



## Developing a multimedia model of chemical dynamics in an urban area

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### Abstract

A multimedia model has been developed to account for the movement of semi-volatile organic compounds (SOCs) in an urban environment. The model, based on a Level III fugacity model of D. Mackay (Multimedia Environmental Models: The Fugacity Approach, Lewis Publishers, Boca Raton, FL, 1991), consists of six compartments: air, surface water, sediment, soil, vegetation, and an organic film that coats impervious surfaces. The latter is a newly identified compartment into which gas-phase SOCs partition and particle-phase SOCs are believed to be efficiently captured (M.L. Diamond, S.E. Gingrich, K. Fertuck, B.E. McCarry, G.A. Stern, B. Billeck, B. Grift, D. Brooker, T.D. Yager, Environ. Sci. Technol., 34 (2000a), 2900–2908). The model, parameterized for downtown Toronto, Ontario, Canada, and run with an illustrative emission rate for selected polycyclic aromatic hydrocarbons and homologues of polychlorinated dibenzodioxins, indicates that the film achieves the highest concentrations among media but that soils are the greatest sink for all but the least hydrophobic chemicals. The film “reflects” the more volatile chemicals into air, facilitates removal to surface waters by wash-off, and provides a surface on which photolytic degradation can occur. As such, the film is a transient sink that increases chemical mobility in urban areas by increasing air concentrations and the cycling of these compounds between air and urban surfaces and increasing water concentrations. Vegetation also accumulates SOCs, a portion of which is transferred to soil that reduces chemical mobility. © 2001 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

Numerous studies have documented elevated concentrations of a wide variety of contaminants in various urban media (e.g., Cotham and Bidleman, 1995;

Makepeace et al., 1995; Ashley and Baker, 1999). The elevated concentrations of contaminants are of concern, since approximately two-thirds of the world's population inhabit cities and this proportion is increasing. As well, urban areas act as point sources for pollutant transport to surrounding areas (Simcik et al., 1997; Cole et al., 1999). These phenomena are not surprising considering the magnitude and variety of chemicals imported into, and emitted to relatively small geographic areas occupied by cities. Despite the importance of urban areas in terms of human habitation and the role of cities as regional point sources, we know surprisingly little about the mechanisms controlling contaminant fate

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within urban areas and are limited in our ability to estimate the magnitude of the urban “plume”. Although numerous stormwater models have been developed to quantify the movement of water, suspended particles, and water-borne chemicals from impervious surfaces into surface water bodies (e.g., Reckow et al., 1985, Novotny and Olem, 1994), they do not explicitly consider chemical movement, nor is chemical movement addressed from a multimedia perspective.

This paper documents the development of a multimedia model that estimates the fate of semi-volatile organic compounds (SOCs) in an urban environment. The model is based on the steady-state, Level III fugacity model of Mackay (1991). It is parameterized to simulate summer conditions in downtown Toronto, Ontario, Canada. The model includes all major media, but is unique in its treatment of impervious surfaces and vegetation. Diamond et al. (2000a) have found that an organic film develops on impervious surfaces. The film, which comprises a wide range of chemicals as well as air particulate matter, provides a compartment into which gas-phase chemicals partition and, it is suggested, particle-phase contaminants are efficiently trapped. The model is run with illustrative emissions of selected polycyclic aromatic hydrocarbons (PAHs) and homologues of polychlorinated dibenzodioxins (PCDDs). Below, we describe the multimedia urban model (MUM) and present illustrative results of relative PAH and PCDD concentrations, amounts and rates of transport to and from the six compartments considered.

## 2. The urban environment

Cities characteristically have large areas of impervious surfaces that include roadways and buildings, radically altered hydrologic regimes, and highly disturbed and simplified biological systems (Pouyat et al., 1994, e.g., grassy lawns with low biological complexity in comparison to forests). The percentage of horizontal impervious surface varies from 5% for low density suburbs to 98% for high density downtown areas, with a typical range of 33–56% (Boyd et al., 1993). Hydrologic flows change as a function of impervious surface area. In forested systems, 40% of water is lost to evapotranspiration, 10% to surface runoff, 25% to shallow infiltration, and 25% to groundwater. With 75–100% impervious surface coverage, these values change to 30% evapotranspiration, 55% runoff, 10% surface infiltration, and 5% to groundwater (USEPA, 1993). The change in water flows with urbanization increases chemical mobility as chemicals are conveyed directly to surface waters in heavily urbanized areas, rather than infiltrating soils that have a high capacity for chemical retention.

Diamond et al. (2000a) have shown that impervious surfaces are coated with an organic film of 30–250 nm

thickness (“pure” film plus particles). The film is derived from primary emissions from vehicles, and transformation products formed by the reaction of primary emissions with oxidants and other reactive species that are abundant in urban air (Law and Diamond, 1998). The bulk film comprises a wide range of organic compounds, particles, and inorganic species (Bahavar, unpubl. data). Gas-phase compounds partition into the film, as indicated by the correspondence between film–air ratios and  $K_{OA}$  for PAHs and PCBs. It is suggested that the film increases the capture efficiency (e.g., dry deposition velocity) of impervious surfaces for fine particles, similarly to that of greased surfaces (Turner and Hering, 1987; Wu et al., 1992). Another implication of the film is that it increases the movement of compounds from impervious surfaces to surface waters upon wash-off (Gingrich, 1999, Diamond et al., 2000b). This would contribute to the correlation between watershed impervious coverage and chemical burdens in urban streams (Schueler, 1994).

Vegetation is well recognized as ameliorating the effects of air pollution (e.g., Nowak et al., 1997). This cleansing effect of vegetation pertains to SOCs as well (e.g., Duarte-Davidson et al., 1997; McLachlan and Horstmann, 1998) suggesting that urban vegetation plays an important role in the fate of SOCs. The vegetative community in cities is highly simplified by the predominance of grasses, with their low leaf area index (LAI) of 1–4, in contrast to forests or agricultural crops that have large LAIs of 4–6 (Müller and Pröhl, 1993). This structural simplification suggests that vegetation will transfer less SOCs to urban soils relative to forested soils, similarly to the difference found between grassland and forested systems (Rotard et al., 1994; Brorström-Lundén and Löfgren, 1998). Another difference between urban and forested ecosystems is that urban tree leaves are usually not incorporated into soils, but rather are collected and transferred out of the urban area. This transfer likely results in the net export of leaf-associated SOCs.

## 3. Model structure

MUM is based on the steady-state Level III fugacity model developed by Mackay and coworkers (Mackay, 1991; Mackay and Paterson, 1991; Mackay et al., 1992) to estimate chemical fate on a regional scale. Below we describe modifications to the Level III model to allow its application to urban areas. The reader is referred to Mackay and Paterson (1991) for complete details of the original model.

MUM comprises 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 com-

partment consists of pure and particulate-phases of specified volume. Chemicals are assumed to be in equilibrium between these phases within each bulk compartment (e.g., between gas and particulate-phases within air). Chemical  $i$  can enter each phase  $j$  through a direct emission,  $E_{ij}$  (mol/h). Chemical can also enter air and water through advection, parameterized as the product of a  $G$  value ( $\text{m}^3/\text{h}$ ) that quantifies bulk movement and the chemical concentration entering the system,  $C_{\text{IN}ij}$ . Chemical can transfer among compartments and can be lost from all compartments through various transformation processes. Chemical can be lost from the system through vertical transfer above the mixed layer (ventilation), leaching to groundwater, burial in deep sediments, and export of litterfall.

### 3.1. $Z$ values

$Z$  values ( $\text{mol}/\text{Pa m}^3$ ), that express the capacity of a phase for a chemical, are derived according to Mackay (1991) and Mackay and Paterson (1991). Their derivations are listed in Table 1. Since the model is intended to be general and relatively simple, we have neglected factors such as relative humidity and the nature of surfaces that affect partitioning (e.g., Goss, 1997; Jang and Kamens, 1998) and hence,  $Z$  values.

The  $Z$  value for aerosols is calculated based on  $K_{\text{OA}}$ , as described below. The  $Z$  value for vegetation,  $Z_V$ , is calculated where only the leaf cuticle is considered with

respect to the plant/air partitioning of SOCs (Paterson and Mackay, 1995). The bulk  $Z$  value for vegetation is then calculated by multiplying the relative fractions of air, water, and cuticle in leaves by their corresponding pure  $Z$  values. The relative 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 (Paterson and Mackay, 1995).

The  $Z$  values for film are calculated as follows. The film is considered to consist of 30% and 70% by mass of organic or pure film and particulate phases, respectively (Diamond et al., 2000a). The pure film phase is assumed to consist entirely of organic matter, with an organic carbon fraction ( $f_{\text{OC}}$ ) of 0.74, that of octanol. Thus, the  $Z$  value for chemicals “dissolved” in the organic film is calculated from measured values of  $K_{\text{OA}}$ , similar to the use of  $K_{\text{OW}}$  to calculate  $Z$  values for compartments in contact with water (e.g., sediment, soil):

$$Z_{\text{F}} = K_{\text{OA}} f_{\text{OC}} Z_{\text{A}} \quad (1)$$

The  $Z$  value for particle-sorbed chemicals in the film is the same as that for aerosols,  $Z_{\text{Q}}$ , the presumed source of particles in film. We use the relationship of Harner and Bidleman (1998a) that correlates the particle–air partition coefficient,  $K_{\text{P}}(\text{m}^3/\mu\text{g})$ , with  $K_{\text{OA}}$ , assuming an organic matter content of aerosols of 0.20 (Bahavar, unpubl. data; Rogge et al., 1993a; Harner and Bidleman, 1998a). The bulk  $Z$  value for the film,  $Z_{\text{BF}}$ , is calculated

Table 1  
 $Z$  values<sup>a</sup>

Compartment	Phase	Equation
Air	Gas-phase	$Z_{\text{A}} = 1/RT$
	Particles	$Z_{\text{Q}} = 10^{(\log K_{\text{OA}} + \log f_{\text{om}} - 11.91)} Z_{\text{A}} \rho_{\text{Q}} \times 10^{9\text{b}}$
	Bulk	$Z_{\text{BA}} = Z_{\text{A}} + (Z_{\text{Q}} \times v_{\text{Q}})$
Water	Dissolved	$Z_{\text{W}} = 1/H = S^{\text{S}}/P^{\text{S}} = S^{\text{L}}/P^{\text{L}}$
	Suspended Part.	$Z_{\text{P}} = Z_{\text{W}} \times \rho_{\text{P}} \times K_{\text{OC}} \times f_{\text{OC,P}}$
	Bulk	$Z_{\text{BW}} = Z_{\text{W}} + (Z_{\text{P}} \times v_{\text{P}})$
Soil	Solids	$Z_{\text{S}} = Z_{\text{W}} \times \rho_{\text{S}} \times 0.41 K_{\text{OW}} \times f_{\text{OC,S}}$
	Bulk	$Z_{\text{BS}} = (v_{\text{A}} \times Z_{\text{A}}) + (v_{\text{W}} \times Z_{\text{W}}) + (v_{\text{S}} \times Z_{\text{S}})$
Sediment	Solids	$Z_{\text{D}} = Z_{\text{W}} \times \rho_{\text{D}} \times 0.41 K_{\text{OW}} \times f_{\text{OC,D}}$
	Bulk	$Z_{\text{BD}} = (v_{\text{W}} \times Z_{\text{W}}) + (v_{\text{D}} \times Z_{\text{D}})$
Vegetation	Leaf cuticle	$Z_{\text{V}} = Z_{\text{W}} \times K_{\text{OW}} \times f_{\text{OC,V}}$
	Bulk	$Z_{\text{BV}} = (v_{\text{A}} \times Z_{\text{A}}) + (v_{\text{W}} \times Z_{\text{W}}) + (v_{\text{V}} \times Z_{\text{V}})$
Film	Dissolved	$Z_{\text{F}} = Z_{\text{A}} \times K_{\text{OA}} \times f_{\text{OC,F}}$
	Particles	$Z_{\text{Q}} = 10^{(\log K_{\text{OA}} + \log f_{\text{om}} - 11.91)} Z_{\text{A}} \rho_{\text{Q}} \times 10^9$
	Bulk	$Z_{\text{BF}} = (Z_{\text{F}} \times \phi_{\text{F}}) + (Z_{\text{Q}} \times \phi_{\text{Q}})$

<sup>a</sup> Subscripts A, Q, W, P, S, D, V, 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,  $H$  the Henry’s law constant ( $\text{Pa m}^3/\text{mol}$ ),  $S^{\text{S}}$  and  $S^{\text{L}}$  the solid and subcooled liquid solubilities ( $\text{mol}/\text{m}^3$ ),  $P^{\text{S}}$  and  $P^{\text{L}}$  the solid and subcooled vapor pressures (Pa), respectively,  $f_{\text{om}}$  the fraction of organic matter,  $f_{\text{OC}}$  the organic carbon fraction,  $\rho$  the density ( $\text{kg}/\text{l}$ ),  $v$  the volume fraction and  $\phi$  is the mass fraction.

<sup>b</sup> Harner and Bidleman (1998a).

as the weighted average of the pure phase values, using the fractional composition listed above.

### 3.2. Intercompartmental transfer

Intercompartmental transfer of chemicals between the four major media and chemical transformation is quantified by  $D$  values that are described in detail by Mackay (1991). In addition to the  $D$  values defined by Mackay and Paterson (1991), MUM includes transport mechanisms to and from the organic film and vegetation. These processes are discussed below and  $D$  values are listed in Table 2.

### 3.3. Organic film on impervious surfaces

The total area of impervious surfaces is calculated using aerial estimates of impervious surface area and an impervious surface index (ISI) developed using typical building arrangements and dimensions as outlined by Theurer (1999) for the purposes of air pollution modelling. This calculation is carried out analogously to that for quantifying the air-vegetation interfacial area using a leaf area index (LAI). As a first estimate, the total interfacial area of impervious surfaces was assumed to be composed of 50% two-dimensional surfaces (e.g., roadways and sidewalks) and 50% three-dimensional structures.

Air-film transfer consists of wet and dry particle deposition, rain dissolution of gas-phase chemical, and bi-directional gas absorption/volatilization ( $D_{AF}$ ). Wet deposition and rain dissolution are formulated as in Mackay (1991). Dry particle deposition ( $D_{DF}$ ) accounts for the film's presumed high capture efficiency for fine particles (due to its "greasy" nature) through the parameterization of the deposition velocity ( $U_P$ ). Bi-directional gas-phase-film transfer is modelled using the conventional Whitman two-film theory. The air-side mass transfer coefficient,  $k_{AF}$  (m/h), is calculated by dividing the mean diffusivity of contaminant in air by the boundary layer thickness,  $\delta^{bl}$  (mm), adjacent to the film surface as outlined in Nobel (1991),

$$\delta^{bl} = \beta \sqrt{\frac{l}{v}}, \quad (2)$$

where  $l$  (m) is the mean length of the surface in the direction of the wind,  $v$  (m/s) the wind speed, and  $\beta$  (mm  $s^{-1/2}$ ) is assigned a value of 6 (in accordance with hydrodynamic theory for an air current adjacent to a flat plate). The film-side mass transfer coefficient,  $k_{FF}$  (m/h), is calculated as in Trapp and Matthies (1997),

$$\text{Log}(k_{FF}) = (0.704 \log K_{OW} - 11.2)/K_{AW}, \quad (3)$$

where  $K_{OW}$  and  $K_{AW}$  are the octanol/water and air/water partition coefficients of the chemical, respectively.

Table 2  
 $D$  value formulations specific to MUM<sup>a</sup>

Transport: from – to	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	$D_{RF} = A_{AF}U_RZ_W$
	Wet dep. of particles	$D_{QF} = A_{AF}U_RQv_QZ_Q$
	Dry dep. of particles	$D_{DF} = A_{AF}U_Pv_QZ_Q$
	Total	$D_{AF} = D_{VF} + D_{RF} + D_{QF} + D_{DF}$
Film–water	Film wash-off	$D_{FW} = A_{AF}k_{FW}Z_{BF}$
Air–vegetation	Gas diffusion	$D_{VV} = 1/[(1/k_{AV}A_{AV}Z_A) + (1/k_{Vv}A_{AV}Z_V)]$
	Wet dep. of gas	$D_{RV} = A_{AV}U_RZ_W\text{If}_W$
	Wet dep. of particles	$D_{QV} = A_{AV}U_RQv_QZ_Q\text{If}_W$
	Dry dep. of particles	$D_{DV} = A_{AV}U_Pv_QZ_Q\text{If}_D$
	Total	$D_{AV} = D_{VV} + D_{RV} + D_{QV} + D_{DV}$
Vegetation–soil	Canopy drip	$D_{CD} = A_{AV}U_R(\text{If}_W - \text{Il}_W)\lambda Z_Q$
	Wax erosion	$D_{WE} = A_{AV}k_{WE}Z_V$
	Litterfall	$D_{LF} = V_V R_{LF} Z_{BV}$
	Total	$D_{VS} = D_{CD} + D_{WE} + D_{LF}$
Soil–vegetation	Rainsplash	$D_{SP} = V_S R_S Z_{BS}$

<sup>a</sup>  $A$ 's are the media interfacial areas ( $m^2$ ),  $k$ 's the mass transfer coefficients (m/h),  $U_R$  the rain rate (m/h),  $U_P$  the dry deposition velocities (m/h),  $\text{If}_W$  and  $\text{If}_D$  the canopy wet and dry interception fractions,  $Q$  the scavenging ratio,  $v$  the volume fraction,  $V$  the medium volume,  $\lambda$  the canopy drip parameter, and  $R_{LF}$  and  $R_S$  are the first-order litterfall and rainsplash rate constants, respectively.

Film–water transfer occurs as a result of precipitation conveying film constituents to surface water. The film is comprised of nonpolar and polar compounds. The polar compounds are believed to accumulate due to the deposition of secondary organic aerosols (SOAs), direct condensation of polar transformation products of atmospheric chemicals (Law and Diamond, 1998), and chemical transformation in the film. The polar compounds solubilize the nonpolar constituents and thus facilitate the wash-off of both groups. This was confirmed in a wash-off experiment in which all SOCs were removed equally by simulated precipitation rather than as a function of chemical solubility in water (Gingrich, 1999; Diamond et al., 2000b). The extent of wash-off is related to the intensity of the precipitation up to a maximum rate of removal and results in a portion of the film remaining. Thus, film–water transfer is estimated as a bulk removal process of a fraction of the film, rather than having any dependency on the physical–chemical properties of chemicals. The process is controlled by a mass transfer coefficient,  $k_{FW}$  (m/h), and is described by

$$k_{FW} = T_F W, \quad (4)$$

where  $T_F$  is the film thickness (m), and  $W$  is the wash-off rate constant ( $\text{h}^{-1}$ ). We believe that the value of  $W$  reaches an asymptote with prolonged rainfall, but are unsure of the relationship with rainfall intensity. To estimate a reasonable value applicable to steady-state rather than event-specific conditions, we determined  $W$  empirically by comparing measured contaminant loadings from sewer outfalls in Toronto (OME, 1995) with measured chemical concentrations in the organic film (Gingrich, 1999), hydrological data, and impervious surface coverage. After removal, all wash-off constituents are conveyed directly to surface waters via storm sewers. We do not consider storage in the sewer system or storm water treatment, as occurs in some cities.

### 3.4. Vegetation

Numerous studies have investigated contaminant transport within the air–vegetation–soil system. We incorporate work that focuses on processes such as vegetative canopy interception (Mahendrappa, 1990; Gash et al., 1995; Carlyle-Moses and Price, 1999) and contaminant partitioning between air and leaves, and air and soil (Simonich and Hites, 1995; Trapp and Matthies, 1997).

We first consider canopy interception for wet and dry conditions that is parameterised as the fraction of chemical, on an aerial basis, that is deposited on leaves. The dry deposition interception fraction,  $\text{If}_D$ , is taken from Whicker and Kirchner (1987),

$$\text{If}_D = 1 - \exp(-2.8B), \quad (5)$$

where  $B$  is the above ground biomass of vegetation ( $\text{kg dry mass/m}^2$ ). The wet deposition interception fraction,  $\text{If}_W$ , depends on the leaf area index (LAI), and the interception coefficient,  $\alpha$ .  $\text{If}_W$  can vary substantially with meteorological conditions and canopy density (Müller and Pröhl, 1993),

$$\text{If}_W = \text{LAI} \alpha \left( 1 - \exp \left( - \ln \frac{2}{3} \times \frac{1}{\alpha} \right) \right). \quad (6)$$

$\text{If}_D$  and  $\text{If}_W$  are then multiplied by terms for dry and wet particle deposition to a surface, respectively (Table 2). The wet deposition interception loss fraction, which is defined as the fraction of total incident precipitation that evaporates off the leaf surface and, consequently, is not transferred to soil, was considered by the term  $\text{Il}_W$ . The fraction of chemical not intercepted by the vegetative canopy, free throughfall, is assumed to be transported directly from the air to soil (Gash et al., 1995).

Next, we consider the transfer of contaminants from vegetation to soil. Under wet conditions SOC transport between vegetation and soil occurs via canopy drip (also known as canopy throughfall) that is the wet removal of particles from vegetation due to the impact of rainfall. The mass transfer coefficient for this process,  $k_{CD}$  (m/h), is described by,

$$k_{CD} = U_R (\text{If}_W - \text{Il}_W) \lambda, \quad (7)$$

where  $U_R$  is the rain rate (m/h),  $\text{If}_W$  and  $\text{Il}_W$  are the wet deposition interception and loss fractions, respectively, and  $\lambda$  is the canopy drip parameter that is related to the efficiency of the removal of particles from the leaf surface. We have assumed that a given fraction of the leaf surface is covered by particles and that, for any given rain event, only a small fraction of these particles is removed because, we suggest, some leaf bound particles reside in pits and cracks of the cuticular wax structure (Turunen and Huttunen, 1990), and hence, resist removal by precipitation.

Under dry conditions two processes convey chemicals from vegetation to soil. First, litterfall occurs in which dead or decaying leaf matter falls from trees to the ground below. We assume this process is controlled by a first-order rate constant,  $R_{LF}$ , that is taken to be  $1/L_G$ , where  $L_G$  is the length of the growing season (Bennett et al., 1998). Since, litterfall in urban areas is typically collected and disposed of outside the city boundary, we have considered it to be a permanent removal process for chemicals in the system. The second process that transports contaminants from vegetation to soil is that of wax erosion whereby a portion of the leaf surface itself is physically removed. Several researchers (van Gardigen et al., 1991; Rogge et al., 1993b; Horstmann and McLachlan, 1996) have concluded that wind and wind-borne particulate abrasion and/or the rubbing motions of leaves against each other can dislodge

contaminant enriched, crystalline-like leaf surface waxes. We expect this process is more important in urban than rural areas for two reasons. First, urban areas have higher concentrations of atmospheric particles that likely lead to greater abrasion rates. Secondly, air pollution that is characteristic of urban areas (e.g., elevated concentrations of O<sub>3</sub>, NO<sub>x</sub>, VOC radicals) increases the production and, we hypothesize, the erosion of plant waxes along with chemical deposited on the cuticle (Sauter et al., 1987; Turunen and Huttunen, 1990; Rogge et al., 1993b). We parameterize leaf wax erosion through a mass transfer coefficient,  $k_{WE}$  (m/h).

Rainsplash transfers particles and particle-sorbed chemical in soil to vegetation surfaces (Whicker and Kirchner, 1987). We assume that this process may be quantified as the product of a first-order rate constant,  $R_S$  (h<sup>-1</sup>), the bulk  $Z$  value for soil ( $Z_{BS}$ ), and soil volume ( $V_S$ ).

Finally, the model considers bi-directional diffusive exchange of gas-phase chemicals between air and leaf cuticle. This is modeled analogously to air–film exchange by using the Whitman two-film theory. The air-side mass transfer coefficient for vegetation is calculated similarly to that for the film, substituting a value of 4 for  $\beta$  in Eq. (2) for vegetative surfaces as outlined in Nobel (1991). The vegetation side mass transfer coefficient is calculated using Eq. (3).

#### 4. Mass balance model

As discussed by Mackay (1991),  $D$  values for chemical transfer between specific compartments can be summed to give total  $D$  values (Table 2). Mass balance equations can then be assembled for each compartment using total  $D$  values for intercompartmental transfer, transformation, and “ultimate” loss processes. The six mass balance equations, one for each compartment, are listed in Table 3. The steady-state solution to these equations is obtained by setting the differentials to zero and solving the equations through substitution. With estimates of fugacities for each compartment, concentrations, amounts, and transport rates can be calculated.

MUM is programmed in MS Visual Basic version 6.0 and runs on the PC platform in a Windows environment.

#### 5. Model application

The model was parameterized to simulate conditions in the lower Don River watershed in downtown Toronto, Ontario, Canada. This area supports approximately 500,000 people. The lower Don watershed is covered by 15% water, 49% impervious surface and 36% open area (MTRCA, 1992). We assumed conditions typical for summer with a temperature of 25°C and trees in full leaf. Parameter values for the Don River watershed summarized in Table 4 and Table 5 contains parameter values for chemical transfer. We ran the model for illustrative purposes with an emission of 1 mol/h into air for two polycyclic aromatic hydrocarbons (PAHs) and three polychlorinated dibenzodioxins (PCDDs). These chemicals were selected because of their range of physical–chemical properties, their importance as urban contaminants, and the availability of data with which to calibrate air–vegetation–soil transfer (Horstmann and McLachlan, 1996; Horstmann et al., 1997). The chemicals or congeners selected, their physical–chemical properties, and their transformation rates (expressed as media half-lives) are listed in Table 6.

We use values from Mackay (1991) for parameter values except where noted below. Advective air flow through the Don River watershed ( $G_A$ ) was calculated as the product of the cross-sectional area of the Don River watershed with a height of 1 km and a wind speed of 2 km/h (Environment Canada, 1998). A water advection rate ( $G_W$ ) of 14,000 m<sup>3</sup>/h was calculated using the daily discharge measurements for the Don River at Todmorden Station (02HC024), located 5 km upstream of the river’s mouth and averaged monthly from 1990 to 1995 (OME unpubl. data). For illustrative purposes, we assumed that inflowing air and water concentrations are zero; all chemicals enter by a single emission of 1 mol/h into air.

Table 3  
Mass balance equations for each medium<sup>a</sup>

Medium	Mass balance equation
Air	$I_A + f_W D_{WA} + f_S D_{SA} + f_V D_{VA} + f_F D_{FA} = f_A D_{TA}$
Water	$I_W + f_A D_{AW} + f_S D_{SW} + f_D D_{DW} + f_F D_{FW} = f_W D_{TW}$
Soil	$I_S + f_A D_{AS} + f_V D_{VS} = f_S D_{TS}$
Sediment	$I_D + f_W D_{WD} = f_D D_{TD}$
Vegetation	$I_V + f_A D_{AV} + f_S D_{SV} = f_V D_{TV}$
Organic film	$I_F + f_A D_{AF} = f_F D_{TF}$

<sup>a</sup> Subscripts A, W, S, D, V, and F represent air, water, soil, sediment, vegetation, and organic film, respectively,  $f$  is fugacity,  $I$  the contaminant input into each medium (advection plus direct emission), and the subscript “T” denotes total  $D$  values.

Table 4  
Model parameter values for the Don River watershed

Compartment	Air	Water	Soil	Sediment	Vegetation	Film
Surface area (m <sup>2</sup> )	$4.7 \times 10^7$	$7.0 \times 10^6$	$1.71 \times 10^7$	$7.0 \times 10^6$	$2.05 \times 10^{7a}$	$4.58 \times 10^{7b}$
Depth (m)	1000	0.38	0.05	0.02	$2 \times 10^{-4c}$	$70 \times 10^{-9}$
Volume (m <sup>3</sup> )	$4.7 \times 10^{10}$	$2.66 \times 10^6$	$8.55 \times 10^5$	$1.4 \times 10^5$	$4.1 \times 10^3$	3.21
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>	–
$V_A$	~1.0	–	0.2	–	0.18	–
$V_W$	–	~1.0	0.3	0.8	0.80	–
$V_{part.}$	$4.17 \times 10^{-11}$ (50 µg/m <sup>3</sup> )	$8.0 \times 10^{-9}$ (0.012 g/m <sup>3</sup> )	0.5	0.2	–	0.7
$v_{lipid}$	–	–	–	–	0.02 <sup>i</sup>	0.3
Advection res. time (h)	7	190	–	–	–	–
Advective flow (m <sup>3</sup> /h)	$6.87 \times 10^9$	$1.4 \times 10^4$	–	–	–	–

<sup>a</sup> Leaf area index of 1.2 from Nowak et al. (1997).

<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: Riederer (1995).

<sup>d</sup> For particulate fraction: Cotham and Bidleman (1995).

<sup>e</sup> For particulate fraction: Law (1996).

<sup>f</sup> For lipid fraction: Paterson and Mackay (1995).

<sup>g</sup> For particulate fraction: Diamond et al. (1996).

<sup>h</sup> Pertains to particulate fraction.

<sup>i</sup> Cuticle volume fraction.

Table 5  
Input parameters and coefficients used by MUM<sup>a</sup>

Parameter	Value	Comments	Reference
$U_R$	$9.3 \times 10^{-5}$ m/h	●average from May to October	OME (1995)
$D_{\text{air}}$	$4.9 \times 10^{-6}$ m <sup>2</sup> /s		Bennett et al. (1998)
$k_{\text{AS}}$	3.5 m/h	●using $\delta^{\text{bl}} = 0.005$ m	Bennett et al. (1998)
$k_{\text{AV}}$	23.0 m/h	●using $\delta^{\text{bl}}$ from Eq. (3)	Nobel (1991)
$k_{\text{AF}}$	15.4 m/h	●using $\delta^{\text{bl}}$ from Eq. (3)	Nobel (1991)
$k_{\text{VV}}$ (veg. side)	Eq. (3)	●chemical dependent	Trapp (1995)
$k_{\text{FF}}$ (film side)	Eq. (3)	●chemical dependent	Trapp (1995)
$v$	2 km/h	●historically average low summer value	Environment Canada (1998)
$l$	7 cm	●illustrative lit. value	Riederer (1995)
$R_S$	$3.58 \times 10^{-7}$ h <sup>-1</sup>		Whicker and Kirchner (1987)
$R_{\text{LF}}$	$2.31 \times 10^{-4}$ h <sup>-1</sup>	● $L_G = 180$ days = 4320 h	Bennett et al. (1998)
$\text{II}_W$	0.19	●illustrative lit. value for a variety of forest stands	Mahendrappa (1990); Carlyle-Moses and Price (1999)
$k_{\text{WE}}$	$8.05 \times 10^{-8}$ m/h		
$W$	0.25	●calibrated from empirical data	OME (1995)
$\lambda$	$8.7 \times 10^{-4}$		
$U_P$	10.2 m/h	●0.3 cm/s	Mackay (1991); Wu et al. (1992)
$U_W$	34.2 m/h	●0.9 cm/s, used in calculating fluxes to surface waters (Mackay, 1991)	Franz et al. (1998)
$B$	0.4 kg/m <sup>2</sup>		Bennett et al. (1998)

<sup>a</sup>  $U_R$  is the rain rate,  $D_{\text{air}}$  the diffusion quotient in pure air,  $k_{\text{AS}}$  the mass transfer coefficient of air over soil,  $k_{\text{AV}}$  the mass transfer coefficient of air over vegetation,  $k_{\text{AF}}$  the mass transfer coefficient of air over film,  $k_{\text{VV}}$  the vegetation-side mass transfer coefficient,  $k_{\text{FF}}$  the film-side mass transfer coefficient,  $v$  the wind velocity,  $l$  the mean length of the surface in the direction of the wind,  $R_S$  the rainsplash rate constant,  $R_{\text{LF}}$  the litterfall rate constant,  $\text{II}_W$  the wet deposition interception loss fraction,  $k_{\text{WE}}$  the leaf wax erosion mass transfer coefficient,  $W$  the film wash-off rate constant,  $\lambda$  the canopy drip parameter, and  $U_P$  and  $U_W$  the dry deposition velocities to surfaces and water, respectively, and  $B$  is the above ground plant dry mass inventory.

Table 6  
Physical–chemical properties of evaluative chemicals at 25°C and their transformation rates (Mackay et al., 1992)<sup>a</sup>

Property	Phenanthrene	Fluoranthene	Tetra-CDD	Penta-CDD	Octa-CDD
MW (g/mol)	178.24	202.3	322.0	356.4	460.0
M.P. (°C)	101.0	111.0	305.0	196.0	322.0
Solub. (g/m <sup>3</sup> )	1.2	$1.29 \times 10^{-3}$	$1.93 \times 10^{-5}$	$1.18 \times 10^{-4}$	$7.36 \times 10^{-7}$
Log( $K_{\text{OW}}$ )	4.6	5.22	6.8	7.4	8.2
Log( $K_{\text{OA}}$ ) <sup>b</sup>	7.61	8.88	9.67	11.37	12.76
$H$ (Pa/m <sup>3</sup> Pa)	3.26	0.92	3.34	0.0266	$6.88 \times 10^{-2}$
V.P. (Pa)	$2.2 \times 10^{-2}$	$1.2 \times 10^{-3}$	$2.0 \times 10^{-7}$	$8.8 \times 10^{-8}$	$1.1 \times 10^{-10}$
$\tau_{1/2}$ Air (h) <sup>c</sup>	8	18	190	350	3850
$\tau_{1/2}$ Water (h)	550	1700	550	550	5500
$\tau_{1/2}$ Soil (h)	5500	17,000	55,000	55,000	55,000
$\tau_{1/2}$ Sed. (h)	17,000	55,000	55,000	55,000	55,000
$\tau_{1/2}$ Veg. (h)	6	14	148	273	3003
$\tau_{1/2}$ Film (h)	5	11	111	205	2252

<sup>a</sup> Specific PCDD congeners chosen were 2,3,7,8-Cl<sub>4</sub> DD, 1,2,3,4,7-Cl<sub>5</sub> DD, Cl<sub>8</sub> DD, hereafter referred to by their homologue groups.

<sup>b</sup> Calculated using an empirical relationship (Harner and Bidleman, 1998b).

<sup>c</sup> Atmospheric half-lives calculated using data from Brubaker and Hites (1997, 1998) assuming that reaction with OH radicals is the primary reactive atmospheric loss processes.

For this steady-state representation, the value of the interception coefficient,  $\alpha$  (defined by  $S/R$ , where  $S$  (mm) is the retention coefficient and  $R$  (mm) is the rainfall for an event), was chosen to be unity. Eq. (6) was then calibrated using experimental data from Gash et al., (1995). Parameterization of the mass transfer coefficients

for vegetation to soil transport is difficult as the relative magnitudes of the three contributing mechanisms are poorly known. To approximate the magnitude of these processes we first adopted the rate constant for litterfall of Bennett et al. (1998). We then equated the litterfall mass transfer coefficient (the product of the litterfall rate



constant and leaf thickness) with the fractional litterfall flux reported by Horstmann et al. (1997). They reported that litterfall accounted for approximately 22% of the flux from vegetation to soil for five PCDD congeners averaged from May to August. Finally, we divided equally the remaining 78% of the vegetation to soil flux between canopy drip and wax erosion process to approximate the two remaining mass transfer coefficients,  $k_{WE}$  (m/h) and  $k_{CD}$  (m/h). To simulate typical urban conditions, we assumed that chemical subject to litterfall is permanently removed from the system as leaves are exported.

Sediment–water exchange is parameterized for a shallow river with minimal sediment accumulation and burial. A shallow sediment depth was assumed as minimal fine-grained sediment accumulates due to mobilization by water currents during and after storm events (Monabbati, unpubl. data).

Chemical transformation rates in all media, especially vegetation and organic film, are highly uncertain and hence, order-of-magnitude estimates are often made based on knowledge of dominant degradative process. Researchers agree that photochemical oxidation by hydroxyl radicals (OH) is the dominant chemical transformation process for most gas-phase organic compounds in the troposphere (Kwok et al., 1995; Anderson and Hites, 1996; Brubaker and Hites, 1998). Studies of chemical transformation in various types of vegetation have shown that photodegradation is an important loss mechanism for many types of organic compounds (McCrary and Maggard, 1993; Schuler et al., 1998). Whereas photodegradation of SOCs is also believed to occur in the film, we postulate that the film promotes direct photolysis by virtue of its large surface area to volume ratio and its direct exposure to sunlight. Researchers such as Böhme et al. (1999) and Simcik et al. (1999) point out, however, that there are many simplifying assumptions inherent in the various estimates of SOC transformation rates in air and vegetation and that, in reality, natural environmental variability causes actual rates to deviate, sometimes substantially, from those reported in the literature.

In order to approximate transformation rates in vegetation and film, we compared rate constants and reported degradation half-lives of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in air and vegetation. We first multiplied the rate constant associated with the photodegradation half-life of 44 h for TCDD-sorbed to vegetation reported by McCrary and Maggard (1993) under controlled laboratory conditions, by the correction factor of 0.3 suggested by Trapp and Matthies (1995), in order to correct for the fraction of time that vegetation is exposed to full sunlight. We then compared this value to the rate constant associated with the reported atmospheric reaction half-life with OH radicals of 189 h (~8 days) (Brubaker and Hites, 1997). This

comparison suggested that transformation in vegetation is about 30% faster than in air. As a first approximation, then, a factor of 30% was applied to the reaction rates in vegetation for the remainder of the chemicals. Transformation rates in the organic film were then taken to be 25% faster than those in vegetation based on the assumption that these rates may be enhanced by the film's comparatively simple architecture, combined with the high concentrations of numerous chemicals that would promote and accelerate indirect photolysis.

## 6. Results and discussion

Chemicals consistently achieve their highest concentrations in the film with sediment, soil, and vegetation following in descending order (Fig. 1). In contrast, soil and sediment accumulate the greatest mass of chemicals (Fig. 2). These results agree with estimates of SOC burdens in European and North American soils and sediments (Alcock et al., 1993; Wild and Jones, 1995; Diamond et al., 1996; Duarte-Davidson et al., 1997).

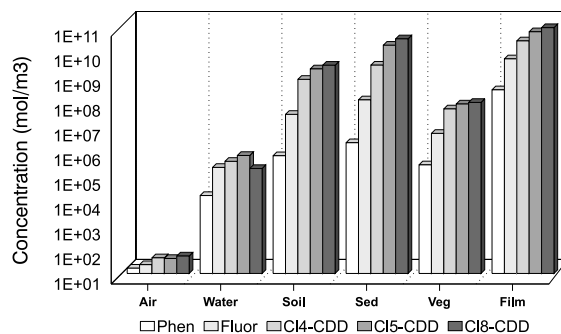


Fig. 1. Estimated concentrations of phenanthrene, fluoranthene, 2,3,7,8-Cl<sub>4</sub>DD, 1,2,3,4,7-Cl<sub>5</sub>DD, Cl<sub>8</sub>DD in the bulk phase (ng/m<sup>3</sup>) based on an emission of 1 mol/h into air.

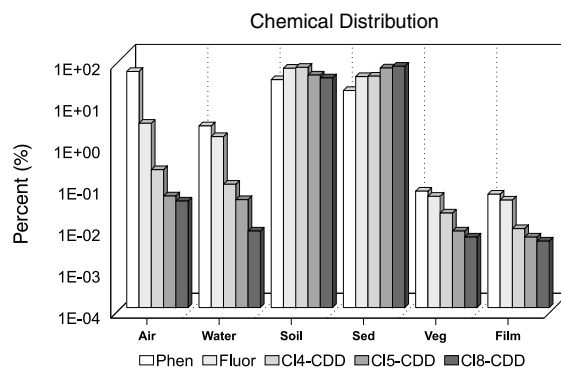


Fig. 2. Estimated distribution of mass of phenanthrene, fluoranthene, 2,3,7,8-Cl<sub>4</sub>DD, 1,2,3,4,7-Cl<sub>5</sub>DD, Cl<sub>8</sub>DD among model compartments (%) based on an emission of 1 mol/h into air.



that accelerated erosion rates in warmer summer months might be due to the increased pliability of the cuticular waxes or an increase in plant metabolism. The latter would result in a mechanism whereby the waxes covering older foliage are discarded and renewed. Other researchers have suggested that pollution exposure might alter cuticular wax composition and accelerate leaf wax erosion (Rogge et al., 1993b; Turunen and Huttunen, 1990; Sauter et al., 1987). Atmospheric aerosols and particles have been shown to contribute to leaf abrasion (van Gardigen et al., 1991). The elevated concentration of these particles in urban systems would aggravate this erosion process.

The model presented here is a first step towards developing a more comprehensive and validated description of SOC fate in urban areas and the influence of urbanization on fate processes. We suggest that further development of a multimedia model of urban areas is warranted since the majority of the world's population lives in urban areas where we are exposed to SOCs through urban media and may pose a health risk. The model results indicate that urban areas increase SOC mobility due to the prevalence of impervious surfaces coated by an organic film. This enhanced mobility can increase our exposure directly (e.g., inhalation) and indirectly by promoting regional and long range transport of the urban plume to agricultural areas followed by our importation and consumption of agricultural produce.

## 7. Conclusions

A multimedia urban model, MUM, has been developed that incorporates mechanisms of chemical transport and transformation in urban systems. The model, an adaptation of Mackay's Level III fugacity model, includes the organic film that coats impervious surfaces and vegetation as additional compartments. The model was run to illustrate the effect of urbanization, or specifically, impervious surfaces, on the fate of SOCs. The model indicates that the film achieves high chemical concentrations. Due to the high concentrations and high surface area to volume ratio, the film reflects SOCs back into the atmosphere and promotes chemical wash-off into surface waters. In contrast, soil and sediment are the greatest sinks for SOCs in urban areas because of inputs from other media and high persistence due to minimal losses. Vegetation accumulates gas- and particle-phase SOCs that are subsequently transferred to surface soils via litterfall, canopy drip and cuticular wax erosion (non-litterfall deposition); chemicals contained in litterfall, however, are typically exported from urban areas and thus become a loss process from the system. The organic film on impervious surfaces acts as a transient sink for gas- and particle-phase SOCs and increases the mobility of SOCs relative to a forested environment.

We acknowledge the uncertainty in many parameter values, however we believe that the model is a useful first step towards improving our understanding of the influence of the built environment on chemical fate.

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