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Environmental multimedia distribution of organics

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Abstract

An integrated spatial-multimedia-compartmental model (ISMCM) of chemical transport and fate was developed to predict environmental partitioning of both volatile and semi-volatile organics. The model is composed of eight compartments namely, air-gaseous phase, air-particulate phase, water, suspended solids (in water), biota (in water), sediment, soil, and vegetation. These compartments are described by a series of ordinary and partial differential equations which are solved simultaneously subject to the appropriate physical boundary conditions. The ISMCM provides a detailed description of intermedia transport processes associated with the gaseous, dissolved, and particle phases. For example, detailed modules are included to describe the rain scavenging of gaseous and particle-bound chemicals, dry deposition, wind erosion and resuspension of soil, rain infiltration, surface runoff, and resuspension and deposition of sediment particles. In addition, the ISMCM accounts for the dependency of atmosphere/soil and atmosphere/water intermedia transport on particle size and the dynamic changes in the atmospheric particle size distribution. The ISMCM is linked to a database of physicochemical and geographical parameters and this database can be expanded by the user.

1 Introduction

In recent years there has been an increasing interest in assessing, from a multimedia perspective, the impact of chemical pollutants on human health and the enviroment[1,2]. The motivation for developing multimedia environmental assessment tools stems from the realization that pollutants, once released to the environment, as the result of a variety of human-related activities (air emissions and/or direct discharge to surface water, etc.), cross environmental boundaries and are therefore found in most media. The significance of intermedia transfers is exemplified by the cycling of polychlorinated biphenyls (PCBs), in the Great Lakes region in North

America[3,4] (e.g., sediment→water, water→atmosphere, atmosphere→ water, water→sediment). Another example is the emissions of polyaromatic hydrocarbons (PAHs) which can deposit from the atmosphere to the ground surface via wet and dry deposition[5]. Thus, PAHs can accumulate in the soil, vegetation and biota compartments[6,7] and also reenter the atmosphere via wind resuspension. Similarly, incineration of waste can also lead to the emissions of aerosols containing trace metals, zinc, cadmium, lead, which are susceptible to intermedia transfers by wet or dry deposition. Various volatile organic compounds have also been shown to be ubiquetous in the environment, although the exposure of the human receptor to these chemicals is generally dominated by the air pathway and to a lesser extent the water pathway.

Multimedia models which incorporate intermedia transfer processes[1,2,8-10] can be particularly useful and inexpensive tools for assessing environmental multimedia pollutant concentration levels and intermedia chemical fluxes (i.e., among the various environmental compartments). Such models can be used to ascertain the environmental impact of present and future chemical releases for a variety of environmental scenarios. While the existing multimedia models incorporate various intermedia transfer processes, most are deficient in the treatment of particle-bound chemicals, prediction intermedia transfer factors (ITFs), and in their ability to guarantee mass conservation[1,9-11]. For example, present multimedia models do not consider the interrelation between the particle size distribution and exchange processes such as dry and wet deposition. Also, in most models the degree of required user input of ITFs (e.g., mass transfer coefficients, dry deposition velocities, etc.) is significant and thus reduces the utility of the model for rapid scenario analysis.

In this work the major objective has been to develop a practical integrated spatial-multimedia-compartmental model (ISMCM) of pollutant transport and fate which is based on a mechanistic description of intermedia transport processes. The ISMCM integrates spatial and well mixed comaprtments using the appropriate mass transfer balances which are coupled through compartmental boundary conditions[1,8,11]. Thus, the ISMCM assures the conservation of mass mass in the multimedia environmental system. Although spatial resolution is sacrificed in this hybrid spatial-compartmental approach, it is well suited for the rapid assessment of multimedia distribution and associated intermedia fluxes of particle-bound organics and volatile organic compounds (VOCs).

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2 The ISMCM Model

2.1 Overview of the ISMCM Structure

The ISMCM is a PC-based model which is based on a detailed mechanistic description of intermedia transfer processes. Thus, the ISMCM can be used to study various scenarios with minimum parameter input requirements . The ISMCM describes the environmental media as composed of eight main compartments which include air, aerosol, soil, water, sediment, suspended solids, biota and vegetation. A schematic representation of the ISMCM is shown in Figure 1. The model incorporates theoretical and empirical descriptions of transport processes associated with the gaseous, dissolved and particle phases to reduce the required user-input. A unique feature of the ISMCM relative to other available multimedia models is the incorporation of the particle-size distribution and the dependence of intermedia transfer processes on particle size. Furthermore, the ISMCM includes the modeling of rainfall events and the associated intermedia transport processes such as precipitation scavenging of contaminants from the atmosphere and contaminant transport in soils due to rain infiltration and runoff. The vegetation compartment includes contaminant uptake from both the soil and the atmosphere. The biota compartment accounts for contaminant uptake from both water and via the food chain. The ISMCM also allows the investigation of the impact of daily and seasonal variations in temeprature, wind speeds, and source release rate on contaminant distribution in the multimedia environment. It is emphasized that the ISMCM is a dynamic model which allows the user to follow the time-evolution of concentration levels in the various compartments.

In the ISMCM the atmospheric compartments (aerosol and gas) and the aquatic compartments (i.e., water, biota, and suspended solids) are treated as well-mixed; thus, the chemical mass balance in these compartments is expressed via ordinary differential equations. The ISMCM has is especially suited for handling particle-bound chemicals (e.g., PAHs, dioxins, PCBs). For such chemicals, the particle size distribution of atmospheric particles has a significant effect on the temporal dynamics of the chemical concentration in the atmosphere and its deposition rate to the terrestreial and aquatic environments[12]. Therefore, in the ISMCM a population balance on the various particle sizes, grouped into about 30 size fractions, is utilized. In this way, the temporal change in the particle size distribution is followed througout the simulation period. For organic chemicals, the distribution between the particle and gas phase is predicted internally by the model using particle/gas parition coefficient correlations proposed by Junge[13] Yamasaki et al.[14] and Pankow[15].

The soil compartment is subdivided into the soil-air, soil-water, and soil-solids phases while the sediment consist of the sediment-water and sediment-solids

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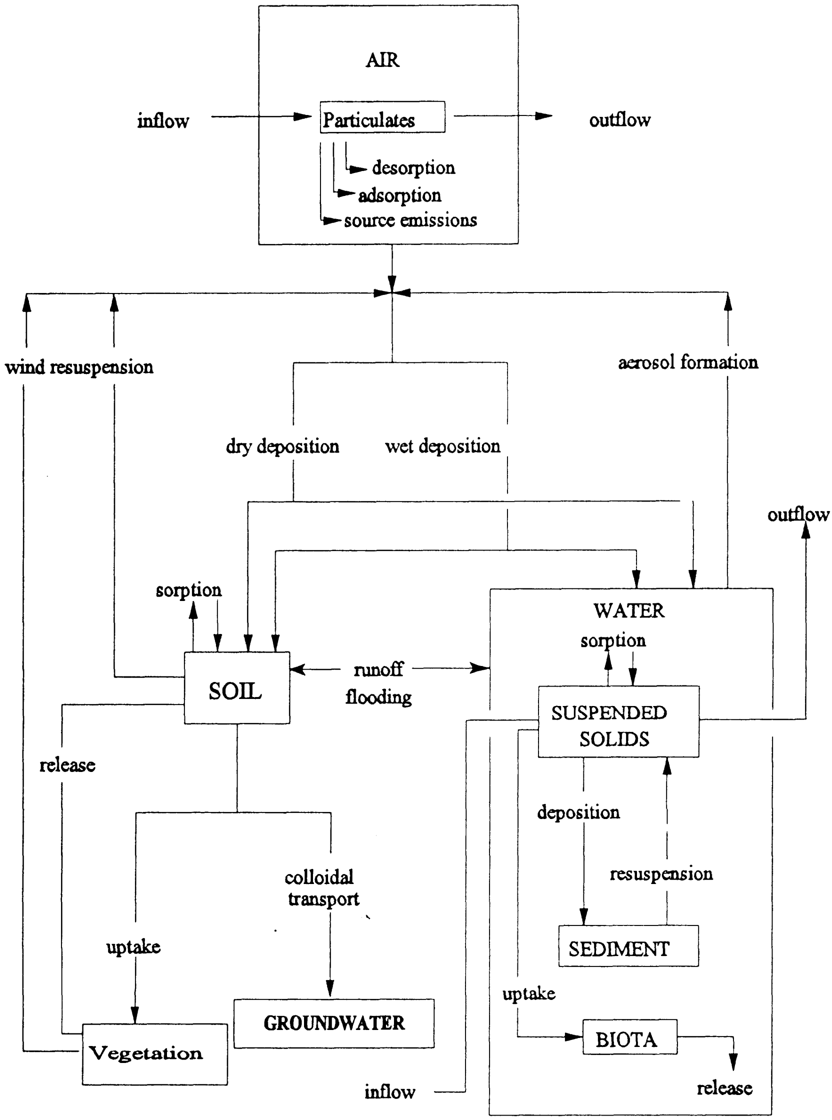

Figure 1. Schematic Representation of the ISMCM.

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phases. The soil and sediment compartments are both taken to be non-uniform where transport is described by one-dimensional convective-diffusion equations. Although lateral contaminant migration in the unsaturated zone is possible, it is assumed that contaminant migration is dominated by transport in the vertical direction; thus, the description of chemical transport in the soil is reduced to a one-dimensional transport equation. Also, in order to simplify the model local equilibrium is assumed to exist between the soil phases[16]. The vegetation compartment is also divided into a number of subcompartments with chemical uptake by convection and diffusion via the roots and by dry and wet deposition via the leaf canopy.

In the ISMCM the processes of sediment resuspension and deposition are included as are chemical input via runoff and atmospheric dry and wet deposition of the particle-bound form of the chemical[11]. Finally, the biota compartment is included as a dynamic compartment where chemical uptake via the water and prey chain is modeled via a five-compartment food-chain chain model[17,18].

The ISMCM structure is flexible and it can be expanded to include any number of compartments to provide a more detailed resolution of pollutant partitioning in the environment. However, it should be noted that with an increased complexity of the compartmental description the requirement for user-input of model parameters also increases.

2.2 Parameter Estimation and User Data Input

In order to reduce the number of model input parameters, the ISMCM utilizes various theoretical and empirical parameter estimation methods. The estimation methods incorporated into the ISMCM follow the approach described by Cohen et al.[3,8] and Cohen and Clay[11]. Estimation methods are included for partition coefficients, mass transfer coefficients, diffusion coefficients and the interpolation schemes for meteorological parameters. Additional modules exist to predict precipitation scavenging of gases, infiltration of dissolved solutes in the soil (due to rain infiltration), intermedia transfers of particle-bound chemicals by dry and wet deposition[8,12], wind resuspension[19] and sediment resuspension and deposition.

The physicochemical properties that the user is required to supply are listed in Tables 1. The partition coefficients are calculated internally using the fugacity representation for the fugacity capacity for each of the phases[8]. A database of physicochemical properties for nearly eighty chemicals is supplied with the ISMCM. The user can select the chemical of interest from a menu of chemicals and the appropriate physicochemical data are automatically written to the input screens. A number of prediction methods are also available to predict some of the physicochemical properties as indicated in Table 1.

Table 1. User-Specified Physicochemical Properties

Chemical Class, Molecular Weight, Molal Volume, Solubility[a]
Vapor pressure, Boiling Point
Henry's Law Constant[b]
Octanol-Water Partition Coefficient[c]
Water-Organic Carbon Partition Coefficient[d]
BCF[e] and BAF[e]
Reaction Rate Constants in the Compartments

(a) Optional input (can be estimated internally by the ISMCM) from K_{ow}.
(b) Can be estimated by ISMCM from solubility.
(c) Can be estimated by the ISMCM given solubility and vapor pressure data.
(d) Can be estimated by the ISMCM.
(e) Optional input (can be estimated by the ISMCM)

Table 2. User-Specified Physical Characteristics for the Air, Aerosol, Water and Biota Comaprtments

Parameter	Compartment			
	Air	Aerosol	Water	Biota
Height or Depth	Mixing height	NA	Depth	NA
Volume, Area or Mass	Air/land and air/water interfacial areas	Initial mass concentration	Area	Volume fraction in the water body.
Convection	Wind speed	NA	Water flow rate	NA
Temperature	Monthly average temperatures	Monthly average temperatures	Monthly average temperatures	(Assumed at water temperature)
Other	-	Type of particle size distribution	-	Species type

NA- not applicable

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Table 3. User-Specified Physical Characteristics for the Soil, vegetation, Sediment, and Suspended Solids Compartments

Parameter	Compartment			
	Soil	Vegetation	Sediment	Suspended Solids
Height, Depth or diameter	Depth	Mass surface density	Depth	Diameter
Volume or Area	Soil/atmosphere interfacial area	Canopy area per unit mass of plant matter	Sediment/water interfacial area	Volume fraction in the water body
Organic Carbon	Organic carbon mass fraction	percent lipid, organic matter and water	Organic carbon mass fraction	Organic carbon mass fraction
Density	Density	Density	Density	Density
Temperature	Average monthly temperatures	roots at soil temeperature. Canopy at ambient temepratture	Assumed at water temperature	Assumed at water temperature
Other	Land slope and land use charateristics.	type	NA	-

NA - not applicable

2.2 Structure of the SMCM Software and User-Interface

The ISMCM software is accessed via a user interface. The structure of the user interface is shown in Figure 2. There are four main menus: (1) internal menu; (2) external menu; (3) databases menu: and (4) input screens menu. An online help capability is provided to guide the user through the menu system, to define the various model parameters and to help the user in selecting the appropriate model parameters. The user interface is designed to also allow the addition of an auxilliary exposure module.

The menu system guides the user, in a logical sequence, through the compilation of information which is required to run the model. The internal menu leads the user to the parameter input screens menu and it also provides access to

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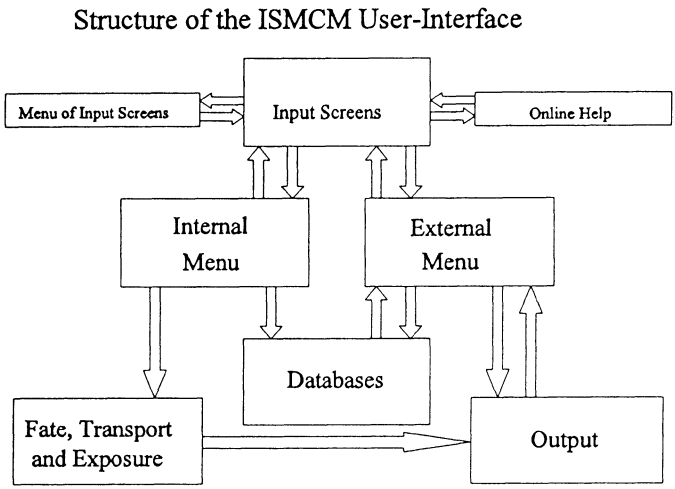

Figure 2. Schemcatic Representation of the ISMCM User-Interface.

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the model simulation. The parameter input screens are divided into three main groups, simulation se tup parameters (e.g., length of simulation, output reproting options, etc.), chemical-specific parameters and geographical parameters. The user can access both a chemical property database and a library of geographical parameters for a number of selected regions in the United States. Physicochemical and geographical information which is entered by the user, through the input screens, can be easily added to a user library of chemicals and geographical profiles. The saved input files can be easliy modified via the full-screen input system to allow for the simulation of various scenarios. Once the model is executed, the user is led to an external menu from which the results can be viewed in either a tabular or graphical format and also exported as ASCII files.

In the ISMCM the user can select a number of different source release scenarios and various initial condition (e.g., initial compartmental concentrations) as shown in Figures 3a and 3b. These source release scenarios can be used to simulate constant sources and intermittent, seasonal and diurnal variations of source releases.

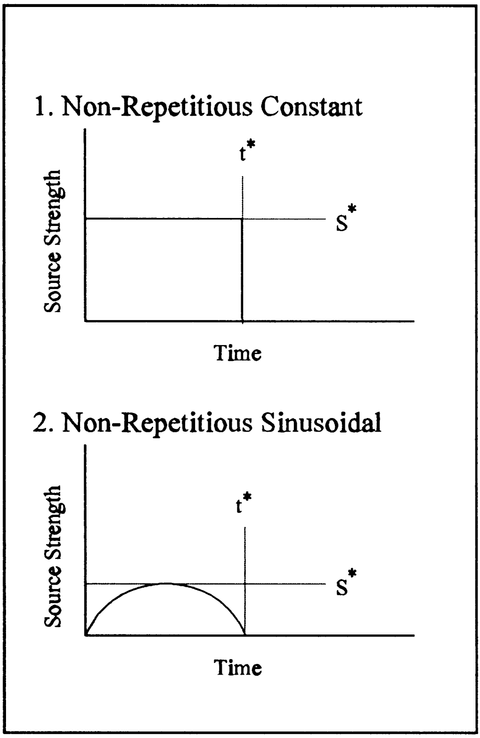

Figure 3a. ISMCM source release options. Non-repetitious constant and non-repetitious sinusoidal source release scenarios.

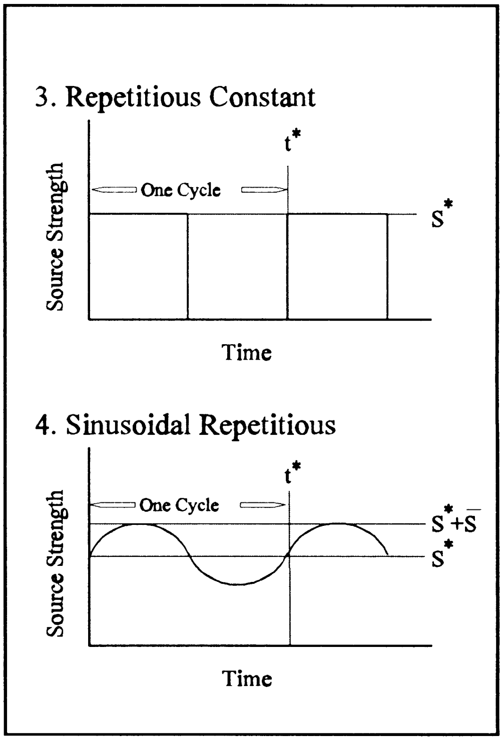

Figure 3b. ISMCM source release options. Repetitious costant and sinusoidal repetitious source release scenarios.

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3 Summary

An integrated spatial-multimedia-compartmental model (ISMCM) was developed to describe the multimedia partitioning of organics in the environment. The ISMCM considers both gaseous, dissolved and particle-bound pollutants and the particle size distribution along with a variety of intermedia transport processes. The current approach allows the determination of intermedia fluxes for the various physical forms of the chemical (e.g., particle-bound, vapor and dissolved forms) and various environmental scenarios.

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