

# Application of the Multimedia Urban Model To Compare the Fate of SOCs in an Urban and Forested Watershed

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A multimedia model has been developed to estimate the dynamics of semivolatile organic compounds (SOCs) in urban areas (1). The model is based on a Level III fugacity model of Mackay (2) and consists of six compartments: air, surface water, sediment, soil, vegetation, and an organic film that coats impervious surfaces. The model was used to illustrate the effect of impervious surfaces in urban areas by parametrization for downtown, Toronto, Canada, and modification of the same area to simulate forested conditions. With illustrative emissions of PCB homologues to air, the model indicates that most chemicals are lost by advection, with the remainder undergoing air-to-surface (organic film or vegetation) transfer. Under urban conditions chemicals with  $\text{Log}[K_{OA}] < 7.5$  volatilize from the film into air where they are susceptible to advection and photolytic degradation. Chemicals with  $\text{Log}[K_{OA}] > 7.5$  are washed off the film to surface waters where they may undergo volatilization, advection, sedimentation, and degradation. Both loss mechanisms from the film increase the overall mobility of SOCs in the urban relative to the forested environment. In forested areas, vegetation more efficiently accumulates gas- and particle-phase SOCs and subsequently transfers them to surface soils, the greatest chemical reservoir, where they are relatively immobile.

## Introduction

Although populations are becoming increasingly urbanized worldwide, we know surprisingly little about the influence of our built environment on chemical fate, particularly from a multimedia perspective. In cities we concentrate raw materials and other resources originating from regional and global sources, for the purposes of general consumption and processing. These activities give rise to urban areas being the geographic focus of numerous chemical emissions and having elevated chemical concentrations in virtually all media (e.g. refs 3–7). This has also led to the recognition that urban areas act as point sources for medium and long-range pollutant transport to surrounding areas (8, 9). In contrast to rural or forested systems, chemicals enter an urban system

in which the environment is characterized by the presence of impervious surfaces, minimal vegetation, and a radically altered hydrologic regime. To understand these influences on contaminant dynamics in urban areas, the built environment must be addressed within a modeling framework.

In this paper, the multimedia urban model (MUM) developed by Diamond and co-workers (1) is presented and used to compare the fate and transport of semivolatile organic compounds (SOCs) in urban and forested areas. The model, based on the steady-state, level III fugacity model of Mackay (2), is parametrized to simulate summer conditions for the urban area of downtown Toronto, Ontario, Canada, and considers all major media as well as impervious surfaces that are specific to urban areas (1). Diamond et al. (7) have found that an organic film is present on impervious surfaces and contains a wide range of chemicals. Its high surface area-to-volume ratio promotes the volatilization of SOCs back into the atmosphere as well as chemical washoff into surface waters. In contrast, soil and sediment are the greatest sinks for SOCs in urban areas due to high chemical persistence in, and minimal losses from, these media. Vegetation accumulates gas- and particle-phase SOCs and subsequently transfers them to surface soils via litterfall, canopy drip, and cuticular wax erosion (nolitterfall deposition); chemicals contained in litterfall, however, are typically exported from urban areas.

Here, the model is used to demonstrate the effect of the built environment on the mobility of SOCs in urban relative to forested areas. We first review the model and then apply it in order to compare results obtained for urban and forested areas. Although there are many uncertainties that accompany parameter values, the model is a useful first step towards understanding the effect of the built environment on SOC fate.

## Multimedia Urban Model (MUM)

The Multimedia urban model (MUM), described in detail by Diamond et al. (1) and summarized here, is based on the Level III fugacity model of Mackay (2) and assumes steady-state conditions. MUM is comprised of six bulk compartments: air [A], surface water [W], soil [S], sediment underlying the water [D], vegetation covering the soil [V], and the organic film on impervious surfaces [F]. Each bulk compartment consists of pure and either aqueous and/or particulate phases of specified volume. Chemicals are assumed to be in equilibrium between these phases within each bulk compartment. Chemicals enter each medium through direct emission,  $E$  (mol/h), and can be transferred among compartments as well as be lost from all compartments through various transport and transformation processes expressed as  $D$  values (mol/Pa·h). Chemicals can also enter air and water through advection, parametrized as the product of a flow rate  $G$  ( $\text{m}^3/\text{h}$ ) that quantifies bulk material movement, and the chemical concentration entering the system  $C$  (mol/ $\text{m}^3$ ). Chemicals can be lost from the system through ventilation to the stratosphere, leaching to groundwater, burial in deep sediments, and export of litterfall.

$Z$  values (mol/Pa· $\text{m}^3$ ) that express the capacity of a phase for a chemical are derived according to Mackay (2) and Mackay and Paterson (10) (Table 1). The  $Z$  value for vegetation,  $Z_v$ , is calculated by assuming that only the leaf cuticle participates in the plant/air partitioning of SOCs (11). The bulk  $Z$  value for vegetation is calculated as the product of the relative fractions of air, water, and cuticle in leaves and their corresponding pure  $Z$  values (12). The relative

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TABLE 1. Z Values<sup>a</sup>

compartment	phase	equation
air	gas phase	$Z_A = 1/RT$
	particulate	$Z_Q = 10^{(\log K_{OA} + \log f_{om} - 11.91)} \cdot Z_A \cdot \rho_Q \cdot 10^9$ <sup>b</sup>
	bulk	$Z_{BA} = Z_A + (Z_Q \times v_Q)$
water	dissolved	$Z_W = 1/H = S^S/P^S = S^L/P^L$
	suspended part.	$Z_P = Z_W \times \rho_P \times K_{OC} \times f_{OC,P}$
soil	bulk	$Z_{BW} = Z_W + (Z_P \times v_P)$
	solids	$Z_S = Z_W \times \rho_S \times 0.41 K_{OW} \times f_{OC,S}$
sediment	bulk	$Z_{BS} = (v_A \times Z_A) + (v_W \times Z_W) + (v_S \times Z_S)$
	solids	$Z_D = Z_W \times \rho_D \times 0.41 K_{OW} \times f_{OC,D}$
vegetation	bulk	$Z_{BD} = (v_W \times Z_W) + (v_D \times Z_D)$
	leaf cuticle	$Z_V = Z_W \times K_{OV} \times f_{OC,V}$
film	bulk	$Z_{BV} = (v_A \times Z_A) + (v_W \times Z_W) + (v_V \times Z_V)$
	dissolved	$Z_F = Z_A \times K_{OA} \times f_{OC,F}$
	particulate	$Z_Q = 10^{(\log K_{OA} + \log f_{om} - 11.91)} \cdot Z_A \cdot \rho_Q \cdot 10^9$
	bulk	$Z_{BF} = (Z_F \times \phi_F) + (Z_Q \times \phi_Q)$

<sup>a</sup> Subscripts A, Q, W, P, S, D, V, and F represent the media of air, aerosols, water, suspended sediment, soil, bulk sediment, vegetation, and organic film, respectively. The subscript B denotes the bulk Z value for that medium. H is the Henry's law constant (Pa·m<sup>3</sup>/mol), S<sup>S</sup> and S<sup>L</sup> are the solid and subcooled liquid solubilities (mol/m<sup>3</sup>), P<sup>S</sup> and P<sup>L</sup> are the solid and subcooled vapor pressures (Pa), respectively, f<sub>om</sub> is the fraction of organic matter, f<sub>OC</sub> is organic carbon fraction, ρ is density (kg/L), v is volume fraction, and φ is mass fraction. <sup>b</sup> Reference 13.

TABLE 2. D Value Formulations Specific to MUM<sup>a</sup>

transport media	process	D value formulation
air–film	gas diffusion	$D_{VF} = 1/[(1/k_{AF}A_{AF}Z_A) + (1/k_{FF}A_{AF}Z_F)]$
	wet dep. of gas	$D_{RF} = A_{AF} \cdot U_R \cdot Z_W$
	wet dep. of particles	$D_{QF} = A_{AF} \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q$
	dry dep. of particles	$D_{DF} = A_{AF} \cdot U_P \cdot v_Q \cdot Z_Q$
	total	$D_{AF} = D_{VF} + D_{RF} + D_{QF} + D_{DF}$
film–water	film washoff	$D_{FW} = A_{AF} \cdot k_{FW} \cdot Z_{BF}$
	gas diffusion	$D_{VV} = 1/[(1/k_{AV}A_{AV}Z_A) + (1/k_{VV}A_{AV}Z_V)]$
air–vegetation	wet dep. of gas	$D_{RV} = A_{AV} \cdot U_R \cdot Z_W \cdot I_{FW}$
	wet dep. of particles	$D_{QV} = A_{AV} \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q \cdot I_{FW}$
	dry dep. of particles	$D_{DV} = A_{AV} \cdot U_P \cdot v_Q \cdot Z_Q \cdot I_{FD}$
	total	$D_{AV} = D_{VV} + D_{RV} + D_{QV} + D_{DV}$
	canopy drip	$D_{CD} = A_{AV} \cdot U_R \cdot (I_{FW} - I_{LW}) \cdot \lambda \cdot Z_Q$
vegetation–soil	wax erosion	$D_{WE} = A_{AV} \cdot k_{WE} \cdot Z_V$
	litterfall	$D_{LF} = V_V \cdot R_{LF} \cdot Z_{BV}$
	total	$D_{VS} = D_{CD} + D_{WE} + D_{LF}$
soil–vegetation	rainsplash	$D_{SP} = V_S \cdot R_S \cdot Z_{BS}$

<sup>a</sup> A's are media interfacial areas (m<sup>2</sup>), k's are mass transfer coefficients (m/h), U<sub>R</sub> is the rain rate (m/h), U<sub>P</sub> is the dry deposition velocity (m/h), I<sub>FW</sub> and I<sub>FD</sub> are the canopy wet and dry interception fractions, I<sub>LW</sub> is the wet deposition loss fraction, Q is the scavenging ratio, v is volume fraction, V is medium volume (m<sup>3</sup>), λ is the canopy drip parameter (dimensionless), and R<sub>LF</sub> and R<sub>S</sub> are the first-order litterfall and rainsplash rate constants, respectively (h<sup>-1</sup>).

magnitudes of these fractions vary from species-to-species, but we have chosen values of 0.18, 0.8, and 0.02 for these parameters, respectively (12). The bulk film is considered to consist of 30 and 70% by mass of organic or "pure" film and particulate phases, respectively (7). The "pure" film phase is assumed to consist entirely of organic matter with an organic carbon fraction (f<sub>OC</sub>) of 0.74, that of octanol. The Z value for particle-sorbed chemicals in the film is the same as that for aerosols, Z<sub>Q</sub>, the presumed source of the particles in film. We use the empirical relationship of Harner and Bidleman (13) that correlates the particle-air partition coefficient, K<sub>P</sub> (m<sup>3</sup>/μg), with the octanol-air partition coefficient, K<sub>OA</sub>, assuming an organic matter content of aerosols of 0.20 (13–16).

Intercompartmental transfer of chemicals between air, water, soil, and sediment, chemical transformations and loss processes are quantified by D values that are described in detail by Mackay (2). In addition to these, MUM includes D values for transport mechanisms to and from the organic film and vegetation (Table 2), full details of which are presented by Diamond et al. (1) and are summarized below. The organic film surface area is calculated as a film thickness (7) and an impervious surface index (ISI) derived using typical building arrangements and dimensions (17). Chemicals are transferred from air to film by wet and dry particle deposition,

D<sub>QF</sub> and D<sub>DF</sub>, respectively, and rain dissolution of gas-phase chemical, D<sub>RF</sub>. Chemicals can undergo bidirectional exchange of gas-phase compounds, D<sub>VF</sub>, where the air-side mass transfer coefficient is calculated as the ratio of a chemical's diffusivity and a boundary layer thickness obtained by consideration of fetch and wind speed (18)

$$\delta^{bl} = \beta \cdot \sqrt{\frac{l}{v}} \tag{1}$$

where l (m) is the mean length of the surface in the direction of the wind, v (m/s) is the wind speed, and β (mm/s<sup>-1/2</sup>) assumes a value of 6 according to hydrodynamic theory for an air current adjacent to a flat plate. The film side mass transfer coefficient is calculated using the empirical relationship developed for plant cuticles by Trapp (19)

$$\text{Log}[k_F] = (0.704 \text{ Log } K_{OW} - 11.2)/K_{AW} \tag{2}$$

Chemicals can also be lost from the film by a bulk removal process of washoff, D<sub>FW</sub>, in which the polar constituents of the film solubilize the nonpolar constituents independently of aqueous solubility and precipitation removes most but not all of the film (20). D<sub>FW</sub> is calculated as the product of

**TABLE 3. Model Parameter Values for the Don River Watershed**

compartment	air	water	soil	sediment	vegetation	film
surface area urban (m <sup>2</sup> )	4.7 × 10 <sup>7</sup>	7.0 × 10 <sup>6</sup>	1.71 × 10 <sup>7</sup>	7.0 × 10 <sup>6</sup>	2.05 × 10 <sup>7</sup> <sup>a</sup>	4.58 × 10 <sup>7</sup> <sup>b</sup>
surface area forested (m <sup>2</sup> )	4.7 × 10 <sup>7</sup>	7.0 × 10 <sup>6</sup>	4.0 × 10 <sup>7</sup>	7.0 × 10 <sup>6</sup>	1.6 × 10 <sup>8</sup> <sup>a</sup>	
depth (m)	1000	0.38	0.05	0.02	2 × 10 <sup>-4</sup> <sup>c</sup>	70 × 10 <sup>-9</sup> <sup>b</sup>
volume: urban (m <sup>3</sup> )	4.7 × 10 <sup>10</sup>	2.66 × 10 <sup>6</sup>	8.55 × 10 <sup>5</sup>	1.4 × 10 <sup>5</sup>	4.1 × 10 <sup>3</sup>	3.21
volume: forested (m <sup>3</sup> )	4.7 × 10 <sup>10</sup>	2.66 × 10 <sup>6</sup>	2.0 × 10 <sup>6</sup>	1.4 × 10 <sup>5</sup>	3.2 × 10 <sup>4</sup>	
organic carbon frac.	0.2 <sup>d</sup>	0.02 <sup>e</sup>	0.02 <sup>e</sup>	0.04 <sup>e</sup>	0.02 <sup>f</sup>	0.74 <sup>g</sup>
density (kg/m <sup>3</sup> )	1.175	1000	1300 <sup>h</sup>	1500 <sup>h</sup>	850 <sup>f</sup>	
V <sub>A</sub>	~1.0		0.2		0.18	
V <sub>W</sub>		~1.0	0.3	0.8	0.80	
V <sub>part.</sub>	4.17 × 10 <sup>-11</sup> (50 μg/m <sup>3</sup> )	8.0 × 10 <sup>-9</sup> (0.012 g/m <sup>3</sup> )	0.5	0.2		0.7
V <sub>lipid</sub>					0.02 <sup>i</sup>	0.3
advection res. time (h)	7	190				
advective flow (m <sup>3</sup> /h)	6.87 × 10 <sup>9</sup>	1.4 × 10 <sup>4</sup>				

<sup>a</sup> Leaf area index of 1.2 (28). <sup>b</sup> An impervious surface index (ISI) is defined analogously to the LAI. This parameter accounts for the three-dimensional nature of the urban landscape. A value of 2 is assumed. <sup>c</sup> Illustrative literature value (17). <sup>d</sup> For particulate fraction (16). <sup>e</sup> For particulate fraction (54). <sup>f</sup> For lipid fraction (12). <sup>g</sup> For particulate fraction (7). <sup>h</sup> Pertains to particulate fraction. <sup>i</sup> Cuticle volume fraction.

**TABLE 4. Physical/Chemical Properties of PCB Homologues at 25 °C (29) and Selected Chemical Transformation Rates Expressed as Half-Lives (h)**

	no. of Cl							
	1	2	3	4	5	6	7	8
MW (g/mol)	188.7	223.1	257.4	292	326.4	360.9	395.3	429.8
mp (°C)	34	37	57	65	77	79	109.5	159
sol (g/m <sup>3</sup> )	5.5	1	0.2	5.2 × 10 <sup>-2</sup>	1.2 × 10 <sup>-2</sup>	5.5 × 10 <sup>-4</sup>	1.2 × 10 <sup>-4</sup>	2.5 × 10 <sup>-4</sup>
Log[K <sub>OW</sub> ]	4.3	5.1	5.7	6.1	6.4	7	7	7.1
Log[K <sub>OA</sub> ] <sup>a</sup>	5.9	7	7.1	7.3	7.7	7.7	8.5	8.8
H (Pa m <sup>3</sup> /mol)	70	31.7	97.2	1.5 × 10 <sup>2</sup>	1.3 × 10 <sup>2</sup>	5.0 × 10 <sup>2</sup>	87.7	45.7
V.P. solid (Pa)	2	0.14	7.8 × 10 <sup>-2</sup>	2.7 × 10 <sup>-2</sup>	4.8 × 10 <sup>-3</sup>	7.6 × 10 <sup>-4</sup>	2.7 × 10 <sup>-5</sup>	2.7 × 10 <sup>-5</sup>
τ <sub>1/2</sub> air <sup>b</sup>	55	90	170	220	315	450	650	940
τ <sub>1/2</sub> H <sub>2</sub> O <sup>c</sup>	550	550	17000	55000	55000	55000	55000	55000
τ <sub>1/2</sub> soil <sup>c</sup>	17000	17000	55000	55000	55000	55000	55000	55000
τ <sub>1/2</sub> sed. <sup>c</sup>	17000	17000	55000	55000	55000	55000	55000	55000
τ <sub>1/2</sub> veg. <sup>d</sup>	43	70	133	172	246	351	507	733
τ <sub>1/2</sub> film <sup>d</sup>	32	53	99	129	184	263	380	550

<sup>a</sup> Calculated using the relationship, K<sub>OA</sub> = (K<sub>OW</sub> · R · T) / H (55). <sup>b</sup> Atmospheric half-lives calculated using data from Anderson and Hites (37), who have assumed that the primary removal mechanism is reaction with OH radicals. <sup>c</sup> Reference 29. <sup>d</sup> Assumed values.

film area, A<sub>AF</sub> (m<sup>2</sup>), a mass transfer coefficient, k<sub>FW</sub> (m/h), and the bulk Z value for film (Z<sub>BF</sub>) where k<sub>FW</sub> is

$$k_{FW} = T_F \cdot W \quad (3)$$

and T<sub>F</sub> is film thickness (m) and W is a washoff rate constant (h<sup>-1</sup>) that is estimated for "average" steady-state conditions rather than on an event basis.

Analogously to the film, chemicals are transferred from air to vegetation by wet and dry particle deposition, D<sub>QV</sub> and D<sub>DV</sub>, respectively, and rain dissolution of gas-phase chemical, D<sub>RV</sub>. Unlike the film, a fraction of the wet deposited chemical is intercepted by the canopy, If<sub>W</sub> (21)

$$If_W = LAI \cdot \alpha \cdot (1 - \exp(-\ln 2/3 \cdot 1/\alpha)) \quad (4)$$

where LAI is the leaf area index and α is an interception coefficient. Similarly, only a fraction of the dry deposited chemical is intercepted by the canopy, If<sub>D</sub> (22)

$$If_D = 1 - \exp(-2.8 \cdot B) \quad (5)$$

where B is the above ground biomass of vegetation (kg dry mass/m<sup>2</sup>). A fraction of the chemical that is intercepted by wet deposition evaporates off the leaf surface, II<sub>W</sub>, and thus is not transferred to soil. Throughfall is defined as the fraction of a chemical that is not intercepted by the canopy (23).

Chemicals are transferred from vegetation to soil by canopy drip or throughfall, D<sub>CD</sub>, in which the fraction of a particulate chemical that is intercepted by the canopy, λ, is removed because of the rough architecture of the leaf surface (e.g., ref 24)

$$k_{CD} = U_R \cdot (If_W - II_W) \cdot \lambda \quad (7)$$

where U<sub>R</sub> is the rain rate (m/h). Under dry conditions wax erosion, D<sub>WE</sub>, that physically removes cuticular waxes and associated chemicals, is calculated as the product of leaf area, A<sub>AV</sub> (m<sup>2</sup>), and a mass transfer coefficient, k<sub>WE</sub> (m/h). Chemical loss by wax erosion is expected to be greater in an urban than forested area because of (1) higher concentrations of atmospheric particles that can abrade leaf surfaces and (2) air pollution, that is characteristic of urban areas, can increase the production, and, it is hypothesized, the erosion of plant waxes (24, 25). Litterfall, D<sub>LF</sub>, is considered to be a permanent loss process since falling leaves are collected and transported outside the model boundary in this application of the model to the downtown Toronto area. Litterfall is calculated using a first-order rate constant, R<sub>LF</sub> (h<sup>-1</sup>), that is the inverse of the length of the growing season (26). Finally, chemicals can be transported from soil back to vegetation by rainsplash, D<sub>SP</sub> (22).

The model consists of six differential equations that quantify the rate of change of chemical mass with time and input and loss processes for each compartment (1). For the

# Homologue

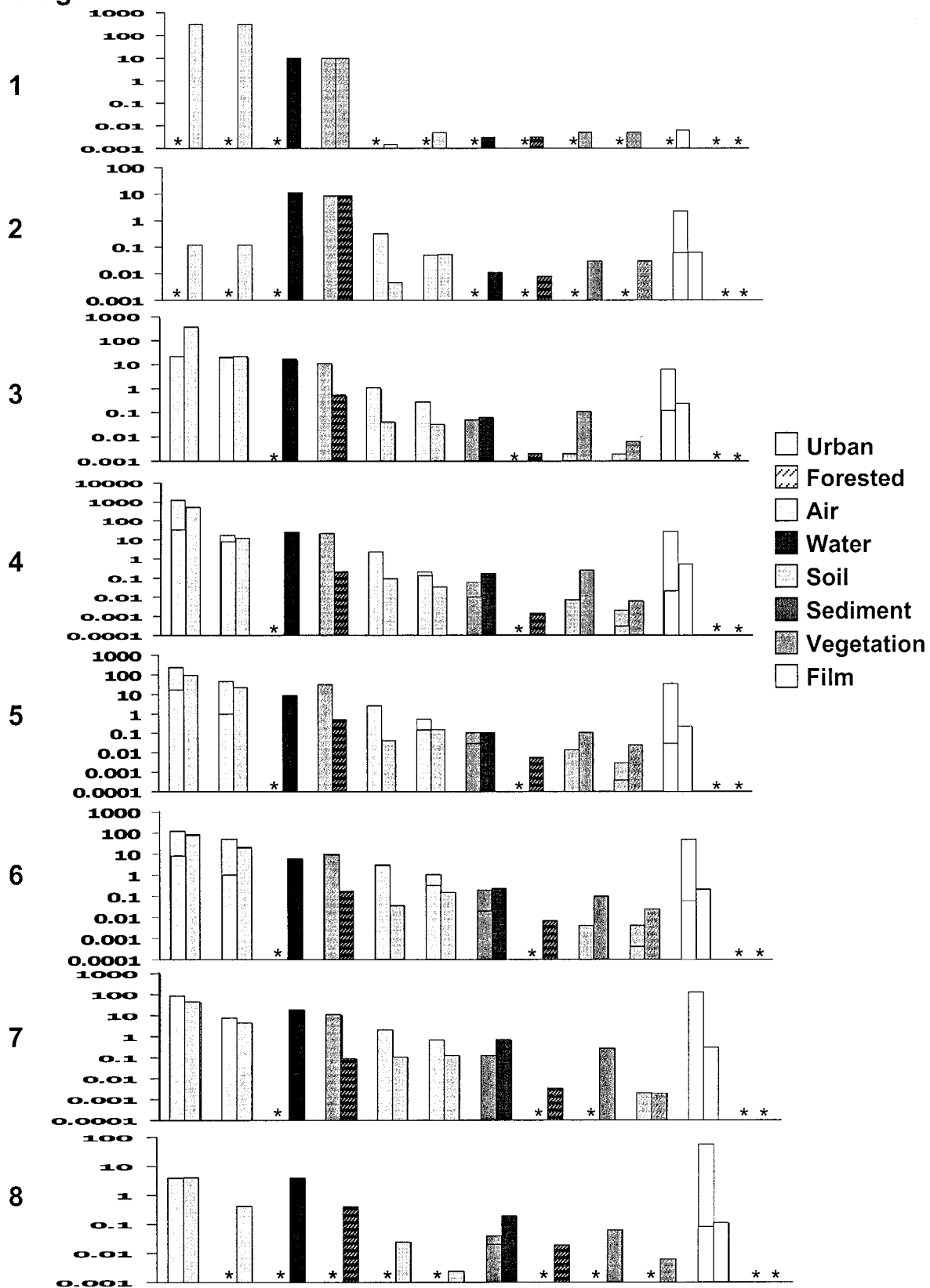


FIGURE 1. Comparison of the relative distributions of measured and modeled PCB homologues. Measured data from the following sources. Urban air ref 16 for Chicago, U.S.A.; ref 35 for London, Manchester, Cardiff, Stevenage, England; ref 56 for London, Manchester; England; ref 57 for Birmingham, England. Forested air ref 49 for Lancaster, England; ref 58 for Lista, Norway. Forested water ref 59 for Manitoba, Canada. Urban soil ref 60 for Birmingham, England. Forested soil ref 49 for Lancaster; England. Urban sediment ref 61 for western Lake Erie, Canada. Urban vegetation ref 57 for Birmingham, England. Measured values converted from dry to wet weight. Forested vegetation ref 62 for England; ref 63 for eight sites, Norway. Measured values converted from dry to wet weight. Urban film ref 64 for Toronto, Canada. Forested film ref 64 for Cambridge, Egbert; ON, Canada.

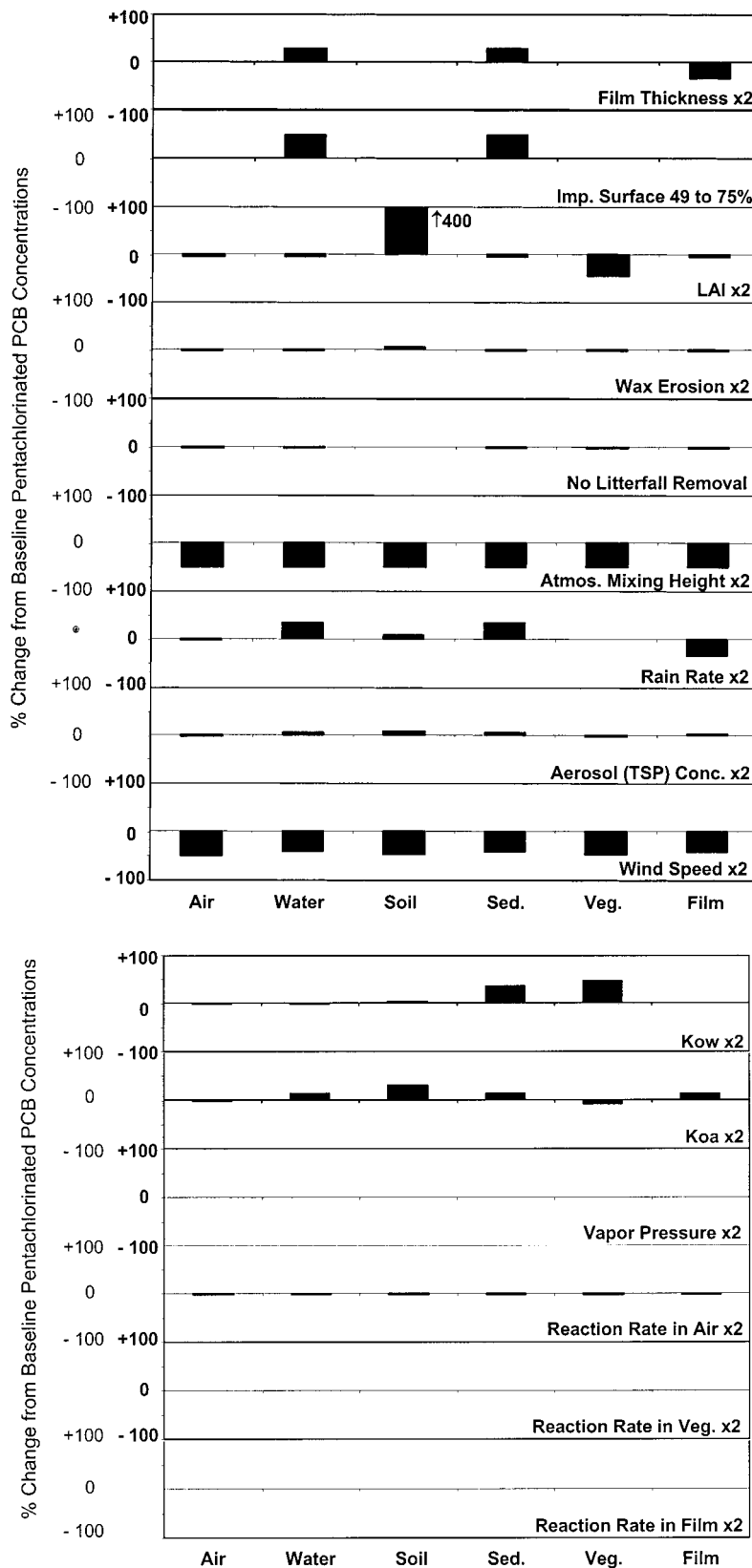


FIGURE 2. Sensitivity of modeled pentachlorinated biphenyl concentrations to the doubling of selected parameter values, except film area that was increased from 49 to 75% and litterfall that was altered from removal from the urban area to incorporation into urban soils: (a) environmental parameters and (b) physical-chemical properties.

steady-state model the differentials are set to zero and the equations are solved for fugacities in each medium. The model is written in Visual Basic 6.0 and runs on a PC platform in a Windows environment.

### Model Application

We used the model to consider SOC fate in an urban area and contrast this with fate in a comparable forested

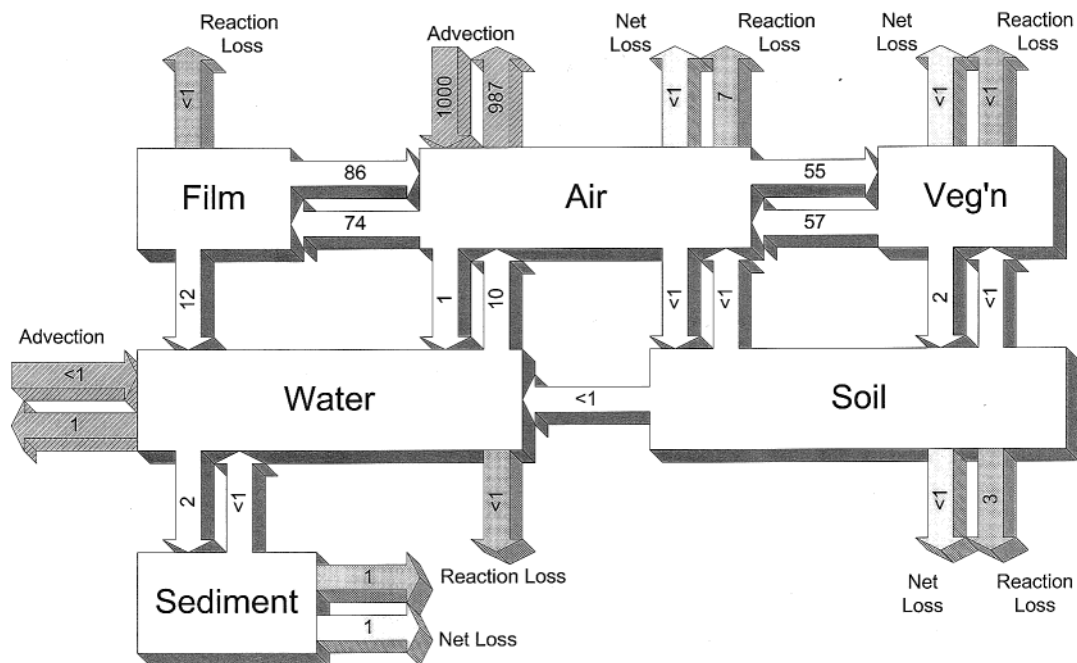


FIGURE 3. Estimated rates of chemical movement and transformation of heptachlorinated PCB under urban conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

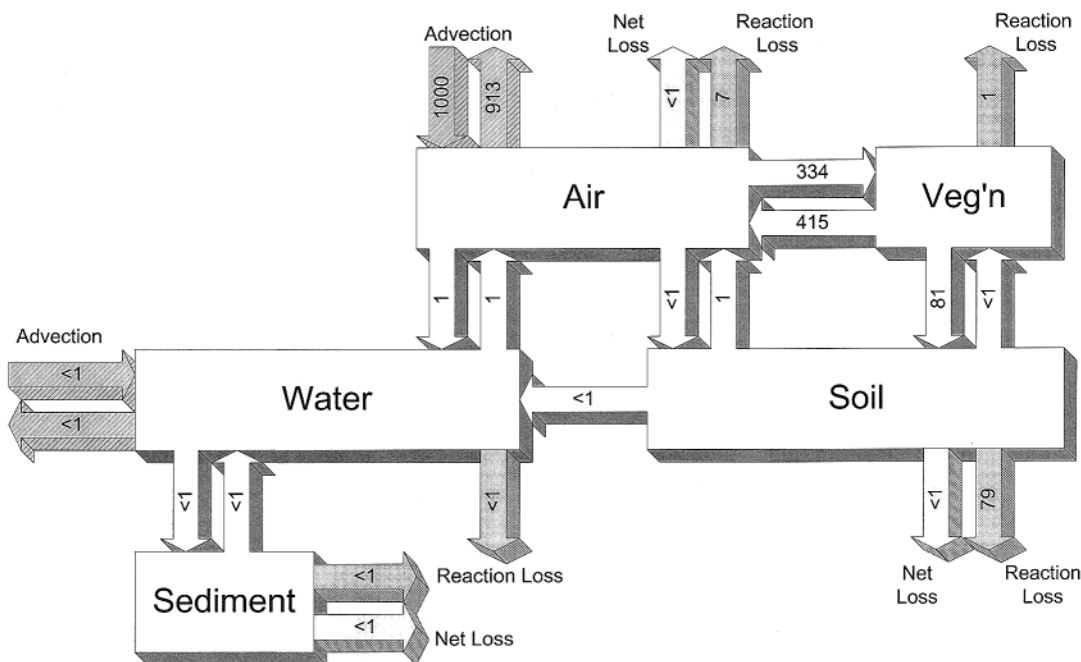


FIGURE 4. Estimated rates of chemical movement and transformation of heptachlorinated PCB under forested conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

environment. The model is parametrized to simulate conditions in the lower Don River watershed in downtown Toronto, Ontario, Canada, which currently supports approximately 500 000 people. Aerial land coverage for the lower Don watershed is characterized by 15% water (Don River), 49% impervious surface, and 36% open area (27). Open area was assumed to consist of vegetation that is underlain by soil. We have assumed typical summer conditions with a temperature of 25 °C for all media, trees in full leaf, and a low wind speed of 1 km/h representative of calm summer conditions. The Don River was parametrized as a shallow river of moderate velocity, with minimal sediment accumulation and burial. Parameter values for the Don River watershed are summarized in Table 3. For comparative

purposes, we have neglected meso- and microclimatic differences between urban and forested conditions.

To simulate forested conditions, the model parameters were changed as follows. First, impervious surfaces were "replaced" with vegetation and soil (i.e. from 36 to 85% air-soil interfacial area). Second, we assumed a leaf area index of 4 that is characteristic of forests and agricultural crops (21) in contrast to a LAI of 1.2 for urban areas (28). This changed the air-vegetation interfacial area from  $2.05 \times 10^7$  to  $1.6 \times 10^8$  m<sup>2</sup> from urban to forested conditions. Compartment volumes and interfacial areas for water and sediment were kept constant, as were all other parameter values.

We ran the model for illustrative purposes for eight PCB homologue groups that span a range of physical-chemical

properties (29) and are relatively abundant in urban areas (e.g. refs 7 and 16). Selected physical-chemical properties and chemical transformation rates, expressed as half-lives, for each homologue group are listed in Table 4.

Chemical transformation rates in all media, especially vegetation and organic film, are highly uncertain, and, hence, order of magnitude estimates were made using the approach adopted by Diamond et al. (1). Photochemical oxidation by hydroxyl radicals (OH) was assumed to be the dominant transformation processes for PCBs in the atmosphere (30, 31), and photodegradation was assumed to be the dominant degradative process in film and vegetation (31, 32). The half-lives for photochemical oxidation of gas-phase mono- to pentachlorinated homologues were calculated based on OH-PCB reaction rate constants that assume pseudo-first-order reaction kinetics (31) and a 24 h globally averaged OH concentration of  $9.7 \times 10^5 \text{ cm}^{-3}$  (32). Half-lives for hexa- to octachlorinated homologues were extrapolated from the calculated half-lives.

Chemical transformation rates in vegetation and film were assumed to be 25% and 30% faster than those in air, respectively. The presumed faster reaction rates for vegetation were based on experimental evidence for dioxins and furans (32, 33). Experimental values are not available for the film; however, we assumed that photodegradation in the film would be enhanced by the film's simple architecture, combined with the high concentrations of numerous chemicals that would promote and accelerate indirect photolysis. Although there is considerable uncertainty in the assumed transformation rates, this uncertainty does not alter model results substantially as minimal chemical in vegetation and film is lost through this pathway. Reaction rates in other media were taken from Mackay et al. (29).

## Results and Discussion

**Model Efficacy.** To assess whether the model provides reasonable estimates of SOC fate, measured distributions of PCB homologues were compared with model estimates (Figure 1). Measured and modeled homologue distributions were compared rather than absolute concentrations of homologues or congeners because emission rates are not known for the Toronto area or for other systems for which measured concentrations are available. To compare distributions, the model was run with an emission of 1 mol/h to air. For forested conditions this is a reasonable scenario since PCBs are delivered by atmospheric transport although soils likely contain accumulated PCBs from the past when usage rates were high. The situation is more complicated for the urban scenario. There are 390 PCB storage sites in the whole of Toronto that contain 10 200 tonnes of PCB contaminated material (34). PCB homologue distributions and variations in PCB concentrations in organic films sampled in Toronto suggest a relatively "fresh" emission of PCBs to air (7). As well, historically accumulated PCBs in soils may be another source to the urban environment; however, the contribution of PCBs from these sources is not known.

The correspondence between the measured and modeled homologue distributions is believed to be reasonable considering the uncertainty in many model parameter values and the lack of parameter calibration. As well, we have assumed "average" values for the physical-chemical properties of the homologues that may not correspond to the congeners measured in the homologue group. The order-of-magnitude correspondence is also reasonable considering that the model estimates steady-state concentrations, whereas measured PCB concentrations in soil and sediment have concentrations elevated by historically high emission rates, i.e., soils and sediments are unlikely to be at steady-state with respect to air concentrations, especially in urban areas where PCBs were used extensively (35).

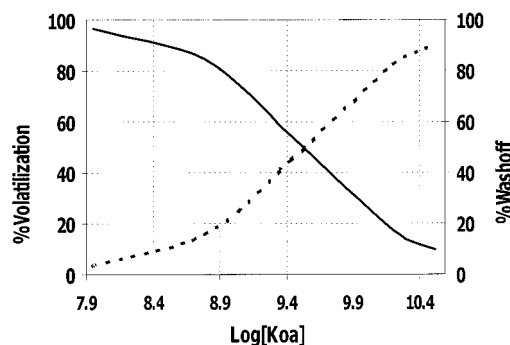


FIGURE 5. Percentage of PCB homologue loss from the organic film by means of volatilization and washoff, as a function of  $\text{Log}[K_{\text{Oa}}]$ .

**Sensitivity Analysis.** Since many parameter values are highly uncertain, a sensitivity analysis was conducted to explore the parameters to which model results are most sensitive. Results for this analysis are presented for the pentachlorinated homologue in the urban scenario, again assuming a unit emission to air. All parameter values were doubled with the exceptions of litterfall for which we assumed that leaves were incorporated into soils rather than being removed from the urban area, and impervious surface coverage was increased from 49 to 75% of aerial coverage since a doubling to 98% impervious surface area was considered to be unreasonable.

Figure 2 illustrates the results of the sensitivity analysis, with the results expressed as deviation from baseline concentrations. Results obtained for the physical-chemical properties indicate that for the pentachlorinated homologue, uncertainties in vapor pressure and reaction rates have minimal effects on the model outcome. This is reassuring considering the great uncertainty in reaction rates, particularly in vegetation and film. Doubling  $K_{\text{OW}}$  and  $K_{\text{OA}}$ , parameters that are well-known, increases concentrations in the condensed phases and for  $K_{\text{OA}}$  increases water and sediment concentrations as a result of washoff of film. A similar effect of increased water and sediment concentrations occurs when film thickness and impervious surface coverage are doubled. Doubling leaf area index increases soil concentrations 4-fold and decreases vegetation concentrations as more chemicals are transferred from air-to-vegetation-to-soil. Doubling of wax erosion and altering litterfall removal has minimal effect on chemical concentrations because most chemicals are transferred from vegetation-to-soil via wet removal processes, as seen by the results obtained from doubling the rain rate. Finally, doubling atmospheric mixing height and wind speed decreases all concentrations as chemicals are diluted in the air compartment and lost via advection, respectively.

**Comparison of Urban and Forested Scenarios.** The overall changes in contaminant dynamics between urban and forested conditions are shown in Figures 3 and 4 for the heptachlorinated biphenyl homologue. The results show that the dominant loss process in both scenarios is advection from air, a result that is consistent with the findings of Mackay and Paterson (10).

Under urban conditions all chemicals achieve the highest concentrations in the film with sediment, soil, and vegetation following in order of decreasing concentration (Figure 1). The film on impervious surfaces efficiently captures all homologues, that vary from being <0.1% (mono-) to almost 50% particle-bound (octochlorobiphenyl). However, the film's high surface area-to-volume ratio of  $1.4 \times 10^7$  prevents it from being a contaminant reservoir. Chemicals in the film undergo three fates: washoff to surface waters, volatilization to air, and transformation. Chemical transformation in the film is slow compared to the first two processes and accounts

# Homologue

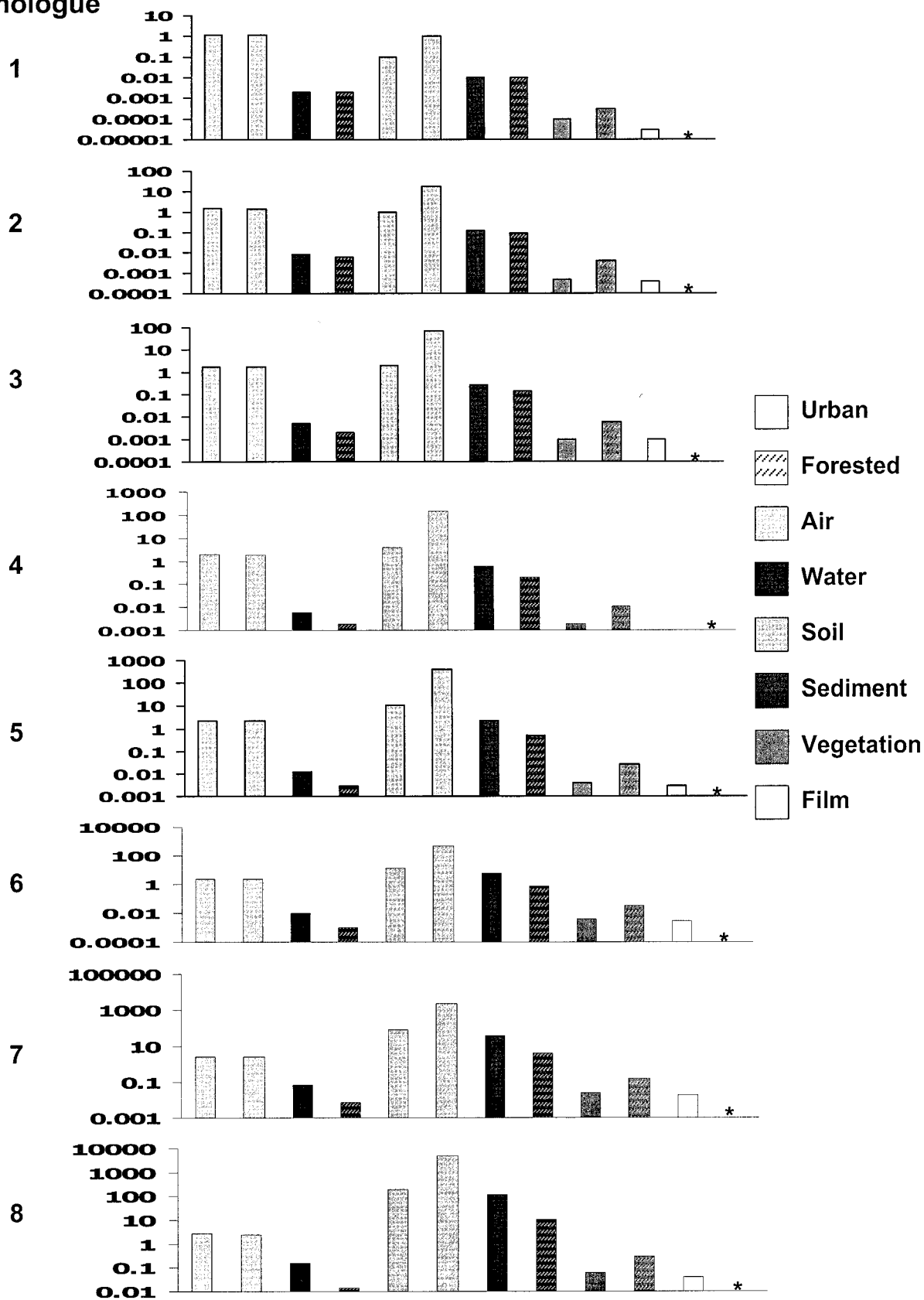


FIGURE 6. Mass of PCB homologues in media under urban and forested conditions.

for losses of less than 1% of inputs to the film. The proportion of a chemical undergoing volatilization versus washoff is a function of the chemical's physical-chemical properties (Figure 5). PCBs with  $\text{Log}[K_{\text{OA}}]$  less than approximately 7.5

almost completely volatilize, whereas the more hydrophobic homologues (pentachlorinated and higher), that are more efficiently captured and retained by the film, undergo increased washoff as  $K_{\text{OA}}$  increases.



The implications of these results are first, that air concentrations are higher in urban than forested conditions, considering the same emissions in both systems. Second, film washoff increases concentrations of the mono- and dichlorinated homologues in surface waters and sediment by 4 and 35%, respectively, between forested to urban conditions, whereas concentrations of the tri- to pentachlorinated homologues are 2–5 times as great, and concentrations of the hexa- to octachlorinated homologues are 8–11 times greater. The mass of the PCB homologues in water and sediment also increases from forested to urban conditions (Figure 6).

The model results demonstrate the importance of the film for increasing chemical mobility despite its very small volume of ~3 m<sup>3</sup>. Air–film–water transfer explains reports by Schueler (36) and others of the correlation between impervious surface coverage and stream degradation. It is well-known that roadways, in particular, accumulate dust that contains elevated concentrations of a wide range of compounds that are flushed by precipitation into surface waters (e.g. ref 37). However, empirical evidence (20) and these modeling results indicate that the film transfers gases as well as particle-phase chemicals from impervious surfaces to surface waters. In addition, since particle-phase compounds are efficiently captured by the greasy nature of the film (i.e. the film increases the dry deposition velocity, ref 38), the film increases air–film–water transfer. We tested this assumption by running the model with a 50% decrease in film thickness (70–35 nm) which decreased by 39–50% the amount of mono- to octachlorinated PCB transported from the film to surface waters. In contrast to the film, chemical export from forested soils via surface runoff is minimal as soils retain most atmospherically deposited chemicals (39).

From 69 to 88% of inputs of mono- to octachlorinated PCB entering water volatilize. This process of input to surface waters via urban runoff and high volatilization fluxes close to these inputs is consistent with measurements of air–water exchange of PAHs in Chesapeake Bay by Baltimore (40, 41) and PAHs and PCBs in Lake Michigan by Chicago (8, 42).

Volatilization from the film and surface waters increases atmospheric residence times by approximately 25% for all but the monochlorinated homologues and concentrations and advective loss from air by 8 and 15% for the hepta- and octachlorinated homologues, respectively, relative to forested conditions; concentrations and advective losses of the mono- to hexachlorinated homologues do not change significantly. These model results suggest that the elevated concentrations of some SOCs in urban air (e.g. refs 35 and 43) and the temperature dependence of these concentrations in the gas-phase (44, 45) is attributable to not only higher emission rates but also to the physical characteristics of the urban environment that increase the importance of the air phase. This deduction also is germane to the conclusion that urban areas serve as point sources to surrounding regions (8, 9, 42).

Total PCB mass in vegetation is, on average, three times greater for urban than rural canopies when normalized per m<sup>2</sup> of soil. The vegetation compartment is, however, almost eight times larger in the forested than urban scenario, and, therefore, chemicals in the forest vegetation (total vegetation) are “diluted” relative to urban vegetation. Concentrations of the mono- to tetrachlorinated homologues in vegetation are similar between the two scenarios, while the concentrations of the penta- and hexachlorinated homologues increase by 5% from forested to urban conditions, and the hepta- and octachlorinated homologues increase by 28 and 64%, respectively.

Under urban conditions the low leaf area index and, hence, air–vegetation interfacial area as well as litterfall export decreases by four to six times the transfer efficiency of PCBs

to urban relative to forested soils. This result is similar to the observation that SOC transfer from vegetation to soil is much less in grasslands than forests (46, 47). With increasing hydrophobicity, PCBs are more efficiently captured by the lipophilic plant wax surfaces (48) and consequently experience greater transfer to soils relative to the lower chlorinated congeners. This difference with homologue group is similar to that with film washoff.

The model indicates that soil is the dominant PCB reservoir for all chemicals in the forest scenario and all but the mono- and dichlorinated homologues in the urban scenario. Urban soils contain only 5% of the mono- and dichlorinated homologue mass in the system because of their greater volatility and remobilization due to volatilization from the film and the scenario of all emissions to air. Under forested conditions the soil compartment contains 30% of the total monochlorinated homologues and 92–99% of the remaining PCB homologues (in comparison to 29–72% in the urban scenario). The high soil burden is achieved by air–vegetation–soil transfer. These results are in agreement with conclusions that the majority of SOC burdens in Europe and North America reside in soils (e.g. ref 49). Soils typically contain the greatest mass of hydrophobic SOCs because they receive relatively high inputs from vegetation and because losses due to volatilization, erosion to surface waters, and leaching to groundwater are minimal (50).

Vegetation is well recognized as ameliorating the effects of air pollution (e.g. refs 28 and 51), including SOCs (e.g. ref 52). Forests decrease the atmospheric half-lives of a variety of environmental contaminants through interception by the canopy and subsequent transfer to soils (48, 52, 53). Hence, forests tend to minimize chemical mobility and long-range atmospheric transport. Model results confirm that air–vegetation–soil transfer is one of the most important mechanisms with respect to reducing SOC mobility in a multimedia system. In contrast, the mobility of SOCs in urban areas is increased by the lack of, and simplified structure of the vegetation (e.g. lawns), and the prevalence of impervious surfaces.

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