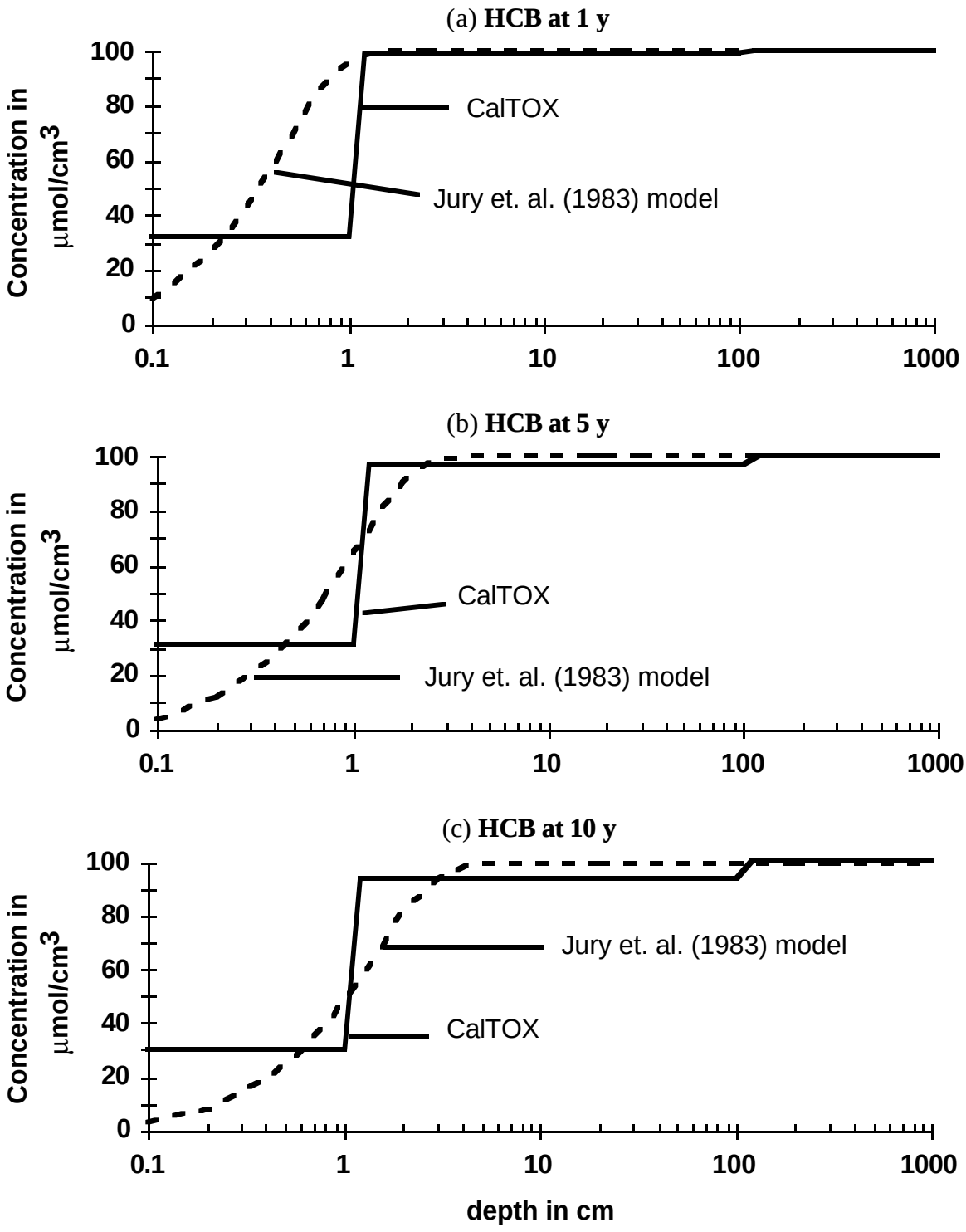


Figure 7. Concentrations in ground-surface (<1 cm depth) root-zone (1 to 100 cm depth) and vadose-zone soil (>100 cm depth) for hexachlorobenzene (HCB) as calculated by CalTOX using a boundary layer model at (a) 1 y, (b) 5 y, and (c) 10 y after placement and compared to the analytical solution based on the model of Jury et al. (1983).

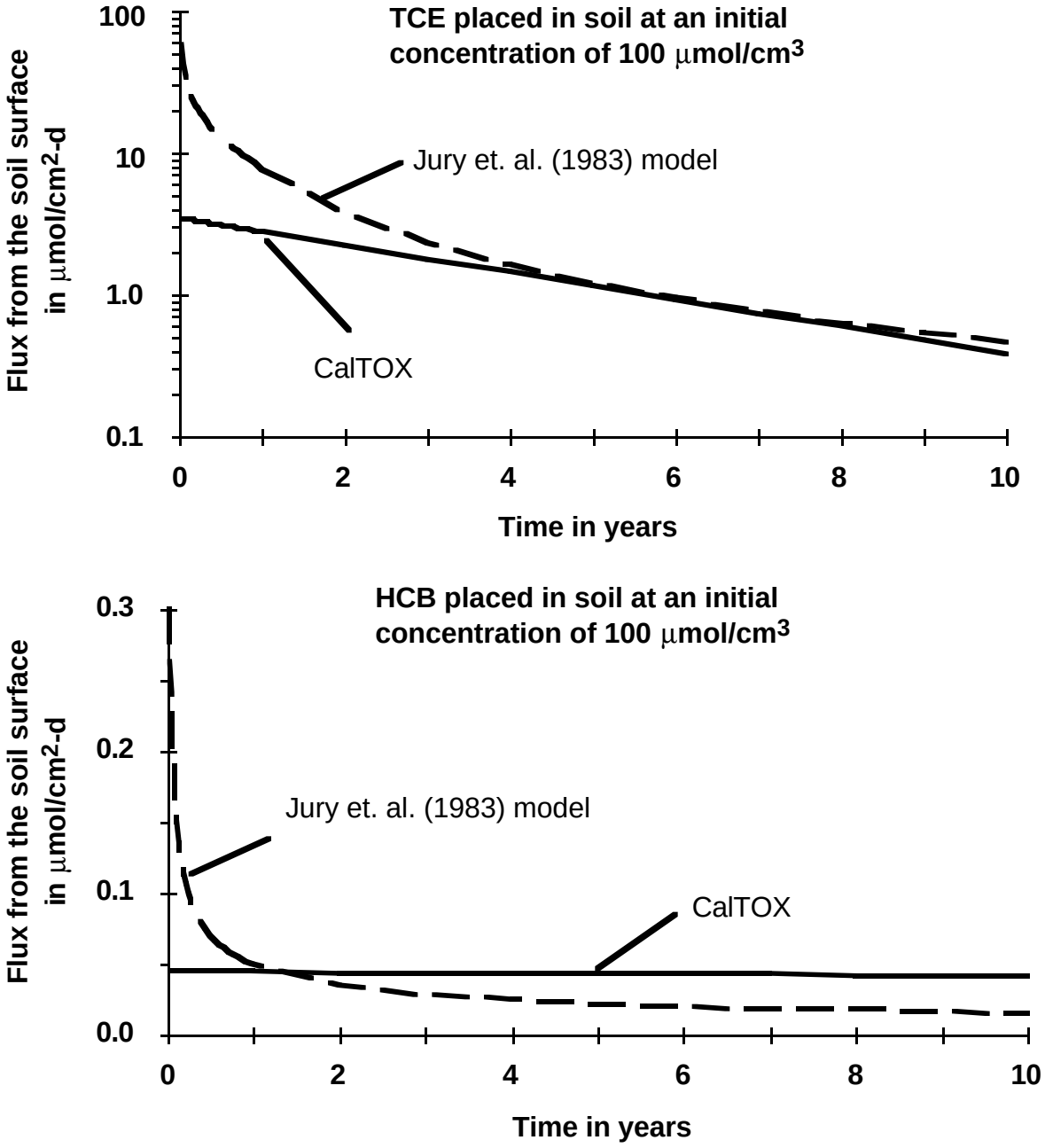


Figure 8. The surface flux of TCE (above) and HCB (below) calculated by CalTOX over a 10-y period using a boundary layer model and compared to the analytical solution used by Jury et al. (1983). The flux calculation is based on the assumption of the initial placement of 100 mmol/cm^3 of a chemical uniformly from the surface to a depth of 1000 cm (10 m).

Diffusive Mass Transfer at the Surface-Water and Sediment Interface

Diffusive mass transfer at the sediment-water interface accounts for the net volatilization of contaminants from sediment and deposition of dissolved contaminants to the sediment layer. In each case, total mass transfer depends on both the water-side and sediment-side boundary layers. The fugacity mass-transfer coefficient on the water side is given by

$$Y_{wd}^{w} = Z_w \frac{D_{water}}{\delta_{wd}} \quad , \qquad [59]$$

where Z_w is the fugacity capacity in the surface-water compartment, D_{water} is the effective diffusivity in the surface-water compartment, and δ_{wd} is the boundary-layer thickness in the water above the sediment layer. The fugacity mass-transfer coefficient on the sediment side is given by

$$Y_{wd}^{d} = Z_d \frac{D_d}{\delta_{dw}} \quad , \qquad [60]$$

where Z_d is the fugacity capacity in the sediment compartment, D_d is the effective diffusivity in the sediment compartment, and δ_{dw} is the boundary-layer thickness in the sediment layer below water. Formica et al. (1988) have described a method for calculating for the sediment layer effective diffusivity based on corrections for the solids content of sediment. This approach is similar to that used by Jury et al. (1983) as described in equations [38] to [39] with the volume fraction of the gas phase set to zero. We use fluxes of radon from the Hudson river estuary measured by Hammond et al. (1975) to estimate the water-side boundary-layer thickness. The reported flux is 200 atoms/m^2-s above sediments with a concentration of radon in water of 2.6×10^9 atoms per m^3 with a diffusion coefficient of 1.4×10^{-9} m^2/s. This implies a boundary-layer thickness of 0.02 m, which is what we use in CalTOX for the water side boundary layer thickness above sediments. For the boundary-layer thickness in sediments below the water column, we use equation [58] with D_d in place of D_s.

Mass Transfer by Advection in Water and Solids

In CalTOX, the cross-media transfer of contaminants by advection is treated as an advection flux. This flux is modeled as the product of the velocity of the moving phase times the contaminant concentration in that phase. This flux has units of

mol/m^2-d, the velocity of the moving phase is in m/d, and the concentration in the moving phase is the product of the contaminant fugacity in that phase, Pa, and the fugacity capacity of that phase in mol/m^3-Pa,

$$advection\ \ flux = velocity \times Z_{ik}\ f_i\ , \qquad [61]$$

where Z_{ik} and f_i represent the fugacity capacity of the moving phase and the fugacity, respectively, in compartment i. As an example, the flux of contaminant from air to surface soil through particle deposition is the product of deposition velocity, v_d; the fugacity capacity of air particles, Z_{ap}; and the total fugacity of the air compartment, f_a:

$$flux \text{ (air to ground-surface soil)} = v_d \times Z_{ap} \times f_a\ . \qquad [62]$$

Advection processes used in the CalTOX model include deposition of aerosol particles, resuspension of particles from soil, water-borne erosion of soil, rainfall, evaporation, runoff of precipitation, infiltration of water through soil, deposition of sediment particles in surface water, resuspension of sediment particles from the sediment layer, and surface water flows. The advective or nondiffusive flux terms used in the CalTOX model are summarized in Table II.

TRANSFORMATION PROCESSES IN THE CalTOX MODEL

The transformation of contaminants in the environment can have a profound effect on their potential for persistence. Chemical transformations, which may occur as a result of biotic or abiotic processes, can significantly reduce the concentration of a substance. For organic chemicals, knowledge of a compound's half-life for any given transformation process provides a very useful index of persistence in environmental media. Because these processes determine the persistence and form of a chemical in the environment, they also determine the amount and type of substance that is available for the exposure of species of interest. Experimental methods (Howard et al., 1978) and estimation methods (Lyman et al., 1982) are available for defining these fate processes in a variety of media. Specific information on the rates and pathways of transformation for individual chemicals of concern must be obtained directly from experimental determinations or derived

Table II. Advective or non-diffusive flux terms used for intermedia transfers in the CalTOX model.

Intermedia Transfer	**Description of the non-diffusive process**	**Formula**
Air to ground-surface soil	Rain scavenging of gaseous contaminants from air to ground	$flux = rain \times Z_{water} \times f_a$
Air to ground-surface soil	Wet and dry deposition of particle-bound contaminants	$flux = v_d \times Z_{ap} \times f_a$
Air to surface water	Rain scavenging of gaseous contaminants from air to ground	$flux = rain \times Z_{water} \times f_a$
Air to surface water	Wet and dry deposition of particle-bound contaminants	$flux = v_d \times Z_{ap} \times f_a$
From air compartment out of the system	Wind induced movement of the air mass out of the landscape boundary	$flux = Z_a \frac{0.23 \times v_w \times d_a}{\sqrt{Area}}$
Ground-surface soil to air	Resuspension of soil particles	$flux = v_d \times Z_{gp} \times f_g$
Ground-surface soil to root-zone soil	Leaching due to ground-water recharge	$flux = recharge \times Z_{water} \times f_g$
Ground-surface soil to surface water	Soil-solution runoff	$flux = runoff \times Z_{water} \times f_g$
Ground-surface soil to surface water	Erosion (mineral runoff) to surface water	$flux = erosion \times Z_{gp} \times f_g$
Root-zone soil to vadose-zone soil	Leaching due to ground-water recharge	$flux = recharge \times Z_{water} \times f_s$
Vadose-zone soil to ground-water zone	Leaching due to ground-water recharge	$flux = recharge \times Z_{water} \times f_v$
Surface water to sediment	Sediment deposition	$flux = deposit \times Z_{wp} \times f_w$
From surface water out of the landscape	Surface water outflow	$flux = outflow \times Z_w \times f_w$
Sediment to surface water	Sediment resuspension	$flux = resuspend \times Z_{dp} \times f_d$

indirectly from information on chemicals that are structurally similar. Consequently, quantitative estimates are difficult to derive for classes of compounds for which empirical data are lacking. In the sections below consideration is given to photolysis, hydrolysis, oxidation/reduction, and microbial degradation as transformation processes.

Photolysis

Most organic contaminants are capable of undergoing photolytic decomposition. Such decompositions can be partial, resulting in the formation of stable byproducts, or complete, resulting in the formation of CO_2 and H_2O. The potential for such photochemical transformations can generally be predicted based on the molecule's ability to absorb radiant energy in the near ultraviolet and visible light range (240-700 nm wavelength). Although solar radiation at the earth's surface is attenuated by the atmosphere, it is generally of sufficiently high wavelength (i.e., >290 nm) to break bonds in many compounds. All compounds that contain aromatic rings absorb energy at environmental wavelengths as do compounds that contain halogen atoms (e.g., Cl, Br) and unsaturated carbon chains (e.g., alkenes and alkynes). Phototransformation of a chemical may result in two effects that are relevant to its environmental fate: (1) fragmentation, in which a molecular bond is broken forming two free radicals; or (2) rearrangement, such as conversion from *cis* to *trans* isomers. Of these two possible reactions, fragmentation is likely to play the greatest role in the fate of contaminants due to its potential for the degradation. Such transformations may result in relatively short half-lives (e.g., hours to days) for contaminants, such as pesticides that are incorporated onto ground-surface soil.

Hydrolysis

Hydrolytic transformation of organic chemicals can be a significant fate process for compounds that are present in aqueous environments. Hydrolysis is most important for chemicals that have functional groups (e.g., amides, esters, carbamates, organophosphates). These compounds can be altered rapidly (e.g., minutes to days) in the presence of water. In contrast, hydrolytic degradation of compounds that contain stable substituents (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 environment can have a dramatic influence on the rate of hydrolysis for any given compound. Hydrolytic transformations that are relatively slow at

neutral pH can occur at rates that are several orders of magnitude greater under acidic or basic conditions (Tinsley, 1979). Therefore, the relative importance of hydrolysis to the environmental fate of a contaminant will depend on the chemical structure of the compound as well as the pH of the environmental media.

Oxidation and Reduction

Many inorganic and organic chemicals can undergo oxidation or reduction reactions in the environment. These reactions are important because they can influence the environmental fate and toxicological properties of the compound and are most significant in aqueous environments (see Stumm and Morgan, 1981). An index of a compound's ability to be oxidized or reduced is provided by a knowledge of its reduction potential (E^0), which is the voltage at which it is transformed to its reduced state. A similar measure of the environment'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 terrestrial subsurface). 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.

Microbial Transformation

The transformation of organic and inorganic compounds by microorganisms that are present in environmental media can have a profound influence on their persistence. Due to their broad range of enzymatic capabilities, microorganisms are capable of transforming many inorganic and organic compounds. Such transformations can result in the partial degradation of a compound (e.g., conversion of DDT to DDE), mineralization (i.e., complete transformation to carbon dioxide and water), or synthesis of a stable product (e.g., formation of methyl arsenicals from arsenate). The susceptibility of many organic compounds to microbial transformation can be predicted based on a knowledge of chemical structure (Boethling and Sabljic, 1989).

MODEL INPUT AND DATA REQUIREMENTS

The CalTOX multimedia transport and transformation model uses two sets of input data, one describing the properties of the contaminants and the other providing properties of the environment or landscape receiving the contaminants. Each of the inputs is described in terms of the physical process associated with the input and with an estimated coefficient of variation, which describes the uncertainty or variability associated with that parameter. The coefficient of variation or CV is the ratio of arithmetic standard deviation to arithmetic mean for a parameter that can have a range of values. Because the process of assigning CVs is itself an uncertain process, we use only five CV values corresponding to five uncertainty or CV classes to characterize these parameters. The term "CVa" represents a parameter that has a CV of 0.1 or less and is considered a highly reliable parameter that will contribute little to the overall uncertainty or variability of the final results so the uncertainty in the parameter need not be expressed. "CVb" represents a CV between 0.1 and 0.3 and indicates a parameter that has been measured or obtained from a highly reliable estimation method. A CV in this range reflects both the typical variability in the measurement and the uncertainty in extrapolating that value from an experimental setting to an environmental setting. "CVc" represents a CV between 0.3 and 3 (log mean CV of 1) and indicates a parameter for which a somewhat reliable estimation method exists. "CVd" represents a CV between 3 and 10 (log mean equal to 5) and is used for parameters for which the estimation method is much less reliable. "CVe" represents a CV between 10 and 15 (log mean equal to 12) and is used for parameters for which the estimated value is highly uncertain.

Chemical and Physical Data

The CalTOX model also requires a set of physical-chemical properties inputs. These inputs and their approximate CVs are described below. Table III provides a list of the chemical properties used in the CalTOX model and their corresponding CV class.

Molecular Weight

For most organic and inorganic compounds, the molecular weight can be reliably obtained from a number of common references. The precision with which molecular weights can be measured is as high as any property used in the transport analysis. This parameter is assigned to the *CVa* uncertainty class.

Table III. The list of chemical and physical properties used to carry out the environmental transport and transformation analysis in CalTOX.

Physical-chemical property	**Symbol**	**CV class**[a]
Molecular weight (g/mol)	MW	a
Octanol-water partition coefficient (L[water]/L[octanol])	K_{ow}	b or c
Melting point of the chemical (K)	T_m	a
Vapor Pressure in Pa	VP	b or c
Solubility in mol/m^3	S	b or c
Henry's law constant (Pa-m^3/mol)	H	b or c
Diffusion coefficient in pure air (m^2/d)	D_{air}	b
Diffusion coefficient in pure water (m^2/d)	D_{water}	b
Organic-carbon partition coefficient (L[water]/kg[carbon])	K_{oc}	c
Sorption Coefficient (L[water]/kg[solid])	K_D	c
Reaction rate constant in air in (day^{-1})	R_a	e
Reaction rate constant in plants in (day^{-1})	R_p	e
Reaction rate constant in root-zone soil in (day^{-1})	R_s	e
Reaction rate constant in vadose-zone soil in (day^{-1})	R_v	e
Reaction rate constant in surface water (day^{-1})	R_w	e
Reaction rate constant in sediment (day^{-1})	R_d	e

[a]The CV classes are as follows, (a) CV of 0.1 or less, (b) CV between 0.1 and 0.3, (c) CV between 0.3 and 3, (d) CV between 3 and 10, and (e) CV between 10 and 15.

Octanol-Water Partition Coefficient, K_{ow}

The octanol-water partition coefficient provides a measure of the extent of chemical partitioning between water and octanol at equilibrium. The greater the K_{ow}, the more likely a chemical is to partition to octanol than to water. The octanol-water partition coefficient is used as a basis for estimating organic carbon partitioning in soils and sediments, bioconcentration factors in aquatic organisms, root-soil and leaf-air partition coefficients in land vegetation, and fat-diet partition coefficients in terrestrial animals. Measured K_{ow} values are available in references such as Howard (1990, 1991a, 1991b) and Verschueren (1983). Estimation methods are discussed in Lyman et al. (1982). For measured values, this parameter is assigned

to the *CVb* uncertainty class. It should be noted that K_{ow}-estimation procedures result in estimation error factors in the range from 1.2 (benzene) to as much as 30 (dioxins), depending on the chemical compound. However, current estimation methods for K_{ow} tend to be somewhat reliable and the example above of dioxins is a likely exception. Thus, when K_{ow} is estimated rather than measured, it should be assigned to the *CVc* uncertainty class.

Melting Point

The melting point is a measured parameter and available for most compounds in the literature. It is assigned to the *CVa* uncertainty class.

Vapor Pressure

Vapor pressure is the pressure exerted by a chemical vapor in equilibrium with its solid or liquid phase. It is used to calculate the rate of volatilization of contaminant from soil or water and for estimating the Henry's law constant for low-solubility chemicals. The higher the vapor pressure, the more likely a chemical is to exist in the gas phase. Measured vapor pressure are often available in references, such as Howard (1989, 1990, 1991) and Verschueren (1983). Estimation methods are discussed in Lyman et al. (1982). For measured values, this property is assigned to the *CVb* class and for estimated values to the *CVc* class.

Water Solubility

This is the upper limit on a chemical's dissolved concentration in pure water at a specified temperature. However, the observed ratio of inventory to volume in surface waters can exceed this solubility limit when there is sorption of the contaminant onto suspended sediments within the water, or there are agents present such as solvents, which increase the apparent water solubility. Measured solubility limit are often available in references, such as Howard (1990, 1991a, 1991b) and Verschueren (1983). Estimation methods are discussed in Lyman et al. (1982). For measured values, this property has *CVb* and for estimated values *CVc*.

Henry's Law Constant

This factor is a measure at equilibrium of the ratio of chemical activity in the gas above a liquid to chemical activity in the liquid. It is the basis for estimating air-water partition coefficients and is often expressed as the partial pressure of chemical in the gas phase divided by the concentration in the water phase. For chemicals with a low solubility limit in water, the Henry's law constant can be estimated as the

vapor pressure of the pure chemical divided by the solubility limit in water. The higher the Henry's law constant, the more likely a chemical is to exist in the gaseous state than remain dissolved in water. Measured solubilities are often available in references such as Howard (1989, 1990, 1991) and Verschueren (1983). Estimation methods are discussed in Lyman et al. (1982). For measured values, this property is assigned to uncertainty class *CVb* and for estimated values to uncertainty class *CVc*.

Diffusion Coefficients in Air and Water

Diffusion coefficients describe the movement of a molecule in a liquid or gas medium as a result of differences in concentration within the medium. They are used to calculate the dispersive component of chemical transport. The higher the diffusion coefficient, the more likely a chemical is to move in response to concentration gradients. Diffusive mass transfer at compartment boundaries is often modeled using a boundary-layer model. The flux of contaminant from the surface to the bulk fluid is proportional to the difference in concentration between the surface and the bulk fluid. This approach is used for mass transfer between air and soil, air and surface water, and surface water and sediments. In order to carry out this approach, one needs estimates of the diffusion coefficients of a chemical in both pure air and pure water. Estimation methods for diffusion coefficients tend to be fairly reliable, thus for both measured and estimated values of diffusion coefficients are assigned to uncertainty class CVb (see, for example equations [36] to [39] and the associated discussions).

Organic-Carbon Partition Coefficient, K_{oc}, and Sorption Coefficient, K_D

As noted above, Karickhoff (1981) has proposed empirical estimation methods for obtaining K_{oc} from K_{ow}. The most general of these is that K_{oc} is equal to 0.48 times K_{ow} with a CV in this estimation of about 1. These estimation methods are intended for nonionic organic compounds. A larger CV could be expected when the estimation is applied to ionic species for which a correction for acid dissociation should be made. When K_{oc} is multiplied by the fraction of organic carbon in a soil or sediment, we obtain an estimate of the soil-water or sediment-water partition coefficient, K_D (Karickhoff, 1981). The CV in this estimation is dominated by the estimation error in K_{oc} and roughly equal to 1.0. For inorganic chemicals, values of K_D can be based on measured values, on values derived from geochemical data, such as that published in Wedepohl (1969-1978), or on estimation

methods described by Bodek et al. (1988). Based on this information, K_{oc} and K_D are both assigned to the *CVc* uncertainty class.

Media-Specific Transformation Rates

Rate constants that express the rate of chemical transformations in each compartment are required as inputs. Experimental methods (Howard et al., 1978) and estimation methods (Lyman et al., 1982) are available for defining these rate constants in a variety of media. Specific information on the rates and pathways of transformation for individual chemicals of concern must be obtained directly from experimental determinations or derived indirectly from information on chemicals that are structurally similar. As noted above, quantitative estimates are difficult to derive for classes of compounds for which empirical data are lacking. Transformation rate constants are perhaps the most uncertain parameters in the CalTOX model and are assigned to the uncertainty class *CVe* unless site and chemical specific data are available.

Landscape Data

Because it is often impractical to develop detailed parameter sets for the landscapes surrounding a large number of facilities, we have developed landscape data sets that are representative of California. The types of data needed to construct a landscape data set include meteorological data such as average annual wind speed, deposition velocities, air temperature, and depth of the mixing layer; hydrological data, such as annual rainfall, runoff, soil infiltration, ground-water recharge, and surface water depth and sediment loads; and soil properties, such as bulk density, porosity, water content, erosion rates, and root zone depth. In Table IV we summarize the landscape data that are needed to represent the California landscape in the CalTOX analyses. Also listed in this table are the CV classes associated with variability and uncertainty in these data. Primary references for these data are van der Leeden et al. (1991), Soil Conservation Service (1975), the U.S. National Oceanic and Atmospheric Administration (1974), U.S. Department of Agriculture (1978), and Gleick (1987). Values used in the CalTOX model to represent residential, commercial and industrial landscapes are listed in a supplemental report on parameter values and ranges for CalTOX.

Table IV. The list of landscape properties used to carry out the environmental transport and transformation analysis for California sites.

Landscape Property	**Symbol**	**CV class**[a]
Contaminated area in m^2	Area	n/a
Annual average precipitation (m/d)	rain	c
Flow of surface water into landscape (m/d)	inflow	n/a
Land surface runoff (m/d)	runoff	c
Atmospheric dust load (kg/m^3)	ρb_a	b
Deposition velocity of air particles (m/d)	v_d	b
Plant dry mass inventory ($kg[DM]/m^2$)	bio_{inv}	b
Plant dry-mass production ($kg[DM]/m^2$-d)	bio_{prd}	b
Plant dry mass fraction	bio_{dm}	b
Plant density kg/m^3	ρ_p	b
Ground-water recharge (m/d)	recharge	c
Evaporation from surface water (m/d)	evaporate	c
Thickness of the ground-soil layer (m)	d_g	c
Soil particle density; ground-surface-soil layer (kg/m^3)	ρs_g	a
Water content in surface soil (volume fraction)	β_g	b
Air content in the surface soil (volume fraction)	α_g	b
Erosion of surface soil (kg/m^2-d)	$erosion_g$	b
Thickness of the root-zone layer (m)	d_s	b
Soil particle density; root-zone soil layer (kg/m^3)	ρs_s	a
Water content of root-zone soil layer (vol. fraction.)	β_s	b
Air content of root-layer (vol. fraction.)	α_s	b
Thickness of the vadose layer (m)	d_v	d
Water content; vadose layer (vol. fraction.)	β_v	b
Soil particle density; vadose soil (kg/m^3)	ρs_v	a
Air content of vadose layer (vol. fraction.)	α_v	b
Fraction of land area in surface water	f_{arw}	b
Average depth of surface waters (m)	d_w	c
Suspended sediment in surface water (kg/m^3)	ρb_w	c

Landscape properties (continued)

Landscape Property	Symbol	CV class[a]
Suspended sediment deposition ($kg/m^2/d$)	deposit	b
Thickness of the sediment layer (m)	d_d	c
Solid material density in sediment (kg/m^3)	ρs_d	a
Porosity of the sediment zone	β_d	b
Sediment resuspension rate ($kg/m^2/d$)	resuspend	d
Ambient environmental temperature (K)	T	a
Surface water current in m/d	$current_w$	c
Organic carbon fraction in surface soil	f_{ocg}	c
Organic carbon fraction in root-zone soil	f_{ocs}	c
Organic carbon fraction in vadose zone	f_{ocv}	c
Organic carbon fraction in sediments	f_{ocd}	c
Boundary layer thickness in air above ground-surface (m)	δ_{ag}	b
Yearly average wind speed (m/d)	v_w	b

[a]The CV classes are as follows, (a) CV of 0.1 or less, (b) CV between 0.1 and 0.3, (c) CV between 0.3 and 3, (d) CV between 3 and 10, and (e) CV between 10 and 15.

TRANSFER-RATE, LOSS-RATE, AND THE GAIN-LOSS EQUATIONS

The dynamic and steady-state equations describing gains and losses in each of the seven compartments are expressed in the general form defined by equation [6] in equations [63] through [69] below. Table I has listed the gains and losses considered for each compartment. We solve for the inventory (and concentration) in each compartment by balancing losses and gains that define the molar inventory in each compartment of the contaminated landscape.

$$L_a N_a = S_a + T_{pa} N_p + T_{ga} N_g + T_{wa} N_w \qquad \text{(air)} \qquad [63]$$

$$L_p N_p = T_{ap} N_a + T_{sp} N_s \qquad \text{(plants)} \qquad [64]$$

$$L_g N_g = S_g + T_{ag} N_a + T_{sg} N_s \qquad \text{(ground-surface soil)} \qquad [65]$$

$$\frac{dN_s}{dt} = -L_s N_s + T_{gs} N_g \qquad \text{(root soil)} \qquad [66]$$

$$\frac{dN_v}{dt} = -L_v N_v + T_{sv} N_s \qquad \text{(vadose soil)} \qquad [67]$$

$$L_w N_w = S_w + T_{aw} N_a + T_{gw} N_g + T_{dw} N_d \qquad \text{(surface water)} \qquad [68]$$

$$L_d N_d = T_{wd} N_w \qquad \text{(sediments)} \qquad [69]$$

In the equations above the N's represent compartment inventories and the T_{ij} (i, j = a, p, g, s, v, w, or d) are transfer rate constants, with units of day^{-1}, that express fraction per unit time of the inventory of compartment i that is transferred to compartment j. The compartment abbreviations are *a* for air, *p* for plants, *g* for ground-surface soil, *s* for root-zone soil, *v* for vadose-zone soil, *w* for surface water, and *d* for sediments. The product of an N term and a T term is the rate of change of inventory in mol/d. $L_i N_i$ represents all losses from compartment *i*, mol/d. The terms S_a, S_g, S_w, in equations [63], [65], and [68] are the rates of contaminant input to the air, ground surface, and surface water compartments, mol/d. In the sections below, the transfer-rate constants are defined in terms of landscape properties, chemical properties, fugacity capacities, and other parameters used to construct them and the loss rate constants are defined in terms of transfer and transformation rate constants.

In terms of fugacity, the balance in mol/d is expressed as a loss from a compartment *i* and transfer to a compartment *j* in the form

$$loss = Area \times v_{ij} \times Z_{ik} \times f_i \ , \qquad [70]$$

where *Area* in m^2 is that across which mass exchange occurs, v_{ij} is the advection or diffusion velocity from i to j at the exchange boundary, and Z_{ik} is the fugacity capacity of the moving phase k from i to j, and f_i represents the fugacity of compartment i. Equation [70] can also be written as

$$loss = T_{ij} N_i \ , \qquad [71]$$

in which

$$N_i = Z_i f_i V_i , \quad [72]$$

$$T_{ij} = \frac{area \times v_{ij}}{V_i} \frac{Z_{ik}}{Z_i} = \frac{v_{ij}}{d_i} \frac{Z_{ik}}{Z_i}, \text{ and} \quad [73]$$

V_i is the compartment volume, d_i is the compartment depth or thickness, and Z_i is the total fugacity capacity of compartment i. This is the general approach used in the sections below to obtain the transfer rate constants.

The Lower-Atmosphere or Air Compartment (a)

In CalTOX, the air compartment is represented by a simple box model in which losses include deposition to soil, vegetation, and surface water; convective losses; and transformation losses. The concentration in this compartment is assumed to be in a steady state condition relative to the deeper soil compartments, which have inventories that are changing with time, but the rate constants for the inventory change in the soil compartments are small enough to make the other compartments behave as though they are in steady state relation with these soil compartments. In the box model used for air, the inventory, N_a in mol, of contaminant in the air compartment is described by equation [63]. L_a is the sum of all loss-rate constants from the air compartment,

$$L_a = T_{ap} + T_{ag} + T_{aw} + T_{ao} + R_a \ . \quad [74]$$

$T_{pa} N_p$, $T_{ga} N_g$, and $T_{wa} N_w$ are the gains from plants, ground-surface soil, and water, mol/d; T_{ag}, T_{ap}, and T_{aw} are the rate constants for deposition losses, to ground-surface soil, plants, and water, day^{-1}; T_{ao} is the rate constant for convective losses, day^{-1} and R_a is the rate constant for transformation losses, day^{-1}.
In steady state and in the absence of net deposition and chemical reaction losses, equation [6
volume V_a and pollution source, S_a in mol/d, is given by

$$C_{air} = N_a / V_a = \frac{c\, S_a}{Area \times v_w} \quad , \quad [75]$$

where *c* is a unitless proportionality constant; *Area* is the area of the region being modeled, and v_w is the long-term average wind speed in m/d. This implies that the inverse of the rate constant, T_{ao}, is the convective residence time and is given by the expression, $c\ d_a / v_w$, where d_a is the atmospheric mixing height. Based on a model for area sources developed by Turner (1970), the constant c can be estimated as $4.3\sqrt{\text{Area}}\ / d_a$, where $\sqrt{\text{Area}}$ is the cross-sectional length of an assumed square area containing the source S_a. Making the appropriate substitutions gives the following expression for the convective loss-rate constant in the air compartment:

$$T_{ao} = \frac{0.23\ v_w}{\sqrt{\text{Area}}} \quad . \qquad [76]$$

The rate constant, T_{ag}, accounts for gross diffusion, rain-water washout, and particle-deposition losses from air to ground surface soil.

$$T_{ag} = (1 - f_{arw}) \times \frac{\left(Y_{ag} + rain \times Z_{water} + v_d \times Z_{ap} \times \frac{\rho b_a}{\rho s_g}\right)}{(Z_a \times d_a)} \quad . \qquad [77]$$

If the land-unit area is greater than or equal to 6×10^8 m^2, then the air-compartment mixing depth, d_a, is 700 m; if the area is less than 6×10^8 m^2, then d_a is $0.22\ (\sqrt{\text{Area}}\ )^{0.8}$ (Hanna et al., 1982). The net diffusion from air ground-surface soil is given by $Y_{ag}(f_a - f_g)$. Thus, $Y_{ag}\ f_a$ is the gross diffusion from air to soil and $Y_{ag}\ f_g$ is the gross diffusion from ground-surface soil to air. Other parameters in this expression are listed in Table IV or have been defined previously.

The rate constant, T_{aw}, accounts for gross diffusion, rain-water washout, and particle deposition losses from air to surface water and has the form

$$T_{aw} = f_{arw} \times \frac{\left(Y_{aw} + rain \times Z_{water} + v_d \times Z_{ap} \times \frac{\rho b_a}{\rho s_g}\right)}{(Z_a \times d_a)} \quad . \qquad [78]$$

The rate constant T_{ap} is derived in the next section.

The Plants Compartment (p)

The plants compartment represents vegetation, which is the major mass-fraction of the terrestrial biosphere. The plants compartment interacts with the air and root-soil compartments. Its inventory is steady-state relative to the deeper soil compartments and its inventory, N_p in mol, is described by equation [64]. L_p is the sum of all loss rate constants from the plants compartment,

$$L_p = T_{pa} + T_{ps} + R_p \quad . \qquad [79]$$

$T_{ap}\ N_a$ and $T_{sp}\ N_s$ are the gains from air and root-soil compartments, mol/d; T_{pa} and T_{ps} are the rate constants for losses due to exchanges with, respectively, air and root-zone soil, day^{-1}; and R_p is the rate constant for transformation losses in plants, day^{-1}. Expressions relating to exchanges between vegetation and air and between vegetation and soil are obtained for nonionic organic chemicals by requiring that the fugacity of plants is the average of the fugacities in air and soil. The basis for this assumption is described previously. This requirement results in the following expressions for transfers between air and plants and between soil and plants,

$$T_{pa} = 0.5 \quad , \qquad [80]$$

$$T_{ps} = 0.01 \, , \qquad [81]$$

$$T_{sp} = \frac{(T_{pa} + T_{ps}) \times Z_p \times V_p}{2\ Z_s \times V_s} \quad \text{, and} \qquad [82]$$

$$T_{ap} = \frac{(T_{pa} + T_{ps}) \times Z_a \times V_a}{2\ Z_p \times V_p} \quad . \qquad [83]$$

Expressions relating to exchanges between vegetation and air and between vegetation and soil are obtained for ionic organic chemicals and inorganic chemicals by requiring that the fugacity of plants equal the fugacity of soil and results in the following expressions for transfers between air and plants and between soil and plants,

$$T_{ap} = 0 \quad , \qquad [84]$$

$$T_{pa} = 0 \ , \qquad [85]$$

$$T_{sp} = \frac{evapotrans \times Z_{water}}{2\, Z_s \times d_s} \ , \text{ and} \qquad [86]$$

$$T_{ps} = T_{sp} \times \frac{Z_s \times V_s}{Z_{water} \times V_p} . \qquad [87]$$

$$evapotrans = rain \times (1 - f_{arw}) - recharge - runoff \ . \qquad [88]$$

The Ground-Surface Soil Compartment (g)

The ground-soil compartment is another compartment that is assumed to be in steady state relative to deeper soil compartments. It represents the thin surface layer of soil in which losses include diffusion to air, diffusion to root-zone soil, infiltration to root-zone soil, runoff to surface water, and transformation processes. The inventory, N_g in mol, of contaminant in the ground-soil compartment is described by equation [65]. L_g is the sum of all loss-rate constants from the ground-surface-soil compartment,

$$L_g = T_{ga} + T_{gs} + T_{gw} + R_g \ . \qquad [89]$$

$T_{ag}\ N_a$ and $T_{sg}\ N_s$ are the gains from air and root-soil compartments, mol/d; T_{ga}, T_{gs}, and T_{gw} are the rate constants for resuspension losses to air, for gross diffusion losses to air and to root soil, for advection losses due to rain-water infiltration and for runoff losses to surface water, day^{-1}; and R_g is the rate constant for transformation losses, day^{-1}. These loss-rate constants are given by

$$T_{ga} = \frac{Y_{ag} + v_d \times \rho b_a \times \dfrac{Z_{gp}}{\rho s_g}}{Z_g \times d_g} \ , \qquad [90]$$

$$T_{gs} = \frac{recharge \times Z_{water} + Y_{sg}}{Z_g \times d_g} \ , \qquad [91]$$

$$T_{gw} = \frac{runoff \times Z_{water} + erosion \times \frac{Z_{gp}}{\rho s_g}}{Z_g \times d_g} \quad \text{, and} \qquad [92]$$

Equation [90] reflects our assumption that resuspension of soil particles is, on average, equal to deposition. Other parameters in these expressions are listed in Table IV or have been defined previously.

The Root-Zone-Soil Compartment (s)

The root-zone-soil compartment is not required to be in steady state and is modeled as a compartment with a dynamic inventory. It represents the layer of soil in which losses include gross diffusion to ground-surface soil, uptake by vegetation, infiltration to vadose-zone soil, and transformation processes. Sources of contamination to this compartment are specified as initial inventories. The inventory, N_s in mol, of contaminant in the root-zone-soil compartment is described by equation [66]. L_s is the sum of all loss-rate constants from the root-zone-soil compartment,

$$L_s = T_{sp} + T_{sg} + T_{sv} + R_s \quad . \qquad [93]$$

$T_{gs}\ N_g$ is the gain by diffusion and infiltration from the ground-soil compartment, mol/d; T_{sp}, T_{sg}, and T_{sv} are the rate constants for uptake losses to vegetation, for gross diffusion losses to ground-surface soil, and for advection losses to the vadose zone due to rain-water infiltration, day^{-1}; and R_s is the rate constant for transformation losses, day^{-1}. These loss-rate constants are given by equations [82] or [86] above and by

$$T_{sg} = \frac{Y_{sg}}{Z_s \times d_s} \quad \text{and} \qquad [94]$$

$$T_{sv} = \frac{recharge \times Z_{water}}{Z_s \times d_s} \quad . \qquad [95]$$

Other parameters in these expressions are listed in Table IV or have been defined previously.

The Vadose-Zone-Soil Compartment (v)

The vadose-zone-soil compartment is also a dynamic compartment. It represents the layer of soil below the root zone and above the water table and in which water flow is predominantly vertical. In the vadose zone, losses include infiltration to ground water and transformation processes. Sources of contamination to this compartment are specified as initial inventories. The inventory, N_v in mol, of contaminant in the vadose-soil compartment is described by equation [67]. L_v is the sum of all loss-rate constants from the vadose soil compartment,

$$L_v = T_{vq} + R_v \quad . \qquad [96]$$

$T_{sv}\ N_s$ is the gain by infiltration from the root-soil compartment, mol/d; T_{vq} is the rate constant for advection losses to the ground-water zone due to rain-water infiltration, day^{-1}; and R_v is the rate constant for transformation losses, day^{-1}. This loss-rate constant is given by

$$T_{sv} = \frac{recharge \times Z_{water}}{Z_v \times d_v} \quad . \qquad [97]$$

Parameters in this expression are listed in Table IV or have been defined previously.

The Surface-Water Compartment (w)

The surface-water compartment is a steady-state compartment. It represents bodies of water in which losses include diffusion to air, diffusion to sediment, deposition to sediment, outflow to other surface-water bodies, and transformation processes. The inventory, N_w in mol, of contaminant in the surface-water compartment is described by equation [68]. L_w is the sum of all loss-rate constants from the ground-surface-soil compartment,

$$L_w = T_{wa} + T_{wd} + T_{wo} + R_w \quad . \qquad [98]$$

$T_{aw}\ N_a$ is the gain by diffusion and deposition from the air compartment, mol/d; $T_{gw}\ N_g$ is the gain by runoff from the surface-soil compartment, mol/d; $T_{dw}\ N_d$ is the gain by diffusion and deposition from the sediment compartment, mol/d; T_{wa}, T_{wd}, and T_{wo} are rate constants for gross diffusion loss to air, for deposition and

gross diffusion losses to sediments, and for loss due to outflow, day^{-1}; and R_w is the rate constant for transformation losses, day^{-1}. The loss-rate constants are given by

$$T_{wa} = \frac{Y_{aw}}{Z_w \times d_w} \quad , \qquad [99]$$

$$T_{wd} = \frac{Y_{wd} + deposit \times Z_{dp} / \rho s_d}{Z_w \times d_w} \quad , \qquad [100]$$

$$T_{wo} = outflow \times \frac{[Z_{water} + (Z_{wp} \times \rho b_w / \rho s_d)]}{Z_w \times d_w \times f_{arw}} \quad , \text{and} \qquad [101]$$

$$outflow = inflow + runoff + rain \times (f_{arw}) - evaporate \quad . \qquad [102]$$

Parameters in these expressions are listed in Table IV or have been defined previously.

The Sediment-Zone Compartment (d)

The sediment compartment is a steady-state compartment. It represents the sediment layer at the bottom of a surface-water column. In this compartment, losses include diffusion to water, resuspension of sediment particles, sediment burial, and transformation processes. The inventory, N_d in mol, of contaminant in the sediment compartment is described by equation [69]. L_d is the sum of loss-rate constants from the ground-surface-soil compartment

$$L_d = T_{dw} + R_d \quad , \qquad [103]$$

$T_{wd}\ N_w$ is the gain by diffusion and deposition from the water compartment, mol/d; T_{dw} is rate constant for gross diffusion and particle resuspension losses to water, day^{-1}; and R_w is the rate constant for sediment burial and for transformation losses, day^{-1}. The loss-rate constant to water is given by

$$T_{dw} = \frac{Y_{wd} + resuspend \times Z_{dp} / \rho s_d}{Z_d \times d_d} \quad . \qquad [104]$$

Parameters in this expression are listed in Table IV or have been defined previously.

Ground-Water (q)

The water in the ground-water compartment is assumed to have the same contaminate concentration as the leachate from the bottom of the vadose zone. This means that the concentration of contaminant in the ground-water is given by

$$C_q = Z_{water}\, f_v \ , \qquad [105]$$

where C_q is the contaminant concentration in leachate going into the ground-water zone, mol/m^3; Z_{water} is the fugacity capacity of pure water, mol/m^3-Pa; and f_v is the fugacity of the vadose-zone soil from which the leachate comes, Pa.

Time-Dependent Solution for Compartment Inventories

We used equations [63] through [69] and exponential methods to develop a closed-form solution for the time-dependent inventories, $N_i(t)$, of contaminant in the seven compartments included in the model. This solution is given by,

$$N_v(t) = \mathbf{a}_7 \exp(-L_v t) + \mathbf{a}_8 \exp(-\lambda_1 t) + \mathbf{b}_5 \ , \qquad [106]$$

$$N_s(t) = \mathbf{a}_6 \exp(-\lambda_1 t) + \mathbf{b}_4 \ , \qquad [107]$$

$$N_g(t) = \mathbf{a}_5 N_s(t) + \mathbf{b}_3 \ , \qquad [108]$$

$$N_a(t) = \mathbf{a}_3 N_g(t) + \mathbf{a}_4 N_s(t) + \mathbf{b}_2 \ , \qquad [109]$$

$$N_w(t) = \mathbf{a}_1 N_a(t) + \mathbf{a}_2 N_g(t) + \mathbf{b}_1 \ , \qquad [110]$$

$$N_d(t) = \frac{T_{wd}}{L_d} N_w(t) \ , \text{ and} \qquad [111]$$

$$N_p(t) = \frac{T_{ap}}{L_p} N_a(t) + \frac{T_{gp}}{L_p} N_g(t) + \frac{T_{sp}}{L_p} N_s(t) \ , \qquad [112]$$

where

$$\lambda_1 = L_s - T_{gs}\,\mathbf{a}_5 \ , \qquad [113]$$

$$\mathbf{a}_8 = \frac{T_{sv}\,\mathbf{a}_6}{(L_v - \lambda_1)} \ , \qquad [114]$$

$$\mathbf{a}_7 = N_v(0) - \frac{T_{sv}\,\mathbf{a}_6}{(L_v - \lambda_1)} - \frac{T_{sv}\,\mathbf{b}_4}{L_v} \ , \qquad [115]$$

$$\mathbf{a}_6 = N_s(0) - \frac{T_{gs}\,\mathbf{b}_3}{\lambda_1} \ , \qquad [116]$$

$$\mathbf{a}_5 = \frac{\left[T_{ag}\,\mathbf{a}_4 + \frac{T_{ag}\,T_{ag}}{L_p}\mathbf{a}_4 + \frac{T_{pg}\,T_{sp}}{L_p} + T_{sg}\right]}{\left[L_g - T_{ag}\,\mathbf{a}_3 - \frac{T_{pg}\,T_{ap}}{L_p}\mathbf{a}_3 - \frac{T_{pg}\,T_{gp}}{L_p}\right]} \ , \qquad [117]$$

$$\mathbf{a}_4 = \frac{\left[\frac{T_{pa}\,T_{sp}}{L_p}\right]}{\left[L_a - \frac{T_{pa}\,T_{ap}}{L_p}\mathbf{a}_3 - T_{wa}\,\mathbf{a}_1\right]} \ , \qquad [118]$$

$$\mathbf{a}_3 = \frac{\left[\frac{T_{pa}\,T_{gp}}{L_p} + T_{wa}\,\mathbf{a}_2 + T_{ga}\right]}{\left[L_a - \frac{T_{pa}\,T_{ap}}{L_p} - T_{wa}\,\mathbf{a}_1\right]} \ , \qquad [119]$$

$$\mathbf{a}_2 = \frac{T_{gw}}{\left[L_w - \frac{T_{wd}\,T_{dw}}{L_d}\right]} \ , \qquad [120]$$

$$\mathbf{a}_1 = \frac{T_{aw}}{\left[L_w - \frac{T_{wd}\,T_{dw}}{L_d}\right]} \ , \qquad [121]$$

$$\mathbf{b}_5 = \frac{T_{sv}\,\mathbf{b}_4}{L_v} \quad , \qquad [122]$$

$$\mathbf{b}_4 = \frac{T_{gs}\,\mathbf{b}_3}{\lambda_1} \quad , \qquad [123]$$

$$\mathbf{b}_3 = \frac{\left[S_g + T_{ag}\,\mathbf{b}_2 + \frac{T_{pg}\,T_{ap}}{L_p}\mathbf{b}_2\right]}{\left[L_g - T_{ag}\,\mathbf{a}_3 - \frac{T_{pg}\,T_{ap}}{L_p}\mathbf{a}_3 - \frac{T_{pg}\,T_{gp}}{L_p}\right]} \quad , \qquad [124]$$

$$\mathbf{b}_2 = \frac{\left[S_a + T_{wa}\,\mathbf{b}_1\right]}{\left[L_a - \frac{T_{pa}\,T_{ap}}{L_p}\mathbf{a}_3 - T_{wa}\,\mathbf{a}_1\right]} \quad \text{, and} \qquad [125]$$

$$\mathbf{b}_1 = \frac{S_w}{\left[L_w - \frac{T_{wd}\,T_{dw}}{L_d}\right]} \quad . \qquad [126]$$

SAMPLE APPLICATIONS

In order to illustrate the use of CalTOX for screening studies, we apply the model here to steady-state inputs of contaminants to air or surface soil in order to estimate concentrations in the adjacent air, plants, soil and water compartments and illustrate the use of the model. These examples are not intended as a validation of the model, but only as an illustration of its use. The examples do indicate that a multimedia model, such as CalTOX can reproduce multimedia concentration data that has been collected regionally.

The contaminants considered in these examples include the volatile organic compounds (VOCs) PCE and TCE, the semi-volatile organic compound benzo(a)pyrene, and the radionuclides tritium (as tritiated water) and uranium-238. The emissions that we selected are assigned magnitudes in mol/m^2-d that correspond to the types of emissions expected in the industrialized regions of the U.S. In Table V are summarized for these emissions the environmental concentrations that result in air, root-zone soil, ground water, and surface water. These concentrations are compared to measured concentrations reported for industrialized regions of the U.S. Data for TCE and PCE are obtained from

Table V. Concentrations derived from CalTOX calculations for the listed contaminants compared to measured or reported concentrations.

Contaminants and compartments	Modeled concentrations	Measured or reported concentrations
Trichloroethylene (TCE)		
Air ($\mu g/m^3$)	0.76	0.1 to 0.5 (U.S. cities)
Soil ($\mu g/kg$)	1.6 to 4.9	n/a
Plants ($\mu g/kg$)	0.92	1 to 3 (grain-based foods)
Ground water ($\mu g/L$)	1.1	2.1 (U.S. public supplies)
Surface water ($\mu g/L$)	0.67	0.1 to 1 (Ohio river)
Tetrachloroethylene (PCE)		
Air ($\mu g/m^3$)	0.96	1 (577 U.S. cities)
Soil ($\mu g/kg$)	1.6 to 4.9	n/a
Plants ($\mu g/kg$)	0.93	2 (U.S. wheat)
Ground water ($\mu g/L$)	0.76	0.6 (27 U.S. cities)
Surface water ($\mu g/L$)	0.77	2.0 (154 U.S. cities)
Benzo(a)pyrene (BaP)		
Air (ng/m^3)	6.2	4.7
Soil ($\mu g/kg$)	240	300 to 500
Plants ($\mu g/kg$)	140	n/a
Ground water (pg/L)	8.3	n/a
Surface water (ng/L)	100	28
Tritium		
Air (mBq/m^3)	8.5	6.7
Soil (Bq/kg)	0.03	0.035
Plants (Bq/kg)	0.26	0.45
Ground water (Bq/L)	0.037	0.02 to 0.1
Surface water (Bq/L)	1.7	0.38 to 0.84
Uranium-238		
Air ($\mu Bq/m^3$)	0.3	1.2
Soil (Bq/kg)	20 to 35	10 to 50 (mean = 25)
Plants (Bq/kg)	0.35	~0.01
Ground water (Bq/L)	0.027	0.025 (U.S. supplies)
Surface water (Bq/L)	0.024	0.025

Verschueren (1983) and Howard (1990), for BaP from Richitt et al. (1982) and from Mackay and Paterson (1991), for tritium from NCRP (1979), and for uranium-238 from UNSCEAR (1988).

Trichloroethylene (TCE)

TCE is a volatile chlorinated hydrocarbon compound that is widely used as a degreasing solvent. Its molecular weight is 131, its octanol-water partition coefficient, K_{ow}, is 260, its vapor pressure 9200 Pa (at 25 °C), and its solubility 8.4 mol/m^3. Production in the U.S. of TCE is on the order of 7.50×10^7 kg/y. For the analysis here, we used a source term of 0.02 mol/km^2-d released to air and deposited to the soil surface as representative of releases in the urbanized regions of the U.S. We estimate the K_D values for TCE in ground-surface and root-zone soil, vadose-zone soil, and sediments as 1.5, 0.25, and 2.5 L/kg, respectively. We estimate the plant-to-soil and plant-to-air partition coefficients as 0.87 and 12.8.

Tetrachloroethylene (PCE)

PCE is also a volatile chlorinated hydrocarbon compound that is a widely used solvent with applications as a dry-cleaning agent, a metal degreaser, and a chemical intermediate in the production of fluorocarbons. Its molecular weight is 166, its octanol-water partition coefficient 400, its vapor pressure 2000 Pa (at 25 °C), and its solubility 0.9 mol/m^3. Production in the U.S. of PCE is on the order of 3.1×10^7 kg/y. For the analysis here, we assumed a source term of 0.01 mol/km^2-d released to air and deposited to the soil surface. We estimate the K_D values for PCE in ground-surface and root-zone soil, vadose-zone soil, and sediments as 2.3, 0.38, and 3.8 L/kg, respectively. We estimate the plant-to-soil and plant-to-air partition coefficients as 0.87 and 9.5. Figure 9 provides an illustration of the type of transport and transformation information for PCE that can be assembled using CalTOX. In this figure, we see the distribution and dynamics of PCE at a time ten years after it was incorporated at a dry-soil concentration of 1 ppm in the root- and vadose-soil compartments.

Tritium

Tritium is the heaviest and only radioactive isotope of hydrogen. Natural production due to cosmic rays is approximately 1.8×10^{17} Bq/y (NCRP, 1979), corresponding to 1 Bq/km^2-d worldwide. Large amounts have also been produced

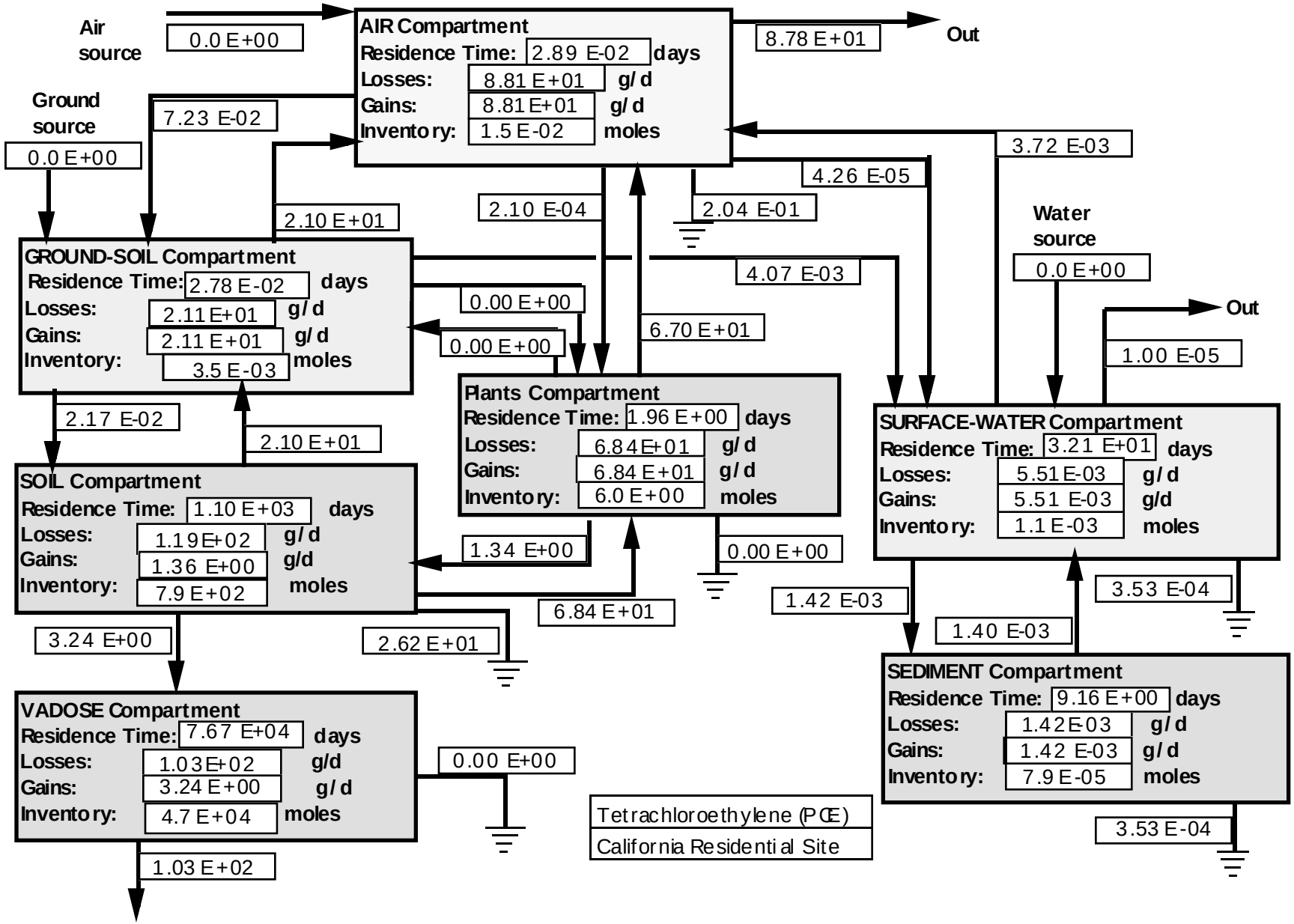


Figure 9. An illustration of the type of transport and transformation information for a contaminant that can be assembled using CalTOX. In this example, we see the distribution and dynamics of PCE at a time ten years after it was incorporated at a dry-soil concentration of 1 ppm in the root- and vadose-soil compartments.

by atomic-energy programs throughout the world. The concentration of tritium in environmental waters due to natural tritium production is reported in the range 0.12 to 0.60 Bq/L (NCRP, 1979). The right-most column of Table V lists the concentrations of tritium that were estimated by the NCRP (1979) to be in the water of various compartments. These numbers are based on the assumption that the absolute humidity of the atmosphere is 11 g(water)/m^3, that the water content of surface soil is 100 L/m^3, and that plants are 80% water. The distribution of tritium that we calculated and report in Table V is based on our assumptions that (1) the concentration in air of water vapor corresponding to 50% saturation above water at 25 °C is 11 g/m^3, (2) concentrations of tritium in above-ground vegetation water are proportional to plant concentrations, (3) the natural source term is 1 Bq/km^2-d, (4) the molecular weight of tritiated water is approximately 20 g/mol, (5) its octanol-water partition coefficient is 0.042, (6) its vapor pressure is 3170 Pa (at 25 °C), (7) its Henry's law constant is 0.063 m^3/mol, and (8) the plant-to-soil and plant-to-air partition coefficients are 8 and 45,000, respectively.

Uranium

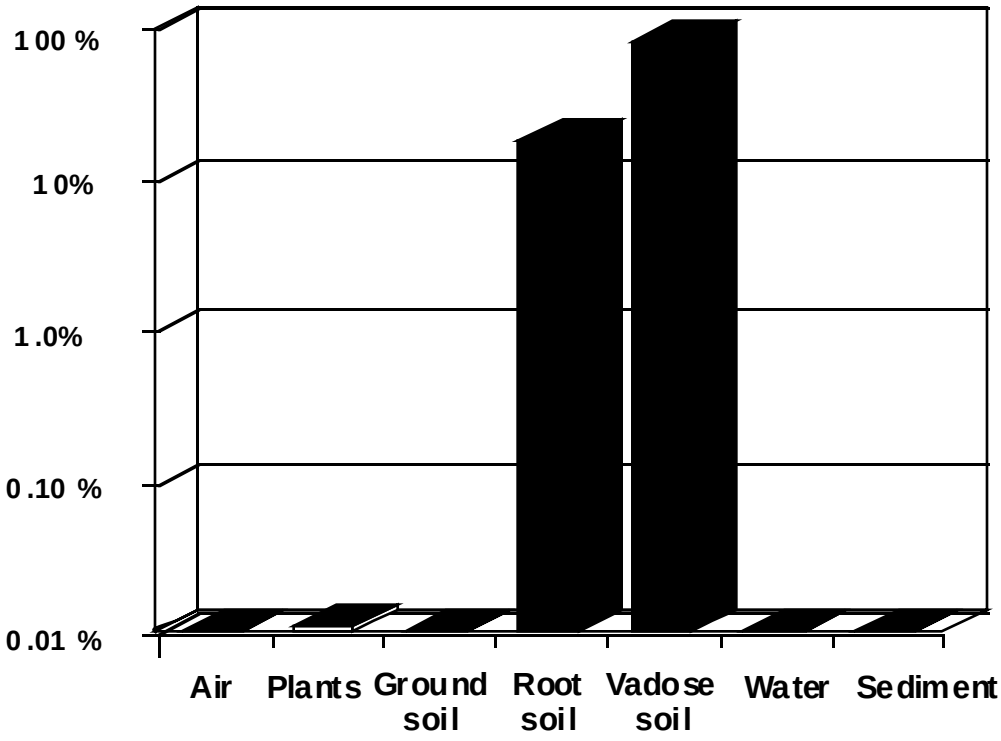
Uranium-238 is a long-lived (half life = 4.5×10^9 y) primordial nuclide that is widely dispersed in the earth's crust. Weathering processes distribute this nuclide among the environmental compartments of the earth's surface. In the atmosphere, the main natural source of uranium is resuspension of dust from the earth's surface. The mean concentration of uranium-238 in soil has been reported as 25 Bq/kg (UNSCEAR, 1988). This along with other environmental concentrations of uranium-238 reported in the UNSCEAR report (1988) are listed in Table V. We modeled the distribution of uranium-238 using a continuous deposition to surface soil of 1.2×10^{-6} Bq/d. Based on environmental abundance data in the UNSCEAR report (1988), we estimate the K_D values for uranium in ground-surface and root-zone soil, vadose-zone soil, and sediments as 20, 100, and 100 L/kg, respectively and we estimate the plant-to-soil partition coefficient as 0.009. Our estimated steady-state concentrations are listed in Table V and compared to the reported concentrations.

Benzo(a)pyrene (BaP)

Benzo(a)pyrene (BaP) is a lipophilic, low solubility ($K_{ow} = 1 \times 10^6$), low vapor pressure (Henry's law constant = 0.048 Pa-m^3/mol) compound that tends to be transported in the environment through binding to dust and sediment particles.

BaP is a by-product of coal-tar processing, petroleum refining, coke processing, and power generation (Mackay and Paterson, 1991). Its molecular weight is 252. Our estimates of the K_D values for BaP in ground-surface and root-zone soil, vadose-zone soil, and sediments are 5800, 960, and 9600 L/kg, respectively. We estimate the plant/soil partition coefficient as 3000. Emissions and multimedia concentrations of BaP in the Ohio River Valley of the U.S. have been measured by Richitt et al. (1982), who reported emissions to this area of 400 km^2 as 40 mol BaP per day. This emission rate was used to calculate the concentrations we report and compared to measured values by Richitt et al (1982) in Table V. Figure 10 illustrates the difference in dispersion of BaP and PCE. The top diagram shows the per cent distribution of PCE in a land unit with landscape properties from Table IV and one year after PCE incorporation in the root- and vadose-soil layers at a concentration of 1 ppm dry soil. The bottom diagram shows per cent distribution of BaP under the same conditions.

As can be seen from the results in Table V, it is possible to make reliable estimates of environmental partitioning in regional environments. Although this exercise provides illustrates the use of multimedia models as screening tools, it should not be considered a definitive validation exercise for the use of CalTOX at hazardous waste sites. First, it should be noted that the emission used in these sample applications were primarily air and surface-soil releases, not contaminants introduced to deeper soils, such as root and vadose. Second, because we did not have precise information on the land area receiving the release or the magnitude of the release for these sample applications, the results only validate the ability of CalTOX to reproduce the relative concentration in a number of compartments but not the absolute level of contamination. The absolute level of contamination can easily be adjusted through selection of the source-area ratio. Finally, the applications above apply to regions of some 100 km^2 or larger and do not reveal the scale at which the reliability of CalTOX breaks down. CalTOX is designed to model a landscape on the order of 1 to 10 km^2 associated with a toxic-substances release site. Smaller landscape areas can be treated with the model, but in such cases, the model is likely to overestimate the persistence of contamination.



PCE

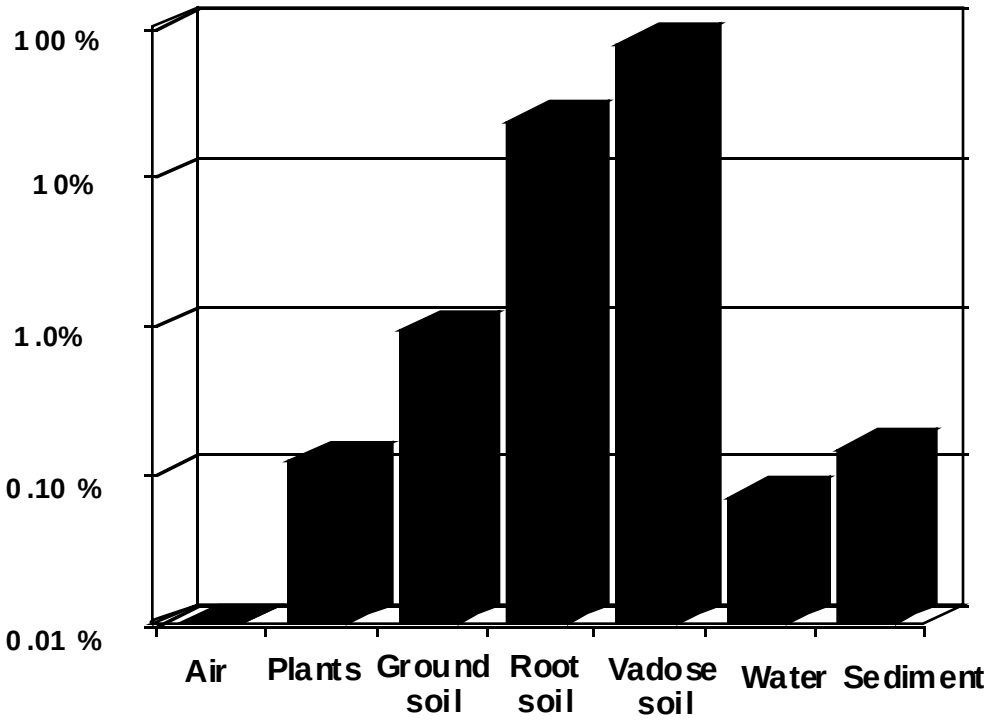


Figure 10. Differences in distribution of BaP and PCE one year after incorporation in the root- and vadose-zone-soil layers at a concentration of 1 ppm dry soil.

SUMMARY AND DISCUSSION

Reports of environmental contaminants in air, drinking water, soil, and food result in public concern about the risks to human health posed by the chemical byproducts of industrial societies. Whether contaminated by pesticide application, waste dumping, or by deposition of airborne pollutants, contaminated soils are among the issues that are foremost in this area of public awareness. As applied to landscapes contaminated by hazardous wastes, risk assessment involves four inter-related steps. These are (1) determination of source concentrations or emissions characteristics, (2) exposure assessment, (3) toxicity assessment, and (4) risk characterization. An important issue in both the risk characterization and subsequent risk management of contaminated soil is how precisely we can characterize the distribution among individuals of potential doses associated with chemical contaminants.

In his treatise *Air, Water, and Places*, the ancient-Greek physician Hippocrates demonstrated that the appearance of disease in human populations is influenced by the quality of air, water, and food; the topography of the land; and general living habits (Wasserstein, 1982). This approach is still relevant and, indeed, the cornerstone of modern efforts to relate public health to environmental factors. What has changed is the precision with which we can measure and model these long-held relationships. Today, environmental scientists recognize that plants, animals, and humans encounter environmental contaminants via complex transfers through air, water, and food and use multimedia models to evaluate these transfers.

In the sections above, we provided an overview of methods that can be used to determine how the interaction among transport and transformation processes results in the distribution of environmental contaminants in time and among compartments. These methods are incorporated into the spreadsheet model, CalTOX.

Summary

We began with a review of multimedia models—how they came about and where they are going. We highlight areas of success, areas of weakness, and areas that need much more work—such as plant-soil-air modeling. We have described methods and models that are incorporated into the CalTOX multimedia-based exposure model for multiple-pathway exposures.

CalTOX contains a seven-compartment regional and dynamic multimedia fugacity-type model that was developed for assessing the spread of contamination among the environmental media at a landscape unit that represents a toxic-substances-release site. It is designed to model a landscape on the order of 1,000 to 10^7 m^2. Smaller landscape areas can be treated with the model, but in such cases the model has greater uncertainty associated with model predictions and the persistence of contamination. CalTOX is a spreadsheet model and has been developed with the EXCEL application on Macintosh and IBM-type personal computers.

We began this report by describing the objectives of the model, critical sensitivities and uncertainties, the chemical classes for which it is appropriate, and situations for which the model should not be used. We also described the fugacity capacities of organic and inorganic chemicals in each CalTOX compartment.

We next provided a detailed overview of the CalTOX multimedia transport and transformation model including the nature of the mathematical models describing chemical transport and fate in this seven-compartment system. Also, we considered for each compartment transport processes that lead to the dispersion of substances within a single environmental medium. Although the CalTOX model does not explicitly deal with intra-media gradients, this information was provided to put our model development in proper perspective. We gave an overview of the types of transformation processes that can be included in the CalTOX model. We then describe the landscape and chemical-property data needed to carry out a multimedia analysis. This is followed by a section in which we developed explicit mathematical descriptions for transformation processes, loss-rate constants, and all inter-compartment rate constants in the CalTOX model. We then show how these rate constants are used to develop the gain-loss equations for a landscape unit and develop a dynamic solution to this set of equations. The use of the CalTOX model was illustrated with several example calculations. The contaminants considered include the volatile organic compounds tetrachloroethylene (PCE) and trichloroethylene (TCE), the semi-volatile organic compound benzo(a)pyrene, and the radionuclides tritium and uranium-238. These sample calculations reveal that it is possible to make reliable estimates of environmental partitioning in regional environments.

The objectives of the multimedia transport and transformation components of CalTOX are to (1) provide realistic (although) uncertain ranges of contaminant concentrations available in environmental media at a contaminated site, (2) provide a relatively simple and accessible model, (3) conserve contaminant mass and comply

with laws of chemical equilibrium, (4) address both transport and transformation processes, (5) allow for a distinction between environmental concentrations and exposure concentrations, (6) be compatible with uncertainty and sensitivity analyses, (7) provide time-varying chemical inventories, and (8) be capable of addressing both continuous inputs and initial concentrations.

The CalTOX model, in descending order of reliability, is capable of handling nonionic organic chemicals, radionuclides, fully dissociating organic and inorganic chemicals, and solid-phase metal species. With careful attention to inputs, the model can be used for partially dissociated organic and inorganic species. The model has not been designed to work with surfactants, inorganic chemicals species with high vapor-pressure-to-solubility ratios, and volatile metals such as mercury.

As is the case with any model, CalTOX was designed for use in a limited range of spatial scales, time scales, geographic conditions, and chemical classes. CalTOX is intended for application over long time scales, several months to decades. It should be used cautiously for time periods less than one year and then only when properly time-averaged landscape properties are employed. It should not be used for landscapes in which water occupies more than 10% of the land surface area. CalTOX is designed for modeling very low concentrations of contamination. When contaminant concentration exceeds the solubility limit in any phase, the results of the model are no longer valid. CalTOX should not be used as substitute for measured data, where it is available. Also, it should not be used when a detailed transport and transformation assessment has been conducted. However, it might be used as a compliment to such an assessment.

Discussion

There is a delicate balance between perceived model reliability (which favors large complex models with big data bases) and utility for policy makers (which favors simple, flexible, easy-to-use models). Because many exposure models are used by policy makers, they should be kept as simple as the science allows. Furthermore, we always must reflect on whether we have done a good job of demonstrating that the science justifies a more simple model. In addition, there is a need to confront the issue of uncertainty and variability in the predictions of human exposure.

A key issue of potential concern for application of the CalTOX model to hazardous waste sites is the appropriateness of the idealized “unit-world” approach with its spatially homogenous compartments. Such an approach, while providing

insight on broad-scale trends and differences in partitioning between different chemicals, may appear to fail in providing sufficient precision when applied to a population at a hazardous waste site. However, CalTOX was designed as a consistent screening mechanism for those sites where full-scale risk assessment might only serve to delay the process of evaluation and remediation. In this context, we believe the unit-world option, with a rigorous and comprehensive implementation as provided by the CalTOX model, is attractive and appropriate. Much of the uncertainty associated with CalTOX is in the transformation factors and in the intermedia transfer factors, particularly in the air/soil, air/water, and soil-layer transfers. The uncertainties about these processes are limiting factors in any transport model, whether simple or complex. In addition, for many applications of CalTOX, source data has large variability and/or uncertainty. This is particularly the case for contaminant measurements in soils.

Properly designed multimedia assessments can be used as tools for decision makers who must select (based on limited information) contaminants and/or contaminant concentrations likely to pose significant health risk and thus require regulatory priority. Health-risk estimates for chemicals are sensitive to the magnitude of the source term, measures of dose-response (or acceptable dose), as well as environmental partition factors, reaction rates, and residence times. For many compounds, the potential risk is clouded by uncertainties about one or more of these factors. In particular, absence of information about environmental degradation could make some estimates of health risks orders of magnitude too conservative. In response to the problem of uncertainty, CalTOX was designed to provide for a systematic evaluation of uncertainties. Currently, uncertainty is not explicitly addressed in many calculations of risk-based exposure standards. Instead, uncertainty is dealt with by using conservative values (e.g., 95% upper-confidence limits) for human exposure factors and (often) median estimates of intermedia transfer factors. This results in an almost unpredictable level of confidence about quantitative expressions of exposure and risk. Consequently, in the past, risk managers could determine neither the size of the safety factor that is incorporated into their standards nor the accuracy of the standards with respect to different sites, populations, and/or individual toxic substances.

Regulatory toxicology and risk assessment often operate under the premise that, with sufficient funding, science and technology will provide an obvious and cost-effective solution for reducing environmental health risks. However, in reality there are many sources of uncertainty and variability in the process of human

health-risk assessment and many of these are not reducible. Effective environmental management policies are possible under conditions of uncertainty, but such policies must directly confront the uncertainty . There exists well-developed theories of decision making under uncertainty. In the context of decision making, CalTOX was designed so that ultimately it can be used to provide flexibility to address margins of error; to consider reducible versus irreducible uncertainty; to separate individual variability from true scientific uncertainty; and to consider benefits, costs, and comparable risks in the decision making process.

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APPENDIX A: PARAMETER LISTS

Constants

R	Universal gas constant (8.31 Pa-m^3/mol-K)

Chemical Source Terms and Initial Inventories

S_a	continuous source term of contaminant to air (mol/d)
S_g	continuous source term of contaminant to soil surface (mol/d)
S_w	continuous source term of contaminant to surface water (mol/d)
$N_s(0)$	initial inventory in the root-zone soil (mol)
$N_v(0)$	initial inventory in the vadose-zone soil (mol)

Chemical Properties

MW	Molecular weight (g/mol)
K_{ow}	Octanol-water partition coefficient (L[water]/L[octanol])
T_m	melting point of the chemical (K)
VP	vapor pressure in Pa
S	solubility in mol/m^3
H	henry's law constant (pa-m^3/mol)
D_{air}	diffusion coefficient in pure air (m^2/d)
D_{water}	diffusion coefficient in pure water (m^2/d)
R_a	reaction rate constant in air in 1/d
R_p	reaction rate constant in plants in 1/d
R_s	reaction rate constant in root-zone soil in 1/d
R_v	reaction rate constant in vadose-zone soil in 1/d
R_w	reaction rate constant in surface water in 1/d
R_d	reaction rate constant in sediment in 1/d

Landscape Properties

Area	area in m^2
rain	precipitation onto land (m/d)
inflow	flow of surface water into the landscape system (m/d)
runoff	land surface runoff (m/d)
ρb_a	atmospheric particle load (kg/m^3)
v_d	deposition velocity of atmospheric particles (m/d)
bio_{inv}	plant dry mass inventory (kg/m^2)

bio_{prd}	plant dry mass production ($kg/m^2/yr$)
bio_{dm}	plant dry mass fraction
ρ_p	plant density kg/L
recharge	ground water recharges (m/d)
evaporate	evaporation of water from surface water (m/d)
d_g	thickness of the ground-soil layer (m)
ρs_g	density of soil particles in the ground-soil layer (kg/m^3[particles])
β_g	water content of the soil in the ground-soil layer (m^3[water]/m^3[soil])
α_g	volumetric air content in the ground-soil layer (m^3[air]/m^3[soil])
erosion	mechanical erosion rate from surface soil (kg/m^2-d)
d_s	thickness of the root-zone soil layer (m)
ρs_s	density of soil particles in the root-zone soil (kg/m^3[particles])
β_s	water content of the soil in the root-zone soil (m^3[water]/m^3[soil])
α_s	volumetric air content in the root-zone soil (m^3[air]/m^3[soil])
d_v	thickness of the vadose layer (m)
β_v	water content of the soil in the vadose layer (m^3[water]/m^3[soil])
ρs_v	density of soil particles in the vadose layer (kg/m^3)
α_v	volumetric air content in the vadose layer (m^3[air]/m^3[soil])
f_{arw}	fraction of the total surface area in surface water
d_w	average depth of surface waters (m)
ρb_w	suspended sediment load in surface water (kg/m^3)
deposit	deposition rate of suspended sediment ($kg/m^2/d$)
d_d	thickness of the sediment layer (m)
ρs_d	density of particles in the sediment layer (kg/m^3[particles])
β_d	porosity of the sediment zone
resuspend	resuspension rate from the sediment layer ($kg/m^2/d$)
T	ambient environmental temperature (kelvins)
$current_w$	surface water current in m/d
f_{ocs}	fraction organic carbon in the root-zone soil
f_{ocv}	fraction organic carbon in the vadose zone
f_{ocd}	fraction organic carbon in sediments
δ_{ag}	boundary-layer thickness in air above ground-surface soil (m)
v_w	yearly average wind speed (m/d)

Calculated Chemical and Landscape Properties

K_{oc} *	organic carbon partition coefficient
K_{Dg} *	water-phase/solid-phase partition coefficient in ground-surface soil
K_{Ds} *	water-phase/solid-phase partition coefficient in root-zone soil
K_{Dv} *	water-phase/solid-phase partition coefficient in the vadose zone
K_{Dd} *	water-phase/solid-phase partition coefficient in surface-water sediments
d_a	height of the air compartment (m)
evapotrans	evapotranspiration of water from soil (m/d)
outflow	total surface water runoff (m/d)
δ_{aw}	air-side boundary layer thickness at the air-water interface (m)
δ_{wa}	water-side boundary layer thickness at the air-water interface (m)
δ_g	boundary layer thickness in the ground-surface-soil compartment (m)
δ_s	boundary layer thickness in the root-zone soil compartment (m)
δ_{wd}	water-side boundary layer thickness at water-sediment interface (m)
δ_{dw}	sediment-side boundary layer thickness at water-sediment interface (m)

* For these properties the default calculation is not used when an input value is provided.

Compartment Volumes

V_a	air compartment volume in m^3
V_p	plant compartment volume in m^3
V_g	ground-surface soil compartment volume in m^3
V_s	root-zone soil compartment volume in m^3
V_v	vadose-zone soil compartment volume in m^3
V_w	surface-water compartment volume in m^3
V_d	sediment compartment volume in m^3

Fugacity Capacities

Z_{air}	fugacity capacity of pure air (mol/m^3-Pa)
Z_{water}	fugacity capacity of pure water (mol/m^3-Pa)
Z_{ap}	fugacity capacity of particles in air (mol/m^3[s]-Pa)
Z_{gp}	fugacity capacity of ground-surface-soil particles (mol/m^3[s]-Pa)
Z_{sp}	fugacity capacity of root-soil compartment particles (mol/m^3[s]-Pa)
Z_{vp}	fugacity capacity of vadose-soil compartment particles (mol/m^3[s]-Pa)
Z_{wp}	fugacity capacity of suspended sediment particles (mol/m^3[s]-Pa)

Z_{dp}	fugacity capacity of bottom sediment particles (mol/m^3[s]-Pa)
Z_a	fugacity capacity of air compartment (mol/m^3-Pa)
Z_p	fugacity capacity of plant biomass (mol/m^3-Pa)
Z_g	fugacity capacity of ground-surface soil (mol/m^3-Pa)
Z_s	fugacity capacity of root-zone soil compartment (mol/m^3-Pa)
Z_v	fugacity capacity of vadose-zone soil compartment (mol/m^3-Pa)
Z_w	fugacity capacity of water compartment (mol/m^3-Pa)
Z_d	fugacity capacity of sediment compartment (mol/m^3-Pa)

Compartment Diffusion Coefficients

D_g	effective diffusion coefficient in ground-surface soil (m^2/d)
D_s	effective diffusion coefficient in root-zone soil (m^2/d)
D_d	effective diffusion coefficient in the sediment compartment (m^2/d)

Fugacity-Based Mass-Transfer Coefficients

Y_{ag}^a	fugacity mass transfer coefficient on the air side of the air-ground-soil interface (mol/Pa-m^2-d)
Y_{ag}^g	fugacity mass transfer coefficient on the ground-soil side of the air-ground-soil interface (mol/Pa-m^2-d)
Y_{gs}^g	fugacity mass transfer coefficient on the ground-soil side of the ground-surface-soil and root-zone-soil interface (mol/Pa-m^2-d)
Y_{gs}^s	fugacity mass transfer coefficient on the root-zone-soil side of the ground-surface-soil and root-zone-soil interface (mol/Pa-m^2-d)
Y_{aw}^a	fugacity mass transfer coefficient on the air side of the air and surface-water interface (mol/Pa-m^2-d)
Y_{aw}^w	fugacity mass transfer coefficient on the water side of the air and surface-water interface (mol/Pa-m^2-d)
Y_{wd}^w	fugacity mass transfer coefficient on the water side of the surface-water and sediment interface (mol/Pa-m^2-d)
Y_{wd}^d	fugacity mass transfer coefficient on the water side of the surface-water and sediment interface (mol/Pa-m^2-d)
Y_{ag}	fugacity mass transfer coefficient at air and ground-surface-soil interface (mol/Pa-m^2-d)
Y_{gs}	fugacity mass transfer coefficient at ground-surface-soil and root-zone-soil interface (mol/Pa-m^2-d)

Y_{aw} fugacity mass transfer coefficient at the air and surface-water interface (mol/Pa-m^2-d)

Y_{wd} fugacity mass transfer coefficient at the sediment and surface-water interface (mol/Pa-m^2-d)

Molar-Transfer-Rate Constants

T_{ap} transfer rate constant from air to plants (day^{-1})

T_{ag} transfer rate constant from air to ground-surface soil (day^{-1})

T_{aw} transfer rate constant from air to surface water (day^{-1})

T_{ao} transfer rate constant from air and out of the landscape (day^{-1})

T_{pa} transfer rate constant from plants to air (day^{-1})

T_{ps} transfer rate constant from plants to root-zone soil (day^{-1})

T_{ga} transfer rate constant from ground-surface soil to air (day^{-1})

T_{gv} transfer rate constant from ground-surface to root-zone soil (day^{-1})

T_{gw} transfer rate constant from ground-surface soil to surface water (day^{-1})

T_{sv} transfer rate constant from root-zone to ground-surface soil (day^{-1})

T_{sp} transfer rate constant from root-zone soil to plants (day^{-1})

T_{sv} transfer rate constant from root-zone to vadose-zone soil (day^{-1})

T_{vo} transfer rate constant from vadose-zone soil to ground water (day^{-1})

T_{wa} transfer rate constant from surface water to air (day^{-1})

T_{wd} transfer rate constant from surface water to sediments (day^{-1})

T_{wo} transfer rate constant from surface water out of the landscape (day^{-1})

T_{dw} transfer rate constant from sediments to surface water (day^{-1})

Loss rate constants

L_a loss rate constant for the air compartment (day^{-1})

L_p loss rate constant for the plants compartment (day^{-1})

L_g loss rate constant for the ground-surface-soil compartment (day^{-1})

L_s loss rate constant for the root-zone-soil compartment (day^{-1})

L_v loss rate constant for the vadose-zone-soil compartment (day^{-1})

L_w loss rate constant for the surface-water compartment (day^{-1})

L_d loss rate constant for the sediments compartment (day^{-1})

APPENDIX B: THE RELATIONSHIP OF THE BOX MODEL TO THE GAUSSIAN-PLUME MODEL FOR PREDICTING AIR DISPERSION

Substances in outdoor (or ambient) air are dispersed by atmospheric advection and diffusion. Meteorological parameters have an overwhelming influence on the behavior of contaminants in the lower atmosphere. Among them, wind parameters (direction, velocity, and turbulence) and thermal properties (stability) are the most important. The standard models for estimating the time and spatial distribution of point sources of contamination in the atmosphere are the Gaussian statistical solutions of the atmospheric diffusion equation. These models are obtained from solution of the classical differential equation for time-dependent diffusion in three dimensions. The standard Gaussian plume model has the form,

$$\chi / Q = \frac{1}{2 \pi v_w} \times g_1 \times g_2 \qquad [B\text{-}1]$$

where g_1 and g_2 represent the respective horizontal and vertical dispersion factors about the plume center line and are given by

$$g_1 = \frac{1}{\sigma_y} \exp\left(- \frac{y^2}{2 \sigma_y^2} \right) \qquad [B\text{-}2]$$

$$g_2 = \frac{1}{\sigma_z} \left\{ \exp\left[- \frac{(z - H)^2}{2 \sigma_z^2} \right] + \exp\left[- \frac{(z + H)^2}{2 \sigma_z^2} \right] \right\} \qquad [B\text{-}3]$$

and where χ / Q is the ratio of contaminant concentration, χ in mol / m^3, to source strength, Q in mole per hour, at a distance y (m) downwind and distance z (m) above the source; v_w is the ground-surface wind speed in m/h, H is the height of the release, in m; and σ_z and σ_y are, respectively vertical and horizontal dispersion parameters (in m) that increase with increasing distance from the source. However, σ_z can be no greater than L, the mixing height of the lower troposphere.

When we consider the cross-wind integral from $y = -\infty$ to $+\infty$ of equation [B-2] above and consider the dispersion over a 22.5 ° ($2 \pi x / 16$) segment of a circle a distance x from the source, then equation [B-2] above gives the average cross-wind dispersion at a distance x from the source as

$$\frac{16}{2\,\pi\,x}\int_{-\infty}^{+\infty} g_1\,dy = \frac{16}{x\sqrt{2\pi}} \quad . \qquad \text{[B-6]}$$

And when we consider the integral from 0 to +∞ of equation [B-3] for a ground-level release (H=0) and the dispersion over a mixing height of depth d_a, then equation [B-3] becomes

$$\frac{1}{d_a}\int_{0}^{+\infty} g_2\,dz = \frac{\sqrt{2\pi}}{d_a} \quad . \qquad \text{[B-5]}$$

Thus, the vertical and cross-wind average concentration at a distance x from the source, $\bar{\chi}$, is given by

$$\bar{\chi} = \frac{1}{2\,\pi\,v_w}\,Q \times \frac{16}{x\sqrt{2\pi}} \times \frac{\sqrt{2\pi}}{d_a} = \frac{16\,Q}{2\,\pi\,x\,v_w\,d_a} = \frac{2.5\,Q}{x\,v_w\,d_a} \qquad \text{[B-6]}$$

Another approach to the dispersion of substances in the atmosphere is based on the application of a mass balance to a volume element, parcel, or box of air. This gives rise to the "box" models. In this approach, the region to be studied is divided into cells or boxes. The concentration in each box is assumed to be uniform and is a function of the box volume, the rate at which material is being imported, emission rates within the box, and the rate at which material is exported from the box. Gifford and Hanna (1973) have shown that, in a simple box model, the yearly average concentration of contaminant within the box is proportional to the source strength in mass per unit area divided by the wind speed. Based on data from U.S. cities, they have developed for both gases and particles proportionality coefficients that can be used to estimate long-term contaminant concentrations.

According to Benarie (1980), the long-term average pollutant concentration in a region bordered by a box model with volume V_a and pollution source, Q mol/h, is given by

$$\bar{\chi} = N_a / V_a = \frac{c\,Q}{\text{Area} \times v_w} \quad , \qquad \text{[B-7]}$$

where N_a is the pollutant inventory in mol,*c* is a unitless proportionality constant; *Area* is the area of the region being modeled in m^2, and v_w is the long-term average wind speed in m/h. Based on a model for area sources developed by Turner (1970), the constant c can be estimated as $4.3\sqrt{Area}\ / d_a$, where $\sqrt{Area}$ is the cross-sectional length of an assumed square area containing the source Q. Putting this in equation [B-7] gives

$$\bar{\chi} = \frac{4.3\ Q}{\sqrt{Area} \times d_a \times v_w} \qquad [B\text{-}8]$$

as the concentration given by the box model. Now, when we recognize that the area occupied by a circle of radius x is πx^2 and make this substitution into equation [B-6], we obtain a very similar relationship,

$$\bar{\chi} = \frac{4.4\ Q}{\sqrt{Area} \times d_a \times v_w} \qquad [B\text{-}9]$$

where Area is the surface area occupied by a circle of radius x. However, equation [B-9] only applies when the vertical dispersion is contained within a mixing height of depth d_a, typically past a distance of several km, and when cross-wind averages of the horizontal concentration are appropriate, that is over long time periods.

Dispersion in the air-compartment of CalTOX is based on the box-model approach. But as shown above, the ratio of concentration to source predicted by the Gaussian plume model is similar in form to that predicted by the box model when this ratio is averaged over long time periods (on the order of one year) and over an area of several km^2 or greater.