

Multimedia partitioning of particle-bound organics

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Abstract

A spatial-multimedia-compartmental approach to modeling the partitioning and intermedia fluxes of particle-bound and volatile organics in the environment was developed with emphasis on a detailed description of intermedia transport processes associated with the gaseous, dissolved, and particle phases. Based on this approach a spatial-multimedia-compartmental model (COSMCM) of chemical transport and fate was developed. The COSMCM is composed of eight compartments, namely, air-gaseous phase, air-particulate phase, water, suspended solids (in water), biota (in water), sediment, soil, and vegetation. The COSMCM includes detailed modules of 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 COSMCM 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. Test cases with benzo(a)pyrene and pyrene distributions in the Los Angeles region revealed that the current approach is of sufficient accuracy and flexibility for estimating pollutant fluxes and multimedia partitioning.

1. Introduction

Pollutants which are released to the environment as the result of a variety of human-related activities (air emissions and/or direct discharge to surface water, etc.) move across environmental boundaries and are therefore found in most media. Although the recognition of the inherent multimedia nature of environmental pollution is not new [1-4], it is now becoming clear that the proper design of air pollution prevention strategies must incorporate a multimedia analysis of pollutant partitioning in the environment and the exposure of the human receptor via multiple exposure pathways.

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The significance of intermedia transfers is exemplified by the cycling of polychlorinated biphenyls (PCBs), in the Great Lakes region (e.g., sediment → water, water → atmosphere, atmosphere → water, water → sediment). Another example, is the emission of volatile compounds, such as benzene, TCE, and chloroform, from Public Owned Treatment Works (POTWs); such emissions contribute to multimedia environmental pollution via the volatilization. Various combustion processes (from either stationary or non-stationary sources) result in the emissions of polyaromatic hydrocarbons (PAHs) which can deposit to the ground surface via wet and dry deposition. 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.

Multimedia analyses of human exposure and risk require the determination of chemical concentrations in all media of concern via direct measurements or appropriate multimedia models that account for intermedia transport between the environmental media. Multimedia models which incorporate intermedia transfer processes are relatively inexpensive to use and can ascertain the environmental impact of present and future chemical releases. Also, using the modeling option, various scenarios can be simulated in order to assess a variety of potential environmental impacts. Multimedia models that incorporate intermedia transfer processes, are not a new concept and detailed reviews can be found elsewhere [2,4-6]. Multimedia transport and fate models vary in their level of complexity depending on the spatial resolution considered and the detailed accounting of intermedia transport processes.

While the existing multimedia models incorporate various intermedia transfer processes, most are deficient in the treatment of particle-bound chemicals. For example, the available models do not consider the interrelation between the particle size distribution and exchange processes such as dry and wet deposition. In most models the degree of required user input of intermedia transport parameters (e.g., mass transfer coefficients, dry deposition velocities, etc.) is significant and thus reduces the utility of the model for rapid analysis of various scenarios. Thus, in this work the major objective has been to develop a practical spatial-multimedia-compartmental model of pollutant transport and fate which is capable of dealing with volatile and particle-bound chemicals. The model developed in this study describes the environmental media as composed of four well-mixed environmental compartments and two non-uniform compartments where chemical transport is described by spatial one-dimensional transport equation. 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). The present multimedia approach incorporates the particle-size distribution and the dependence of intermedia transfer processes on particle size. Also, the present model incorporates theoretical and empirical descriptions of transport processes associated with the gaseous, dissolved and particle phases to reduce the required level of parameter input by the user. Furthermore, included in the present model is the modeling of rainfall events and the associated processes of rain scavenging of volatile organic compounds and particle-bound organics.

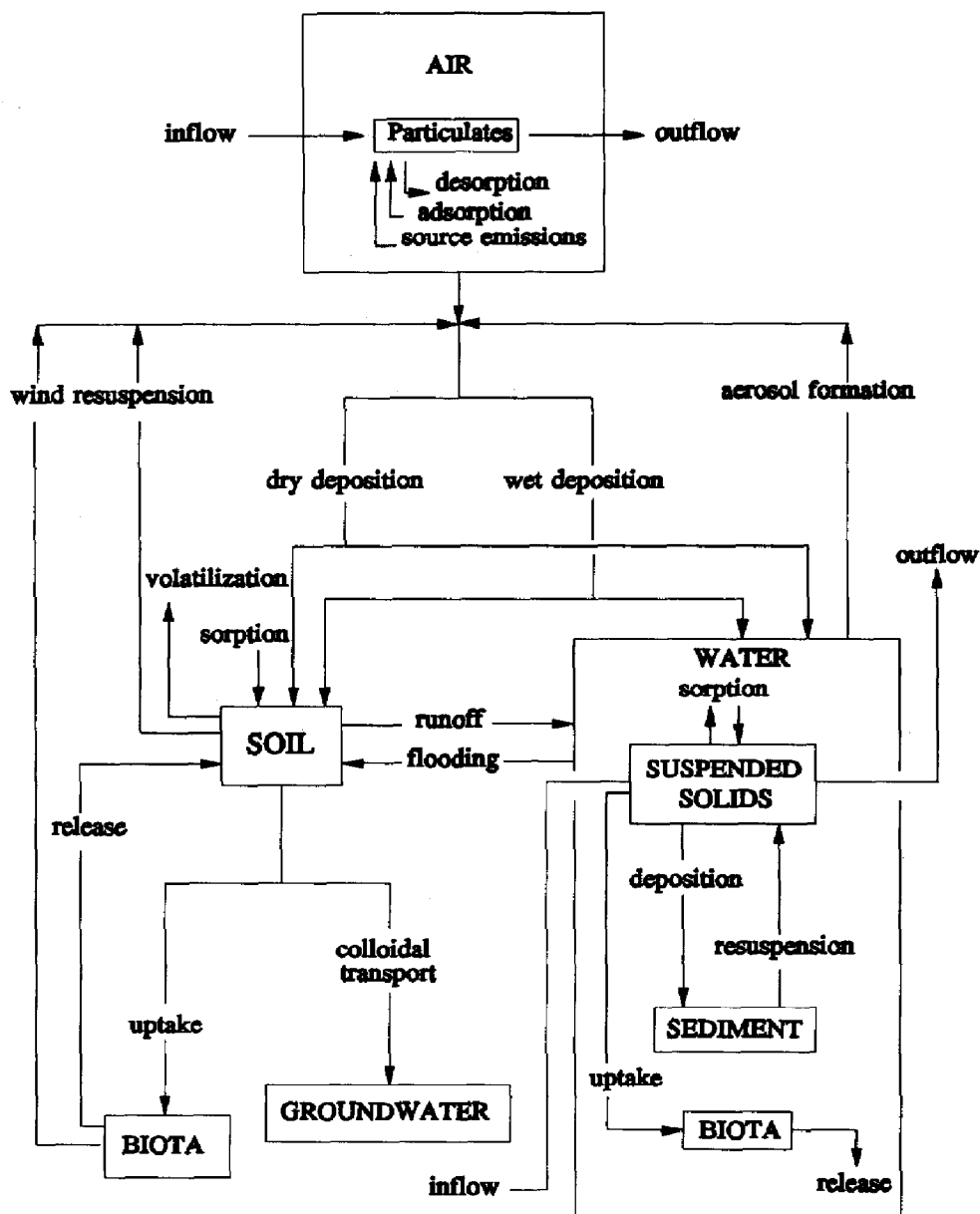


Fig. 1. Schematic representation of the COSMCM.

2. The COSMCM model

2.1. Overview

The comprehensive-spatial-multimedia-compartmental model (COSMCM) consists of six major environmental compartments, air, water, soil, sediment, suspended solids, and biota. A schematic representation of the COSMCM is shown in Fig. 1. The

air, water, biota, and suspended solids are treated as well-mixed compartments and thus, the mass balance of the chemical in these compartments can be expressed via ordinary differential equations. 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 phases. The soil and sediment compartments are taken to be non-uniform where transport is described by a one-dimensional convective-diffusion equation. The COSMCM structure is flexible and it can be expanded to include any number of compartments to provide a more detailed resolution of pollutant partitioning. However, it should be noted that with an increase of the complexity of the compartmental description the requirement for user input of model parameters also increases. It is beyond the scope of this paper to review all of the model equations and features and here only the major compartments and the associated intermedia interactions are presented.

2.2. Particle-bound chemical in the atmosphere

The chemical mass balance for the air compartment must consider the separate gas and particles phases. The basis for this approach originates from the fact that the modes of transport are a function of the physical state of the chemical (e.g., gaseous, liquid aerosol, or particle-bound). The mass balance on a pollutant present in the particulate form is given by:

$$\begin{aligned} \frac{d(V_a C_{ja}^{(p)})}{dt} = & (Q_{ia} C_{j,ia}^{(p)} - Q_{oa} C_{ja}^{(p)}) - C_{ja}^{(p)} (V_{dw,j} A_{aw} + V_{ds,j} A_{as}) \\ & - C_{ja}^{(p)} J_{rain} (A_{as} + A_{aw}) \Lambda_{jp} - k_a^{(p)} V_a C_{ja}^{(p)} + S_{ja}^{(p)} \\ & + R_{rsp} A_{as} (C_{j,sm}/H_{sm,sp})|_{z=0} + K_{jp} A_{jp} (C_a^{(g)} - C_a^{(g)*}|_p), \quad j = 1, \dots, M \end{aligned} \quad (1)$$

in which the subscripts and superscripts a, w, s, p, sm, and sp denote the air, water, soil, particle (in the atmosphere), soil matrix and soil–particles phases, respectively. The concentration of the particle-bound chemical in the atmosphere, in particle size range j (i.e. $a_j - a_{j+1}$, where a is the particle radius), is given by $C_{ja}^{(p)}$ (ng/m³ air) where $C_{j,ia}^{(p)}$ is the background concentration of the particle-bound chemical, A_{jp} (m²) is the corresponding surface area for particle size range j , and M is the number of particle size ranges. The particle surface area for particle fraction j is denoted by A_{jp} (m²). The volume of the air compartment is V_a (m³), A_{ij} is the interfacial area (m²) between media i and j , and Q_{ia} and Q_{oa} are the volumetric air flow rates (m³/h) into and out of the air compartment, respectively. The rain scavenging of particle-bound chemicals is quantified using the rain scavenging coefficient, Λ_{jp} (i.e. $C_{j,wf}/C_{ja}^{(p)}$, where $C_{j,wf}$ is the pollutant chemical concentration, in the particle-bound form, in rain water at ground level), which varies with the rate of rainfall J_{rain} (m/h). The dry deposition rate for the

particle-bound chemical to the water and soil surfaces is quantified using the dry deposition velocities, $v_{dw,j}$ and $v_{ds,j}$ (m/h), respectively. Particles can reenter the atmosphere via the process of wind resuspension quantified by R_{rsp} , the resuspension rate coefficient of soil particles (m/h). The rate of chemical exchange between the gas phase and the particle phase is governed by the mass transfer coefficient K_{jp} (m/h) and the chemical concentration in the air phase that would be in equilibrium with the particulate phase is denoted by $C_a^{(s)*|p}$ (ng/m³). The source input to the atmosphere for the chemical associated with particle size range j is given by $S_a^{(p)}$ (mol/h) and the chemical degradation of the chemical in the atmosphere is assumed to follow a first-order kinetics with $k_a^{(p)}$ denoting the first-order reaction rate constant (h⁻¹).

The terms in Eq. (1) represent the various interactions of the atmospheric phase with other environmental media. The left-hand side of Eq. (1) accounts for the rate of accumulation of the particle-bound chemical in the atmosphere. The first term on the right-hand side of Eq. (1) (term i) accounts for the net convective flow of the particle-bound chemical into the air compartment. Term (ii) represents the transport of the particle-bound chemical from the atmosphere to the water compartment and land surface by dry deposition. Term (iii) represents the intermedia transfers of the particle-bound chemical from the atmosphere, due to rain scavenging of the particle-bound organic to the land and surface water. Term (iv) represents the production or degradation of the chemical pollutant in the particulate phase (e.g., due to heterogeneous reactions), term (v) represents the net input of the particle-bound chemical into the atmosphere from source emissions, and term (vi) accounts for potential introduction of the particle-bound chemical from the soil matrix phase via wind resuspension of soil particles. Finally, the last term (vii) represents the mass exchange rate of the chemical between the atmospheric gas phase and the particulate phase.

The particle size distribution of atmospheric particles affects the temporal dynamics of the contaminant in the particle phase. For example, Tsai et al. [7] have shown that failing to account for the variation in particle size distribution during rain can result in a significant overprediction of the rate of wet deposition. Therefore, when the model parameters are dependent upon the particle size distribution (e.g., deposition velocity), the mass balance on the particle-bound chemical, as described in Eq. (1), may be insufficient. Thus, if the temporal variation in the particle size distribution is significant, over the time scale of the simulation, then the temporal variation of the number concentration of particles, in the different particle size ranges, can be included by the following population mass balance equation on the particulate phase:

$$\begin{aligned} \frac{d(V_a N_{j,a}^{(p)})}{dt} = & (Q_{ia} N_{j,ai}^{(p)} - Q_{oa} N_{j,a}^{(p)}) - N_{j,a}^{(p)} (V_{dw,j} A_{aw} + V_{ds,j} A_{as}) \\ & - N_{j,w}^{(p)} J_{rain} (A_{as} + A_{aw}) \Lambda_p + S_j^{(p)} + R_{j,rsp} A_{as} N_{j,sm}|_{z=0}, \quad j = 1, \dots, M \end{aligned} \quad (2)$$

in which $N_{j,a}^{(p)}$ is number concentration of particles for size range j in a unit volume of air (number/m³ of air), $N_{j,ai}^{(p)}$ is the number concentration of particles for size range

j outside the region of study, $N_{j,sm}^{(p)}|_{z=0}$ is the number concentration of particles in size range j at the soil surface layer (number/m³ of soil), and $N_{j,w}^{(p)}$ is the number concentration of particles of size range j in rain water (number/m³ of water). The dry deposition velocities to the soil and water surface are denoted by $v_{dw,j}$ and $v_{ds,j}$ respectively, and $R_{j,rs}$ is the resuspension rate coefficient (m/h) of soil particles of size range j (m/h) [8]. Finally, $S_j^{(p)}$ is the source emission of particles of size range j into the atmosphere (number/m³ of air). In the application of the current model equations the initial particle size distribution is taken to be a trimodal log-normal distribution [9,10] with the appropriate distribution parameters for the selected scenario.

2.3. Chemical in the vapor phase in the atmosphere

The mass balance for the pollutant fraction which is present as a vapor phase in the atmosphere can be described by the following mass balance equation:

$$\begin{aligned} \frac{d(V_a C_a^{(g)})}{dt} = & (Q_{ia} C_{ia}^{(g)} - Q_{oa} C_a^{(g)}) + K_{aw} A_{aw} (H_{aw} C_w - C_a^{(g)}) \\ & + K_{as} A_{as} [(C_{sm}/H_{sm,sa})_{z=0} - C_a^{(g)}] - C_a^{(g)} H_{wa} J_{rain} (A_{aw} + A_{as}) \Lambda_g^* \\ & - k_a^{(g)} V_a C_a^{(g)} + S_a^{(g)} - K_p A_p (C_a^{(g)} - C_a^{(g)*}|_p) \end{aligned} \quad (3)$$

in which $C_a^{(g)}$ is the concentration of the gaseous chemical in the atmospheric phase (ng/m³ air) and C_{sm} is the chemical concentration in the soil matrix (ng/m³). The air/water and soil matrix/atmosphere partition coefficients are indicated by H_{aw} (i.e. $H_{aw} = C_a/C_w$) and $H_{sm,sa}$, respectively. K_{aw} is the overall gas phase mass transfer coefficient for the mass transfer of chemicals from air to water (or water to air) (m/h) and K_{as} gas-side mass transfer coefficient (m/h) for the mass transfer of chemicals from air to soil (or soil to air). Λ_g^* is the normalized gas scavenging ratio ($W_g H_{aw}$, where W_g is the gas scavenging ratio defined as $C_w^{(d)}/C_a^{(g)}$, and $C_w^{(d)}$ is the dissolved chemical concentration in rain water) that represents the effectiveness of the scavenging process with a range of values between one (i.e. equilibrium between the gas phase and water phase) and zero (i.e. the raindrops are pollutant free). Finally, $k_a^{(g)}$ is the first-order reaction rate constant (h⁻¹) for the chemical degradation in the gaseous phase.

The left-hand side of Eq. (3) defines the rate of accumulation of the gaseous chemical in the atmospheric environment. Term (i) describes the net convective flow of the gaseous chemical, terms (ii) and (iii) account for the rate of interfacial mass transfer of the gaseous chemical between the atmosphere and the water and soil compartments, term (iv) accounts for rain scavenging of the pollutant, term (v) accounts for the reaction and/or production of the contaminant, and term (vi) is the net input of gaseous chemical into the atmosphere from source emissions. Finally, term (vii) represents the rate of chemical mass exchange between the atmospheric gas and particle phases.

The rate of mass transfer between the particulate and gaseous phases can be extremely rapid leading to a stiff set of differential equations. However, it is useful to note that, when the time scale for the rate of mass transfer process is small relative to the time step of integration, for the complete set of mass balance equations, the particulate and gaseous phases can be assumed to be in equilibrium. In this situation Eqs. (1) and (3) can be combined using a relationship between the gas and particulate phase concentrations expressed using an appropriate gas/particle partition coefficient. For organic chemicals it is often possible to express the fraction of the organic chemical associated with the particle phase using an appropriate adsorption isotherm [11,12]. For example, the correlation of Junge [12] expresses the fraction of the organic chemical adsorbed onto the particle phase, ϕ , as

$$\phi = \frac{bS_t}{P_{\text{sat}} + bS_t} \quad (4)$$

where P_{sat} is the chemical saturation vapor pressure (mmHg), S_t is the total surface area of particles per unit volume of air (m^2/m). Finally, b is a parameter dependent upon the molecular weight, the surface concentration needed for a monolayer coverage, and the difference of the surface heat of desorption and the liquid phase heat of desorption (mmHg m). Other gas/particle partition coefficients such as the correlations proposed by Yamasaki et al. [13] and Pankow [14] can also be used provided that they are first converted to partition coefficients which are based on the total particle surface area.

2.4. *Water compartment, suspended solids and biota*

The mass balance equations for the water compartment, in the COSMCM, follow the approach of Cohen et al. [5]. However, as with the atmospheric compartments separate mass balances are written for the dissolved and particle-bound phases of the chemical. In the COSMCM 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 chemical. Finally, the biota compartment is included as a dynamic compartment with the rate of chemical exchange governed by an overall volumetric mass transfer coefficient as employed by Cohen et al. [5].

2.5. *Soil and sediment compartments*

The soil and sediment are considered as non-uniform compartments since significant concentration gradients exist in these compartments in which transport is strongly affected by molecular diffusion. Although lateral contaminant migration in the unsaturated zone is possible, in the present screening-level model 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-air, soil-water and soil-solids phases. Accordingly, the total

chemical concentration in the sediment or soil matrix is defined as

$$C_{am} = \theta_{as}C_{as} + \theta_{aw}C_{aw} + \theta_{aa}C_{aa} \quad (5)$$

where the subscript α represents either the soil (s) or sediment (sd), θ_{as} is the solids volume fraction, θ_{aw} is the water volume fraction, θ_{aa} is the air volume fraction (assumes a value of zero for the sediment), C_{as} is the chemical concentration in the soil or sediment solids, C_{aw} is the concentration in the soil or sediment water and C_{aa} is the concentration in the soil air (note that the sediment air content is normally set to zero).

The structure of the transport equation for the soil and sediment is given below

$$\frac{\partial C_{am}}{\partial t} = \frac{\partial}{\partial z} \left(D_{am} \frac{\partial C_{am}}{\partial z} \right) - V_{am} \frac{\partial C_{am}}{\partial z} - r_{am}(C_{am}) \quad (6)$$

where C_{am} is the overall soil or sediment matrix chemical concentrations defined in Eq. (5) (e.g. ng/m³), D_{am} is the effective diffusion coefficient in the soil or sediment (m²/h) as defined by Ryan and Cohen [15], V_{am} is the effective convective velocity in the soil matrix (m/h) [5], and $r_{am}(C_{am})$ is the reaction rate (positive for production and negative for degradation of the chemical) in the soil or sediment (ng/m³ h⁻¹). In most cases of interest a first-order kinetics is appropriate for a screening-level analysis but other kinetic expressions can also be used without a loss of generality. Eq. (6) only reflects the transport of chemicals in the soil in either the dissolved or vapor forms. The transport of rain scavenged particles through the soil column can be estimated separately with an appropriate colloidal transport model. However, for most cases of interest the transport of colloids through the soil column is restricted to the top layer of the soil column; thus, the accumulation of particle-bound chemicals is limited to the surface region.

The initial concentration profile in the soil or sediment columns serves as the initial condition expressed as

$$C_{am} = C_{am}(z) \text{ at } t = 0. \quad (7)$$

Two boundary conditions for the soil, at the air-soil interface and at the groundwater-unsaturated soil zone interface (at the bottom of the soil column) are possible. The top boundary condition, at the air-soil interface, can be expressed as follows:

$$\begin{aligned} V_{sm}C_{sm} - D_{sm} \left(\frac{\partial C_{sm}}{\partial z} \right) = & C_a^{(s)} J_{rain} H_{wa} \Lambda_g^* + k_{a,sm} (C_a^{(s)} - C_{sm}/H_{sm,sa}) \\ & \text{(i)} \qquad \qquad \qquad \text{(ii)} \\ & - R_{rsp} C_{sm}/H_{sm,sp} + C_a^{(p)} v_{ds} + C_a^{(p)} J_{rain} \Lambda_p \quad \text{(8)} \\ & \text{(iii)} \qquad \qquad \text{(iv)} \qquad \qquad \text{(v)} \end{aligned}$$

in which $C_a^{(p)}$ is the concentration of the particle-bound chemical in the air phase (ng/m³), v_{ds} is the overall dry deposition velocity for the particle phase, R_{rsp} is the overall wind-resuspension rate coefficient for the soil particles, Λ_p is the overall particle rain scavenging coefficient [7], and the atmosphere/soil mass transfer coefficient is denoted by $K_{a,sm}$ (m/h). Finally, $H_{sm,sp}$ and $H_{sm,sa}$ denote the soil matrix/soil solids and soil matrix/soil air partition coefficients, respectively. The left-hand side of

Eq. (8) accounts for chemical exchange at the atmosphere/soil interface due to gaseous rain scavenging (term i), gaseous diffusion (term ii), resuspension of the soil (term iii), dry deposition of the particle-bound chemical (term iv), and rain scavenging of the particle-bound chemical (term v).

The bottom boundary condition for the soil as employed in the COSMCM is a flux boundary condition at the groundwater table beneath the unsaturated soil column.

$$V_{sm}C_{sm} - D_{sm} \left(\frac{\partial C_{sm}}{\partial z} \right) = k_{gw,sm}(C_{sm}/H_{sm,sw} - C_{gw}) \quad (9)$$

in which $H_{sm,sw}$ is the soil matrix/soil water partition coefficient, C_{gw} is the groundwater concentration at the groundwater table level, and $k_{gw,sm}$ is the soil matrix/ground water mass transfer coefficient. An alternative boundary condition is the no-flux boundary condition where the right-hand side of Eq. (9) is set to zero.

The boundary condition for the sediment is a flux boundary conditions at the sediment/water interface:

$$V_{sdm}C_{sdm} - D_{sdm} \left(\frac{\partial C_{sdm}}{\partial z} \right) = \underbrace{R_{sed}C_{ss}H_{w,ss}}_{(i)} + \underbrace{k_{w,sdm}(C_w - C_{sdm}^i/H_{sdm,w})}_{(ii)} - \underbrace{R_{res}C_{sdm}/H_{sdm,sdp}}_{(iii)} \quad (10)$$

in which V_{sdm} is the apparent water convective velocity ($V_{sdm} = V_w/H_{sdm,sw}$, where V_w is the water interstitial velocity in the sediment), C_{sdm}^i is the sediment matrix concentration at the sediment/water interface, C_w is the dissolved chemical concentration in the bulk water phase, $k_{w,sdm}$ is the water/sediment mass transfer coefficient (based on the water-side), R_{sed} and R_{res} are the sedimentation and resuspension rates for sediment particles, and $H_{sdm,w}$ and $H_{sdm,sdp}$ are the sediment/water and sediment/sediment particles partition coefficients, respectively.

3. Parameter estimation and user data input

In order to reduce the number of model input parameters, it is useful to utilize parameter estimation methods where possible. The reduction in the required number of input parameters can be accomplished using various theoretical and empirical parameter estimation methods. The estimation methods incorporated into the COSMCM, following the SMCM model of Cohen et al. [5], include the estimation of partition coefficients, mass transfer coefficients, diffusion coefficients and the meteorological parameters. Additional parameter estimations techniques developed explicitly for the COSMCM are for rain 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, wind resuspension and sediment resuspension and deposition.

The required user-specified characteristics for the various environmental compartments are given in Tables 1a and 1b and the required chemical-specific physicochemical properties are given in Table 2. Partition coefficients are calculated internally using

Table 1a
User-specified physical characteristics for air, water and biota

Parameter	Compartment		
	Air	Water	Biota
Height or depth	Mixing height	Depth	NA
Volume or area	Air/land and air/water interfacial areas	Area	Volume fraction in the water body
Convection	Wind speed	Water flow rate	NA
Temperature	Monthly average temperatures	Monthly average temperatures	(Assumed at water temperature)

NA denotes not applicable.

Table 1b
User-specified physical characteristic for soil, sediment, and suspended solids

Parameter	Compartment		
	Soil	Sediment	Suspended solids
Height, depth or diameter	Depth	Depth	Diameter
Volume or area	Soil/atmosphere interfacial area	Sediment/water interfacial area	Volume fraction in the water body
Organic carbon	Organic carbon fraction	Organic carbon fraction	Organic carbon fraction
Density	Density	Density	Density
Temperature	Average monthly temperatures	Assumed at water temperature	Assumed at water temperature
Physical property	Land slope	NA	Particle size

NA denotes not applicable.

Table 2
User-specified physicochemical properties

Chemical property
Molecular weight
Molal volume
Solubility
Boiling point
Octanol-water coefficient
Henry's law constant
Reaction rate constants
Source strength for the different compartments

the fugacity representation for the fugacity capacity for each of the phases [5,16]. Finally, runoff, soil drying and rain infiltration are determined by various sub-modules using user-input regarding rainfall, monthly averaged temperatures and basic geographical information. Table 3 provides a summary of the major parameter estimation methods incorporated into the COSMCM and the corresponding literature references.

4. Multimedia distribution of pyrene and benzo(a)pyrene in the Los Angeles area

As a demonstration of the utility of the COSMCM model, the environmental distributions of two polyaromatic hydrocarbons (PAHs), pyrene and benzo(a)pyrene (B(a)P), were evaluated for the Los Angeles area. B(a)P resides mostly in the particle phase [17,18] while pyrene exhibits moderate partitioning between the particle and gas phases. The pertinent physicochemical properties of B(a)P and pyrene are given in Table 4a and the environmental degradation rate constants are given in Table 4b. Since in the Los Angeles area the major sources of the above two chemicals are from vehicular sources, a source that varies diurnally about the average source value was assumed. The source emission rates were estimated following the approach of Tsai et al. [7] and the data of Benner et al. [19] and Handa et al. [20]. Accordingly, an average mobile source emission of 46 $\mu\text{g}/\text{vehicle km}$ was determined for pyrene, while an average value of 1.75 $\mu\text{g}/\text{vehicle km}$ was determined for B(a)P. These values correspond to an average emission rate of 472 g/h and 18 g/h for pyrene and B(a)P, respectively, for the Los Angeles study region. In the simulation of vehicular emissions, a time variable emission rate was estimated from the above average emission rate assuming a sinusoidally varying emission rate where the maximum emission rate represented the rush hour periods [7].

The regions included in the Los Angeles simulations encompass the major four counties in the region, i.e. Los Angeles County, Orange County, San Bernardino County, and Ventura County. Characterization of the distribution of pollutants for the Los Angeles region required information of the surface topology, water/river–air interfacial area, land surface area and specific compartmental data and the detailed information is available elsewhere [5,7]. The dynamic partitioning of pyrene and B(a)P emitted into the Los Angeles region are illustrated for two scenarios. In the first scenario, the multimedia chemical partitioning due to a constant average emission rate was evaluated (labeled constant emission). In the second case, the multimedia partitioning of the study chemicals, associated with a sinusoidal emission source was evaluated (labeled periodic emission). Both simulations incorporated a stochastic rainfall simulation based on rainfall information for Los Angeles and the test cases were run for a simulation time period of 10000 h (i.e. 417 d).

As an illustration the temporal buildup of the concentration levels, for the sinusoidal emission scenarios, are shown in Fig. 2a for pyrene and in Fig. 2b for B(a)P. It is noted that although the complete concentration profiles with depth were obtained for the sediment and soil compartments, only the average concentrations for the top ten centimeters of these compartments are reported here. The multimedia

Table 3
 Estimation methods utilized in the COSMCM

Parameter	Reference Source
Partition coefficients	
Fugacity capacities for the air and water (Z_a, Z_w)	Cohen et al. [5]
Fugacity of the sorbed phase (Z_{sp})	Mackay and Paterson [16]
Octanol/water partition coefficient (K_{ow})	Chiou and Schmedding [26], Chiou [27], Lyman et al. [28], Mailhot and Peters [29]
Correlation of the organic carbon partition coefficient with K_{ow}	Karickhoff [30,31], Lyman et al. [28]
Bioconcentration factors	Lyman et al. [28], Barber et al. [32], Thomann [33]
Particle/gas partition coefficient	Junge [12], Pankow [11]
Intermedia transfer processes and intermedia transfer factors	
Overall mass transfer coefficients (K_{oij})	Lewis and Whitman [34]
Gas-side mass transfer coefficient at the atmosphere–soil ($k_{a,sm}$)	Fernandez de la Mora and Friedlander [35]
Overall volumetric water/biota mass transfer coefficients	Cohen and Ryan [36]
Water-side mass transfer at the water/suspended solid interface	Rowe et al. [37]
Sediment–water mass transfer coefficient (water-side)	Thibodeaux and Becker [38]
Air–water mass transfer coefficient (air-side)	Brutsaert [39]
Particle dry deposition (land surface)	Slinn [40]
Particle dry deposition (water surface)	Williams [41]
Runoff rate (R_o) and soil erosion	Smith and Cherry [42], Heimstra [43], Novotny and Chesters [44], Whelan et al. [45], Goldman et al. [46]
Partition coefficients	
Soil drying rate	Van Bavel [47]
Rain infiltration (into soil)	Broadbridge and White [48]
Resuspension and sedimentation of sediment particles (in water)	Ackers and White [49], Sheng and Lick [50], Clay [8]
Wind resuspension of soil particles	Cowherd et al. [51], Gillette et al. [52]
Diffusion coefficients	
Air phase diffusion coefficient (D_a)	Reid et al. [53]
Water phase diffusion coefficient (D_w)	Reid et al. [53]
Effective diffusivity in the soil matrix (D_{sm})	Ryan and Cohen [15]
Air and water phase tortuosities (τ_a and τ_w)	Sallam et al. [54]
Effective diffusivity in the sediment (D_{sam})	Cohen et al. [5]
Soil diffusivity and conductivity for water infiltration	EPA [55]
Meteorological parameters	
Daily temperature	Jamison [56]
Rainfall rate and duration	Cohen et al. [5]

Table 4a
Physicochemical properties of pyrene and B(a)P

Physicochemical property	Pyrene	Benzo(a)pyrene
Molecular weight (g/mol)	202.3	252.3
Boiling point (°C)	311	398
Solubility (µg/l)	129–165	3.8
Henry's law constant (Pa m ³ /mol)	0.52	0.05
Vapor pressure (Pa 25 °C)	3.3×10^{-4}	7.5×10^{-7}
Octanol/water partition coefficient	7.8×10^4	1.35×10^6

Table 4b
Chemical reaction rate constants for pyrene and B(a)P

Chemical	Reaction rate constants (h ⁻¹) ^a			
	Air-gas	Air-particle	Soil	Water
Pyrene	0.0864	2.06×10^{-3}	1.52×10^{-5}	0.340
B(a)P	0.630	3.61×10^{-3}	5.45×10^{-5}	0.630

^a Values are obtained from Howard et al. (1991) [79] and ATSDR toxicological profile for PAHs (1990) [80].

mass distribution at the end of the simulation for the periodic emission scenario are displayed graphically in Figs. 3a and 3b for pyrene and B(a)P, respectively.

The results for the two semi-volatile chemicals display obvious trends (Table 5). The atmospheric distribution between the particulate and gaseous phases for the chemicals is such that about 27% and 99.00% of the atmospheric pyrene and B(a)P, respectively, resides in the particulate phase. This is in good agreement with the reported composition of these PAHs in the gaseous phase in Los Angeles, i.e., less than 30% and 0.5% of pyrene and B(a)P is present in the gas phase, respectively [15]. The partitioning of the chemicals in environment is predominately to the soil media, with 98.6% and 99.4% of the pyrene and B(a)P present in the environment partitioning to these media, respectively (Figs. 3a and 3b). The partitioning of both chemicals to the water compartment is extremely low which is to be expected given the low solubility of pyrene and B(a)P in water and the small area of total surface water in the region. However, it is interesting to note that the suspended solids phase in the water compartment, i.e. suspended solids, contains almost all of the chemical present in the water compartment. The effect of rain scavenging is evident by the significant variation in the compartmental concentrations during rain events (Figs. 2a and 2b). It is interesting to note the sharp increase in the compartmental concentrations for the water, sediment, and suspended solids compartments due to rain scavenging. In contrast, the atmospheric concentrations of B(a)P and pyrene decrease significantly as a consequence of rain scavenging.

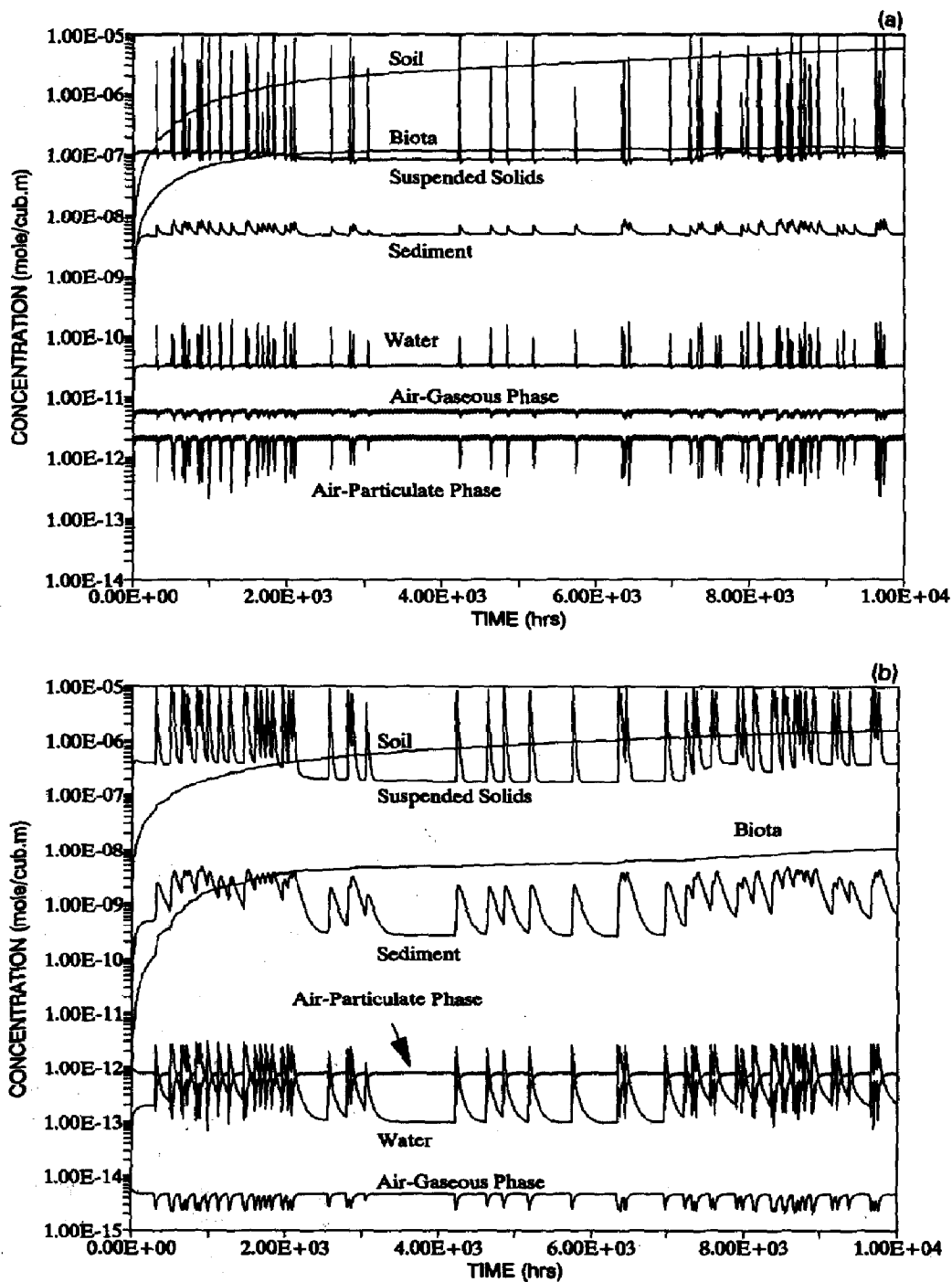


Fig. 2. (a) Temporal variation of environmental pyrene concentrations for the Los Angeles region (periodic emission rate). (b) Temporal variation of environmental B(a)P concentrations for the Los Angeles region (periodic emission rate).

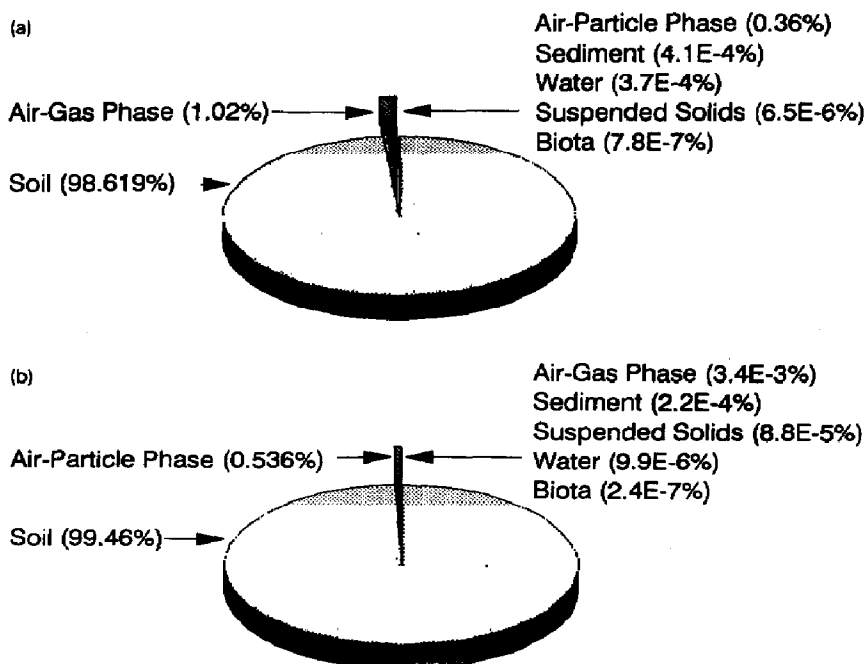


Fig. 3. (a) Mass distribution of pyrene in the Los Angeles region (periodic emission rate). (b) Mass distribution of B(a)P in the Los Angeles region (periodic emission rate).

Table 5
COSMCM predicted environmental concentrations for pyrene and B(a)P

Chemical	Concentrations						
	Air-Particle (ng/m ³)	Air-Gas (ng/m ³)	Water (ng/l)	Soil (ng/kg)	Sediment (ng/kg)	Biota (ng/kg)	S.S. (ng/kg)
Periodic emission rate at the end of the simulation (average pyrene emission rate 472 g/h, average B(a)P emission rate 18 g/h)							
Pyrene	0.39	1.1	6.4×10^{-3}	786	0.65	26.9	14.8
B(a)P	0.19	1.2×10^{-3}	5.7×10^{-5}	268	0.11	2.75	67.4
Constant emission rate at the end of the simulation (i.e. after 2000 h of source removal) (average pyrene emission rate 472 g/h, average B(a)P emission rate 18 g/h)							
Pyrene	0.011	0.029	1.6×10^{-4}	392	0.019	5.0	0.38
B(a)P	0.036	2.2×10^{-4}	1.1×10^{-5}	215	0.022	2.01	12.4

The removal of the emission source (at $t = 8000$ h) is illustrated in Fig. 4 for B(a)P for the scenario of a constant emission rate. Fig. 4 shows that the concentrations in the atmospheric phase, water phase, and sediment phase decrease significantly once emissions are eliminated. For example, the atmospheric B(a)P concentration decreases

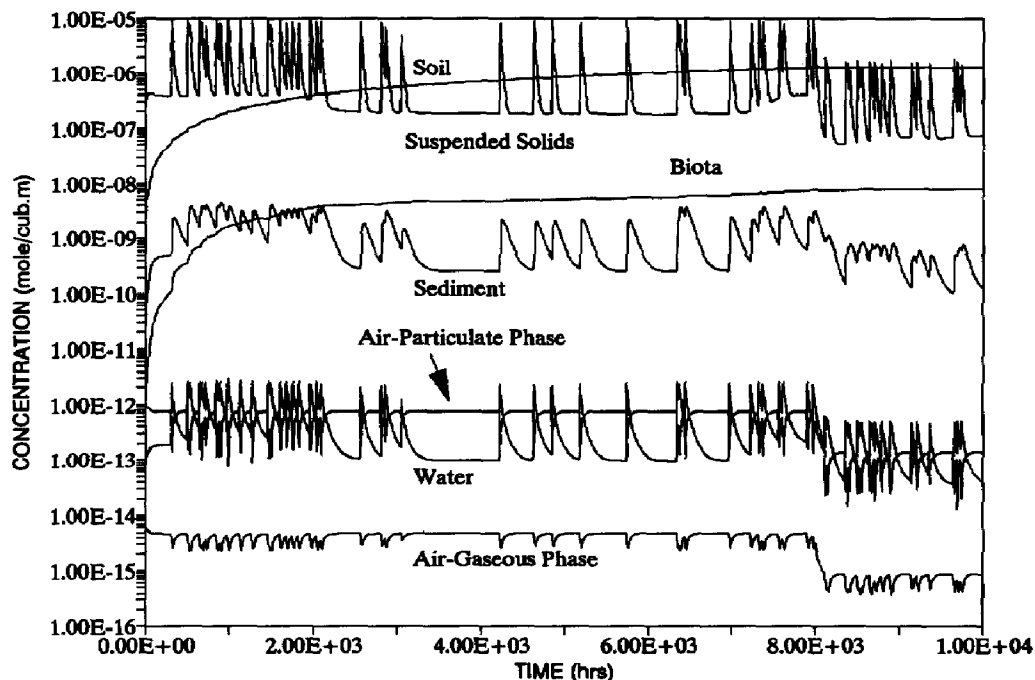


Fig. 4. Temporal variation of environmental B(a)P concentrations (for a constant emission rate) and the effect of source removal in the Los Angeles region.

by about an order of magnitude over a period of about eighty days (Fig. 4). As the concentration of B(a)P in the atmosphere decreases, to the point where the chemical potential driving force for intermedia transport of B(a)P is reversed, and B(a)P is then slowly released from the soil to the atmosphere via volatilization where it continues to degrade in the atmosphere, transported from the atmosphere to other media, and convected outside of the study region. Finally, it is worth noting that the biota compartment responds slowly to removal of sources consistent with the tendency of B(a)P to bioaccumulate.

Multimedia interactions can be illustrated as depicted in Fig. 5 for the annual average movement of B(a)P through the environment for the scenario of a periodic emission rate. In this particular example, the total amount of B(a)P contained in the modeled environment (at $t = 10000$ h) is 147.6 kg. The air/soil transfer rate is dominant with significantly lower intermedia transfer rates from air to water and the water to sediment, suspended solids, and biota. Also given in Fig. 5 are the percentages of the total amount of B(a)P accumulated within the environment, for each compartment, at the end of the simulation run (at $t = 10000$ h). A significant fraction of the total annual source of B(a)P was found to deposit to the soil compared to only about 10% of the annual pyrene source which deposits to the soil compartment. The lower amount of pyrene which accumulates in the soil can be attributed to the greater partitioning of pyrene to the gas phase in the atmosphere where pyrene reacts quickly with the OH^- radical. This is in contrast to B(a)P, for which a much lower partitioning

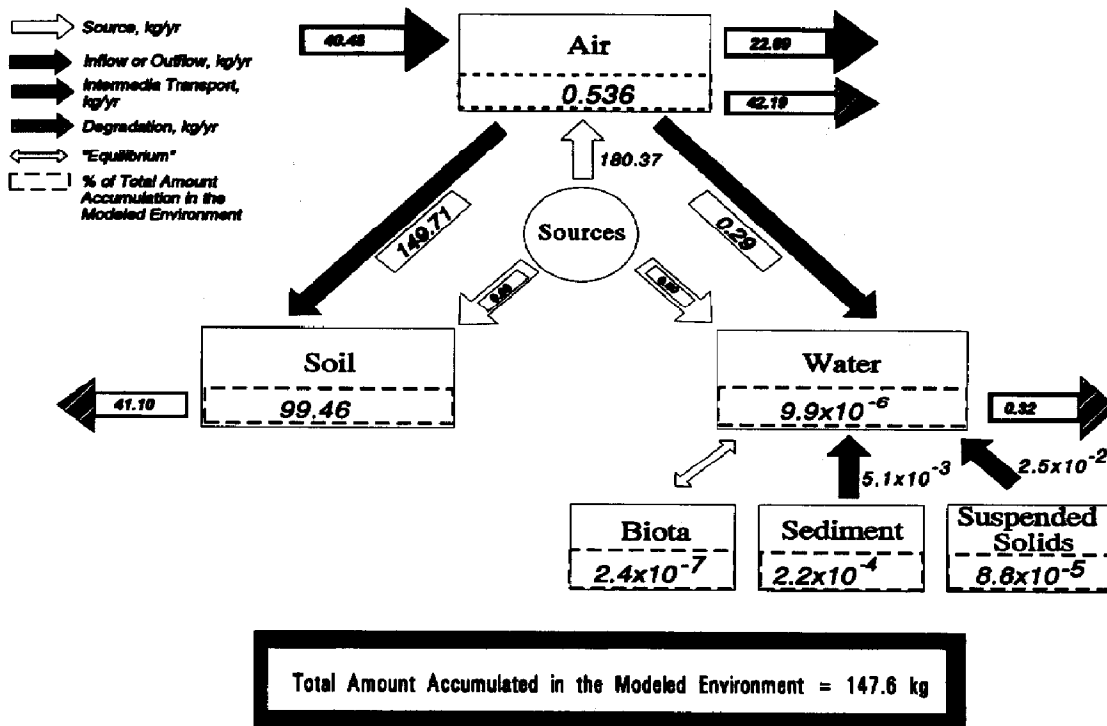


Fig. 5. Multimedia partitioning and intermedia pathways for B(a)P in the Los Angeles region (periodic Oemission rate).

to the gaseous phase is observed. Finally, a significant portion of both chemicals released to the air is convected and dispersed outside of the modeled region.

The predicted atmospheric concentrations of pyrene and B(a)P agree favorably with measured ambient concentrations. Average ambient atmospheric concentrations of 0.7 ng/m [21] and 3.6–3.8 ng/m [18] for pyrene and 0.24–0.29 ng/m³ [18] for B(a)P have been reported for the Los Angeles area and it is obvious that the predicted total atmospheric concentrations (Table 5) are within the limits of a 'screening level' model. Unfortunately, data for pyrene and B(a)P concentrations in surface waters and soil are lacking for the Los Angeles area. The predicted total water concentrations for pyrene and B(a)P combined is approximately 0.6 ng/L which is at the lower limit of reported total PAHs for typical surface water [22]. Predicted soil concentrations (786 ng/kg and 268 ng/kg for B(a)P and pyrene, respectively) are significantly below those that have been measured in typical soils [22]. It should be noted, however, that the present simulation was only carried out for a period of little over a year while the soil concentration of PAH is expected to rise with time due to continuing dry and wet deposition. For example, Ryan and Cohen [17] demonstrated, in their analysis of B(a)P in the Southeast Ohio river valley region, that B(a)P concentration could reach levels in excess of 100 µg/kg for B(a)P due to dry and wet deposition over a period of about 12 yr. Also, it is noted that in the results of the present simulation are restricted to the case of vehicular emissions; thus, actual environmental soil concentrations are expected to be higher than presented in the above illustrations.

Finally it is instructive to compare the COSMCM prediction of the dry deposition velocity and rain scavenging coefficient with available field data. The chemical dry deposition velocity for B(a)P in the Los Angeles area has been estimated to be approximately 0.15–0.20 cm/s [23] which is in excellent agreement with the COSMCM predicted value of 0.22 cm/s. Finally, the average particle rain scavenging ratio for pyrene has been reported to be approximately 9100 for the Portland, Oregon region [24,25] relative to the range of 100000–200000 predicted by the COSMCM model. These differences are expected due to the difference in the geographical regions and given that the reported field values are based on average values which do not consider the temporal variations in the scavenging ratio during a rain event [7].

5. Conclusions

The results of this study have demonstrated the utility of a multimedia partitioning approach that considers the particle size distribution along with a variety of intermedia transport processes for the particulate, gaseous and dissolved forms of the chemical under consideration. 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. Current work is focused on the design of a user-friendly interface for the COSMCM in order to facilitate the rapid evaluation of various scenarios.

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