

Multimedia Environmental Distribution of Toxics (Mend-Tox). I: Hybrid Compartmental-Spatial Modeling Framework

Yoram Cohen¹ and Ellen J. Cooter²

Abstract: An integrated hybrid spatial-compartmental modeling approach is presented for analyzing the dynamic distribution of chemicals in the multimedia environment. Information obtained from such analysis—which includes temporal chemical concentration profiles in various media, mass distribution, and intermedia chemical mass fluxes—can be used for subsequent exposure and risk analyses. The hybrid modeling framework consists of both uniform (air, water, suspended solids, vegetation, biota, suspended solids, and atmospheric aerosols) and nonuniform (soil and sediment) environmental compartments. The interactive system of model equations for the uniform compartments (ordinary differential equations) and nonuniform compartments (1D partial differential equations) must be solved simultaneously to ensure conservation of mass. In order for the approach to be of practical use, parameter input could be minimized through the use of theoretical or empirical description of intermedia transfer processes and estimation methods for associated intermedia transport parameters. Environmental problems are complex, and there are numerous possible multimedia analysis scenarios that may be of interest. Therefore, efficient and user-friendly implementations of such models are essential if multimedia analysis is to become a standard environmental tool.

DOI: 10.1061/(ASCE)1090-025X(2002)6:2(70)

CE Database keywords: Hybrid methods; Chemicals; Multimedia; Models; Toxicity.

Introduction

Environmental management is becoming increasingly dependent on quantitative analysis of environmental and health risks associated with exposure to chemical contaminants. Exposure to chemical pollutants can occur via primary pathways (e.g., inhalation of polluted air or drinking contaminated water) and/or secondary pathways (e.g., ingestion of contaminated food) and therefore requires information on chemical distribution in the environment (Cohen 1986a,b,c).

The distribution of chemicals in the multimedia environment is the consequence of complex physical, chemical, and biological processes, as illustrated schematically in Fig. 1. For example, a chemical that is released to the atmosphere can be deposited onto vegetation, soil, and surface water by both dry and wet deposition. Many examples of multimedia pollutant partitioning have been documented. Examples of chemicals that have been detected in multiple environmental media include DDT (Harrison et al. 1970; Woodwell et al. 1971; Cramer 1973; Singh and Agarwal 1995; Spencer et al. 1996); trichloroethylene and chloroform (Khalil et al. 1983; Cohen and Ryan 1985); benzene (Fishbein 1984; Hattemer-Frey et al. 1990; Duarte-Davidson et al. 2001);

polycyclic aromatic hydrocarbons (Ryan and Cohen 1986; Osborne and Crosby 1987; Vaessen et al. 1988; Lioy and Greenberg 1990; Yaffe et al. 2001); dioxins (Travis and Hattemer-Frey 1989; Hwang 1990; Suzuki et al. 1998, 2000); polychlorinated biphenyls (PCBs) (Nisbet and Sarofin 1972; Swackhammer and Armstrong 1986; Baker and Eisenreich 1990; Macdonald and Metcalfe 1991; Loganathan et al. 1997; Notarianni et al. 1998); lead (Huntzicker et al. 1975; Chadha et al. 1998); mercury (Anderberg et al. 1989; Schroeder et al. 1989; Palusova et al. 1991; Hamasaki et al. 1995; Richardson et al. 1995; Stein et al. 1996; Rasmussen et al. 1998); and chromium (VI) (Kimbrough et al. 1999).

Multimedia field monitoring of all chemicals of concern is not feasible. Therefore, multimedia models of pollutant fate and transport are attractive tools for assessing the potential for multimedia impact of chemical pollutants (Taboas 1993; Renner 1995; Eisenberg et al. 1998). Multimedia models range from simple compartmental models (Cohen 1986a,b,c; Mackay 1991; Cohen and Clay 1994; Cowan et al. 1994; Maddalena et al. 1995; Eisenberg et al. 1998; Trapp and Matthies 1998) to complex models of detailed spatial resolution (Onishi et al. 1990; Mills et al. 1997; Johnston et al. 2000). Multimedia models are useful tools that can complement field monitoring, assist in forecasting and/or rank potential exposure and human health problems, and help reconcile emissions with estimated or monitored environmental contaminant concentrations.

Multimedia analysis is typically a tiered process. A screening-level multimedia analysis is the first phase that can serve to identify major exposure pathways and monitoring data gaps. Therefore, information from such analysis can also be used in the design of monitoring field studies. Subsequent phases, if required, may consist of detailed single-medium models or more extended multimedia analysis coupled with monitoring studies. Examples of such multimedia approaches are the Neuse River Basin of North Carolina study (Cooter et al. 1999a,b) and the Lake Michigan Mass Balance (LMMB) study (USEPA 1997a). Other recent

¹Multimedia Envirosoft Corp., 2288 Westwood Blvd., Suite 214, Los Angeles, CA 90064.

²National Oceanic and Atmospheric Administration/ARL, Atmospheric Sciences Modeling Div., Applied Modeling Research Branch, Mail Drop 80, Research Triangle Park, NC 27711.

Note. Discussion open until September 1, 2002. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on October 3, 2001; approved on October 10, 2001. This paper is part of the *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, Vol. 6, No. 2, April 1, 2002. ©ASCE, ISSN 1090-025X/2002/2-70-86/\$8.00+\$5.00 per page.

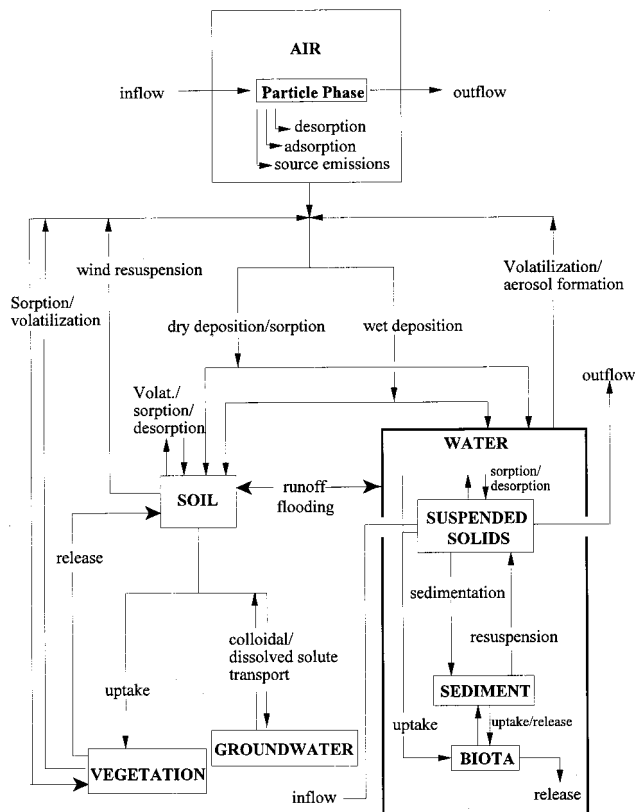


Fig. 1. Intermedia transport processes in multimedia system

multimedia modeling research supported by the U.S. Environmental Protection Agency (USEPA) includes the finite-source multimedia, multipathway, and multireceptor risk assessment (3MRA) (USEPA 1999b) and the Hazardous Waste Identification Rule frameworks (FRAMES-HWIR) (USEPA 1999a), the Total Risk Integrated Methodology (TRIM) system (USEPA 1996), and the Multimedia Integrated Modeling System (MIMS) (Johnston et al. 2000).

Overview of Multimedia Transport and Fate Modeling

Multimedia models of environmental fate and transport are mathematical constructs that describe the entry, movement, and distribution of chemicals within the environment. In the context of integrated multimedia analysis, the environment includes both abiotic and biotic media (including the human receptor) with intermedia transport processes leading to chemical mass exchange among the various media. There are basically four types of multimedia modeling approaches:

1. Integrated spatial multimedia models;
2. Linked spatial single-medium models;
3. Compartmental ("well-mixed" media) models; and
4. Integrated spatial-multimedia-compartmental models (ISMCM).

Integrated spatial-multimedia models may be defined as models that describe chemical transport and fate in all the pertinent media via spatial models, with interactions among media specified through well-posed intermedia boundary conditions, and where the set of medium-specific transport equations are solved simultaneously. Such models are not yet fully developed and,

given their expected complexity, significant computational resources, and data needs, are likely to be slow to emerge as practical tools.

Linked spatial single-medium models consist of serially linked, single-medium transport models (that is, for air, water, soil, and other media of interest) that first solve for concentrations in a given specific medium. Calculated intermedia fluxes (for example, due to dry deposition) are then used as pseudo-source inputs to solve for contaminant concentrations in other adjoining media. Therefore, if feedback mechanisms are not built through the physical mathematical boundary conditions, mass conservation cannot be guaranteed. Examples of the above type of multimedia models include UTM-TOX (Patterson et al. 1984); ALWAS (Tucker et al. 1984); TOX-SCREEN (Hetrick and McDowell-Boyer 1984); MEPAS (Mills et al. 1997; McDonald and Gelston 1998); MMSOILS (USEPA 1988; Stasko and Fthenakis 1993); GENII (Maheras et al. 1994; Maheras 1995); RESRAD (Cheng and Yu 1993); and HWIR (USEPA 1999a). Detailed comparisons of MEPAS, MMSOILS, and RESRAD were published by Mills et al. (1997) and Laniak et al. (1997), and a detailed review of MEPAS, MMSOILS, GENII, and RESRAD was conducted by the U.S. Department of Energy (DOE 1993).

In order to reduce the potential for gross mass conservation errors, software implementations of these linked models have typically utilized executive modules to monitor accumulated contaminant mass and mass transfer from one medium to another. This approach, however, falls short of creating a dynamic system in which temporal compartmental interactions can be accurately evaluated. The above multimedia models have proven useful for hazardous waste-site analyses, but they require significant user training and a large number of input parameters due to their site-specific character.

Compartmental mass-balance models, which have become popular over the last decade, are simpler and easy to execute relative to linked model systems and require fewer parameters (about 1 to 2 orders of magnitude less than for serially linked models). The literature makes a distinction between compartmental and fugacity-type multimedia models. Compartmental fugacity-type models express the driving forces for diffusional interfacial mass transfer (among compartments) in terms of fugacity (or chemical potential) instead of concentration-driving forces (Appendix) (Mackay 1991; Trapp and Matthies 1998). Expressing model output in terms of media-specific chemical fugacities is useful for interpreting the tendency of pollutants to accumulate in various media (Appendix).

In general, however, writing mass-balance equations in terms of concentration variables is more convenient, especially when spatial transport (for example, diffusion in soil and sediment) and intermedia processes that are unconstrained by equilibrium are involved (for instance, dry and wet deposition of particle-bound chemicals and wind resuspension of soil) (Cohen and Clay 1994; Yaffe et al. 2001). Most available models require user input of intermedia transport parameters (or default parameters) and thus are cumbersome to use when temporal dynamics (that is, due to source variations and meteorology) and region-specific parameters need to be considered. Multimedia mass-balance models that employ well-mixed compartments (Cohen 1986a,c, 1987) include, for example, GEOTOX (McKone et al. 1987); CalTox (CalEPA 1993); the fugacity-based models [Mackay (1991), Suzuki et al. (1998), Trapp and Matthies (1998), Edwards et al. (1999), and references therein]; and mass-balance models such as Kinetic (Wiersma 1979). An expanded multimedia compartmental model that improves spatial resolution by using multiple subcom-

partments per given medium is the Total Risk Integrated Model (TRIM) (USEPA 1996).

The compartmental models listed above typically assume that the soil and sediment are well mixed or consist of a number of well-mixed subcompartments. Intermedia processes, such as dry and wet deposition and wind resuspension, are typically incorporated by specifying as input intermedia fluxes or associated intermedia parameters (e.g., average dry-deposition velocity). Most compartmental models do not account for the effect of the particle-size distribution on intermedia transport of particle-bound chemicals. Time variability of sources and meteorological parameters can significantly influence multimedia dynamics, but these are also usually omitted due to the added complexity. It is also noted that vegetation is usually not considered as an integral part of the overall multimedia mass balance model.

ISMCMs include both "well-mixed" and spatial compartments tightly integrated through well-posed intermedia physical boundary conditions. The spatial-multimedia-compartmental model (SMCM) represents an early application of the approach (Cohen et al. 1990a,b; Onishi et al. 1990; Hsieh and Quimette 1994) followed by the COSMCM, which included tracking of particle-bound chemicals (Cohen and Clay 1994; Cohen and Van de Water 1994; Cooter et al. 1999b; USEPA 1997b). The above models demonstrated a wide range of applicability, but lacked internal estimates of intermedia transport parameters and were deficient in accounting for time-dependent parameter variability.

In this first part of a two-paper series (Cohen and Cooter 2002), a general multimedia modeling framework is presented that extends the earlier ISMCM approach. The approach is based on a combination of spatial and compartmental transport elements to form a hybrid model suitable for integrated environmental multimedia analysis. The model is formulated with the following requirements: (1) mathematical integration of all environmental media to ensure mass conservation; (2) mechanistic description of intermedia transport parameters is a priority whenever possible, followed by empirical approaches as a second choice; and (3) biotic media (for example, vegetation) are integral components of the multimedia system. In the subsequent sections of Part I, the basic modeling approach is reviewed, with emphasis on the issues that are of interest to the environmental multimedia analyst. The software implementation of the model and illustrative examples are provided in Part II of this paper (Cohen and Cooter 2002).

Modeling Multimedia Environmental Distribution for Toxics (Mend-Tox)

Overview

The modeling framework for assessing the multimedia environmental distribution of toxics (Mend-Tox) is based on describing the environment as a combination of coupled uniform and non-uniform media. The various media interact via intermedia transport processes, as illustrated in Fig. 1. In the soil and sediment media, which are taken to be nonuniform compartments, transport is described by a 1D convective-diffusion partial differential equation (PDE). All other media are treated as uniform compartments. This modeling approach sacrifices spatial resolution, especially in the atmosphere and water compartments. However, we note that limited evaluation of spatial changes can be carried out by sequential runs of adjacent regions, with the output from one used as the input to the next. A more elaborate expansion of the approach could allow for multiple compartments for each medium, but at the expense of adding model parameters.

In the Mend-Tox modeling approach, temporal dynamics are retained to allow assessment of the impact of temporal variations of meteorological parameters (for example, temperature and wind speed) and source-emission rates. Transport equations for the various media are coupled through intermedia transport processes (Tables 1 and 2 and Fig. 1). Clearly, in order to reduce the number of model parameters, implementation of the overall multimedia model (or simulator) for practical applications requires internal theoretical or empirical descriptions of intermedia transport processes associated with the gaseous, dissolved, and particle phases (Tables 1 and 2). The basic equations used to describe the multimedia system are discussed in the following section.

Model Equations

Uniform Compartments

The air-gas, air-particle, water, suspended solids, vegetation (plant foliage and root subcompartments), and aquatic biota compartments are all considered to be uniform. The atmospheric particle phase is divided into up to 300 size fractions (or subcompartments), each also taken to be a uniform compartment, to account for the dependence of dry and wet deposition on particle size. The general form of the chemical balance equation for a uniform (that is, "well-mixed") compartment is expressed as

$$\frac{d}{dt}[C_i V_i] = \sum_{k=1}^N (Q_{ki}^{in} C_{ki}^{in} - Q_i^{out} C_i) + \sum_{l=1}^M \sum_{j=1}^{P^{(l)}} I_{li}^{j} - \sum_{l=1}^M K_{il} A_{il} (C_i - C_l H_{il}) + \zeta_i k_i^r C_i V_i + S_i; \quad i=1, \dots, M \quad (1)$$

where V_i is the volume (m^3) of compartment i in which the chemical concentration is denoted by C_i ($gmol/m^3$); C_{ki}^{in} =chemical concentration in the advective input stream, Q_{ki}^{in} (m^3/h) flowing from adjacent compartment k to compartment i ; N =number of adjacent compartments to i for which convective mass exchange takes place; Q_i^{out} =convective outflow from compartment i ; and A_{il} =interfacial area between compartment l and compartment i (m^2). The overall mass-transfer coefficient from transport between compartments i and l the system of M compartments, K_{il} (m/h), can be expressed as the combination of the resistances to mass transfer in the adjoining phases given by

$$\frac{1}{K_{il}} = \frac{1}{k_i} + \frac{H_{il}}{k_l H_{il}} \quad (2)$$

where k_i and k_l =phase i and l mass-transfer coefficient for compartment i (m/h), and H_{il} =dimensionless equilibrium partition coefficient that quantifies the ratio between the chemical concentration in compartment i and the chemical concentration in compartment l [that is, $H_{il}=C_i/C_l$, where C_l is the chemical concentration ($gmol/m^3$) in compartment l]. It is often convenient in numerical models to express partition coefficients in terms of fugacity capacity ratios, as presented in the Appendix. The reaction term is signified with a coefficient, ζ_i , and assigned values of +1 for a pollutant-producing reaction and -1 for a consumption reaction; and a first-order reaction rate coefficient, k_i^r ($1/h$). The rates of physical intermedia transport processes (other than interfacial diffusion) between compartments l and i are denoted by I_{li}^j ($gmol/h$), where j denotes the specific transport process (for example, wet deposition of gaseous and particle-bound contaminants, dry deposition of particle-bound pollutants, resuspension of contaminated soil particles, sedimentation/resuspension of sediment particles, and chemical transport from soils due to runoff),

Table 1. Intermedia Transport Fluxes

Intermedia transport pathways ^a	Transport mechanism	Intermedia transport flux (gmol/m ² h)	Nomenclature ^b
Air⇒surface water	Gas absorption/volatization	$k_{wa}(C_a^{(g)}H_{aw} - C_w)$	k_{wa} —Water/air mass transfer coefficient H_{aw} —Air/water partition coefficient $C_a^{(g)}$ —Chemical concentration in gas phase C_w —Chemical concentration in water
	Precipitation scavenging of gases	$C_a^{(g)}H_{wa}\hat{R}\Lambda^{(g)}$	$\Lambda^{(g)}$ —Gas phase rain scavenging coefficient \hat{R} —Rainfall intensity (m/h) $H_{wa} = I/H_{aw}$
Air⇒suspended solids (in water)	Wet deposition of particles	$C_a^{(p)}\hat{R}\Lambda^{(p)}$	$C_a^{(p)}$ —Atmospheric chemical concentration in particle phase $\Lambda^{(p)}$ —Precipitation washout ratio for particle-bound chemical
	Dry deposition of particles	$C_a^{(p)}v_d^w$	v_d^w —Dry deposition velocity to water (m/h)
Air⇒soil	Volatilization/absorption (dry deposition) and wet deposition (chemical transfer due to rainwater infiltration)	Soil/air boundary condition (@ $z=0$): $V_{sm}^{eff}C_{sm} - D_{sm}^{eff}(\partial C_{sm}/\partial z)$ $= C_{wr}K_w^r - k_{a,sm}[C_{sm}/H_{sm,sa} - C_a^{(g)}]$	C_{wr} —Chemical concentration in rainwater C_{sm} —Chemical concentration in soil matrix V_{sm}^{eff} —Effective velocity in soil (m/h) $H_{sm,sa}$ —Soil matrix/soil air partition coefficient D_{sm}^{eff} —Effective soil matrix diffusivity (m ² /h) K_w^r —Water infiltration velocity at surface (m/h) $k_{a,sm}$ —Air/soil matrix mass transfer coefficient (m/h)
	Wet deposition of particles	$C_a^{(p)}\hat{R}\Lambda^{(p)}$	
	Dry deposition of particles	$C_a^{(p)}v_d^s$	v_d^s —Chemical dry deposition velocity to soil (m/h)
	Wind resuspension of particle-bound pollutants	$-v_{resp}(C_{sm}/H_{sm,sp})_{z=0}$	v_{resp} —Effective wind soil resuspension velocity (m/h) $H_{sm,sp}$ —Soil matrix/soil particle partition coefficient
Air (gas phase)⇒ Particulate phase	Gas/particle sorption/desorption	$k_{gp}(C_a^{(g)} - H_{gp}C_a^{(p)})$	k_{gp} —Gas/particle mass transfer coefficient H_{gp} —Gas/atmospheric particle partition coefficient
Surface water⇒ Sediment	Uptake/release of dissolved chemical	Water/sediment surface boundary condition @ $z=0$: $V_{sdm}^{eff}C_{sdm} - D_{sdm}^{eff}(\partial C_{sdm}/\partial z)$ $= k_{w,sdm}[C_w - C_{sdm}/H_{sdm,sdw}]$	$k_{w,sdm}$ —Water/sediment mass transfer coefficient $H_{sdm,sdw}$ —Sediment/sediment water partition coefficient V_{sdm}^{eff} —Effective convective velocity in sediment (m/h) D_{sdm}^{eff} —Effective diffusion coefficient in sediment (m ² /h) C_{sdm} —Chemical concentration in sediment matrix
Surface water⇒ suspended solids	Adsorption/desorption	$k_{w,ss}(C_w - H_{w,ss}C_{sus})$	$k_{w,ss}$ —Water/suspended solids mass transfer coefficient $H_{w,ss}$ —Water/suspended solids partition coefficient C_{sus} —Chemical concentration in suspended solids

Table 1. (Continued).

Intermedia transport pathways ^a	Transport mechanism	Intermedia transport flux (gmol/m ² h)	Nomenclature ^b
Suspended solids (in water)⇒sediment	Sedimentation of suspended solids	$R_{sed}C_{sus}$	R_{sed} —Suspended solids sedimentation velocity (m/h)
	Resuspension of sediment solids	$-R_{rsp}C_{sdm}/H_{sdm,seds}$	$H_{sdm,seds}$ —Sediment matrix/sediment solids partition coefficient R_{rsp} —Effective resuspension velocity (m/h)
Sediment⇒groundwater	Exchange at sediment/groundwater boundary	Sediment/groundwater boundary condition @ $z = d_s$: $V_{sdm}^{eff}C_{sdm} - D_{sdm}^{eff}(\partial C_{sdm}/\partial z)$ $= k_{I,sdm}[(C_{sdm}/H_{sdm,I}) - C_I]$	$k_{I,sdm}$ —Sediment/bottom interface mass transfer coefficient $H_{sdm,I}$ —Sediment/groundwater partition coefficient C_I —Interfacial concentration in the porous matrix phase at bottom boundary
Soil⇒surface water	Runoff of wet scavenged chemical (dissolved in rainwater)	$f_w R_0 C_a^{(g)} H_{wa} \Lambda^{(g)}$	R_0 —Runoff (m/h) f_w —Fraction of runoff diverted to water body
Soil⇒suspended solids (in water)	Runoff of precipitation scavenged particle-bound chemical	$f_w R_0 C_a^{(p)} \Lambda^{(p)}$	
Soil⇒groundwater	Exchange between and groundwater	Boundary condition @ $z = L_s$ $V_{sm}^{eff}C_{sm} - D_{sm}^{eff}(\partial C_{sm}/\partial z) = k_{gw,sm}[(C_{sm}/H_{sm,sw}) - C_{gw}]$	$k_{gw,sm}$ —Groundwater/soil matrix mass transfer coefficient $H_{sm,sw}$ —Soil matrix/soil water partition coefficient C_{gw} —Chemical concentration in groundwater
Air⇒foliage	Absorption/volatilization	$k_{af}(C_a^{(g)} BCF_{fa} - C_f)$	k_{af} —Air/foliage mass transfer coefficient C_f —Chemical concentration in foliage BCF_{fa} —Foliage/air bioconcentration factor
	Dry deposition of particle-bound chemical	$v_{d,veg} C_a^{(p)} I_{fd} I_{fp}$	$v_{d,veg}$ —dry deposition onto foliage (m/h) I_{fd} —Fraction of dry particles intercepted by foliage I_{fp} —Fraction of intercepted chemical absorbed by foliage
	Wet scavenging of particle-bound chemicals	$\hat{R} \Lambda^{(p)} I_f^{(r)} C_a^{(p)}$	$I_f^{(r)}$ —Fraction of rainfall intercepted by foliage
	Wet scavenging of gases	$\hat{R} I_f^{(r)} \Lambda^{(g)} H_{wa} C_a^{(g)}$	
	Chemical loss from foliage due to evapotranspiration	$-T_r f_{T_r} BCF_{af} H_{wa} C_f$	C_f —Chemical concentration in foliage (gmol/m ³) T_r —Water uptake rate via roots (m ³ /h) f_{T_r} —Evapotranspiration fraction of water uptake BCF_{af} —Chemical air/foliage bioconcentration factor (= 1/BCF _{fa})
Foliage⇒soil	Washoff from foliage surface (during rainfall)	$\dot{V}_w^f C_a^{(p)} \Lambda^{(p)}$	\dot{V}_w^f —Foliage surface water loss rate/foliage (leaf)area during rainfall (m ³ /m ² h) h_∞ —Water volume retained by foliage per foliage area during rainfall (m ³ /m ²) $\dot{V}_w^f = \alpha' h_\infty (1 - e^{-\alpha' t}) A_f$; $\alpha' = (\hat{R} A_s F_{veg} I_f^{(r)})/h_\infty$

Table 1. (Continued).

Intermedia transport pathways ^a	Transport mechanism	Intermedia transport flux (gmol/m ² h)	Nomenclature ^b
Root⇒foliage (leaf)	Translocation of chemical from root to foliage (leaf)	$T_r(C_r/BCF_{rw})(1-\sigma_r)$	BCF_{rw} —Root/water bioconcentration factor σ_r —Membrane reflection coefficient for foliage/root transport C_r —Chemical concentration in the roots (gmol/kg)
Foliage (leaf) ⇒root	Chemical transport from foliage (leaf) to root by water transport	$T_r(1-f_{Tr})BCF_{af}H_{wa}\sigma_r C_f$	
Soil⇒root	Diffusional mass transfer	$k_{sr}[\bar{C}_s - (C_r/BCF_{rs})]$	\bar{C}_s —Average concentration in the soil root zone (gmol/kg) k_{sr} —Soil/root mass transfer coefficient (m/h) BCF_{rs} —Root/soil matrix bioconcentration factor
	Chemical transport via soilwater uptake by roots	$T_r\bar{C}_sBCF_{rs}/BCF_{rw}$	
Water⇒biota	Uptake/release	$k_{wb}(C_w - C_b/H_{bw})$	C_b —Concentration in biota (gmol/m ³) k_{wb} —Overall water/biota mass transfer coefficient (m/h) H_{bw} —Biota/water partition coefficient

Note: For mass transfer and partition coefficients, when either one of two interacting media are designated by more than a one-letter subscript, the subscripts are separated by a comma.

^aUnits: concentration (gmol/m³); mass transfer coefficients (m/h); area (m²); volume (m³); partition coefficients are dimensionless.

^bA positive flux is in the direction of the arrow in column 1.

and $P^{(l)}$ =number of such exchange processes between compartments l and i . Finally, S_i =source emission rate into compartment i (gmol/h). Various intermedia transport processes (Fig. 1) are responsible for the coupling of the multimedia system of equations (Eq. 1). Table 1 provides a list of the various intermedia transport fluxes in Eq. (1), with the literature sources for the associated major transport parameters given in Table 2.

The set of equations represented by Eq. (1) is most conveniently expressed in a matrix format:

$$\dot{\underline{C}} = \underline{K}\underline{C} + \underline{S} \quad (3a)$$

with the initial conditions specified as

$$\underline{C} = \underline{C}(0) \quad \text{at } t=0 \quad (3b)$$

where \underline{C} and $\underline{C}(0)$ =concentration vectors at time t and initially, respectively; $\dot{\underline{C}}$ =time rate of change of concentrations in the various media; \underline{K} =parameter matrix, which can be time-dependent due to temporal variations of meteorological parameters (for example, temperature and wind speed) affecting various model parameters; and \underline{S} =source emission rate vector. In the present approach, the above set of equations is solved numerically using a corrector-predictor method (Davis 1984; Cohen et al. 1990b) suitable for stiff ordinary differential equations (ODEs). In the integrated model, uniform compartments are coupled with nonuniform compartments (soil and sediment) through intermedia fluxes at the soil/air, soil/vegetation, and sediment/water boundaries (see the section on nonuniform components).

Chemicals in the atmosphere can be present in either a gaseous or aerosol-bound form (both particles and liquid aerosols). In a strict sense, in the present model, only particles are considered for the aerosol phase. However, one can use the same model equations, given appropriate gas/particle partition coefficients, to also simulate liquid aerosols, although not simultaneously with atmo-

spheric particles. It is convenient to express the total concentration of the chemical in the atmosphere, C_a , as the sum of the chemical gaseous and particle-bound concentrations (gmol/m³ air), given by

$$C_a = C_a^{(g)} + C_a^{(p)} \quad (4)$$

where $C_a^{(g)}$ and $C_a^{(p)}$ are the chemical concentration (gmol/m³) in the vapor and particle-bound forms, respectively. In the special case when the air gaseous and particle phases can be assumed to be in equilibrium, the fraction of the chemical in the air phase that is bound to atmospheric particles, θ_p (dimensionless), is defined as

$$\theta_p = C_a^{(p)}/C_a \quad (5)$$

and is related to the gas/particle partition coefficient, H_{gp} ($=C_a^{(g)}/C_a^{(p)}$) as

$$\theta_p = 1/(H_{gp} + 1) \quad (6)$$

When the above equilibrium approximation is invoked, the overall mass balance for the chemical in the atmospheric compartment is simply the sum of the chemical balance equations for the gaseous and particle-bound forms of the chemical. If gas/particle equilibrium cannot be invoked, then separate chemical mass balances must be written for each of the gas and particle phases (Cohen and Clay 1994).

The atmospheric particle-size distribution can significantly impact atmospheric intermedia processes (for example, dry and wet deposition) of particle-bound chemicals (Tsai et al. 1991; Seinfeld and Pandis 1998) and their accumulation in the soil and water media (Tsai et al. 1991; Cohen and Clay 1994). Temporal variations in the number concentration of particles can be evaluated by a size-fraction (population) mass-balance equation on the particulate phase:

Table 2. Summary of Selected Intermedia Model Parameters

Parameter	Source of Mend-Tox input information ^a
(a) Partition coefficients	
Fugacity capacities	Appendix and Table 5
Octanol/water partition coefficient (K_{ow})	User-input
Organic carbon/water partition coefficient (K_{oc})	User-input
Bioconcentration factors (aquatic)	User-input
Henry's law constant	User-input
Correlations of foliage (leaf)/atmosphere and root/soil partition coefficients	Bacci et al. (1990, 1992), Briggs et al. (1982, 1983), Topp et al. (1986), Trapp and Matthies (1995), Paterson et al. (1994)
Correlations of particle/gas partition coefficient	Junge (1977), Pankow (1987, 1991)
Soil/air and sediment/water partition coefficient	Appendix, Non-Uniform Compartments section
(b) Intermedia transfer processes and intermedia transfer factors	
Gas-side mass transfer coefficient at the atmosphere-soil interface ($k_{a,sm}$)	Fernandez de la Mora and Friedlander (1982) Brutsaert (1975)
Overall volumetric water/biota mass transfer coefficients	Cohen and Ryan (1985), Barber et al. (1991)
Waterside mass transfer at water/suspended solid interface	Rowe et al. (1965)
Sediment-water mass transfer coefficient (water-side)	Thibodeaux and Becker (1982), Mayer (1988)
Air-water mass transfer coefficient (water-side)	Cohen and Ryan (1985), Mackay and Yeun (1983), Shen et al. (1993)
Air-water mass transfer coefficient (airside)	Brutsaert (1975), Mackay and Yeun (1983)
Plant-air mass transfer coefficient	Paterson et al. (1994)
Particle dry deposition to land surface	Slinn (1982), Sehmel and Hodgson (1980)
Particle dry deposition velocity to water surface	Williams (1982)
Rain scavenging coefficient (particles and gas)	Tsai et al. (1991)
Runoff rate (R_0) and soil erosion	Heimstra (1968), Novotny and Chesters (1981), Goldman et al. (1986)
Soil drying rate	Van Bavel (1966)
Rain infiltration (into soil)	Broadbridge and White (1988a,b), Broadbridge et al. (1996)
Resuspension and sedimentation of sediment particles (in water)	Ackers and White (1975), Vohra (1996), Farley and Morel (1986), Hunt (1982), Lick (1994), Luettich et al. (1990), Hawley and Lesht (1992)
Wind resuspension of soil particles	Cowherd et al. (1985,1988), Gillette et al. (1980)
(c) Diffusion coefficients	
Air phase diffusion coefficient (D_a)	Reid et al. (1987), Fuller et al. (1966)
Water phase diffusion coefficient (D_w)	Reid et al. (1987), Wilke and Chang (1955), Hayduk and Laudie (1974), Hayduk et al. (1982)
Effective diffusivity in the soil matrix (D_{sm})	Eq. (17)
Air and water phase tortuosities (τ_a and τ_w)	Sallam et al. (1984), Grifoll and Cohen (1996)
Effective diffusivity in the sediment (D_{sdm})	Eq. (17)
(d) Meteorological parameters	
Temperature	Monthly average for atmosphere and water, seasonal average for soil
Wind speed	Seasonal average and fastest-mile wind speed frequency
Rainfall rate and duration	User input with stochastic distribution by Mend-Tox

^aLiterature references for correlations or estimation methods for intermedia parameters or transport process.

$$\begin{aligned} \frac{d(V_a N_{j,a}^{(p)})}{dt} = & (Q_a^{\text{in}} N_{j,a}^{(p),\text{out}} - Q_a^{\text{out}} N_{j,a}^{(p)}) - N_{j,a}^{(p)} (v_{dw,j} A_{aw} + v_{ds,j} A_{as}) \\ & - N_{j,a}^{(p)} \hat{R} (A_{as} + A_{aw}) \Lambda^{(p)} + \hat{S}_j^{(p)} V_a \\ & + R_{j,rs} A_{as} N_{j,sm}^{(p)} \Big|_{z=0}; \quad j = 1 \dots M \end{aligned} \quad (7)$$

where the subscripts a and p denote the atmospheric and the particle phases, respectively; subscript j denotes a given particle size range for particle size distribution divided into M size ranges; V_a =atmospheric compartment volume (m^3); A_{aw} and A_{as} =atmosphere-water and atmosphere-soil interfacial areas (m^2), respectively; $N_{j,a}^{(p)}$ =number concentration of particles for size range j in a unit volume of air [that is, $N_{j,a}^{(p)} = n_j(D)d(D)$; number particles/ m^3 of air, where D denotes the particle diameter (μm) and $n_j(D)$ =particle size distribution]; $N_{j,a}^{(p),\text{out}}$, $N_{j,sm}^{(p)} \Big|_{z=0}$, $N_{j,w}^{(p)}$ =number concentrations of particles for size range j (number/ m^3 of air) outside the study region, at ground level (number/ m^3 soil), and in rainwater (number/ m^3 of water), respectively; Q_a^{in} and Q_a^{out} =flow rates into and out of the atmospheric compartment; \hat{R} =rainfall rate (m/h); and $\Lambda^{(p)}$ =particle-rain scavenging ratio ($\Lambda^{(p)} = N_{j,w}^{(p)} / N_{j,a}^{(p)}$). The dry, deposition velocities to the water and soil surfaces are denoted by $v_{dw,j}$ and $v_{ds,j}$, respectively; $R_{j,rs}$ =resuspension rate coefficient (m/h) of soil particles of size range j ; and $\hat{S}_j^{(p)}$ =source emission of particles of size range j into the atmosphere (number particles/ $\text{m}^3 \cdot \text{h}$). A convenient representation of the initial particle-size distribution is the trimodal lognormal distribution (Whitby 1978; Jaenicke 1993), with the appropriate particle size distribution parameters for specific scenarios.

In the water compartment, suspended solids represent a distinct compartment designated to track the particle-bound form of the chemical in the aquatic environment. The suspended solids (in water) interact with the water compartment (chemical adsorption and desorption); sediment (deposition and resuspension); atmosphere (through dry and wet deposition); and soil (through runoff). In the present level of multimedia modeling, the dynamics of the suspended-solids size distribution is not considered. The size distribution of suspended particles could be tracked at a multimedia level of analysis, but at the cost of significant added overall model complexity.

The aquatic biota is a complex medium that may be modeled by a suitable food-web model (Thomann 1989; Barber et al. 1991, 1994; Vohra 1996; Campfens and Mackay 1997). However, in many situations the simple one-compartment model or linear food-chain model may be sufficient for first-order analysis. A one-compartment model is a reasonable screening-level approach where chemical uptake is by interfacial diffusion [see third term on the right-hand side of Eq. (1)]. Even with such a simple model, a variety of simulation scenarios can be explored by specifying a bioconcentration or bioaccumulation factor and a biota/water mass transfer coefficient. The coupling of Mend-Tox analysis with a food-chain model is discussed in Part II of this work (Cohen and Cooter 2002).

The vegetation compartment can be modeled at different levels of complexity (Trapp and McFarlane 1995). In the present approach, a simple vegetation model is used whereby the vegetation compartment is divided into foliage and roots, with transport between these compartments facilitated primarily by the shoots. The accumulation of particle-bound chemical on the foliage surface is modeled by the following mass balance equation:

$$\frac{dm_f}{dt} = N_{d_{\text{veg}}} A_s F_{\text{veg}} + N_{wf}^{(\text{rain})} A_s F_{\text{veg}} - J_w^{(f)} - N_r^{(f,s)} M_f \quad (8)$$

where m_f =mass of particle-bound chemical accumulated on the leaf surface; $N_{d_{\text{veg}}}$ and $N_{wf}^{(\text{rain})}$ =chemical fluxes ($\text{gmol}/\text{m}^2\text{h}$) due to dry and wet deposition of particle-bound chemicals (from the atmosphere) onto foliage; $N_r^{(f,s)}$ =rate of degradation per unit mass of foliage ($\text{gmol}/\text{kg}/\text{h}$); M_f =foliage mass; A_s =soil surface area (m^2); and F_{veg} =fraction of soil surface covered by vegetation. The rate of chemical washoff (gmol/h) from the leaf surface $J_w^{(f)}$ (Table 1) is proportional to the water washoff rate (during rainfall); $\dot{V}_w^{(f)}$ ($\text{m}^3/\text{m}^2/\text{h}$), which can be estimated from an approximate water balance on the leaf canopy of area (Table 1). Net chemical accumulation in foliage involves exchange of the dissolved and gaseous forms between foliage and roots, and foliage and the atmosphere, as expressed by

$$\frac{d}{dt} (C_f V_f) = N_{af} A_f + N_{d_{\text{veg}}} A_s + J_{rf} - J_{ev} - J_{c_{fr}} - J_r^{(f)} \quad (9)$$

where C_f and V_f =foliage chemical concentration (gmol/m^3) and volume (m^3), respectively; N_{af} =air-to-leaf gaseous flux ($\text{gmol}/\text{m}^2\text{h}$); $N_{d_{\text{veg}}}$ =chemical penetration flux into the interior of the foliage compartment ($\text{gmol}/\text{m}^2\text{h}$) associated with dry deposition of the particle-bound chemical; J_{rf} =root-to-foliage exchange rate (gmol/h); J_{ev} =chemical loss rate via evapotranspiration (gmol/h); $J_{c_{fr}}$ =convective chemical transport rate from foliage to roots (gmol/h); $J_r^{(f)}$ =rate of chemical degradation (gmol/h) in the foliage compartment; and A_f and A_s denote the surface areas (m^2) of foliage and soil surface (in the vegetated region), respectively. Chemical accumulation in the root compartment involves exchange with foliage and uptake from the soil (Topp et al. 1986; Boersma et al. 1988; Trapp and Matthies 1995; Trapp and McFarlane 1995), as described by the following mass balance:

$$\frac{d}{dt} (C_r V_r) = N_{sr} A_r + J_{sr} + J_{fr} - J_{rf} - J_r^{(r)} \quad (10)$$

where C_r and V_r =root chemical concentration (gmol/m^3) and volume (m^3), respectively; N_{sr} =chemical uptake flux ($\text{gmol}/\text{m}^2\text{h}$) from the soil by diffusion; J_{sr} =soil-to-root uptake rate via water uptake (gmol/h); J_{fr} and J_{rf} =chemical transport rates (gmol/h) from foliage to root and root to foliage by water movement, respectively; $J_r^{(r)}$ =degradation rate in the roots (gmol/h); and A_r =root-soil interfacial area (m^2).

Nonuniform Compartments

The soil compartment consists of soil-solids, soil-air, and soil-water, and the sediment compartment consists of soil-water and soil-solids. Chemical migration down a soil or sediment column is a slow process, and local equilibrium is often assumed to exist between the above phases of the soil or sediment matrices (Sawhney and Brown 1989; Luckner and Schestakow 1991; Ghadiri and Rose 1992; Grifoll and Cohen 1994). This assumption is appropriate if chemical transport in the soil occurs over time scales that are significantly larger than the transport time scales for other media. Chemical movement through the soil and sediment compartments, for most multimedia scenarios of interest, can be described via a 1D convective-diffusion model in which the local equilibrium assumption is invoked. Accordingly, in the present simplified multimedia approach, the transport equation, in terms of the matrix concentration, C_m (gmol/m^3), can be obtained by

summing the transport equations for the individual soil or sediment phases (Sawhney and Brown 1989; Grifoll and Cohen 1994, 1996) leading to

$$\begin{aligned} \frac{\partial C_m}{\partial t} &= \sum_{j=1}^n \frac{\partial(\theta_j C_j)}{\partial t} \\ &= \sum_{j=1}^n \left[\frac{\partial}{\partial z} \left(\theta_j D_j^{\text{eff}} \frac{\partial \overline{H_{jm} C_m}}{\partial z} \right) - \frac{\partial(v_j \theta_j \overline{H_{jm} C_m})}{\partial z} \right. \\ &\quad \left. + \theta_j \zeta_j k_j \overline{H_{jm} C_m} \right] + N_r, \quad j=1..n \end{aligned} \quad (11)$$

where θ_j =volume fraction of phase j of the porous matrix (dimensionless) consisting of n soil phases; C_j =chemical concentration in phase j of the matrix (gmol/m^3); v_j =convective velocity of phase j ; and N_r designates net rate ($\text{gmol/m}^3 \cdot \text{h}$) of chemical root-soil exchange or sediment-buried organisms exchange. The overall matrix concentration, C_m , is defined as

$$C_m = \sum_{j=1}^n \theta_j C_j \quad (12)$$

where C_j =concentration of the contaminant in phase j of the matrix (gmol/m^3), and the individual porous matrix phase/matrix partition coefficient, $\overline{H_{jm}}$, is defined as

$$\overline{H_{jm}} = C_j / C_m = \frac{H_{jw}}{\sum_{i=1}^m \theta_i H_{iw}} \quad (13)$$

where H_{jw} and H_{iw} =partition coefficients between a given porous matrix phase phase j and the water phase (selected here as the reference phase)

$$H_{jw} = \frac{C_j}{C_w} \quad (14)$$

where C_w =chemical concentration in the soil-water phase (gmol/m^3), and the effective diffusivity in phase j , D_j^{eff} (m^2/h), is defined as

$$D_j^{\text{eff}} = \frac{D_j}{\tau_j} + D_{jD} \quad (15)$$

where D_j , D_{jD} , and τ_j =molecular mass diffusivity (m^2/h), dispersion coefficient (m^2/h), and tortuosity factor in phase j , respectively.

For the special case when the partition coefficient, $\overline{H_{jm}}$, is depth-invariant, Eq. (11) can be expressed as

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial z} \left(D_m^{\text{eff}} \frac{\partial C_m}{\partial z} \right) + \frac{\partial(V^{\text{eff}} C_m)}{\partial z} + R_{\text{eff}} + N_r \quad (16)$$

where the effective diffusion coefficient, D_m^{eff} (m^2/h); effective chemical infiltration velocity, V^{eff} (m/h); and overall reaction rate, R_{eff} ($\text{gmol/cm}^3 \cdot \text{h}$), are defined as

$$D_m^{\text{eff}} = \sum_{j=1}^n \theta_j D_j^{\text{eff}} \overline{H_{jm}} \quad (17)$$

$$V^{\text{eff}} = \sum_{j=1}^n v_j \theta_j \overline{H_{jm}} \quad (18)$$

$$R_{\text{eff}} = \sum_{j=1}^n (\theta_j \zeta_j k_j^r \overline{H_{jm} C_m}) \quad (19)$$

The initial condition for solving Eq. (16) for the soil or sediment matrices can be specified as

$$C_{lm} = C_{lm}(z) \quad \text{at } t=0 \quad (20)$$

where the subscript l designates either the soil or sediment matrices. For chemicals present in the gaseous and dissolved phases (in water), the soil/atmosphere boundary condition is given as

$$V_{sm}^{\text{eff}} C_{sm} - D_{sm}^{\text{eff}} \left(\frac{\partial C_{sm}}{\partial z} \right) = C_w^r K_w^r - k_{a,sm} \left(\frac{C_{sm}}{H_{sm,sa}} - C_a^{(g)} \right) \quad @ \quad z=0 \quad (21)$$

where the first and second terms on the right-hand side of Eq. (21) represent the contribution of wet deposition and atmosphere/soil gas phase mass transfer (that is, dry deposition) of the chemical, respectively, where the subscript sm denotes the soil matrix; C_w^r =chemical concentration in rainwater (at ground level); K_w^r =rainwater infiltration velocity (m/h) at the soil surface; $k_{a,sm}$ =atmosphere/soil mass transfer coefficient (m/h); $H_{sm,sa}$ =soil matrix/soil air partition coefficient, and $C_a^{(g)}$ =chemical concentration (gmol/m^3 air) in the atmosphere (gas phase). During rain events, when the condition of soil ponding is reached, excess water (that is, runoff) is transported outside of the study region or to a water body within the region. A practical approach, in hybrid spatial-compartmental models, is to utilize analytical solutions for the time to ponding, moisture content profile, and infiltration velocity during rainfall (Broadbridge and White 1987, 1988a,b; Broadbridge and Rogers 1990; Broadbridge et al. 1996).

The bottom boundary condition for the soil is a flux-type condition at the soil/groundwater boundary or a zero flux at the soil/impermeable zone boundary:

$$V_{sm}^{\text{eff}} C_{sm} - D_{sm}^{\text{eff}} \left(\frac{\partial C_{sm}}{\partial z} \right) = k_{gw,sm} \left(\frac{C_{sm}}{H_{sm,sw}} - C_{gw} \right) \quad \text{at } z=L_s \quad (22)$$

where $k_{gw,sm}$ =soil/groundwater mass transfer coefficient (m/h); $H_{sm,sw}$ =dimensionless soil matrix/soil water partition coefficient; C_{gw} =contaminant concentration in groundwater (gmol/m^3), and L_s =depth of the soil compartment (m). An impermeable bottom boundary condition (that is, no flux) can be specified by setting the mass-transfer coefficient to be identically zero.

The accumulation of particle-bound chemicals at the soil surface can be evaluated subject to the approximation that deposited particle-bound chemicals are equilibrated with the atmospheric phase or rainwater (that is, at ground level) and also do not infiltrate the soil matrix. Accordingly, the accumulated mass of particle-bound chemical at the soil surface region, $M_s^{(p)}$, is tracked using the following chemical mass balance:

$$\begin{aligned} \frac{dM_s^{(p)}}{dt} &= N_{d_s}^{(p)} A_s (1 - F_{\text{veg}}) + N_{\text{rain}}^{(p)} A_s (1 - F_{\text{veg}}) \\ &\quad + N_{d_f}^{(p)} A_s F_{\text{veg}} (1 - I_f) + N_{\text{veg}}^{(p)} A_s F_{\text{veg}} \\ &\quad - N_{\text{res}}^{(p)} A_s (1 - F_{\text{veg}}) - J_s^r \quad \text{at } t=0 \end{aligned} \quad (23)$$

where $N_{d_s}^{(p)}$ and $N_{\text{rain}}^{(p)}$ =mass fluxes of the particle-bound chemical onto the soil surface due to dry and wet deposition, respectively; $N_{d_f}^{(p)}$ =dry deposition flux onto vegetation areas ($\text{gmol/m}^2 \cdot \text{h}$); F_{veg} =fraction of soil surface area covered by vegetation; I_f =fraction of dry-deposited chemical intercepted by foliage; $N_{\text{veg}}^{(p)}$ =flux from vegetation to the soil surface ($\text{gmol/m}^2 \cdot \text{h}$) due to falloff and washoff from foliage; $N_{\text{res}}^{(p)}$ =chemical loss flux

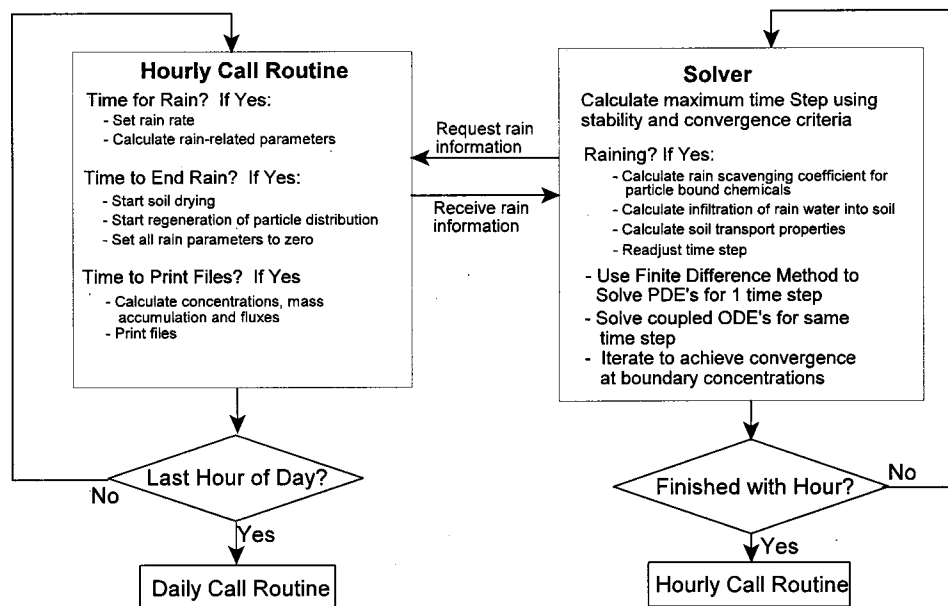


Fig. 2. Solution scheme of coupled transport equations for uniform (ODEs) and nonuniform (soil and sediment PDEs) equations

($\text{gmol}/\text{m}^2 \cdot \text{h}$) due to wind resuspension of particulate matter; and J'_s = chemical degradation rate (gmol/h) at the surface region. While it is known that colloidal size particles can infiltrate the soil along with infiltrating rainwater, the mechanism of colloidal transport in porous media is complex and parameterization of present models is impractical for inclusion in current multimedia analysis.

The sediment/water boundary condition for diffusive transport is treated in a manner analogous to Eq. (22);

$$V_{\text{sdm}}^{\text{eff}} C_{\text{sdm}} - D_{\text{sdm}}^{\text{eff}} \left(\frac{\partial C_{\text{sdm}}}{\partial z} \right) = k_{w,\text{sdm}} \left(C_w - \frac{C_{\text{sdm}}}{H_{\text{sdm},\text{sdw}}} \right) \quad \text{at } z=0 \quad (24)$$

where the subscript "sdm" denotes the sediment matrix; $z=0$ designates the sediment/water interface; C_{sdm} = chemical concentration in the sediment matrix (gmol/m^3); $D_{\text{sdm}}^{\text{eff}}$ = effective diffusivity in the sediment matrix (m^2/h); $V_{\text{sdm}}^{\text{eff}}$ = effective convective velocity in the sediment matrix (m/h); $k_{w,\text{sdm}}$ = water-side mass transfer coefficient water-sediment exchange (m/h); and $H_{\text{sdm},\text{sdw}}$ = sediment/sediment water partition coefficient. At the bottom sediment boundary, a flux condition is specified:

$$V_{\text{sdm}} C_{\text{sdm}} - D_{\text{sdm}} \left(\frac{\partial C_{\text{sdm}}}{\partial z} \right) = k_{l,\text{sdm}} \left(\frac{C_{\text{sdm}}}{H_{\text{sdm},l}} - C_l \right) \quad \text{at } z=d_s \quad (25)$$

where d_s = sediment depth (m); $k_{l,\text{sdm}}$ = water-side mass transfer coefficient at the bottom boundary (m/h); C_l = chemical concentration in a given porous matrix phase (solids or water) at the bottom boundary (gmol/m^3) just at the underside of the sediment bottom interface; and $H_{\text{sdm},l}$ = corresponding chemical partition coefficient.

The accumulation of suspended solid-bound chemical at the sediment surface, $M_{\text{sdm}}^{(ss)}$ (gmol), subject to the assumption of chemical equilibrium between suspended solids and water at the sediment/water boundary, can be described by the following chemical mass balance:

$$\frac{dM_{\text{sdm}}^{(ss)}}{dt} = (N_{\text{sdm},\text{sed}}^{(ss)} - N_{\text{sdm},\text{res}}^{(ss)}) A_{\text{sdm}} - J'_{\text{sdm}} \quad (26)$$

where $N_{\text{sdm},\text{sed}}^{(ss)}$ and $N_{\text{sdm},\text{res}}^{(ss)}$ = sedimentation and resuspension fluxes of the suspended solids-bound chemical ($\text{gmol}/\text{m}^2 \cdot \text{h}$); A_{sdm} = sediment/water interfacial area (m^2), and J'_{sdm} = chemical degradation rate (gmol/h) in the sediment/water surface region. Eq. (26) is coupled with the suspended solids compartment through the exchange of chemical mass via sedimentation and resuspension. It is emphasized that tracking the accumulation of particle-bound chemicals as described above [for the soil and sediment: Eqs. (23) and (26)] is a simplification. In reality, the structure and topologies of the soil and sediment surface regions are constantly changing. However, the added modeling difficulty is not warranted for the present level of multimedia model complexity.

The complete multimedia model consists of the set of coupled ODEs and PDEs presented in this section. Model simulations are carried out by a simultaneous solution of the coupled system of ODEs and PDEs using appropriate time steps. The overall solution procedure consists of alternating between the ODEs and PDEs using an iterative process, until convergence is reached for the boundary concentrations at the soil/air and sediment/water interfaces (Fig. 2). Details of the model structure and solution procedure are described in the companion paper (Cohen and Cooter 2002).

Scenario Design

The building blocks of an environmental simulation include specification of chemical properties, compartmental structure and properties, source-emission scenarios and background concentrations, and intermedia transport processes. Chemical-input parameters at a basic level are required to run a successful simulation (Table 3). It is important to recognize that the propensity of pollutants to accumulate and/or persist in the environment can be significantly impacted by biotic and abiotic transformation rates. The description of these transformation reactions by pseudo-first-order reaction kinetics is suitable for most levels of environmental analyses; however, more complex kinetic models can be specified [for example, see Eqs. (1) and (16)] without a loss of generality.

Table 3. Chemical Information

Required chemical parameters	Advanced chemical parameters ^a
Molecular weight	Temperature dependent Henry's Law Parameters ^a
Molar volume	Chemical vapor pressure ^e
Boiling temperature	Diffusion Coefficients ^f
Henry's law constant	Rain scavenging coefficients ^g
Organic carbon/water partition coefficient	Water/biota mass transfer coefficient ^b
Octanol/water partition coefficient	Temperature dependent reaction rate coefficients ^a
Bioconcentration factor ^b	
Reaction rate coefficients ^c	
Gas/particle partition coefficient ^d	

^aOptional parameter.

^bRequired if biota compartment is selected.

^cRequired if reactions are selected.

^dEstimation method must be specified.

^eRequired if a specific gas/particle partition coefficient estimation method is selected.

^fEstimated internally but can be specified based on experimental data.

^gEstimated internally accounting for dependence on meteorological conditions; however, constant values can be specified.

Although multimedia analysis is often conducted isothermally, it is worth noting that partition coefficients and reaction-rate coefficients are temperature-dependent, and such behavior can be easily incorporated in a dynamic model.

Geographical characteristics such as media dimensions (for example, volume, surface area, and depth) and other properties (for example, organic carbon content for soil and sediment) are

required to describe the multimedia system (Table 4). The volume of the air compartment can be determined based on the total surface area in contact with the soil and water compartments and the atmospheric mixing height. Mixing heights vary diurnally and seasonally; however, the use of an average mixing height is often a reasonable first-order approximation for the majority of screening-level multimedia analyses. The volumes of the water,

Table 4. Major Geographical Compartmental Properties

Compartment	Height, depth, or other size parameters	Interfacial area, volume, or mass	Other physical parameters
Air (gas)	Mixing height	Air/soil Air/water	Atmospheric pressure
Atmospheric particles	Size distribution	Particle/air surface area and particle volume determined from size distribution	Density Porosity
Soil	Depth Land slope	Air/soil	Density of soil solids Initial soil air porosity and water content Organic carbon content Land use
Water	Depth Width (river only)	Air/water	
Suspended solids (in water)	Average diameter	Volume fraction in water	Density of suspended solids Organic carbon fraction Sphericity
Biota (in water)		Volume fraction of water body	
Sediment	Depth	Sediment/water	Density of sediment solids Porosity Organic carbon fraction
Plant	Average height (at full growth) Root diameter	Plant areal density Initial and full-grown mass foliage (leaf) area/foliage (leaf) mass ratio	Growth-rate parameters Bulk density Fraction of foliage in plant Fraction of root hairs in roots Crop type

soil, and sediment compartments are defined by their area and depth. The volumes of biota and suspended solids can often be specified in terms of the fraction of water volume they occupy. For example, available information regarding the concentration of suspended solids and the particle-size fraction (or average diameter) can be used to determine the volume fraction of suspended solids in water. The size of the plant compartment is specified as the fraction of soil covered by vegetation, area density of foliage (kg/m^2), depth of the root zone, size information for the plant roots, and plant growth parameters.

Convective flow rates in the water, air, and soil compartments can be specified as volumetric flow rates or velocity. Although the air and water compartments are considered to be uniform, one can utilize a correction for nonideal mixing. For example, given a convective residence time that accounts for nonideal mixing, $t_{i_{\text{res}}}$ (h), the volumetric flow rate is specified as $Q_i = V_i / t_{i_{\text{res}}}$, where V_i = compartmental volume (m^3). Residence times may be available in the literature or calculated from appropriate convective dispersion models. Water movement in soil can be obtained from a numerical solution of the Richards (1931) equation. However, adding such complexity to the Mend-Tox framework may not be justified for most scenarios of interest. Therefore, it is often more feasible to utilize analytical solutions for water movement in the soil (see section on nonuniform compartments).

Media temperatures are necessary to calculate chemical-specific parameters (for example, mass diffusivities, partition coefficients, mass-transfer coefficients, and reaction-rate constants). In the present approach, monthly average temperatures are used to obtain average daily air and water temperatures using a polynomial fit of the average monthly temperatures. Since temporal soil temperature data are not readily available, it may be reasonable to specify the soil temperature as weighted averages of the air and water temperatures. Interfacial air/soil and air/water can be different from bulk temperatures; therefore, one can also approximate these interfacial temperatures as weighted temperatures of the adjoining compartments. In addition to temperature, temporal variability of wind speed may be of interest at various temporal scales. Average monthly wind speeds are available for most regions. However, greater temporal resolution has to be specified when the wind resuspension process is included in the simulation.

Although the impact of rainfall is episodic, wet scavenging of chemicals can significantly impact the distribution of chemicals in the multimedia system. Conducting full rainfall simulations over long simulation periods (for example, months to years) requires considerable rainfall data. Moreover, rainfall simulations are computationally intensive due to additional complexities associated with the transport of particle-bound chemicals and rainfall infiltration in soil. Therefore, it may be preferred to first evaluate the impact of a single rainfall event on the multimedia system to assess the merit of conducting full rainfall simulations.

Chemical emissions directly impact the dynamics of multimedia chemical partitioning. Three basic types of sources can be used for most multimedia scenarios of interest: (1) uniformly distributed air source; (2) uniformly distributed water source; and (3) buried chemical simulation. Release rates to air and water can be constant or time-dependent. Uniform source simulations are best suited for distributed sources and for regions where the analysis time scale is greater than the chemical mixing time in the compartment where the release occurs. Clearly, the design of system boundaries should consider the location of sources within the region relative to the system boundaries. It is also possible to construct multiple regions, where simulation output from one is used

as input for an adjacent region, through a sequential set of simulations. Buried source simulations for the soil or sediment can be implemented by specifying initial concentration profiles for these media. Although soil and sediment contamination scenarios and source emissions to air and/or water can be specified independently of each other, the simulation must be well posed. For example, if sources are not specified (for any of the compartments), then an initial concentration greater than zero must be specified for at least one of the media in the environmental system. In fact, initial and background [C_{ki}^{in} ; see Eq. (1)] concentrations must be specified for all media.

Multimedia simulation results that are generally of interest include time slices of chemical mass distributions in the environment, temporal media concentration and fugacity profiles, concentration-depth profiles for the nonuniform compartments, and intermedia chemical fluxes, as well as rates of chemical flows into and out of compartments due to various transport processes. Detailed presentation of simulation results can help unravel the complexity of simulation scenarios that are affected by the number and types of included intermedia transport processes. For example, intermedia transport of particle-bound chemicals will increase model complexity and required computational resources. Similarly, processes associated with rainfall (for example, rain scavenging, rainfall infiltration into soil, and runoff) also increase the complexity of interactions among media.

Therefore, in most cases, it is best to first evaluate a system's response with a minimum number of intermedia processes. Subsequently, through sequential simulations, one can add intermedia processes to study and interpret a more complex behavior of the multimedia system. Clearly, there is an advantage to formulating the model structure so as to allow one to include only the desired environmental media and intermedia processes. Implementation of the above features can be accomplished via object-oriented model construction with a suitable user interface built to allow analyses that are consistent with the approach taken by multimedia analysts. Such an approach and illustrative simulation examples are described in a subsequent publication dealing with the implementation of the Mend-Tox approach (Cohen and Cooter 2002).

Summary

Environmental multimedia distribution of chemical contaminants can be assessed using multimedia models ranging in complexity from simple compartmental models to systems of linked, fully spatial single-medium models. The hybrid spatial-compartmental multimedia model formation presented in this paper consists of a mixture of "well-mixed" and nonuniform compartments with a mechanistic description of intermedia transport processes. Such models provide a greater degree of realism relative to simple compartmental models. A wide range of model simulations can be conducted, and thus the modeling approach can form the basis for designing a sophisticated yet practical environmental simulator for conducting multimedia analyses at both the research and instructional levels.

Disclaimer

The information in this document has been funded in part by the U. S. Environmental Protection Agency. It has been subjected to agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 5. Summary of Fugacity Capacities

Environmental medium	Fugacity capacity	Parameter definitions
Air	$Z_a = 1/RT$	T —Temperature (K) R —Gas constant (8.31, Pa·m ³ /gmol·K)
Water	$Z_w = 1/H_w$	H_w —Henry's law constant (e.g., Pa·m ³ /gmol) Note: $H_{aw} = H_w/RT$
Sorbed phase	$Z_{sp} = (K_p \rho_{sp})/H_w$ (Note: for a linear adsorption isotherm)	K_p —Linear sorption coefficient (ml solution/g sorbent) ρ_{sp} —Density of solid sorbent (g/cm ³)
Biota	$Z_B = BCF \rho_B / H_w$	ρ_B —Biota density BCF—Bioconcentration factor (dimensionless)
Multiphase compartment (e.g., soil, sediment, foliage, and roots)	$Z_m = \sum_{i=1}^n \theta_i Z_i$	Z_i —Fugacity capacity of phase i θ_i —Volume fraction of phase i n —Number of phases
Roots	$Z_r = (1/H_w) BCF_{rw}$	BCF_{rw} —Roots/water partition coefficient
Foliage	$Z_f = BCF_{fa} Z_a$	BCF_{fa} —Foliage/air partition coefficient

Appendix: Fugacity and Concentration

The driving force for interfacial mass transfer between adjacent media, associated with diffusional processes, is the chemical potential difference. It is often convenient to map the chemical potential to the function known as fugacity. The fugacity of a chemical in a given environmental phase (for example, air, soil, and water) is related to its chemical potential, μ_i , by the following relation (Prausnitz 1999):

$$f_i = f_i^r \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \quad (27)$$

where μ_i^0 is the standard-state chemical potential and f_i and f_i^r are the chemical fugacity and its reference fugacity, respectively. The accepted unit for fugacity is pressure (typically atmosphere or Pascal). The fugacity of a chemical is typically written using the following simple relation (Prausnitz 1999)

$$f_i = x_i \phi_i f_i^r \quad (28)$$

where x_i =mole fraction; ϕ_i =fugacity coefficient; and f_i^r =reference fugacity. For environmental applications, it is more convenient to write Eq. (28) in molar concentration units:

$$f_i = \left(\frac{C_i}{\rho_m^{\text{phase}}}\right) \phi_i f_i^r \quad (29)$$

where C_i =molar concentration of the pollutant under consideration, and ρ_m^{phase} =molar density of the environmental phase (for example, water, air, and so on). Eq. (29) can be simplified by introducing the so called "fugacity capacity," $Z_i = (\rho_m^{\text{phase}}/\phi_i f_i^r)$, which leads to the following relation between the fugacity and concentration (Mackay 1991):

$$f_i = \frac{C_i}{Z_i} \quad (30)$$

In a multimedia system of M compartments at equilibrium, the equality of the chemical fugacities in the various compartments (for a given chemical and standard-state reference chemical potential) requires that the following condition holds:

$$f_1 = f_2 = f_3 = \dots = f_i = f_j; \quad i, j = 1, \dots, M \quad (\text{where } i \neq j) \quad (31)$$

or using Eq. (30)

$$\frac{C_i}{Z_i} = \frac{C_j}{Z_j} \quad \text{where } i \neq j \quad (32)$$

Since the fugacity capacity for a given chemical in a specific phase is only a function of the nature of the chemical and density of the phase, Eq. (32) can be rearranged to obtain a simple definition for the environmental partition coefficients:

$$H_{ij} = \frac{C_i}{C_j} = \frac{Z_j}{Z_i} \quad \text{where } i \neq j \quad (33)$$

As the number of compartments in a multimedia system increases, it is convenient to store a fugacity capacity vector rather than a matrix of partition coefficients. Also, given values of fugacity capacities, which for a given environmental system and chemical only vary with temperature (the effect of pressure under normal atmospheric conditions is usually negligible), one can easily determine from Eqs. (31) and (33) the fugacities for a given chemical in any desired compartment. Expressions for fugacity capacities of the major media are provided in Table 5. The partition coefficient between any single-phase compartment j and a multiphase compartment m is determined as

$$H_{jm} = \frac{Z_j}{Z_m} = \left(\sum_{i=1}^M \theta_i H_{ij}\right)^{-1} \quad (34)$$

where θ_i =specific porous matrix phase water volume fraction,

and Z_j and Z_m = fugacity capacities of the porous matrix and phase j within this matrix, respectively (Table 5).

References

- Ackers, P., and White, W. R. (1975). "Sediment transport: New approach and analysis." *J. Hydraul. Div., Am. Soc. Civ. Eng.*, 101, 621–625.
- Anderberg, S., Bergback, B., and Lohm, U. (1989). "Flow and distribution of chromium in the Swedish environment—A new approach to studying environmental pollution." *Ambio*, 18(4), 216–220.
- Bacci, E., Cerejeira, M. J., Gaggi, C., Chemello, G., Calamari, D., and Vighi, M. (1990). "Bioconcentration of organic chemical vapors in plant leaves: The Azalea model." *Chemosphere*, 21(4–5), 525–535.
- Bacci, E., Cerejeira, M. J., Gaggi, C., Chemello, G., Calamari, D., and Vighi, M. (1992). "Chlorinated dioxins: Volatilization from soils and bioconcentration in plant leaves." *Bull. Environ. Contam. Toxicol.*, 48(3), 401–408.
- Baker, J. E., and Eisenreich, S. J. (1990). "Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface at Lake Superior." *Environ. Sci. Technol.*, 24, 342–352.
- Barber, M. C., Suarez, L. A., and Lassiter, L. L. (1991). "Modeling bioaccumulation of organic pollutants in fish with an application to PCB's in Great Lake salmonids." *Can. J. Fish. Aquat. Sci.*, 48, 318–337.
- Barber, M. C., Suarez, L. A., and Lassiter, L. L. (1994). *FGETS version 3.0-12 user's manual and database*, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.
- Boersma, L., Lindstrom, F. T., McFarlane, C., and McCoy, E. L. (1988). "Uptake of organic chemicals by plants: A theoretical model." *Soil Sci.*, 146(6), 403–417.
- Briggs, G. G., Bromilow, R. H., and Evans, A. (1982). "Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley." *Pestic. Sci.*, 13, 495–504.
- Briggs, G. G., Bromilow, R. H., Evans, A., and Williams, M. (1983). "Relationship between lipophilicity and the distribution of nonionized chemicals in barley shoots following uptake by the roots." *Pestic. Sci.*, 14, 492–500.
- Broadbridge, P., Edwards, M. P., and Kearton, J. E. (1996). "Closed-form solutions for unsaturated flow under variable flux boundary conditions." *Adv. Water Resour.*, 19, 207–213.
- Broadbridge, P., and Rogers, C. (1990). "Exact solutions for vertical drainage and redistribution in soils." *J. Eng. Math.*, 24, 25–43.
- Broadbridge, P., and White, I. (1987). "Time to ponding: Comparison of analytic quasi-analytic and approximate predictions." *Water Resour. Res.*, 23, 2302–2310.
- Broadbridge, P., and White, I. (1988a). "Constant rate rainfall infiltration: A versatile nonlinear model. Part 1: Analytic solution." *Water Resour. Res.*, 24(1), 145–154.
- Broadbridge, P., and White, I. (1988b). "Constant rate rainfall infiltration: A versatile nonlinear model. Part 2: Applications of solutions." *Water Resour. Res.*, 24(1), 155–162.
- Brutsaert, W. (1975). "A theory for local evaporation (or heat transfer) from rough and smooth surfaces at ground level." *Water Resour. Res.*, 11(4), 543–550.
- California Environmental Protection Agency (CalEPA). (1993). *CalTox: A multimedia total exposure model for hazardous-waste sites, Technical Rep.*, Dept. of Toxic Substances Control, Office of Scientific Affairs.
- Campfens, J., and Mackay, D. (1997). "Fugacity-based model of PCB bioaccumulation in complex aquatic food webs." *Environ. Sci. Technol.*, 31(2), 577–583.
- Chadha, A., McKelvey, L. D., and Mangis, J. K. (1998). "Targeting lead in the multimedia environment in the continental United States." *J. Air Waste Manage Assoc.*, 48(1), 3–15.
- Cheng, J. J., and Yu, C. (1993). "Using the RESRAD computer code to evaluate human health risks from radionuclides and hazardous chemicals." *J. Haz. Mat.*, 35(3), 353–367.
- Cohen, Y. (1986a). "Intermedia transport modeling in multimedia systems." Y. Cohen, ed., *Pollutants in a multimedia environment*, Plenum Press, New York.
- Cohen, Y. (1986b). "Organic pollutant transport: Improved multimedia model techniques are the key to predicting the environmental fate of organic pollutants." *Environ. Sci. Technol.*, 20(6), 538–544.
- Cohen, Y., (ed.). (1986c). *Pollutants in a multimedia environment*, Plenum Press, New York.
- Cohen, Y. (1987). "Modeling of pollutant transport and accumulation in a multimedia environment." S. J. Draggan, J. Cohnssen, and R. E. Morrison, eds., in *Geochemical and Hydrological Processes and Their Protection*, Praeger, New York.
- Cohen, Y., and Clay, R. E. (1994). "Multimedia partitioning of particle-bound organics." *J. Haz. Mat.*, 37, 507–526.
- Cohen, Y., and Cooter, E. J. (2002). "Multimedia environmental distribution of toxics (Mend-Tox). II: Software implementation and case studies." *Prac. Period. Hazard., Toxic, Radioact. Waste Manage.*, 6(2) 87–101.
- Cohen, Y., and Ryan, P. A. (1985). "Multimedia modeling of environmental transport: trichloroethylene test case." *Environ. Sci. Technol.*, 19, 412–417.
- Cohen, Y., Tsai, W.-T., and Chetty, S. L. (1990a). "Partitioning of pollutants in the multimedia environment: SMCM software." *CACHE News*, 30, 18–26.
- Cohen, Y., Tsai, W.-T., Chetty, S. L., and Mayer, G. J. (1990b). "Dynamic partitioning of organic chemicals in regional environments: A multimedia screening-level modeling approach." *Environ. Sci. Technol.*, 24, 1549–1558.
- Cohen, Y., and Van de Water, R. B. (1994). "Environmental distribution of organics." *Computer techniques in environmental studies V, Vol. I: Pollution modeling*, Zannetti, ed., Computational Mechanics Publications, Southampton, U.K., 267–278.
- Cooter, E. J., Cohen, Y., and Hill, J. B. (1999a). "Application of a hybrid compartmental model to the Neuse River Basin of North Carolina." *Proc., A&WMA Symposium on Measurements of Toxics and Related Air Pollutants '98*. Vol. II, Air and Waste Management Association and USEPA, 735–746.
- Cooter, E., Hill, J. B., and Cohen, Y. (1999b). "Impact of secular precipitation changes on the deposition of benzo(a)pyrene to the Neuse River Basin of North Carolina." Pre-Prints of the *11th Conf. on Applied Climatology*, January 10–15, 1999, Dallas, 383–389.
- Cowan, C. E., et al. (1994). *The multi-media fate model*, Society of Environmental Toxicology and Chemistry (SETAC) Press, Pensacola, Fla.
- Cowherd, C., Muleski, G., Englehart, P. J., and Gillette, D. A. (1985). "Rapid assessment of exposure to particulate emissions from surface contamination sites." *Rep. EPA/600/8-85/002*, Environmental Protection Agency.
- Cowherd, C., Muleski, G. E., and Kinsey, J. S. (1988). "Control of open fugitive dust sources." *NTIS, Rep. No. PB89-103691*, U.S. Government Printing Office, Washington, D.C.
- Cramer, J. (1973). "Model of the circulation of DDT on Earth." *Atmos. Environ.*, 7(3), 241–256.
- Davis, M. E. (1984). *Numerical methods and modeling for chemical engineering*, Wiley, New York.
- Duarte-Davidson, R., Courage, C., Rushton, L., and Levy, L. (2001). "Benzene in the environment: An assessment of the potential risks to the health of the population." *Occup. Environ. Med.*, 58(1), 2–13.
- Edwards, F. G., Egemen, E., Brennan, R., and Nirmalakhandan, N. (1999). "Ranking of toxics release inventory chemicals using a level III fugacity model and toxicity." *Water Sci. Technol.*, 39(10–11), 83–90.
- Eisenberg, J. M. S., Bennett, D. H., and McKone, T. E. (1998). "Chemical dynamics of persistent organic pollutants: A sensitivity analysis relating soil concentration levels to atmospheric emissions." *Environ. Sci. Technol.*, 32, 115–123.
- Farley, K. J., and Morel, F. M. M. (1986). "Role of coagulation in the kinetics of sedimentation." *Environ. Sci. Technol.*, 20, 187–195.

- Fernandez de la Mora, J., and Friedlander, S. K. (1982). "Aerosol and gas deposition to fully rough surfaces: Filtration model for blade-shaped elements." *Int. J. Heat Mass Transf.*, 25, 1725–1735.
- Fishbein, L. (1984). "An overview of environmental and toxicological aspects of aromatic hydrocarbons. I: Benzene." *Sci. Total Environ.*, 40, 189–218.
- Fuller, B. N., Schettler, P. D., and Giddings, J. C. (1966). "A new method for prediction of binary gas-phase diffusion coefficients." *Ind. Eng. Chem.*, 58, 19–27.
- Ghadiri, H., and Rose, C. W. (1992). *Modeling chemical transport in soils*, Lewis, Chelsea, Mich.
- Gillette, D. A., Adams, J., Endo, A., and Smith, D. (1980). "Threshold velocities for input of soil particles into the air by desert soils." *J. Geophys. Res.*, 85(C10), 5621–5630.
- Goldman, S. J., Jackson, K., and Bursztynsky, T. A. (1986). *Erosion and sediment control handbook*, McGraw-Hill, New York.
- Grifoll, J., and Cohen, Y. (1994). "Chemical volatilization from the soil matrix: Transport through the air and water phases." *J. Haz. Mat.*, 37, 445–457.
- Grifoll, J., and Cohen, Y. (1996). "Contaminant migration in the unsaturated soil zone: The effect of rainfall and evapotranspiration." *J. Contaminant Hydrology*, 23, 185–211.
- Hamasaki, T., Nagase, H., Yoshioka, Y., and Sato, T. (1995). "Formation, distribution, and ecotoxicity of methylmetals of tin, mercury, and arsenic in the environment." *Crit. Rev. in Environ. Sci. Technol.*, 25(1), 45–91.
- Harrison, H. L., et al. (1970). "Systems studies of DDT transport." *Science*, 170, 502–508.
- Hattemer-Frey, H. A., Travis, C., and Land, M. L. (1990). "Benzene: Environmental partitioning and human exposure." *Environ. Res.*, 53, 221–232.
- Hawley, N., and Lesht, B. (1992). "Sediment resuspension in Lake St. Clair." *Limnol. Oceanogr.*, 37(8), 1720–1737.
- Hayduk, W., and Laudie, H. (1974). "Prediction of diffusion coefficients for non-electrolytes in dilute aqueous solutions." *AIChE J.*, 20, 611.
- Hayduk, W., Minhas, B. S., and Lan, J. (1982). "Correlations for prediction of molecular diffusivities in liquid." *Can. J. Chem. Eng.*, 60, 295.
- Heimstra, L. (1968). PhD dissertation, "Frequencies of runoff for small basins," Colorado State Univ., Fort Collins, Colo.
- Hetrick, D. M., and McDowell-Boyer, L. M. (1984). *A user's manual for TOX-SCREEN: A multimedia screening-level program for assessing the potential fate of chemicals released to the environment*, ORNL-6041; EPA-560/5-85-024, Oak Ridge National Laboratory, Oak Ridge, Tenn., and U.S. EPA, Office of Toxic Substances, Washington, D.C.
- Hsieh, C. R., and Quimette, J. R. (1994). "Comparative study of multimedia modeling for dynamic partitioning of fossil fuels-related pollutants." *J. Haz. Mat.*, 37, 489–505.
- Hunt, J. R. (1982). "Particle dynamics in seawater: Implications for predicting the fate of discharged particles." *Environ. Sci. Technol.*, 16(6), 303–309.
- Huntzicker, J. J., Friedlander, S. K., and Davidson, C. I. (1975). "Material balance for automobile emitted lead in the Los Angeles basin." *Environ. Sci. Technol.*, 9, 448.
- Hwang, S. T. (1990). "Estimation of multimedia environmental contamination of 2,3,7,8-TCDD emissions from municipal waste incinerators." *Environ. Prog.*, 9(2), 93–97.
- Jaenicke, R. (1993). *Tropospheric aerosols, in aerosol-cloud-climate interactions*, P. V. Hobbs, ed., Academic, San Diego.
- Johnston, J. M., Novak, J. H., and Kraemer, S. R. (2000). "Multimedia integrated modeling for environmental protection: Introduction to a collaborative framework." *Environ. Monit. Assess.*, 63(1), 253–263.
- Junge, C. E. (1977). "Fate of pollutants in the air and water environment." I. H. Suffet, ed., *Advances in environmental science and technology*, Wiley, New York.
- Khalil, M. A. K., Rasmussen, R. A., and Hoyt, S. D. (1983). "Atmospheric chloroform (CHCl₃): Ocean-air exchange and global mass balance." *Tellus*, 35(B), 266–74.
- Kimbrough, D. E., Cohen, Y., Winer, A. M., Creelman, L., and Mabuni, C. (1999). "A critical assessment of chromium in the environment." *Crit. Rev. Environ. Sci. Technol.*, 29(1), 1–46.
- Laniak, G. F., Droppo, J. G., Faillace, E. R., and Gnanapragasam, E. K. (1997). "An overview of a multimedia benchmarking analysis for three risk assessment models: RESRAD, MMSOILS, and MEPAS." *Risk Anal.*, 17(2), 203–214.
- Lick, W. (1994). "Chapter 4: The flocculation, deposition and resuspension of fine-grained sediments." *Transport and transformation of chemicals near the sediment water interface*, J. V. De Pinto, W. Lick, and J. F. Paul, eds., Lewis, Chelsea, Mich.
- Lioy, P. J., and Greenberg, A. (1990). "Factors associated with human exposure to polycyclic aromatic hydrocarbons." *Toxicol. Ind. Health*, 6, 209–223.
- Loganathan, B. G., Irvine, K. N., Kannan, K., Pragatheeswaran, V., and Sajwan, K. S. (1997). "Distribution of selected PCB congeners in the Babcock Street sewer district: A multimedia approach to identify PCB sources in combined sewer overflows discharging to the Buffalo River." *New York Archives of Environmental Contamination and Toxicology*, 33(2), 130–140.
- Luckner, L., and Schestakow, W. (1991). *Migration processes in the soil and groundwater zone*, Lewis Publishers, Chelsea, Mich.
- Luettich, R., Harleman, D., and Somlyody, L. (1990). "Dynamic behavior of suspended sediment concentrations in a shallow lake perturbed by episodic wind events." *Limnol. Oceanogr.*, 35(5), 1050–1067.
- Macdonald, C. R., and Metcalfe, C. D. (1991). "Concentration and distribution of PCB congeners in isolated Ontario lakes contaminated by atmospheric deposition." *Can. J. Fish. Aquat. Sci.*, 48(3), 371–381.
- Mackay, D. (1991). *Multimedia environmental models: The fugacity approach*, Lewis, Chelsea, Mich.
- Mackay, D., and Yeun, A. T. K. (1983). "Mass transfer coefficients correlations of organic solutes from water." *Environ. Sci. Technol.*, 17, 4.
- Maddalena, R. L., Mckone, T. E., Layton, D. W., and Hsieh, D. P. H. (1995). "Comparison of multi-media transport and transformation models—Regional fugacity model vs. CALTOX." *Chemosphere*, 30(5), 869–889.
- Maheras, S. J. (1995). "GENII VERSION 1.485." *Health Phys.*, 68(1), 119–121.
- Maheras, S. J., Ritter, P. D., Leonard, P. R., and Moore, R. (1994). "Benchmarking of the CAP-88 and GENII computer codes using 1990 and 1991 monitored atmospheric releases from the Idaho National Engineering Laboratory." *Health Phys.*, 67(5), 509–517.
- Mayer, G. J. (1988). "The spatial multimedia compartmental model (SMCM): A user friendly screening level pollutant distribution model." MS thesis, Univ. of California, Los Angeles.
- McDonald, J. P., and Gelston, G. M. (1998). "Description of the Multimedia Environmental Pollutant Assessment System (MEPAS, Version 3.2), with application to a hypothetical soil contamination scenario." *J. Soil Contaminat.*, 7(3), 283–300.
- McKone, T., Gratt, L., Lyon, M., and Berry, P. (1987). "GEOTOX: Multimedia compartmental model users guidance Volume 1: User guide," Lawrence Livermore National Laboratory, Livermore, Calif.
- Mills, W. B., Cheng, J. J., Droppo, J. G., and Faillace, E. R. (1997). "Multimedia benchmarking analysis for three risk assessment models: RESRAD, MMSOILS, and MEPAS." *Risk Anal.*, 17(2), 187–201.
- Nisbet, C. T., and Sarofin, A. F. (1972). "Rates and routes of transport of PCB's in the environment." *Environ. Health Perspect.*, 1, 21–38.
- Notarianni, V., Calliera, M., Tremolada, P., Finizio, A., and Vighi, M. (1998). "PCB distribution in soil and vegetation from different areas in Northern Italy." *Chemosphere*, 37(14–15), 2839–2845.
- Novotny, V., and Chesters, G. (1981). *Handbook of nonpoint pollution*, Van Nostrand Reinhold, New York, 81–83.
- Onishi, Y., Shuyler, L., and Cohen, Y. (1990). "Multimedia modeling of toxic chemicals." *Proc., Int. Symposium on Water Quality Modeling of Agricultural and Non-Point Sources*, Part II, D. G. DeCoursey, ed., ARS-81. U.S. Dept. of Agriculture, Washington, D.C., 479–509.
- Osborne, M. R., and Crosby, N. T. (1987). *Benzopyrenes*, Cambridge University Press, Cambridge, U.K.
- Palusova, O., Ursinyova, M., and Uhnak, J. (1991). "Mercury levels in

- the components of the environment and diets." *Sci. Total Environ.*, 101(1-2), 79-82.
- Pankow, J. F. (1987). "Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere." *Atmos. Environ.*, 21(11), 2275-2283.
- Pankow, J. F. (1991). "Common γ -intercept and single compound regressions of gas-particle partitioning data vs. $1/T$." *Atmos. Environ., Part A*, 25(10), 2229-2239.
- Paterson, S., Mackay, D., and McFarlane, C. (1994). "A model of organic chemical uptake by plants from soil and the atmosphere." *Environ. Sci. Technol.*, 28(13), 2259-2266.
- Patterson, M. R., et al. (1984). "A user's manual for the UTM-TOX: A unified transport model," ORNL-6064,
- Prausnitz, J. M. (1999). *Molecular thermodynamics of phase equilibria*, Prentice-Hall, Upper Saddle River, N.J.
- Rasmussen, P. E., Friske, P. W. B., Azzaria, L. M., and Garrett, R. G. (1998). "Mercury in the Canadian environment: Current research challenges." *Geosci. Can.*, 25(1), 1-13.
- Reid, R., Prausnitz, J., and Sherwood, T. (1987). *The properties of gases and liquids*, 4th Ed., McGraw-Hill, New York.
- Renner, R. (1995). "Predicting chemical risks with multimedia fate models." *Environ. Sci. Technol.*, 29, A556-A559.
- Richards, L. A. (1931). "Capillary conduction of liquids in porous media." *Physics*, 1, 318-333.
- Richardson, M., Mitchell, M., Coad, S., and Raphael, R. (1995). "Exposure to mercury in Canada—A multimedia analysis." *Water Air Soil Pollut.*, 80(1-4), 21-30.
- Rowe, P. N., Claxton, K. T., and Lewis, J. B. (1965). *Trans. Inst. Chem. Eng.*, 43, 714.
- Ryan, P. A., and Cohen, Y. (1986). "Multimedia transport of particle bound organics: Benzo(a)pyrene test case." *Chemosphere*, 15, 21-47.
- Sallam, A., Jury, W. A., and Letey, J. (1984). *Soil Sci. Soc. Am. J.*, No. 48, 3.
- Sawhney, B. L., and Brown, K., eds. (1989). "Reactions and movement of organic chemicals in soils." SSSA and ASA, *SSSA Special Publication No. 22*.
- Schroeder, W. H., Munthe, J., and Lindqvist, O. (1989). "Cycling of mercury between water, air, and soil compartments of the environment." *Water Air Soil Pollut.*, 48(n-4), 337-347.
- Sehmel, G. A., and Hodgson, W. H. (1980). "A model for predicting dry deposition of particles and gases to environmental surfaces." *AIChE Symp. Ser.*, 76(196), 218-231.
- Seinfeld, J. M., and Pandis, S. N. (1998). *Atmospheric chemistry and physics*, Wiley, New York.
- Shen, T., Schmidt, C. E., and Card, T. (1993). "Assessment and control of VOC emissions from waste treatment and disposal facilities," Van Nostrand Reinhold, New York.
- Singh, D. K., and Agarwal, H. C. (1995). "Persistence of DDT and nature of bound residues in soil at higher altitude." *Environ. Sci. Technol.*, 29(9), 2301-2304.
- Slinn, W. G. N. (1982). "Prediction for particle deposition to vegetation canopies." *Atmos. Environ.*, 16(7), 1785-1794.
- Spencer, W. F., Singh, G., Taylor, C. D., Lemert, R. A., Cliath, M. M., and Farmer, W. J. (1996). "DDT persistence and volatility as affected by management practices after 23 years." *J. Environ. Qual.*, 25(4), 815-821.
- Stasko, S., and Fthenakis, V. M. (1993). "MMSOILS, Version 2.2." *Risk Anal.*, 13(5), 575-579.
- Stein, E. D., Cohen, Y., and Winer, A. M. (1996). "Environmental distribution and transformation of mercury compounds." *Crit. Rev. Environ. Sci. Technol.*, 26, 1-43.
- Suzuki, N., Yasuda, M., Sakurai, T., and Nakanishi, J. (1998). "Model simulation of environmental profile transformation and fate of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans by the multimedia environmental fate model." *Chemosphere*, 37(9-12), 2239-2250.
- Suzuki, N., Yasuda, M., Sakurai, T., and Nakanishi, J. (2000). "Simulation of long-term environmental dynamics of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans using the dynamic multimedia environmental fate model and its implication to the time trend analysis of dioxins." *Chemosphere*, 40(9-11), 969-976.
- Swackhammer, D., and Armstrong, D. (1986). "Estimation of the atmospheric and nonatmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes." *Environ. Sci. Technol.*, 20, 879-883.
- Taboas, A. L. (1993). "Principles of a multimedia, risk-based market-driven environmental approach." *Environ. Int.*, 19(3), 217-220.
- Thibodeaux, L., and Becker, B. (1982). "Chemical transport rates near the surface of wastewater impoundments and similar water bodies." *Environ. Prog.*, 1(4), 296-300.
- Thomann, R. V. (1989). "Bioaccumulation model of organic chemical distribution in aquatic food chains." *Environ. Sci. Technol.*, 23, 699-707.
- Topp, E. M., Scheunert, I., and Korte, F. (1986). *Ecotoxicol. Environ. Saf.*, 11, 219-228.
- Trapp, S., and Matthies, M. (1995). "Generic one-compartment model for uptake of organic chemicals by foliar vegetation." *Environ. Sci. Technol.*, 29(9), 2333-2338.
- Trapp, S., and Matthies, M. (1998). *Chemodynamics and environmental modeling*, Springer, Berlin.
- Trapp, S., and McFarlane, J. C. (1995). *Plant contamination*, Lewis Publishers, Boca Raton, Fla.
- Travis, C., and Hattemer-Frey, H. A. (1989). "Multimedia partitioning of dioxin." *Intermedia pollutant transport: Modeling and field measurements*, D. T. Allen, Y. Cohen, and I. R. Kaplan, eds., Plenum, New York, 257-268.
- Tsai, W., Cohen, Y., Sakugawa, H., and Kaplan, I. R. (1991). "Dynamic partitioning of semi-volatile organics in gas/particle/water phases during rain scavenging." *Environ. Sci. Technol.*, 25, 2012-2023.
- Tucker, W., Eschenroeder, A., and Magil, G. (1984). "Air Land Water Analysis System (ALWAS): A multimedia model for toxic substances." NTIS Publication No. PB84-171743, USGPO, Washington, D.C.
- U.S. Dept. of Energy (DOE). (1993). *Rep. of the Peer Review Committee for Multimedia Models for Use in the DOE Programmatic Environmental Impact Statement Risk Assessment*, Office of Environmental Restoration and Waste Management, Nov. 24.
- U.S. Environmental Protection Agency (USEPA). (1988). "Methodology for estimating multimedia exposures to soil contamination (MMSOIL)." Office of Health and Environmental Assessment, Exposure Assessment Group,
- U.S. Environmental Protection Agency (USEPA). (1996). "Evaluation of existing approaches for assessing non-inhalation exposure and risk with recommendations for implementing TRIM." prepared by *International Technology Air Quality Services and TRJ Environmental*, Contract No. 68, for the USEPA, Office of Air Quality Planning and Standards, RTI, NC.
- U.S. Environmental Protection Agency (USEPA). (1997a). "Lake Michigan mass budget/mass balance work plan." *EPA-905-R-97-018*, USEPA and Great Lakes National Program Office,
- U.S. Environmental Protection Agency (USEPA). (1997b). "Overview and key feature of the Integrated Spatial Multimedia Compartmental Model (ISMCM): An addendum to evaluation of existing approaches for assessing non-inhalation exposure and risk with recommendations for implementing TRIM." prepared by *International Technology Air Quality Services*, Contract No. 68, for the USEPA, Office of Air Quality Planning and Standards, RTI, NC.
- U.S. Environmental Protection Agency (USEPA). (1999a). *FRAMES-HWIR: Technology software system for 1999, Vol. 1. System overview*, U.S. Environmental Protection Agency, Office of Research and Development (DRAFT, July).
- U.S. Environmental Protection Agency (USEPA). (1999b). *A framework for finite-source multimedia, multipathway and multireceptor risk assessment: 3MRA*, U.S. Environmental Protection Agency, Office of Solid Waste (DRAFT, July).
- Vaessen, H. A. M. G., Jekel, A. A., and Wilbers, A. A. M. M. (1988). "Dietary intake of polycyclic aromatic hydrocarbons." *Tox. Environ. Chem.*, 16, 281-294.

- Van Bavel, C. H. M. (1966). "Potential evapotranspiration: The combination concept and its experimental verification." *Water Resour. Res.*, 2(3), 455–467.
- Vohra, R. (1996). "Dynamic partitioning and intermedia transport of hydrophobic chemicals in aquatic systems." Masters thesis, Chemical Engineering Dept., Univ. of California, Los Angeles.
- Whitby, K. T. (1978). "The physical characteristics of sulfur aerosols." *Atmos. Environ.*, 12, 135–139.
- Wiersma, G. B. (1979). "Kinetics and exposure commitment analyses of lead behavior in a biosphere reserve." *Technical Rep.*, Monitoring and Assessment Research Center, Chelsea College, Univ. of London, London.
- Wilke, C. R., and Chang, P. (1955). "Correlation of diffusion coefficients in dilute solutions." *AIChE J.*, 1, 264–270.
- Williams, R. M. (1982). "A model for the dry deposition of particles to natural water surfaces." *Atmos. Environ.*, 16, 1933–1938.
- Woodwell, G., Craig, P., and Johnson, H. (1971). "DDT in the biosphere: Where does it go?" *Science*, 174, 1101–1107.
- Yaffe, D., Cohen, Y., Arey, J., and Grosovsky, A. J. (2001). "Multimedia analysis of PAHs and nitro-PAH daughter products in the Los Angeles basin." *Risk Anal.*, 21, 275–294.