

**THE MULTIMEDIA URBAN MODEL:
ASSESSING THE FATE AND TRANSPORT OF
SEMIVOLATILE ORGANIC COMPOUNDS IN URBAN AREAS**

By

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ABSTRACT

A multimedia model has been developed to account for the movement of semi-volatile organic compounds in an urban environment. The model consists of six compartments: air, surface water, sediment, soil, vegetation, and an organic film that coats impervious surfaces. The model, parameterized for downtown Toronto, Ontario, Canada, indicates that soils are the greatest sink for most chemicals but that the film achieves the highest concentrations. The film reflects chemicals back into the atmosphere and/or transfer them to surface waters via a washoff mechanism, resulting in increased contaminant mobility. This may account for the elevated concentrations of SOC_s in urban media, as well as the magnitude of the urban “plume”. Results contrast those observed for forested areas where air-borne pollutants are transferred to soils via the vegetative canopy and are immobilized. The model has been shown to be most sensitive to the parameterization of air, film, and vegetation and related transport processes.

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CHAPTER 1

THE MULTIMEDIA FATE AND TRANSPORT OF TOXIC CONTAMINANTS IN URBAN AREAS: AN INTRODUCTION

1.1 INTRODUCTION

As the world's industrialized nations continually strive to increase their output and productivity, thousands of chemicals are generated and subsequently discharged into the environment on a daily basis. While only a small fraction of these chemicals are present in detectable quantities in the environment (Mackay et al. 1992), their impacts on human and ecosystem health are often far-reaching, and hence, should be of paramount concern. At the centre of the issue of environmental contamination lies urban areas. Perhaps more so than any other environmental setting, urban areas exemplify these adverse impacts as they are home to almost three-quarters of the population in industrialized countries and the primary source of many toxic contaminants as well as having elevated concentrations of them (e.g.- Halsall et al. 1995, Simcik et al. 1997).

Despite the potential for these adverse effects, we know surprisingly little about the magnitude of the sources of many pollutants, their behavior upon release, and impacts on the surrounding ecosystem. Once emitted into the atmosphere or water these chemicals, notably semivolatile organic compounds (SOCs), can migrate or partition into other environmental media and/or undergo various transformation and degradative processes. One of the most important factors in determining the eventual fate of these chemicals, however, is the *nature* of the environment into which it is released (Mackay et al. 1992). Only with a sound understanding of the mechanisms and pathways along which contaminants move through our

urban areas, will we be able to undertake meaningful and effective measures to improve the environmental quality of human populated areas.

The urban landscape consists of soil, vegetation, surface water bodies, and sediments. It also characterized as having large areas of impervious surfaces such as roadways and buildings, radically altered hydrologic regimes, and highly disturbed and simplified biological systems (e.g.- Pouyat et al. 1994, Theurer 1999). These variations must be taken into account when assessing contaminant dynamics in urban areas.

In this regard environmental researchers have many tools at their disposal with which to investigate the manner in which chemicals interact with their surroundings. Field and laboratory experiments allow scientists to isolate and examine specific environmental mechanisms, such as the uptake of SOC_s by vegetation (Simonich and Hites 1995, Horstmann and McLachlan 1998), or the deposition and accumulation of SOC_s in lakes and sediments (Pirrone et al. 1995, Pearson et al. 1997). However, over the past decade, multimedia modeling has been used increasingly to elucidate the environmental pathways along which SOC_s move under a variety of different conditions. Using mathematic representations to describe complex environmental interactions allows researchers to adopt a more comprehensive and robust approach to studying contaminant dynamics, and the elements by which these interactions are most influenced.

1.2 MULTIMEDIA MODELING

Mathematical models have been used to examine the environmental behavior of persistent organic pollutants (POPs) under a variety of conditions. Recently, many researchers have focused on assessing the role of vegetation within the realm contaminant fate and transport due to its ubiquity and geographic and interspecies variability. Paterson et al. (1991), Kömp and McLachlan (1997), and McLachlan and Horstmann (1998), have constructed models that examine the factors controlling organic pollutant exchange between the atmosphere and plant surfaces. Trapp and Matthies (1995, 1996) and Braud et. al. (1996), have developed similar models in which the atmosphere-vegetation-soil system is considered. Nowak et al. (1997) and Bruse and Fleer (1998) considered similar interactions within a specifically urban framework.

The modeling efforts of Gash et al. (1995), Whelan and Anderson (1996), and Carlyle-Moses and Price (1999), have focused on the hydrological properties of various types of vegetative canopies (i.e.- throughfall and interception). Whicker and Kirchner (1987) and Müller and Pröhl (1993), have addressed these hydrological properties as well, but within the context of modeling the radiological consequences of nuclear accidents. Hoff et al. (1995) and Wania et al. (1998, 1999) have addressed the complex issue of seasonal variations by developing a modeling framework for the interpretation of SOC dynamics within snow packs.

Mackay and co-workers have pioneered the use of generic multimedia models for assessing the fate and transport of organic chemicals for a variety of “evaluative” environments (Mackay 1991, Mackay and Paterson 1991, Mackay et al. 1992, Mackay and Wania 1995).

These models make use of physical-chemical properties, reactivity data, and key intermedia transfer processes, to render a comprehensive treatment of contaminant dynamics. Transport amongst four major media (air, water, soil, and sediment) is typically considered, and general or bulk values are used for many of the required input parameters as chemical and/or media-specific values are often poorly known, if at all. While simplifications such as these may seem to limit the usefulness of generic models, their ease of reformulation with minimal changes to the fundamental model structure only serves to broaden their range of applications. Generic models are often used to highlight the dominant transport pathways for various sets of environmental conditions, explore “what if?” scenarios, and are frequently able to give results consistent to within an order of magnitude with available experimental observations. At the heart of many of these multimedia models, however, lies the means by which their ease of parameterization is facilitated; the fugacity concept.

1.3 THE FUGACITY APPROACH

The fugacity concept was first introduced by G.N. Lewis in 1901 as a convenient alternative to using chemical potential in the analysis of thermodynamic equilibria (Mackay 1991). Chemical potentials cannot be measured absolutely and are not linearly correlated with chemical concentration, hence, using this property to quantify multimedia environmental transport is both difficult and undesirable. The fugacity concept then represents a straightforward yet robust approach to modeling the fate and transport of environmental contaminants. Despite its introduction almost 100 years ago, however, only in about the last 20 years has this concept been applied to chemical equilibria and partitioning between environmental media.

The word ‘fugacity’ comes from the root *fugere* which denotes a ‘fleeing’ or ‘escaping’ tendency. Under ideal conditions fugacity is identical to partial pressure and hence, is assigned units of Pascals (Pa). As previously alluded to, using fugacity over chemical potential has two primary advantages. First, fugacity is logarithmically related to chemical potential, meaning it can be linearly or near-linearly correlated with concentration. Secondly, absolute values of fugacity can be established because at low partial pressures and under ideal conditions, fugacity and partial pressure become equal (Mackay 1991). Thus, transport between media is driven by the difference in fugacity between the source and destination phases.

Fugacity is linearly correlated to chemical concentration by means of *Z*-values also known as “fugacity capacities” as shown in equation 1.1,

$$C = Z \cdot f \quad (1.1)$$

where *C* is the concentration ($\text{mol}\cdot\text{m}^{-3}$), *Z* is the fugacity capacity ($\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$), and *f* is the fugacity (Pa). The fugacity capacity is analogous to heat capacity in the traditional sense, being the amount of chemical required to increase the fugacity of 1m^3 of a given phase by 1 Pa. *Z*-values for various environmental compartments are calculated in a variety of ways but in general they depend on the properties of the chemical, the medium of interest, and temperature.

The parameterization of intermedia transport within a fugacity modeling framework is made possible by the use of D-values which are equal to the product of the fugacity capacity and a flow rate,

$$D = G \cdot Z \quad (1.2)$$

where D is the transport parameter ($\text{mol} \cdot \text{Pa}^{-1} \cdot \text{h}^{-1}$) and G is the phase flow rate (m^3/h). D-values can be defined for a range of different processes including diffusive and non-diffusive transport as well as reaction and advective losses. Chemical transport rates are then defined as the product of these D-values and the fugacity of originating phase,

$$N = D \cdot f \quad (1.3)$$

where N is the chemical transport rate ($\text{mol} \cdot \text{h}^{-1}$). While the derivation of specific Z and D -values can be difficult at times, the relationships developed by Mackay and co-workers allow us to describe the complex multimedia behavior of environmental pollutants using relatively simple and elegant sets of equations.

There are four main levels of models (i.e.- Level I, II, III, & IV) with each successive level adding additional complexity. In Level I models, in which chemicals are at equilibrium and steady-state, the evaluative environment is considered to be a closed system with no chemical losses by reaction or advection (e.g.- photodegradation, inflow or outflow of air, sediment burial, etc.). While Level I calculations can be illustrative, they are rarely used in practical applications due to their simplicity.

Level II models improve upon this treatment by allowing for a continuous discharge of chemical into the environment as well as net losses by reaction and advection. Equilibrium

and steady-state conditions are still assumed to apply and therefore, as before, all environmental compartments share a common fugacity. Level II fugacity models provide rough estimates of chemical distribution but are overly simple for site-specific or more particular uses. For example, the assumption of equilibrium conditions among all media implies the compartment into which chemical is emitted is unimportant, which is not the case.

Level III models are perhaps the most useful fugacity models for assessing the multimedia fate and transport of organic chemicals. The primary advantage of Level III over Level II formulations is that intercompartmental transfer is explicitly considered, and whereas steady-state conditions apply, the various media are not assumed to be in equilibrium with one another. This treatment enables researchers to construct intricate and comprehensive representations of real-world environmental systems from which meaningful conclusions can be drawn.

Level IV fugacity models are similar in structure to Level III models, the difference being that they consider time dependent or unsteady-state conditions. This type of representation illustrates explicitly the response of the environment to various perturbations. Nevertheless, this added level of complexity is not entirely necessary in this regard as response times can be inferred from the characteristic times (VZ/D) of the various processes (Mackay 1991).

Due to the simplicity, and yet effectiveness of the fugacity concept, fugacity models have been used by researchers for a diversity of applications ranging from large scale, multimedia

environmental models to smaller scale models that focus on of a few key mechanism within a single medium. For example, Gobas et al. (1999) developed a multimedia fugacity model to illustrate the biomagnification of selected organic contaminants in food chains. In this case the four compartments considered were along the digestive tract of a fish. Di Guardo et al. (1994), developed a fugacity model of pesticide runoff to surface waters. As the primary focus in this case was chemical mobility within the soil, chemical transport within sub-compartments of the soil itself were considered (i.e.- air, water, organic matter, and mineral matter). On a larger scale, Bennet et al. (1998, 1999) employed a fugacity approach to determine the characteristic travel distance and time respectively, for the transport of airborne semivolatile organic pollutants. In the first treatment, the four compartments considered were air, vegetation, surface soil, and root-zone soil, and in the second case only air, water, and soil were considered.

The goal of this research is to use the fugacity approach to develop a multimedia model of contaminant dynamics in urban areas that incorporates elements unique to the urban environment and improves upon previous representations.

1.4 THE MULTIMEDIA URBAN MODEL (MUM)

In this thesis, I describe the development of, and the results obtained from, the Multimedia Urban Model, a Level III fugacity model designed to assess the fate and transport of semivolatile organic compounds (SOCs) in urban areas. Although several models have been developed to quantify various transport mechanisms within an urban framework (e.g.- Reckow et al. 1985, Nowak et al. 1997, Bruse and Fleer 1998), a comprehensive treatment of

chemical movement within a broader multimedia perspective has yet to be undertaken. This model improves upon previous representations of SOC dynamics in that it includes the four major media typically considered in such models (air, water, soil, and sediment) plus two additional media, vegetation and an organic film on impervious surfaces. These additional media to play integral roles in chemical transport and hence, inclusion in the model renders a more complete picture of contaminant dynamics in urban areas.

The model was initially parameterized to simulate summer conditions in downtown Toronto, Ontario, Canada. The model includes a data set of physical/chemical and related environmental properties for 23 SOC's as individual compounds or homologues from various families (e.g.- polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), etc.). In Chapter 2, I explore the field of multimedia reaction rates by discussing the pathways primarily responsible for chemical transformation. In Chapter 3, I present, in detail, the development of MUM as well as its application to the Toronto environment. This chapter has been submitted for publication in the journal *Chemosphere* and was the result of a collaborative effort with Miriam Diamond (University of Toronto) and Neely Law (University of North Carolina). My role in the project involved doing much of the modelling work and in particular, the air-film-water and air-vegetation-soil transfer. All of the geographical data for Toronto were compiled by Neely Law who also assembled the initial Level II model. Chapters 4 and 5 are undergoing preparation for publication as well. As such, there is repetition of the model structure and parameterization. In Chapter 4, I present the results obtained by modifying the model's parameterization to contrast urban and rural conditions. This was done to highlight the effect

of impervious surfaces on SOC transport. Finally, in Chapter 5, I investigate the sensitivity of the model to parameter uncertainty and environmental variability. I also contrast results obtained by simulating winter and summer conditions in an effort to assess the impacts of natural variability on urban contaminant dynamics.

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CHAPTER 2

MULTIMEDIA REACTION RATES: A REVIEW

2.1 INTRODUCTION

Media-specific chemical reaction and transformation rates are among the most poorly known model variables and can vary substantially with physical/chemical properties and environmental conditions (Mackay 1991, Anderson and Hites 1996, Brubaker and Hites, 1997, Lee et al. 1999). Reaction rates of most SOC_s in media such as soil, sediment, and even water are often simply expressed as “long”, with half-lives on the order of many years (Mackay et al. 1992, Corneliseen et al. 1997). In fact, concentrations of the more hydrophobic SOC_s, such as chlorinated hydrocarbons, in these media can take decades to decline, owing to slow loss mechanisms (Miyamoto and Urano 1996). Such mechanisms include reaction with oxidizing agents, photolytic reactions, as well as microbial degradation and hydrolysis. Unfortunately, photochemical oxidation and photolysis do not generally occur in subterranean media and most hydrophobic contaminants undergo very slow microbial degradation and hydrolysis (Mackay 1991, Koester and Hites 1992, Schuler et al. 1998). This chapter reviews the literature on reaction rates of SOC_s in air and vegetation, and comments on what those rates are likely to be in the organic film on impervious surfaces. The aim of the review is to improve the parameterization of reaction rates and to shed light on what these rates are likely to be in the film.

2.2 REACTION IN AIR

Photochemical oxidation by hydroxyl radicals (OH) is considered to be the dominant chemical transformation process for most gas-phase organic compounds in the troposphere,

especially in urban areas where elevated atmospheric OH concentrations are common (Wayne, 1991, Kwok et al. 1995, Anderson and Hites 1996, Brubaker and Hites, 1998). Until recently, laboratory measurements of OH-SOC reaction kinetic at environmentally significant temperatures were experimentally difficult to obtain due to the low vapour pressures of many SOC. Advances in experimental detection methods (Anderson and Hites, 1996, Brubaker and Hites, 1997) have now allowed researchers to more accurately characterize the rate constants of many photochemical reactions involving OH radicals.

Anderson and Hites (1996) determined experimentally the rate constants for the gas-phase reaction of 14 mono- to pentachlorinated PCB congeners with OH radicals over a temperature range of 323-363K. The calculated temperature dependences of the reactions were then used to estimate OH-PCB reaction rate constants at 298K. From their results, estimates of atmospheric lifetimes can be determined by assuming pseudo first-order reaction kinetics with a 24-h globally averaged OH concentration of $9.7 \times 10^5 \text{ cm}^{-3}$ (Prinn et al. 1995). The calculated lifetimes increase with increasing chlorination and agree with previous estimates of tropospheric lifetimes (Table 2.1).

Table 2.1. Comparison of calculated atmospheric PCB lifetimes for reaction with OH.

# Cl Atoms	Atmospheric Lifetime (days)	
	Anderson and Hites (1996)	Kwok et al. (1995)
0	2	2
1	2-4	2.7-5.1
2	5-6	3.4-7.2
3	9-12	6.9-15
4	12-14	8.5-40
5	14-34	16-48

Brubaker and Hites (1997, 1998) employed a similar method to measure the rate constants of the gas-phase reactions between OH and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Calculated dioxin half-lives ranged from 1 to 8 days for the mono- to tetrachlorinated congeners, 15-31 days for the penta- and hexachlorinated congeners and 62-160 days for the hepta- and octachlorinated congeners, using a globally averaged OH concentration of $9.7 \times 10^5 \text{ cm}^{-3}$. These results agreed well with half-lives previously predicted by the structure-activity method (Atkinson 1988). In general, the dioxins were found to be more reactive than furans (assuming equal degrees of chlorination) owing to the increased electrophilicity of the dioxin substituents.

The same authors conducted similar experiments with environmentally common polycyclic aromatic hydrocarbons (PAHs), pointing out that the primary route of reaction for any PAH is expected to be OH attack of the aromatic ring. The rate at which this attack proceeds for specific PAHs, however, is not straight forward and depends on the structure of the chemical itself (i.e.-the geometry of the ring formations). Atmospheric lifetimes for naphthalene, fluoranthene, and phenanthrene were 12, 26, and 11 hours respectively and were in good agreement with those of others (e.g.-Atkinson 1989).

2.3 REACTION IN VEGETATION

Many researchers agree that the main accumulation pathway for SOC in a multimedia environment is from air to leaf surface (Patterson and Mackay, 1991, Schreiber and Schönherr 1992, Bromilow and Chamberlain, 1995, Kömp and McLachlan, 1997). Contaminant uptake from soil is often minimal for most lipophilic compounds in many types

of vegetation. While these compounds may partition into the epidermis of the plant root or to the organic carbon in soil particles, they are not drawn into the inner root or xylem due to their low water solubilities. (Simonich and Hites, 1995, Wagrowski and Hites, 1998). The partitioning of lipophilic pollutants from the outer to the inner leaf is also a slow process (Simonich and Hites, 1995). Hence, most atmospherically deposited contaminants are sorbed to, or settle on, cuticular plant waxes. The cuticular wax coating of the leaves acts as an organic solvent (Riederer 1995) and, as such, photodegradation in this matrix is the dominant loss process (McCrary and Maggard 1993, Schuler et al. 1998). The reaction rate depends on environmental factors as well as the properties of the plants themselves (Trapp and Matthies 1995, Ockenden et al. 1998, Böhme et al. 1999).

Schuler et al. (1998), measured the photodegradation rate constants of selected PCDD/Fs in the cuticular waxes of the Laurel Cherry. Their experiments involved dissolving PCDD/Fs in these waxes and subsequently coating petrie dishes with thin wax layers. The dishes were then exposed to both natural and artificial sunlight generated by mercury lamps for a given period of time and kinetic parameters were derived from the measured loss rates. From the measured rate constants, degradative lifetimes in vegetation were calculated ranging from 28 h for the tetrachlorinated dioxins to 6 h for the octachlorinated dioxins, and from 13 h for the tetrachlorinated furans to 5 h for the heptachlorinated furans. Under “real” environmental conditions, however, these lifetimes will depend on chemical concentrations, the formation of lower chlorinated congeners, heterogeneity of light exposure, differences in wax composition and constitution, and most importantly, the proportion of chemical sorbed to particles.

McCrary and Maggard (1993), conducted experiments to determine the rates of photodegradation and volatilization of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin from grass foliage. Under controlled conditions they reported a photodegradation half-life of 44 h and the 128 h for volatilization, both of which are fast compared to atmospheric reaction with OH radicals for which the half-life is 8 days (Brubaker and Hites 1997, 1998).

These measured reaction rates are likely maximum values as environmental factors such as the intensity and duration of the incoming solar radiation and canopy architecture will reduce actual rates. Trapp and Matthies (1995) have sought to correct for local meteorological conditions and amount of daylight hours in their vegetation model by multiplying their photodegradation rate constant by a factor of 0.3, the relative amount of time that they believe vegetation is present in full sunlight. In terms of canopy architecture, gaseous diffusion transports chemicals to both the top and underside of the plant foliage, however, only the top side of the leaves of many species is exposed to the sunlight (Schuler et al. 1998). In addition, foliage below the top of the canopy will be sheltered. Overall, in trees and forests, where much of the foliage is often obscured, photodegradation of chemicals in cuticular plant waxes can be significantly inhibited, however, the magnitude of this reduction is uncertain.

Another factor that may contribute to slower photodegradation rates in plant waxes is the composition or architecture of the waxes themselves. The waxes can form finger-like

projections (Turunen and Huttunen, 1990, Rogge et al. 1993) and contaminants that accumulate between these projections can be shielded from UV radiation.

2.4 REACTION IN THE ORGANIC FILM

Diamond et al. (subm) have shown that impervious surfaces are coated with an organic film of 25 to 250 nm thickness. The film is believed to be 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 film has been characterized as being similar to plant waxes in terms of its tendency to accumulate gaseous and particle-bound atmospheric SOC_s (Law and Diamond, 1998). This similarity combined the film's widespread coverage in urban environments, leads us to believe that photodegradation will be the dominant transformation process of chemicals here as well.

The organic film possesses a much larger surface area to volume ratio than vegetation (a factor of almost 3000) and its simple architecture minimizes shadowing in comparison to vegetation. Thus, because the film is thin, it is unlikely to shield contaminants from the photolytic degradative processes, which may occur in the thicker leaf cuticle (Schuler et al. 1998). Therefore, under the same prevailing meteorological conditions, impervious surfaces will likely experience greater losses of SOC_s due to photolysis than in leaf cuticles. In addition, transformation rates may be enhanced by high concentrations of numerous chemicals that would promote and accelerate indirect photolysis. At present there are no

measured data on the reaction rates of SOC_s in film. In the absence of this data, however, reaction rates of SOC_s of vegetation may be used as first approximation.

2.5 SUMMARY

Examining the rates of reaction of SOC_s in air, vegetation, and the organic film on impervious surfaces is important as these media act as the primary conduits for contaminant transport to terrestrial media. Reaction with OH radicals is the dominant loss process for most gas-phase SOC_s in the atmosphere while most SOC_s sorbed to plant cuticles are lost by photolytic degradation. This is the presumed mechanism for reaction losses within the film. Generally, chemical transformation rates in all media, especially air, vegetation, and organic film are highly uncertain and are slower under natural conditions than those measured under laboratory conditions. For these reasons, reaction rates used in model simulations are, at best, order-of-magnitude estimates. Improvements in these estimates awaits further experimental research.

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CHAPTER 3

DEVELOPING A MULTIMEDIA MODEL OF CHEMICAL DYNAMICS IN AN URBAN AREA *

3.1 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). In turn, this has led to the recognition that urban areas act as point sources for pollutant transport to surrounding areas (Simcik et al. 1997, Cole et al. 1999). This recognition is not surprising when one considers the magnitude and variety of chemicals emitted to relatively small geographic areas occupied by cities (Diamond and Pouyat, in prep). The next step lies in estimating the magnitude of the urban “plume” and understanding the mechanisms controlling contaminant fate within urban areas. 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., Reckhow et al. 1985, Novotny and Olem 1994), they do not explicitly consider chemical movement, nor is chemical movement addressed from a multimedia perspective.

This chapter 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.

* This chapter has been submitted for publication in *Chemosphere* as Diamond, Priemer, and Law.

Diamond et al. (subm) have found that an organic film develops on impervious surfaces. The film, which is comprised of 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, run with illustrative emissions of selected polycyclic aromatic hydrocarbons (PAHs) and homologues of polychlorinated dibenzodioxins (PCDDs), suggests that the film attains elevated concentrations of chemicals, however soil is the greatest reservoir for the majority chemicals. Depending on chemical hydrophobicity, chemicals volatilize back into the air where they are more susceptible to advection and photolytic degradation, or are transferred to surface waters via washoff where they may undergo volatilization, degradation, advection, or burial. Both mechanisms of chemical loss from the film result in an increase in contaminant mobility.

This chapter describes the multimedia urban model, MUM, and presents illustrative results of relative PAH and PCDD concentrations, amounts and rates of transport to and from the six compartments considered.

3.2 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 impervious surface varies from 5% for low density suburbs to 98% for high density downtown areas, with a median 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 evapo-transpiration, 10% to surface runoff, 25% to shallow infiltration, and 25% to groundwater. With 75-100% impervious surface coverage these values change to 30% evapo-transpiration, 55% runoff, 10% surface infiltration, and 5% to groundwater (U.S. EPA 1993). This change in water flows with urbanization increases chemical mobility as chemicals are shunted directly to surface waters in heavily urbanized areas, rather than infiltrating soils that have a high capacity for chemical retention.

Diamond et al. (subm) have shown that impervious surfaces are coated with an organic film of 25 to 250 nm thickness. The film is believed to be derived from primary emissions from vehicles, and transformation products formed by the reaction of primary emissions with oxidants and other reactive species which are abundant in urban air (Law and Diamond 1998). The bulk film is comprised of 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 its compounds into surface waters upon washoff (Gingrich 1999). 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 SOC_s as well (e.g., Duarte-Davidson et al. 1997, McLachlan and Horstmann 1998) suggesting that urban vegetation is an important filter for SOC_s. The vegetative community in cities is highly simplified by the predominance of grasses, with their low leaf area index (LAI) of 1-4, as opposed to than forests or agricultural crops that have large LAIs of 4-6 (Müller et al. 1993). This structural simplification suggests that vegetation will transfer less SOC_s 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 SOC_s.

3.3 MODEL STRUCTURE

The multimedia urban model (MUM) is based on the steady-state Level III fugacity model developed by Mackay and Paterson (1991) and 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 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 (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 (m^3/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 ventilation to the stratosphere, leaching to groundwater, burial in deep sediments, and export of litterfall.

3.3.1 Z Values

Z values ($\text{mol}/\text{Pa}\cdot\text{m}^3$) 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 3.1. Because 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_{OA} , as described below. The Z value for vegetation, Z_V , is calculated as in Paterson and Mackay (1995) where only the leaf cuticle is considered with respect to the plant/air partitioning of SOC. 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, as in Paterson and Mackay (1995).

Table 3.1 Z Values. 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 is the Henry's law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}$), S^S and S^L are the solid and subcooled liquid solubilities (mol/m^3), P^S and P^L are the solid and subcooled vapor pressures (Pa) respectively, f_{om} is the fraction of organic matter, f_{OC} is organic carbon fraction, ρ is density (kg/L), v is volume fraction, ϕ is mass fraction.

Compartment	Phase	Equation
Air	Gas Phase	$Z_A = 1/RT$
	Particulate	$Z_Q = 10^{(\log K_{OA} + \log f_{om} - 11.91)} \cdot Z_A \cdot \rho_Q \cdot 10^9$ ^a
	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.	$Z_P = Z_W \times \rho_P \times K_{OC} \times f_{OC,P}$
	Bulk	$Z_{BW} = Z_W + (Z_P \times v_P)$
Soil	Solids	$Z_S = Z_W \times \rho_S \times 0.41 K_{OW} \times f_{OC,S}$
	Bulk	$Z_{BS} = (v_A \times Z_A) + (v_W \times Z_W) + (v_S \times Z_S)$
Sediment	Solids	$Z_D = Z_W \times \rho_D \times 0.41 K_{OW} \times f_{OC,D}$
	Bulk	$Z_{BD} = (v_W \times Z_W) + (v_D \times Z_D)$
Vegetation	Leaf Cuticle	$Z_V = Z_W \times K_{OW} \times f_{OC,V}$
	Bulk	$Z_{BV} = (v_A \times Z_A) + (v_W \times Z_W) + (v_V \times Z_V)$
Film	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	$Z_{BF} = (Z_F \times \phi_F) + (Z_Q \times \phi_Q)$

^a Harner and Bidleman (1998)

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. subm). The “pure” film phase is assumed to consist entirely of organic matter, with an organic carbon fraction (f_{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_{OA} , similar to the use of K_{OW} to calculate Z values for compartments in contact with water (e.g., sediment, soil):

$$Z_F = K_{OA} \cdot f_{OC} \cdot Z \quad (3.1)$$

The Z value for particle-sorbed chemicals in the film is the same as that for aerosols, Z_Q , the presumed source of the particles in film. We use the empirical relationship of Harner and

Bidleman (1998) that correlates the particle-air partition coefficient, K_P ($\text{m}^3/\mu\text{g}$), with K_{OA} , assuming an organic matter content of aerosols of 0.20 (Bahavar, unpubl. data, Rogge et al. 1993a, Cotham and Bidleman 1995, Harner and Bidleman 1998). The bulk Z value for the film, Z_{BF} , is calculated as the weighted average of the pure phase values, using the fractional composition listed above.

3.3.2 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 3.2.

3.3.3 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, δ^{bl} (mm) adjacent to the film surface as outlined in Nobel (1991),

$$\delta^{bl} = \beta \times \sqrt{\frac{l}{\nu}} \quad (3.2)$$

where l (m) is the mean length of the surface in the direction of the wind, ν (m/s) is the wind speed, and β (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_F (m/h) is calculated as in Trapp and Matthies (1995),

$$\text{Log}[k_F] = (0.704 \text{ Log } K_{OW} - 11.2) / K_{AW} \quad (3.3)$$

where K_{OW} and K_{AW} are the octanol/water and air/water partition coefficients of the chemical, 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 washoff of both groups. Gingrich (1999) confirmed this

process: in a washoff experiment, all SOC_s were removed equally by simulated precipitation rather than as a function of chemical water solubility. The extent of washoff 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

$$k_{FW} = T_F \cdot W \quad (3.4)$$

where T_F is the film thickness (m), and W is the washoff rate constant (h^{-1}). Currently 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 washoff 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.

3.3.4 Vegetation

Numerous studies have investigated contaminant transport within the air-vegetation-soil system. We have incorporated 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 which is parameterised as the fraction of chemical, on an aerial basis, that is deposited on leaves. The dry deposition interception fraction, If_D , is taken from Whicker and Kirchner (1987),

$$If_D = 1 - \exp(-2.8 \cdot B) \quad (3.5)$$

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

$$If_W = LAI \times \alpha \times (1 - \exp(-\ln 2/3 \cdot 1/\alpha)). \quad (3.6)$$

If_D and If_W are then multiplied by the terms for dry and wet particle deposition to a surface, respectively (Table 3.2). Another term which was used in our calculations was Il_W , the wet deposition interception loss fraction, defined as the fraction of total incident precipitation which evaporates off the leaf surface and consequently, is not transferred to the soil below. The fraction of contaminants not intercepted at all by the vegetative canopy, free throughfall, is assumed 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) which 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,

$$k_{CD} = U_R \cdot (If_W - Il_W) \cdot \lambda \quad (3.7)$$

where U_R is the rain rate (m/h), I_{fW} and I_{lW} are the wet deposition interception and loss fractions respectively, and λ is the canopy drip parameter which 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 are removed. We believe this is due to some leaf bound particles residing in pits and cracks in the cuticular wax structures (Turunen and Huttunen 1990), and hence, are minimally removed 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. This process is assumed to be controlled by a first order rate constant, (R_{LF}), which is taken to be $1/L_G$ where L_G is the length of the growing season (Bennett et al. 1998). Since, in urban centres, litterfall 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, which 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 accentuated in urban relative to rural areas for two reasons. First, urban areas have higher concentrations of atmospheric particles that likely lead to greater abrasion rates. Secondly, air pollution, characteristic of urban areas (e.g.- elevated concentrations of O_3 , NO_x , VOC radicals) increases the production and, we hypothesize, the erosion of plant

waxes along with chemical deposited on the cuticle (Rogge et al. 1993b, Turunen and Huttunen 1990, Sauter et al. 1987). We parameterize leaf wax erosion through a mass transfer coefficient, k_{WE} (m/h).

Table 3.2 D Value formulations specific to MUM. A's are media interfacial areas (m^2), k's are mass transfer coefficients (m/h), U_R is the rain rate (m/h), U_P is the dry deposition velocities (m/h), If_w and If_D are the canopy wet and dry interception fractions, Q is the scavenging ratio, v is volume fraction, V is medium volume, λ is the canopy drip parameter, and R_{LF} and R_S are the first-order litterfall and rainsplash rate constants respectively.

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	$D_{RF} = A_{AF} \cdot U_R \cdot Z_W$
	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	$D_{FW} = A_{AF} \cdot k_{FW} \cdot Z_{BF}$
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	$D_{RV} = A_{AV} \cdot U_R \cdot Z_W \cdot If_w$
	Wet Dep. Of Particles	$D_{QV} = A_{AV} \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q \cdot If_w$
	Dry Dep. Of Particles	$D_{DV} = A_{AV} \cdot U_P \cdot v_Q \cdot Z_Q \cdot If_D$
	TOTAL	$D_{AV} = D_{VV} + D_{RV} + D_{QV} + D_{DV}$
Vegetation – Soil	Canopy Drip	$D_{CD} = A_{AV} \cdot U_R \cdot (If_w - If_w) \cdot \lambda \cdot Z_Q$
	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	$D_{SP} = V_S \cdot R_S \cdot Z_{BS}$

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^{-1}), 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 cuticle. This was 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 β in equation 3.2 for vegetative surfaces as outlined in Nobel (1991). The vegetation side mass transfer coefficient is calculated using equation 3.3.

2.4 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 3.2). 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 3.3. 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.

Table 3.3 Mass balance equations for each medium. Subscripts A,W,S,D,V, and F represent air, water, soil, sediment, vegetation, and organic film respectively. f is fugacity, I is contaminant input into each medium (advection + direct emission), and the subscript “T” denotes total D values.

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	$I_F + f_A D_{AF} = f_F D_{TF}$

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

3.5 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 are summarized in Table 3.4 and Table 3.5 contains parameter values for chemical transfer. We ran the model for illustrative purposes with an emission of 1 mol/h into air for 2 polycyclic aromatic hydrocarbons (PAHs) and 3 polychlorinated dibenzodioxins (PCDDs). These 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 3.6.

We have used values from Mackay (1991) 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 taken to a height of 1 km, and a wind speed of 12 km/h (Environment Canada 1998). A water advection rate (G_W) of 14,000 m³/h was calculated using the daily discharge measurements for the Don River at Todmorden Station (02HC024), located about 5 km from the river's mouth and averaged monthly from 1990 to 1995 (OME unpubl. data). For simplicity we assumed that inflowing air and water concentrations were zero; all chemicals enter the system by a single emission of 1 mol/h into air.

Table 3.4 Model parameter values for the Don River watershed.

Compartment	Air	Water	Soil	Sediment	Vegetation	Film
<i>Surface Area</i> (m^2)	4.7×10^7	7.0×10^6	1.71×10^7	7.0×10^6	2.05×10^7 ^a	4.58×10^7 ^b
<i>Depth (m)</i>	1000	0.38	0.05	0.02	2×10^{-4} ^c	70×10^{-9}
<i>Volume (m³)</i>	4.7×10^{10}	2.66×10^6	8.55×10^5	1.4×10^5	4.1×10^3	3.21
Organic Carbon frac.	0.2 ^d	0.02 ^e	0.02 ^e	0.04 ^e	0.02 ^f	0.74 ^g
<i>Density</i> (kg/m^3)	1.175	1000	1300 ^h	1500 ^h	850 ^f	--
v_A	~ 1.0	--	0.2	--	0.18	--
v_W	--	~1.0	0.3	0.8	0.80	--
$v_{part.}$	4.17×10^{-11} (50 $\mu g/m^3$)	8.0×10^{-9} (0.012 g/m^3)	0.5	0.2	--	0.7
v_{lipid}	--	--	--	--	0.02 ⁱ	0.3
<i>Advection</i> <i>Res. Time (h)</i>	7	190	--	--	--	--
<i>Advective</i> <i>Flow (m³/h)</i>	6.87×10^9	1.4×10^4	--	--	--	--

^a Leaf area index of 1.2 from Nowak et al. (1997).^b An Impervious Surface Index (ISI) is defined analogously to the LAI. This parameter accounts for the 3-dimensional nature of the urban landscape. A value of 2 is assumed.^c Illustrative literature value (Riederer 1995)^d For particulate fraction: Cotham and Bidleman (1995)^e For particulate fraction: Law (1996)^f For lipid fraction: Paterson and Mackay (1995)^g For particulate fraction: Diamond et al. (1996)^h Pertains to particulate fraction.ⁱ Cuticle volume fraction

Table 3.5 Input parameters and coefficients used by MUM. U_R is the rain rate, D_{air} is the diffusion quotient in pure air, k_{AS} is the mass transfer coefficient of air over soil, k_{AV} is the mass transfer coefficient of air over vegetation, k_{AF} is the mass transfer coefficient of air over film, k_{VV} is the vegetation-side mass transfer coefficient, k_{FF} is the film-side mass transfer coefficient, v is the wind velocity, l is the mean length of the surface in the direction of the wind, R_S is the rainsplash rate constant, R_{LF} is the litterfall rate constant, Il_w is the wet deposition interception loss fraction, k_{WE} is the leaf wax erosion mass transfer coefficient, W is the film washoff rate constant, λ is the canopy drip parameter, and U_P and U_W are the dry deposition velocities to surfaces and water respectively, and B is the above ground plant dry mass inventory.

Parameter	Value	Comments	Reference
U_R	9.3×10^{-5} m/h	• average from May to Oct.	MOE 1995
D_{air}	4.9×10^{-6} m ² /s		Bennett et al. 1998
k_{AS}	3.5 m/h	• using $\delta^{bl} = 0.005$ m	Bennett et al. 1998
k_{AV}	23.0 m/h	• using δ^{bl} from eq. 3.2	Nobel 1991
k_{AF}	15.4 m/h	• using δ^{bl} from eq. 3.2	Nobel 1991
k_{VV} (veg. side)	Eq. 3	• chemical dependent	Trapp 1995
k_{FF} (film side)	Eq. 3	• chemical dependent	Trapp 1995
v	12 km/h	• historically average summer value	Environ. Canada 1998
l	7 cm	• illustrative lit. value	Riederer 1995
R_S	3.58×10^{-7} h ⁻¹		Whicker and Kirchner 1987
R_{LF}	2.31×10^{-4} h ⁻¹	• $L_G = 180$ days = 4320 hours	Bennett et al. 1998
Il_w	0.19	• illustrative lit. value for a variety of forest stands.	Carlyle-Moses and Price 1999. Mahendrappa 1990.
k_{WE}	8.05×10^{-8} m/h		
W	0.25	• calibrated from empirical data	OME 1995
λ	8.7×10^{-4}		
U_P	10.2 m/h	• 0.3 cm/s	Mackay 1991, Wu et al. 1995
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 ²		Bennett et al. 1998

Table 3.6 Physical-chemical properties of evaluative chemicals at 25 °C and their transformation rates (Mackay et al. 1992).^a

<i>Property</i>	<i>Phenanthrene</i>	<i>Fluoranthene</i>	<i>Tetra-CDD</i>	<i>Penta-CDD</i>	<i>Octa-CDD</i>
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 ³)	1.2	1.29×10 ⁻³	1.93×10 ⁻⁵	1.18×10 ⁻⁴	7.36×10 ⁻⁷
Log(K _{ow})	4.6	5.22	6.8	7.4	8.2
Log(K _{OA})	7.61	8.88	9.67	11.37	12.76
H (Pa/m ³ Pa)	3.26	0.92	3.34	0.0266	6.88×10 ⁻²
V.P. (Pa)	2.2×10 ⁻²	1.2×10 ⁻³	2.0×10 ⁻⁷	8.8×10 ⁻⁸	1.1×10 ⁻¹⁰
τ _{1/2} Air (h) ^c	8	18	190	350	3850
τ _{1/2} Water (h)	550	1700	550	550	5500
τ _{1/2} Soil (h)	5500	17000	55000	55000	55000
τ _{1/2} Sed. (h)	17000	55000	55000	55000	55000
τ _{1/2} Veg.(h)	6	14	148	273	3003
τ _{1/2} Film (h)	5	11	111	205	2252

^a specific PCDD congeners chosen where 2,3,7,8-Cl₄DD, 1,2,3,4,7-Cl₅DD, Cl₈DD, hereafter referred to by their homologue groups.

^b Calculated using an empirical relationship (Harner and Bidleman, 1998).

^c 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 the purpose of our steady-state representation, the value of the interception coefficient, α (defined by S/R , where S (mm) is the retention coefficient and R (mm) is the amount of rainfall of a rain event), was chosen to be unity. Equation 3.6 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) to 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 minimal sediment depth was assumed as the fine grain sediment in the Don River is easily mobilized 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 processes for most gas-phase organic compounds in the troposphere (Kwok et al. 1995, Anderson and Hites 1996, Brubaker and Hites, 1998). In addition, studies of chemical transformation in various types of vegetation have shown photodegradation to be an important loss mechanism for many types of organic compounds (McCrady and Maggard 1993, Schuler et al. 1998). While photodegradation of SOC 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 Simick 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 values to deviate, sometimes substantially, from those reported in the literature. Thus, in order to approximate transformation rates in vegetation as a function of those in air we compared the available degradation half-lives of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in both media.

We first assumed the photodegradation half-life of 44 h reported by McCrady and Maggard (1993) under controlled laboratory conditions to be accurate. Next, we multiplied the rate constant associated with this half-life by the correction factor of 0.3 suggested by Trapp and Matthies (1995), in order to correct for the relative amount of time these authors believe vegetation is present in 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 degradation in vegetation is about 30% faster than in air. As a first approximation, then, this factor was then applied to the reaction rates in air 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.

3.6 RESULTS AND DISCUSSION

Chemicals consistently achieve their highest concentrations in the film with sediment, soil, and vegetation following in descending order (Figure 3.1). In contrast, soil and sediment accumulate the greatest mass of chemicals (Figure 3.2). This is in agreement with estimates

of SOC burdens in European and North American soils and sediments (Alcock et al. 1993, Wild and Jones 1995, Duarte-Davidson et al. 1997, Diamond et al. 1996).

Chemical distribution and fate processes are integrated into the estimates of chemical persistence which, at steady state, is the ratio of mass to input or output rate for a compartment (Figure 3.3). Persistence in air is less than 1 day for all chemicals due to high advective losses. Indeed, advection from air accounts for the greatest chemical loss from the system (Figure 3.4). Advection from water also controls chemical loss from, and persistence in, water for the less hydrophobic contaminants that do not appreciably partition into sediments.

It is interesting to contrast soil and sediment with the organic film. These compartments which lie at two ends of the spectrum in terms of mass accumulation and chemical persistence. Soil and sediment contain the greatest mass of chemical because they receive relatively high inputs from air, water and vegetation, and because losses are minimal. Losses from soil occur through volatilization, soil erosion to surface waters, and leaching to groundwater, and from sediment due to burial (chemical transformation occurs in both media). Volatilization from soil is minimal (Jones and Duarte-Davidson 1997). Soil erosion rates are poorly known for urban systems: Wolman (1967) proposed that rates are high during urban development but decline as the city matures. Thus, soil erosion is not likely a major process that removes SOC from soils in the case simulated here. Leaching to groundwater is a slow process for most SOC and thus does not account for large losses. Finally, transformation can play an important role in SOC removal but is nonetheless slow

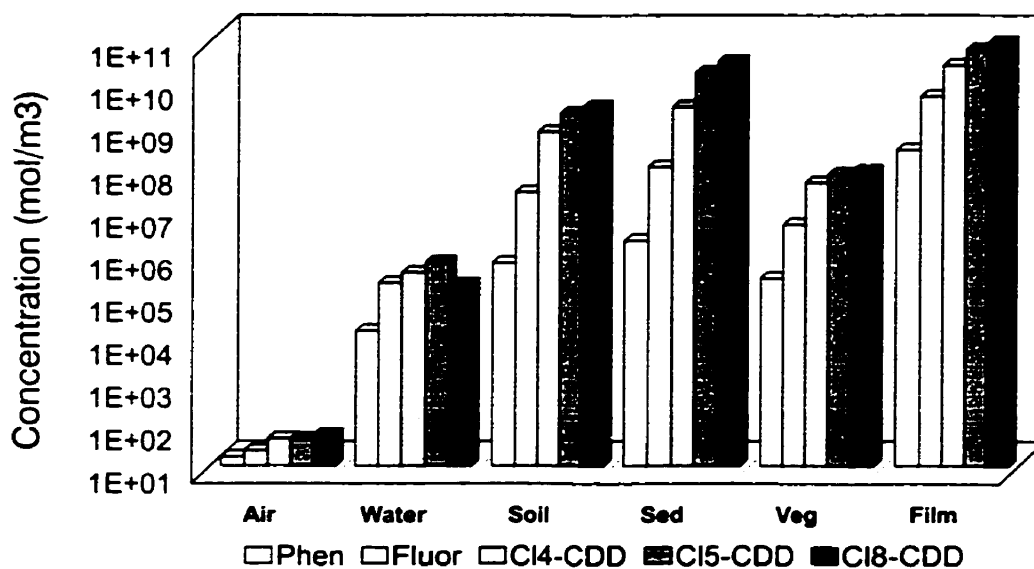


Figure 3.1 Estimated chemical concentrations in the bulk phase (ng/m³).
Emission of 1 mol/h into air is assumed.

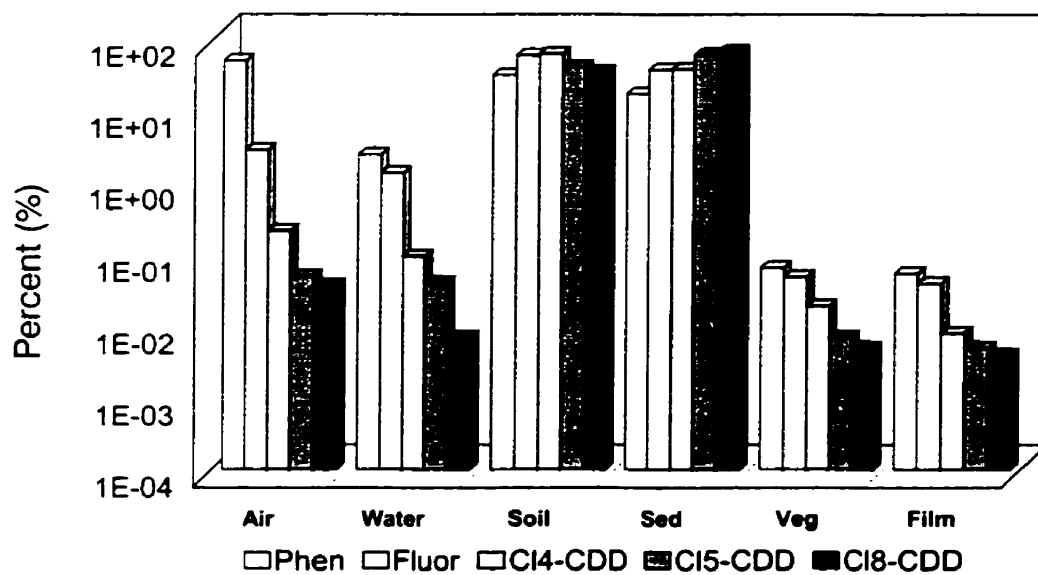


Figure 3.2 Estimated distribution of chemicals among model compartments (%).
Emission of 1 mol/h is assumed.

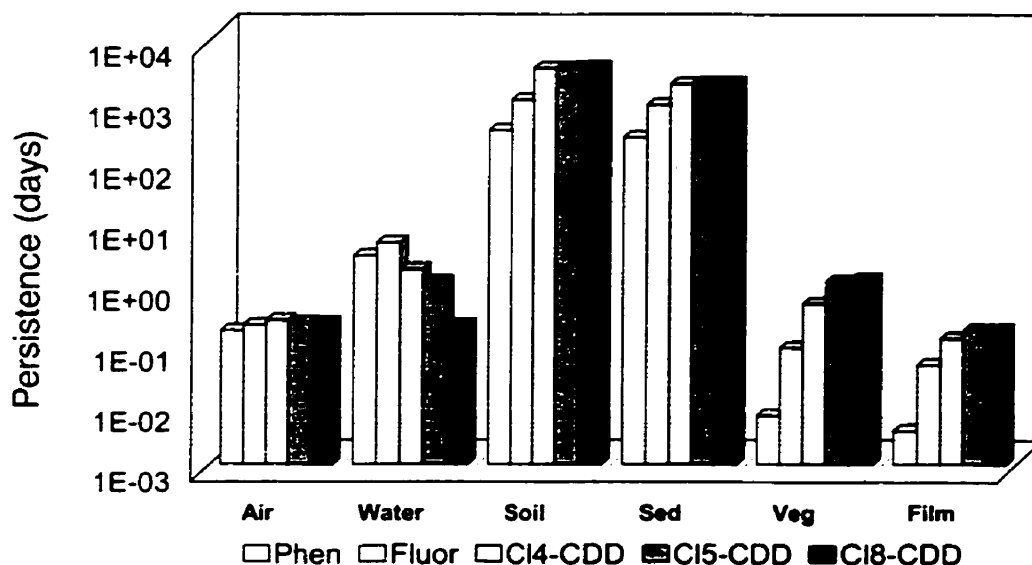


Figure 3.3 Estimated chemical persistence in each compartment (days).

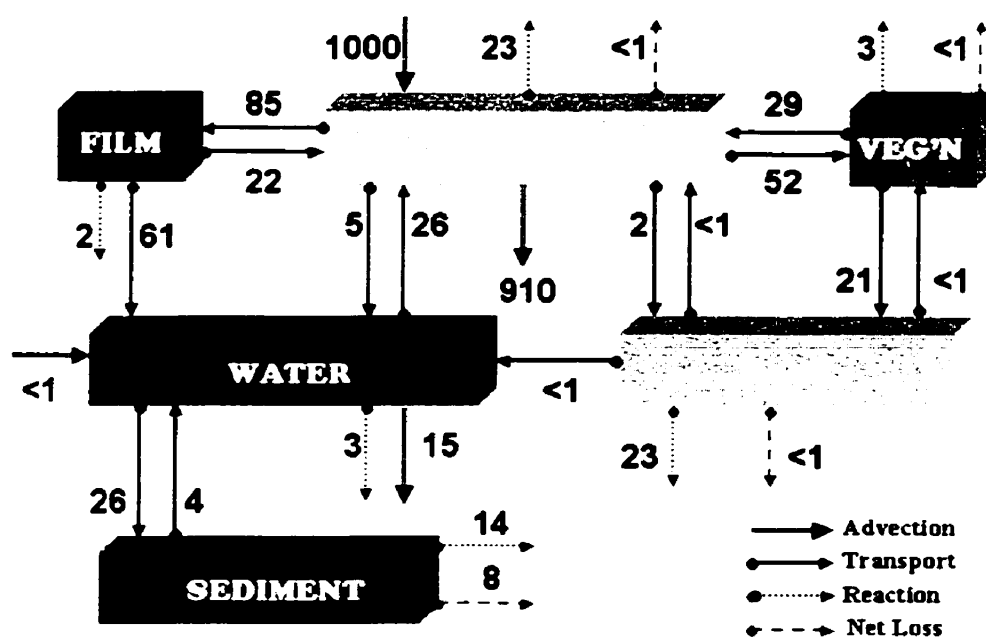


Figure 3.4 Estimated rates of chemical movement and transformation for 2,3,7,8-Cl₄DD. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

for most hydrophobic compounds. Together, these processes lead to the high persistence of chemical in soil and sediment on the order of nine years, which is in agreement with experimental results (Eisenberg et al. 1998).

In contrast to soil, sediment and indeed, all other compartments, the organic film achieves very high concentrations but holds minimal chemical mass. Despite its low chemical mass, the significance of the film lies in its large surface area and rapid exchange rates which affect chemical fate in the system. The film has a surface area to volume ratio of 1.4×10^7 which results in high inputs from atmospheric deposition and, depending on chemical hydrophobicity, promotes loss by either film-air exchange or washoff, as well as reaction by photolysis. Film washoff is the main route of chemical transfer to surface waters. The high total loss rate results in a relatively short chemical residence time of less than 1 day to several weeks and thus low accumulated mass. In contrast, soil and sediment greatly reduce chemical mobility and hence, act as important sinks. Thus, the film in urban areas increases surface-air and surface-water exchange and chemical mobility relative to areas with high soil coverage. These processes may help explain the elevated concentrations of some SOC_s in urban air that can not be accounted for by emission patterns (e.g.- Halsall et al. 1995, Currado and Harrad 1998) and the strong positive relationship between temperature and gas phase SOC_s at urban, relative to rural sites (Gustafson and Dickhut 1997, Cleaverly et al. 1999).

Vegetation also plays an important role in urban systems. Vegetation captures SOC_s (e.g., McLachlan and Horstmann 1998) and transfers them to soil where they are relatively immobile and highly persistent, as noted above. The mechanisms contributing to this

transport are complex. As was previously mentioned, in addition to vegetative canopy drip, SOC_s are transferred to soil by the erosion and subsequent deposition of contaminant-enriched plant waxes. The rate at which this erosion occurs depends on environmental factors and species of vegetation. Horstmann et al. (1997) suggest 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 et al. 1990, Sauter et al. 1987). Atmospheric aerosols and particles have been shown to contribute leaf abrasion (van Gardigen et al., 1991), hence the elevated concentration of these particles in urban systems would serve to aggravate the erosion process.

3.7 CONCLUSIONS

A multimedia urban model 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 a vegetation compartment as well as a compartment for the organic film that coats impervious surfaces. The model was run to illustrate the effect of urbanization, or specifically, impervious surfaces, on the fate of SOC_s. The model indicates that the film achieves high chemical concentrations and its high surface area to volume ratio serves to "reflect" SOC_s back into the atmosphere and promote chemical washoff into surface waters. In contrast, soil and sediment are the greatest sinks for SOC_s in urban areas due to inputs from other media and high persistence due to minimal losses. Vegetation

accumulates gas and particle phase SOC_s and subsequently transfers them 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. These results are consistent with literature reports of processes that contribute to chemical movement and fate. 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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CHAPTER 4

COMPARISON OF THE MULTIMEDIA FATE AND TRANSPORT OF SOCs IN URBAN AND FORESTED AREAS: APPLICATION OF THE MULTIMEDIA URBAN MODEL

4.1 INTRODUCTION

As populations become increasingly urbanized worldwide, our concerns with respect to quantifying the influence of our built environment on chemical fate become more pressing. Raw materials and other resources concentrate in urban areas 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.- Horstmann and McLachlan 1995, Crunkilton and DeVita 1997, Wagrowski and Hites 1997, Mayer 1999, Diamond et al. *subm*). This has also led to the recognition that urban areas act as point sources for medium and long range pollutant transport to surrounding areas (Simcik et al. 1997, Cole et al. 1999). 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 radically altered hydrologic regimes. These unique properties must be addressed within a modeling framework in order to get a more complete and accurate picture of contaminant dynamics in urban areas.

In this chapter, the Multimedia Urban Model (MUM) developed by Diamond and co-workers (Chapter 3) is used to compare the fate and transport of semi-volatile organic compounds (SOCs) in urban and forested areas. The model, based on the steady-state, Level III fugacity model of Mackay (1991), is parameterized 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 (Chapter 3). Diamond et al. (subm.) 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 SOC_s back into the atmosphere as well as chemical washoff into surface waters. In contrast, soil and sediment are the greatest sinks for SOC_s in urban areas due to high chemical persistence in, and minimal losses from, these media. Vegetation accumulates gas- and particle-phase SOC_s and subsequently transfers them 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.

Here, the model is used to demonstrate the increased mobility of SOC_s in urban relative to forested areas. I first review the model, and then apply it in order to compare results obtained for urban and forested areas.

4.2 MULTIMEDIA URBAN MODEL (MUM)

The Multimedia Urban Model (MUM) is based on the Level III fugacity model of Mackay (1991) 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. Chemical enters each medium through direct emission and can be transferred among compartments as well as be lost from all compartments through various transformation

processes. Chemical can also enter air and water through advection, parameterized as the product of a flow rate G (m^3/h) that quantifies bulk movement, and the chemical concentration entering the system C (mol/m^3). Chemical can be lost from the system through ventilation to the stratosphere, leaching to groundwater, burial in deep sediments, and export of litterfall.

Z values ($\text{mol}/\text{Pa}\cdot\text{m}^3$) that express the capacity of a phase for a chemical, are derived according to Mackay (1991) and Mackay and Paterson (1991) (Table 4.1). The Z value for vegetation, Z_v , is calculated by assuming that only the leaf cuticle participates in the plant/air partitioning of SOC_s (Riederer 1995). 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 (Paterson and Mackay 1995). 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 bulk film is considered to consist of 30 and 70% by mass of organic or “pure” film and particulate phases respectively (Diamond et al. *subm*). The “pure” film phase is assumed to consist entirely of organic matter with an organic carbon fraction (f_{OC}) of 0.74, that of octanol. The Z value for particle-sorbed chemicals in the film is the same as that for aerosols, Z_Q , the presumed source of the particles in film. We use the empirical relationship of Harner and Bidleman (1998) that correlates the particle-air partition coefficient, K_p ($\text{m}^3/\mu\text{g}$), with the octanol-air partition coefficient, K_{OA} , assuming an organic matter content of aerosols of 0.20 (Bahavar, *unpubl. data.*, Rogge et al. 1993, Cotham and Bidleman 1995, Harner and Bidleman 1998).

Table 4.1. Z Values. 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 is the Henry's law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}$), S^S and S^L are the solid and subcooled liquid solubilities (mol/m^3), P^S and P^L are the solid and subcooled vapor pressures (Pa) respectively, f_{om} is the fraction of organic matter, f_{OC} is organic carbon fraction, ρ is density (kg/L), v is volume fraction, ϕ is mass fraction.

Compartment	Phase	Equation
Air	Gas Phase	$Z_A = 1/RT$
	Particulate	$Z_Q = 10^{(\log K_{OA} + \log f_{om} - 11.91)} \cdot Z_A \cdot \rho_Q \cdot 10^9{}^a$
	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.	$Z_P = Z_W \times \rho_P \times K_{OC} \times f_{OC,P}$
	Bulk	$Z_{BW} = Z_W + (Z_P \times v_P)$
Soil	Solids	$Z_S = Z_W \times \rho_S \times 0.41 K_{OW} \times f_{OC,S}$
	Bulk	$Z_{BS} = (v_A \times Z_A) + (v_W \times Z_W) + (v_S \times Z_S)$
Sediment	Solids	$Z_D = Z_W \times \rho_D \times 0.41 K_{OW} \times f_{OC,D}$
	Bulk	$Z_{BD} = (v_W \times Z_W) + (v_D \times Z_D)$
Vegetation	Leaf Cuticle	$Z_V = Z_W \times K_{OW} \times f_{OC,V}$
	Bulk	$Z_{BV} = (v_A \times Z_A) + (v_W \times Z_W) + (v_V \times Z_V)$
Film	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	$Z_{BF} = (Z_F \times \phi_F) + (Z_Q \times \phi_Q)$

^a Harner and Bidleman (1998)

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 (1991). In addition to these, MUM includes D values for transport mechanisms to and from the organic film and vegetation (Table 4.2).

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. For the 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.

Table 4.2. D Value formulations specific to MUM. A's are media interfacial areas (m^2), k's are mass transfer coefficients (m/h), U_R is the rain rate (m/h), U_P is the dry deposition velocities (m/h), If_W and If_D are the canopy wet and dry interception fractions, Q is the scavenging ratio, v is volume fraction, V is medium volume, λ is the canopy drip parameter, and R_{LF} and R_S are the first-order litterfall and rainsplash rate constants respectively.

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	$D_{FW} = A_{AF} \cdot k_{FW} \cdot Z_{BF}$
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	$D_{RV} = A_{AV} \cdot U_R \cdot Z_W \cdot If_W$
	Wet Dep. Of Particles	$D_{QV} = A_{AV} \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q \cdot If_W$
	Dry Dep. Of Particles	$D_{DV} = A_{AV} \cdot U_P \cdot v_Q \cdot Z_Q \cdot If_D$
	TOTAL	$D_{AV} = D_{VV} + D_{RV} + D_{QV} + D_{DV}$
Vegetation – Soil	Canopy Drip	$D_{CD} = A_{AV} \cdot U_R \cdot (If_W - If_D) \cdot \lambda \cdot Z_Q$
	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	$D_{SP} = V_S \cdot R_S \cdot Z_{BS}$

4.3 MODEL APPLICATION

We used the model to consider SOC fate in an urban area and contrast this with fate in a comparable forested environment. The model is parameterized 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 (MTRCA 1992). Open area was assumed to consist of vegetation under soil. We have assumed typical summer conditions with a temperature of 25°C and trees in full leaf. The Don River was parameterized to reflect that it is a shallow river of moderate velocity. On average, minimal sediment accumulates and is buried as high flows resuspend most

deposited sediment. Parameter values for the Don River watershed are summarized in Table 4.3.

Table 4.3. Model parameter values for the Don River watershed.

Compartment	Air	Water	Soil	Sediment	Vegetation	Film
<i>Surface Area</i> (m^2)	4.7×10^7	7.0×10^6	1.71×10^7	7.0×10^6	2.05×10^7 ^a	4.58×10^7 ^b
<i>Depth</i> (m)	1000	0.38	0.05	0.02	2×10^{-4} ^c	70×10^{-9}
<i>Volume</i> (m^3)	4.7×10^{10}	2.66×10^6	8.55×10^5	1.4×10^5	4.1×10^3	3.21
Organic Carbon frac.	0.2 ^d	0.02 ^e	0.02 ^e	0.04 ^e	0.02 ^f	0.74 ^g
<i>Density</i> (kg/m^3)	1.175	1000	1300 ^h	1500 ^h	850 ^f	--
v_A	~ 1.0	--	0.2	--	0.18	--
v_W	--	~1.0	0.3	0.8	0.80	--
$v_{part.}$	4.17×10^{-11} ($50 \mu g/m^3$)	8.0×10^{-9} ($0.012 g/m^3$)	0.5	0.2	--	0.7
v_{lipid}	--	--	--	--	0.02 ⁱ	0.3
<i>Advection</i> <i>Res. Time</i> (h)	7	190	--	--	--	--
<i>Advective</i> <i>Flow</i> (m^3/h)	6.87×10^9	1.4×10^4	--	--	--	--

^a Leaf area index of 1.2 from Nowak et al. (1997).

^b An Impervious Surface Index (ISI) is defined analogously to the LAI. This parameter accounts for the 3-dimensional nature of the urban landscape. A value of 2 is assumed.

^c Illustrative literature value (Riederer 1995)

^d For particulate fraction: Cotham and Bidleman (1995)

^e For particulate fraction: Law (1996)

^f For lipid fraction: Patterson and Mackay (1995)

^g For particulate fraction: Diamond et al. (1996)

^h Pertains to particulate fraction.

ⁱ Cuticle volume fraction

The environmental parameters listed in Table 4.3 were used to simulate urban conditions. In order to simulate forested conditions, the model parameters were changed as follows. First, impervious surfaces were mathematically replaced with soil and overlying vegetation (i.e.- from 36 to 85% air-soil interfacial area). Secondly, we assumed a leaf area index of 4 which is characteristic of forests and agricultural crops (Müller et al. 1993) in contrast to a LAI of

1.2 for urban areas (Nowak et al. 1997). This changed the air-vegetation interfacial area from 2.05×10^7 to 1.6×10^8 m² 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 (Mackay et al. 1992) and are relatively abundant in urban areas (e.g.- Cotham & Bidleman, 1995, Diamond et al. subm.). PCBs were widely used in North America from the 1930s until the 1970s, when they were banned in applications requiring an inert, non-flammable, insulating fluid (Wallace and Hites 1996). To this day the persistence of PCBs has been noted in many environmental media particularly in biota where PCBs have been shown to bioaccumulate, reaching levels where their teratogenic and carcinogenic properties are of concern (Honrath et al. 1997). Selected physical-chemical properties for each homologue group are listed in Table 4.4.

Table 4.4 Physical/chemical properties of PCB homologues at 25 °C (Mackay et al. 1992).

# Cl	MW (g/mol)	M.P. (°C)	Sol (g/m ³)	Log[K _{ow}]	Log[K _{OA}] ^a	H (Pa/m ³ Pa)	V.P. solid (Pa)
1	188.7	34.0	5.5	4.3	5.9	70.0	2.0
2	223.1	37.0	1.0	5.1	7.0	31.7	0.14
3	257.4	57.0	0.2	5.7	7.1	97.2	7.8×10^{-2}
4	292.0	65.0	5.2×10^{-2}	6.1	7.3	1.5×10^2	2.7×10^{-2}
5	326.4	77.0	1.2×10^{-2}	6.4	7.7	1.3×10^2	4.8×10^{-3}
6	360.9	79.0	5.5×10^{-4}	7.0	7.7	5.0×10^2	7.6×10^{-4}
7	395.3	109.5	1.2×10^{-4}	7.0	8.5	87.7	2.7×10^{-5}
8	429.8	159.0	2.5×10^{-4}	7.1	8.8	45.7	2.7×10^{-5}

^a Calculated using the relationship, $K_{OA} = (K_{OW} \cdot R \cdot T) / H$ (Harner and Bidleman, 1998).

Table 4.5 shows chemical transformation rates, expressed as half-lives, that are used in the model. 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 in Chapter 3. Photochemical oxidation by hydroxyl radicals (OH) was assumed to be the dominant transformation processes for PCBs in the atmosphere (Kwok et al. 1995, Anderson and Hites 1996), and photodegradation was assumed to be the dominant degradative process in the film and vegetation (McCrary and Maggard 1993, Schuler et al. 1998). As before, a scaling factor relating transformation rates in air to those in vegetation, obtained by comparing measured transformation rates in these two media, was used. Chemical transformation rates in vegetation were taken to be 30% faster than those in air and transformation rates in the film were 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. Reaction half-lives were assumed to be representative of the PCB homologues.

Table 4.5 Selected chemical transformation rates expressed as half-lives (h).

# Cl	$\tau_{1/2}$ Air ^a	$\tau_{1/2}$ Water ^b	$\tau_{1/2}$ Soil ^b	$\tau_{1/2}$ Sed. ^b	$\tau_{1/2}$ Veg. ^c	$\tau_{1/2}$ Film ^c
1	55	550	17000	17000	43	32
2	90	550	17000	17000	70	53
3	170	17000	55000	55000	133	99
4	220	55000	55000	55000	172	129
5	315	55000	55000	55000	246	184
6	450	55000	55000	55000	351	263
7	650	55000	55000	55000	507	380
8	940	55000	55000	55000	733	550

^a Atmospheric half-lives calculated using data from Anderson and Hites (1996), who have assumed that the primary removal mechanism is reaction with OH radicals.

^b Mackay et al. (1992)

^c Assumed values, as described in the text.

4.4 RESULTS AND DISCUSSION

In order to assess whether the model provides reasonable estimates of chemical distribution, measured concentrations of PCB homologues were compared with model estimates. This necessitated back-calculating reasonable emission rates since there are virtually no emission data available. Measured chemical concentrations were compiled from a variety of sources for various urban and forested locations. The back-calculation was accomplished by assuming a single emission to air and no inputs via air or water advection, and estimating the air emission by maximizing the correspondence between measured and observed air concentrations. If air concentrations were unavailable, the air emission was back-calculated by maximizing the correspondence between measured and observed water and then film concentrations. In cases where concentrations were available for only one particular scenario (i.e.- either urban or forested), equal emissions were assumed for illustrative purposes. The back-calculated emissions for mono- to octachlorinated homologues are shown in Table 4.6.

Table 4.6 Back-calculated atmospheric emission rates (mol/h) for urban and forested conditions for each homologue group.

#Cl	1	2	3	4	5	6	7	8
Urban	1.2×10^{-2}	4.0×10^{-3}	1.0×10^{-2}	1.2×10^{-2}	2.0×10^{-3}	1.5×10^{-3}	7.0×10^{-4}	6.8×10^{-5}
Forested	1.2×10^{-2}	4.0×10^{-3}	6.0×10^{-4}	3.0×10^{-4}	5.0×10^{-4}	4.0×10^{-4}	7.6×10^{-5}	6.8×10^{-5}

Modelled concentrations agree within one to two orders of magnitude with measured values (Table 4.7). Whereas homologue-specific PCB concentrations for media such as air were readily available for both urban and forested locations, there were few data for other urban media such as soil, surface waters, sediment, and vegetation. The inability to calibrate and test the model with measured data represents a weakness inherent to many multimedia models (Mackay and Paterson 1991). Where data were available for comparison, the

correspondence is believed to be reasonable considering the uncertainty in many model parameter values and the lack of parameter calibration. This 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 (Halsall et al. 1995).

Table 4.7 Estimated and measured multimedia chemical concentrations.

#Cl / Source	Air (pg/m ³)		Water (pg/L)		Soil (ng/g)		Sed. (ng/g)		Veg. (ng/g)		Film (ng/m ²)	
	Urb. ^a	For. ^b	Urb.	For. ^c	Urb.	For. ^d	Urb. ^e	For.	Urb.	For. ^f	Urb. ^g	For. ^g
1 Meas.				10							0	
Model	304	300	10	9.7	0.0015	0.005	0.003	0.003	0.005	0.0052	0.006	---
2 Meas.				8.4							0.06-2.21	0
Model	0.12	0.12	11	8.5	0.0046	0.053	0.011	0.008	0.03	0.03	0.063	---
3 Meas.		19-25		11		0.28	0.05			0.13-0.19	0.12-7.18	0.03-0.78
Model	370	22	17	0.54	0.042	0.033	0.063	0.002	0.11	0.0063	0.24	---
4 Meas.	33-1350	8-18		21		0.13	0.01-0.06			0.031-0.154	0.02-28.5	0.04-0.31
Model	500	12	25	0.21	0.092	0.033	0.17	0.0014	0.25	0.0061	0.52	---
5 Meas.	17-252	1-48		30		0.15	0.03-0.11			0.039-0.285	0.03-38.1	0.02-0.36
Model	94	23	9.1	0.51	0.042	0.16	0.11	0.0059	0.11	0.026	0.23	---
6 Meas.	8-115	1-48		9		0.31	0.02-0.18			0.042-0.414	0.06-45.8	0.05-0.55
Model	78	20	5.6	0.17	0.035	0.15	0.22	0.0067	0.094	0.024	0.2	---
7 Meas.	2-75	1-7		10		0.13	0.01-0.12			0.021-0.167	0.02-114.2	0.02-0.12
Model	40	4	17	0.084	0.1	0.12	0.66	0.0033	0.26	0.0019	0.29	---
8 Meas.	4						0.02-0.04				0.08-56.5	0.02
Model	4.1	0.42	4	0.4	0.024	0.0024	0.19	0.019	0.063	0.0063	0.11	---

^a Cotham and Bidleman (1995) (Chicago, U.S.A.),
Halsall et al. (1995) (London, Manchester, Cardiff, Stevenage; England),
Coleman et al. (1997) (London, Manchester; England)

^b Cousins & Jones (1998) (Lancaster; England)
Haugen et al. (1999) (Lista; Norway)

^c Rawn et al. (1998) (Miami; Manitoba, Canada)

^d Cousins & Jones (1998) (Lancaster; England)

^e Gewurtz et al. (subm.) (Detroit River, U.S.A.)

^f Thomas et al. (1998), (England)

Ockenden et al. (1998) (8 sites, Norway)

^g Gingrich (1999) (Toronto, Cambridge, Egbert; Ontario, Canada)

In order to illustrate the multimedia behavior of the PCB homologues and contrast their behavior in urban and forested conditions, we used an emission rate of 1 mol/h into the air compartment. Flow diagrams illustrating the overall changes in contaminant dynamics between urban and forested conditions are shown in figures 4.1 and 4.2 for heptachlorinated homologues. The results show that the dominant loss processes in both scenarios is advection from air which is consistent with the findings of Mackay and Paterson (1991). Individual processes are discussed in detail below.

Under urban conditions all chemicals achieve the highest concentrations in the film with sediment, soil, and vegetation following in order of decreasing concentration (Table 4.8).

Table 4.8 Multimedia PCB concentrations for urban and forested conditions (assuming equal emissions of 1 mol/h into air).

#Cl	Air (ng/m ³)		Water (ng/L)		Soil (ng/g)		Sed. (ng/g)		Veg. (ng/g)		Film (ng/m ²)	
	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.
1	26	26	1	1	0.1	0.4	0.2	0.2	0.4	0.4	0.5	--
2	31	31	3	2	1	13	3	2	7	7	9	--
3	37	37	2	1	4	56	6	3	11	11	14	--
4	42	41	2	1	8	111	14	5	21	20	25	--
5	47	46	5	1	20	314	53	12	54	52	65	--
6	52	51	4	0.4	23	365	146	17	63	60	76	--
7	57	53	24	3	142	1914	942	100	375	292	416	--
8	62	54	58	5	350	3714	2804	253	922	561	913	--

The model shows that the film on impervious surfaces efficiently captures a wide range of gas- and particle-phase contaminants. However, it's high surface area to volume ratio of 1.4×10^7 prevents it from being a contaminant reservoir. Chemicals in the film undergo one of three fates: washoff to surface waters, volatilization to air, or transformation. Chemical transformation in the film is slow compared to the first two processes and accounts for losses of less than 1% of inputs to the film.

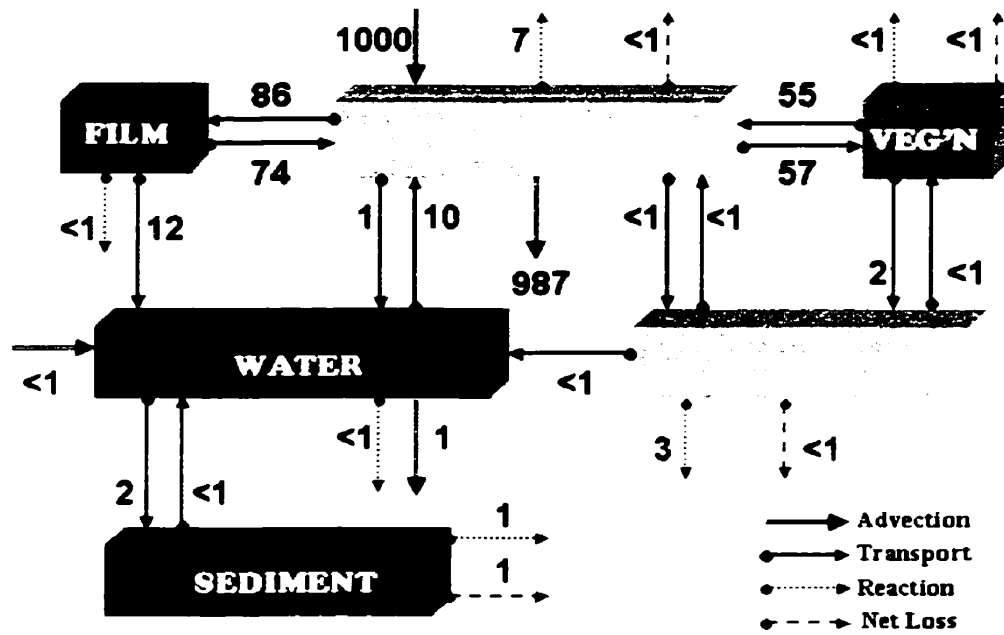


Figure 4.1 Estimated rates of chemical movement and transformation of heptachlorinated PCB under urban conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

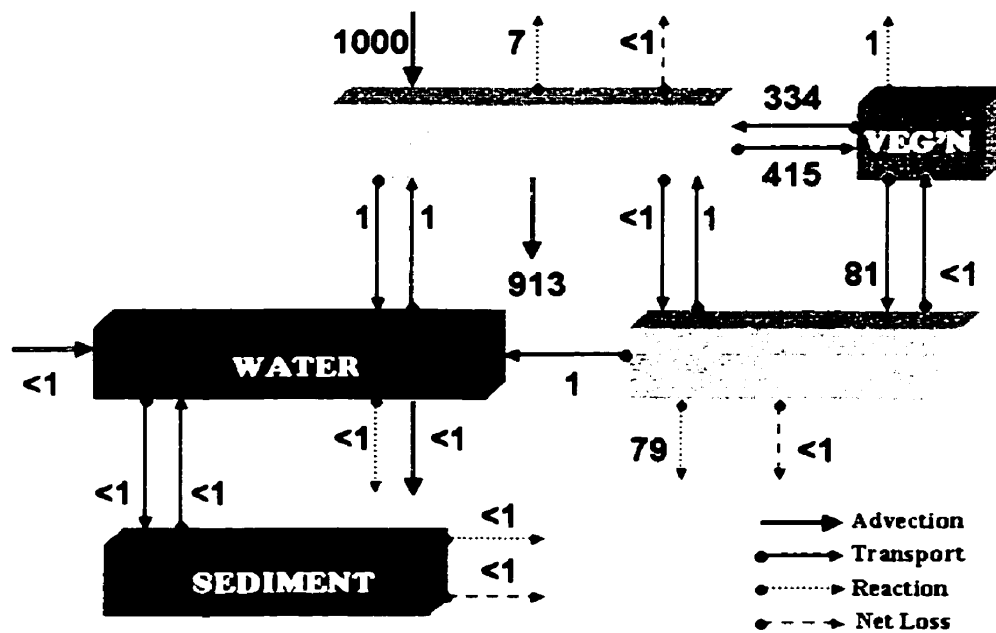


Figure 4.2 Estimated rates of chemical movement and transformation of heptachlorinated PCB under forested conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

Figure 4.3 shows the percentages of chemical volatilization and film washoff as a function of $\text{Log}[K_{OA}]$ or hydrophobicity. PCBs with $\text{Log}[K_{OA}]$ less than approximately 7.5, are almost completely “reflected” back into the atmosphere. In contrast, the more hydrophobic homologues (pentachlorinated and higher) which are more efficiently captured and retained by the film, experience increased washoff as K_{OA} increases.

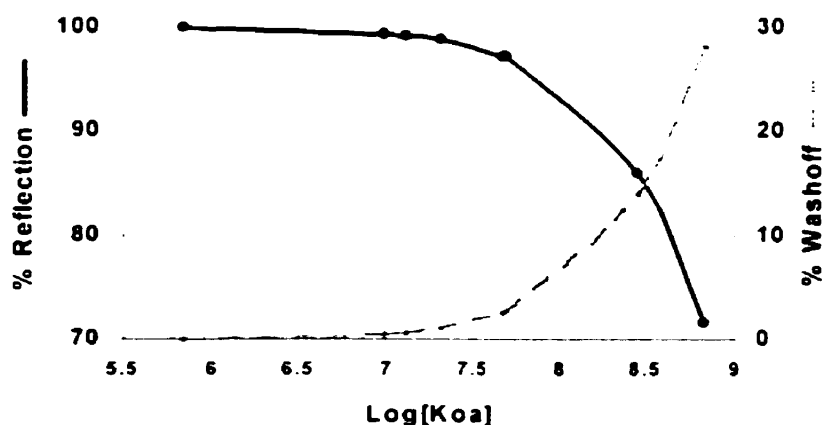


Figure 4.3 Percentage of PCB homologue loss from the organic film by means of volatilization and washoff, as a function of $\text{Log}[K_{OA}]$.

The implications of these results are first that air concentrations are higher in urban than forested conditions, considering the same emissions in both systems (Table 4.8). Secondly, film washoff causes concentrations of the mono- and dichlorinated homologues in surface waters and sediment to increase by 4 and 35% respectively between forested to urban conditions, while concentrations of the tri- to pentachlorinated homologues are two to five times as great, and concentrations of the hexa- to octachlorinated homologues are 8 to 11 times greater. The mass of the PCB homologues in water and sediment also increased from forested to urban conditions (Table 4.9).

Table 4.9 Mass of PCB in each medium for urban and forested conditions (assuming equal emissions of 1 mol/h into air).

#Cl	Air (kg)		Water ($\times 10^{-3}$ kg)		Soil (kg)		Sed. ($\times 10^{-3}$ kg)		Veg. ($\times 10^{-3}$ kg)		Film ($\times 10^{-3}$ kg)	
	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.	Urb.	For.
1	1.2	1.2	2	2	0.1	1	10	10	0.1	0.3	0.03	--
2	1.5	1.4	8	6	1	17	118	88	0.5	4	0.4	--
3	1.7	1.7	5	2	2	72	266	139	1	6	1	--
4	2.0	1.9	6	2	4	144	591	200	2	11	1	--
5	2.2	2.2	12	3	11	408	2213	495	4	27	3	--
6	2.4	2.4	10	1	13	475	6133	704	4	31	3	--
7	2.7	2.5	65	7	79	2488	39560	4191	25	153	19	--
8	2.9	2.5	155	14	194	4828	117800	10630	62	295	42	--

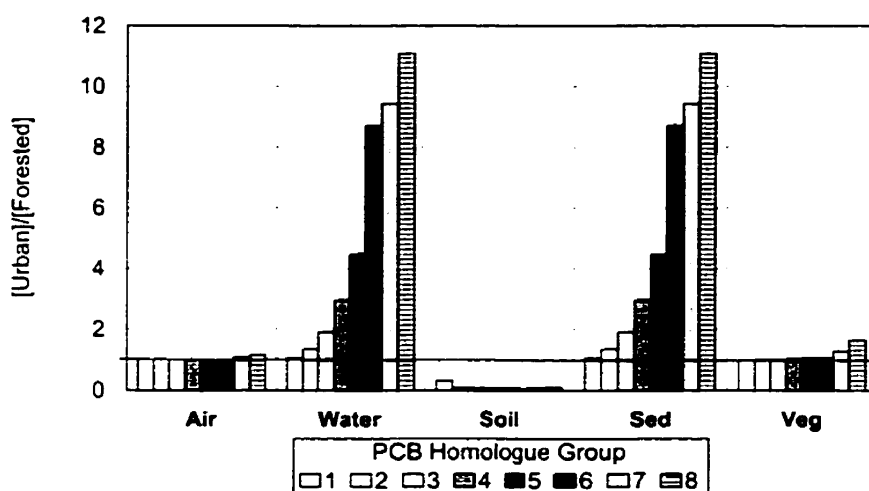


Figure 4.4 Ratio of chemical concentrations between urban and forested conditions. (assuming emissions of 1 mol/h to air).

The observed trends highlight the importance of the film for increasing chemical mobility despite the very small volume of this compartment ($\sim 3\text{m}^3$). Air-film-water transfer explains reports by Schuler (1994) 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 which are flushed by precipitation into surface waters (e.g.- Faure et al. 2000). However, empirical evidence (Gingrich 1999) and these modeling results indicate that the film transfers gas- as well as

particle-phase chemicals from impervious surfaces to surface waters. In addition, since particle-phase compounds are believed to be efficiently captured by the greasy nature of the film, air-film-water transfer is increased beyond that expected in absence of the film. In contrast, chemical export from forested soils via surface runoff is minimal as soils retain most atmospherically deposited chemicals (Dierkes and Geiger 1999).

It is important to note that 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 (Nelson et al. 1998, Bamford et al. 1999) and PAHs and PCBs in Lake Michigan by Chicago (Zhang et al. 1999).

Volatilization from the film and surface waters increase 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 SOC in urban air (e.g., Halsall et al. 1995, Currado and Harrad 1998) and the temperature dependence of these concentrations in the gas-phase (Gustafson and Dickhut 1997, Cleaverly et al. 1999), is attributable to not only higher emission rates, but also 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 (Simcik et al. 1997, Zhang et al. 1999).

Total PCB mass in vegetation is, on average, three times greater for urban than rural canopies when normalized per m² of soil. The vegetation compartment is, however, almost 8 times as large in the forested than urban scenario, and therefore, chemicals in the forest 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 28 and 64%, respectively.

Under urban conditions the low leaf area index, and hence, air-vegetation interfacial area, as well as litterfall export, decreases the transfer efficiency of PCBs to urban relative to forested soils by four to six times (Table 4.10) thereby leading to the accumulation of hydrophobic SOC in vegetation. This result is similar to the observation that SOC transfer from vegetation to soil is much less in grasslands than forests (Rotard et al. 1994, Brorström-Lundén and Löfgren 1998).

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. The efficiency with which the vegetative canopy intercepts airborne chemicals and transfers them to the soil, depends on the air-vegetation interfacial area that is parameterized as the leaf area index.

Table 4.10 PCB fluxes (mmol/h) from the air to vegetation and from vegetation to soil for urban and forested conditions (emission of 1 mol/h into air is assumed).

# Cl	Urban		Forested	
Flux (mmol/h)	Air to Veg	Veg to Soil	Air to Veg	Veg to Soil
1	21	6×10^{-3}	164	3×10^{-1}
2	55	8×10^{-2}	424	4
3	56	1×10^{-1}	436	5
4	57	2×10^{-1}	438	8
5	57	4×10^{-1}	440	17
6	58	4×10^{-1}	442	18
7	57	2	416	81
8	57	5	338	143

Ninety-two % of this increase in PCB fluxes from vegetation to soil is attributable to the increase in leaf area index and only 8% to the increase in vegetative coverage. With increasing hydrophobicity, PCBs are more efficiently captured by the lipophilic plant wax surfaces (McLachlan and Horstmann 1998), and consequently are transferred to soils more efficiently relative to the lower chlorinated congeners. This difference with homologue group is similar to that with film washoff. Wax erosion is parameterized in the same fashion for both urban and forested conditions. Results show this mechanism to be responsible for 38-50% of the PCB flux to soil under urban conditions, and 9-10% under forested conditions. This trend is due to the larger interception capacity of the forest canopy (83% vs. 25% for urban canopy) and hence, the increased contribution of the canopy drip transport mechanism in forests.

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. The soils do not accumulate the mono- and dichlorinated homologues because of their greater volatility and remobilization due to volatilization from the film. Under forested conditions the soil compartment contains 30% of the total monochlorinated homologues, and 92-99% of the

remaining PCB homologues. This high 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 (Alcock et al. 1993, Wild and Jones 1995, Duarte-Davidson et al. 1996, Cousins and Jones 1998). Soils typically contain the greatest mass of hydrophobic SOC because they receive relatively high inputs from vegetation and because losses due to volatilization, erosion to surface waters, and leaching to groundwater are minimal (Jones and Duarte-Davidson 1997). In contrast, under urban conditions soils contain only 5% of the monochlorinated homologues, 29-62% of the di- to tetrachlorinated homologues, and 62-72% of the penta- to octachlorinated homologues due to differences in PCB dynamics caused by the film on impervious surfaces.

Vegetation is well recognized as ameliorating the effects of air pollution (e.g.- Nowak et al. 1997, 2000), including SOC (e.g., Duarte-Davidson 1997, McLachlan and Horstmann 1998). As discussed by Simonich and Hites (1995) and McLachlan and Horstmann (1998), forests *decrease* the atmospheric half-lives of a variety of environmental contaminants through interception by the canopy and subsequent transfer to soils. Hence, forests tend to minimize chemical mobility and long-range atmospheric transport. The lack of vegetation and the simplified structure of the vegetation in urban areas (e.g.- lawns) serves to increase chemical mobility (along with impervious surfaces) relative to forested systems.

4.5 CONCLUSIONS

The Multimedia Urban Model, an expansion of the Level III model of Mackay and co-workers, was parameterized to simulate conditions in an urban area (Don River watershed in

Toronto, Canada) and a fictitious forested area identical in dimensions (urban impervious surfaces were “replaced” with forest and leaf area index was increased). Model estimates of PCB homologue concentrations were within one to two orders of magnitude of measured values obtained from the literature. This correspondence was achieved by back-calculating a single emission rate into air. The model indicates that the large area of impervious surface, and the organic film with which these surfaces are coated, influences contaminant movement by virtue of (1) volatilization of SOCs “dissolved in the film” back into the atmosphere, and (2) the transfer the more hydrophobic chemicals to surface waters via washoff. Volatilization from the film increases atmospheric concentrations, residence times, and advective losses. Film washoff increases urban surface water and sediment concentrations and air concentrations via volatilization. Thus the film increases overall chemical mobility in comparison to forested systems. In forested areas, the dense foliage is able to efficiently collect contaminants and transfer them to surface soils where they are relatively immobile. In urban areas, the higher atmospheric concentrations combined with the lower leaf areas results in greater contaminant loadings in vegetation, a portion of which is exported from the system in litterfall rather than being transferred to soil as occurs under forested conditions.

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CHAPTER 5

THE IMPACT OF ENVIRONMENTAL VARIABILITY ON THE MULTIMEDIA FATE AND TRANSPORT OF SOCs IN URBAN AREAS

5.1 INTRODUCTION

In recent years many researchers have sought to gain insight into the fate and transport of semivolatile organic compounds (SOCs) by constructing multimedia models of contaminant dynamics (e.g.- Mackay et al. 1992, Müller and Pröhl 1993, Bennett et al. 1998, Bruse and Fler 1998). These efforts have largely centred around investigating the primary pathways and mechanisms by which chemical dynamics are controlled. If multimedia models are to be used increasingly as analytical rather than illustrative tools, we must first explore, and second minimize the major uncertainties associated with approximations made through parameterization. As well, it must be appreciated that whereas the models provide a single, deterministic view of chemical dynamics, in reality, conditions are constantly changing in predictable (e.g.- seasonal changes) and unpredictable (e.g.- major storm events) ways. Thus, it is important to quantify the ranges of chemical dynamics that are likely.

Models vary in their sensitivity to uncertainty and variability. Knowledge of this sensitivity and the range of model responses to variable inputs is important for focusing research efforts and critical if the model is to be used for decision making. In this chapter, I examine the sensitivity of the Multimedia Urban Model (MUM) to parameter uncertainty and seasonal variability. The Multimedia Urban Model described in Chapter 3 describes the multimedia fate and transport of SOCs in urban areas. The model is based on the steady-state, Level III fugacity model of Mackay (1991) but is modified for urban systems. The model includes all

major media, however, it is unique in its treatment of impervious surfaces and vegetation. An analysis of the model's sensitivity and uncertainty with regards to variations in many of the critical environmental parameters is addressed, followed by an examination of the model's response to simulated seasonal changes between summer and winter.

5.2 SENSITIVITY AND UNCERTAINTY ANALYSIS

5.2.1 Multimedia Urban Model (MUM)

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 and chemicals are assumed to be in equilibrium between these phases within each bulk compartment. Chemical enters each medium through direct emission and can be transferred among compartments as well as be lost from all compartments through various transformation processes. Chemical can also enter air and water through advection, parameterized as the product of a flow rate (m^3/h) that quantifies bulk movement and the chemical concentration entering the system (mol/m^3). Chemical can be lost from the system through ventilation to the stratosphere, leaching to groundwater, burial in deep sediments, and export of litterfall (in urban centres litterfall is typically collected and disposed of outside the city boundary making it a permanent removal process for chemicals in the system).

Z values ($\text{mol}/\text{Pa}\cdot\text{m}^3$) that express the capacity of a phase for a chemical, are derived according to Mackay (1991) and Mackay and Paterson (1991) and their equations are shown

in Table 5.1. The derivations for model-specific equations of the Z value for vegetation, Z_V , and of the organic film, Z_F , are outlined in Chapter 3. The Z value for particle-sorbed chemicals in the film is the same as that for aerosols, Z_Q , the presumed source of the particles in film. We use the empirical relationship of Harner and Bidleman (1998a) that correlates the particle-air partition coefficient, K_P ($\text{m}^3/\mu\text{g}$), with the octanol-air partition coefficient, K_{OA} , assuming an organic matter content of aerosols of 0.20 (Rogge et al. 1993, Cotham and Bidleman 1995, Harner and Bidleman 1998a).

Table 5.1. Z Values. 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 is the Henry's law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}$), S^S and S^L are the solid and subcooled liquid solubilities (mol/m^3), P^S and P^L are the solid and subcooled vapor pressures (Pa) respectively, f_{om} is the fraction of organic matter, f_{OC} is organic carbon fraction, ρ is density (kg/L), v is volume fraction, ϕ is mass fraction.

Compartment	Phase	Equation
Air	Gas Phase	$Z_A = 1/RT$
	Particulate	$Z_Q = 10^{(\log K_{OA} + \log f_{om} - 11.91)} \cdot Z_A \cdot \rho_Q \cdot 10^9^a$
	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.	$Z_P = Z_W \times \rho_P \times K_{OC} \times f_{OC,P}$
	Bulk	$Z_{BW} = Z_W + (Z_P \times v_P)$
Soil	Solids	$Z_S = Z_W \times \rho_S \times 0.41 K_{OW} \times f_{OC,S}$
	Bulk	$Z_{BS} = (v_A \times Z_A) + (v_W \times Z_W) + (v_S \times Z_S)$
Sediment	Solids	$Z_D = Z_W \times \rho_D \times 0.41 K_{OW} \times f_{OC,D}$
	Bulk	$Z_{BD} = (v_W \times Z_W) + (v_D \times Z_D)$
Vegetation	Leaf Cuticle	$Z_V = Z_W \times K_{OW} \times f_{OC,V}$
	Bulk	$Z_{BV} = (v_A \times Z_A) + (v_W \times Z_W) + (v_V \times Z_V)$
Film	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	$Z_{BF} = (Z_F \times \phi_F) + (Z_Q \times \phi_Q)$

^a Harner and Bidleman (1998a)

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 (1991). In addition to these, MUM also includes D values for transport mechanisms to and from the organic film and vegetation that are summarized in Table 5.2.

Table 5.2 D Value formulations specific to MUM. A's are media interfacial areas (m^2), k's are mass transfer coefficients (m/h), U_R is the rain rate (m/h), U_P is the dry deposition velocities (m/h), If_W and If_D are the canopy wet and dry interception fractions, Q is the scavenging ratio, v is volume fraction, V is medium volume, λ is the canopy drip parameter, and R_{LF} and R_S are the first-order litterfall and rainsplash rate constants respectively.

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	$D_{FW} = A_{AF} \cdot k_{FW} \cdot Z_{BF}$
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	$D_{RV} = A_{AV} \cdot U_R \cdot Z_W \cdot If_W$
	Wet Dep. Of Particles	$D_{QV} = A_{AV} \cdot U_R \cdot Q \cdot v_Q \cdot Z_Q \cdot If_W$
	Dry Dep. Of Particles	$D_{DV} = A_{AV} \cdot U_P \cdot v_Q \cdot Z_Q \cdot If_D$
	TOTAL	$D_{AV} = D_{VV} + D_{RV} + D_{QV} + D_{DV}$
Vegetation – Soil	Canopy Drip	$D_{CD} = A_{AV} \cdot U_R \cdot (If_W - If_W) \cdot \lambda \cdot Z_Q$
	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	$D_{SP} = V_S \cdot R_S \cdot Z_{BS}$

5.2.2 Model Application: Sensitivity Analysis

The model was initially parameterized to simulate conditions in the lower Don River watershed in downtown Toronto, Ontario, Canada that currently supports approximately 500,000 people. The lower Don watershed is characterized by 15% water, 49% impervious surface and 36% open area with respect to aerial land coverage (MTRCA 1992). Typical summer conditions prevail with an air temperature of 25°C and trees in full leaf. Parameter values for the Don River watershed are summarized in Table 5.3.

Table 5.3 Initial model parameter values for the Don River watershed.

Compartment	Air	Water	Soil	Sediment	Vegetation	Film
<i>Surface Area</i> (m^2)	4.7×10^7	7.0×10^6	1.71×10^7	7.0×10^6	2.05×10^7 ^a	4.58×10^7 ^b
<i>Depth</i> (m)	1000	0.38	0.05	0.02	2×10^{-4} ^c	100×10^{-9}
<i>Volume</i> (m^3)	4.7×10^{10}	2.66×10^6	8.55×10^5	1.4×10^5	4.1×10^3	3.21
Organic Carbon frac.	0.2 ^d	0.02 ^e	0.02 ^e	0.04 ^e	0.02 ^f	0.74 ^g
<i>Density</i> (kg/m^3)	1.175	1000	1300 ^h	1500 ^h	850 ^f	--
v_A	~ 1.0	--	0.2	--	0.18	--
v_W	--	~1.0	0.3	0.8	0.80	--
$v_{part.}$	4.17×10^{-11} (50 $\mu g/m^3$)	8.0×10^{-9} (0.012 g/m^3)	0.5	0.2	--	0.7
v_{lipid}	--	--	--	--	0.02 ⁱ	0.3
<i>Advection</i> <i>Res. Time</i> (h)	7	190	--	--	--	--
<i>Advective</i> <i>Flow</i> (m^3/h)	6.87×10^9	1.4×10^4	--	--	--	--

^a Leaf area index of 1.2 is assumed (Nowak et al. 1997)^b An Impervious Surface Index (ISI) is defined analogously to the LAI. This parameter accounts for the 3-dimensional nature of the urban landscape. A value of 2 is assumed.^c Illustrative literature value (Riederer 1995)^d For particulate fraction: Cotham and Bidleman (1995)^e For particulate fraction: Law (1996) ^f For lipid fraction: Patterson and Mackay (1995)^g For particulate fraction: Diamond et al. (1996)^h Pertains to particulate fraction. ⁱ Cuticle volume fraction

For ease of comparison we have restricted our application of the model to the pentachlorinated PCB homologue group. Temperature dependent physical/chemical properties were calculated from empirical log-linear relationships of the type $\text{Log}[\text{property}] = A - B/T$ reported by Paasivirta et al. (1999) and Harner and Bidleman (1996) for selected parameters (Table 5.4). Multimedia transformation rate constants for this homologue group are the same as those given in Table 4.5.

Table 5.4 Temperature dependent equation coefficients and selected physical/chemical properties for the pentachlorinated PCB homologue group at 25 °C.

<i>Property</i>	MW ^a (g/mol)	M.P. ^a (°C)	Sol ^{b*} (mol/m ³)	Log[K _{ow}] ^a	Log[K _{oa}] ^c	H ^b (Pa/m ³ Pa)	V.P. ^{b*} (Pa)
A	--	--	-0.723	--	-5.05	13.59	12.81
B	--	--	1128	--	4317	3568	4711
Value	326.4	77.0	2.9×10 ⁻⁵	6.4	9.4	4.1×10 ²	1.0×10 ⁻³

^a Mackay et al. 1992

^b Paasivirta et al. 1999

^c Harner and Bidleman 1996

* Properties of the sub-cooled liquid.

The model was used to assess the sensitivity of MUM to changes in the parameters shown in Table 5.5. These parameters were chosen for their relevance to urban areas as well as for their spatial and/or temporal variability. For consistency, with the exception of the litterfall removal, and impervious surface coverage, all parameters were scaled up by a factor of two. Presently, litterfall removal is assumed to be a permanent loss mechanism for chemicals in the urban system. In one case, then, litterfall was assumed to not be removed.

Table 5.5 Parameters included in MUM sensitivity analysis.

<i>Property</i>	<i>Change</i>
Film thickness	× 2
Impervious surface area coverage	49 to 75%
Leaf Area Index	× 2
Wax erosion coefficient	× 2
Litterfall removal	No removal
Atmospheric mixing height	× 2
Rain Rate	× 2
Aerosol (TSP) concentration	× 2
Wind speed	× 2
K _{ow}	× 2
K _{oa}	× 2
Vapour Pressure	× 2
Reaction rates in all media	× 2

A doubling of the impervious surface coverage from 49 to 98% would not be realistic within our urban framework as insufficient soil area exists with which to make the switch. Therefore, an increase from 49 to 75% aerial coverage was assumed in one case. Sensitivity was assessed by varying one variable at a time and noting the percentage deviation from the base case of an emission of 1 mol/h to air for the summer scenario.

5.2.3 Results and Discussion: Sensitivity Analysis

The results of our sensitivity analysis reveal a delineation between the two types of parameters examined, with the “environmental” changes having a generally more significant impact on the output than the changes in the properties and behavior of the chemicals themselves. Figures 5.1 and 5.2 show the results of our analysis illustrated by the relative changes from baseline media concentrations for changes in environmental and physical/chemical parameters respectively (our results indicate that the model is relatively insensitive to changes in reaction half-life variations in water, soil, and sediment and therefore, these changes are not shown in figure 5.2).

Chemical transformation rates in various environmental media can vary by many orders of magnitude for a given species depending of the prevailing conditions in those media. Estimated concentration changed by less than 2% in response to doubling of reaction rates in air, vegetation, and film. A similar lack of sensitivity to these properties was reported by Diamond et al. (1996) for their models of aquatic fate. While the amount of net chemical lost in vegetation and the organic film nearly doubles upon doubling the transformation rates, these reactions account for less than 0.1% of the total net environmental loss.

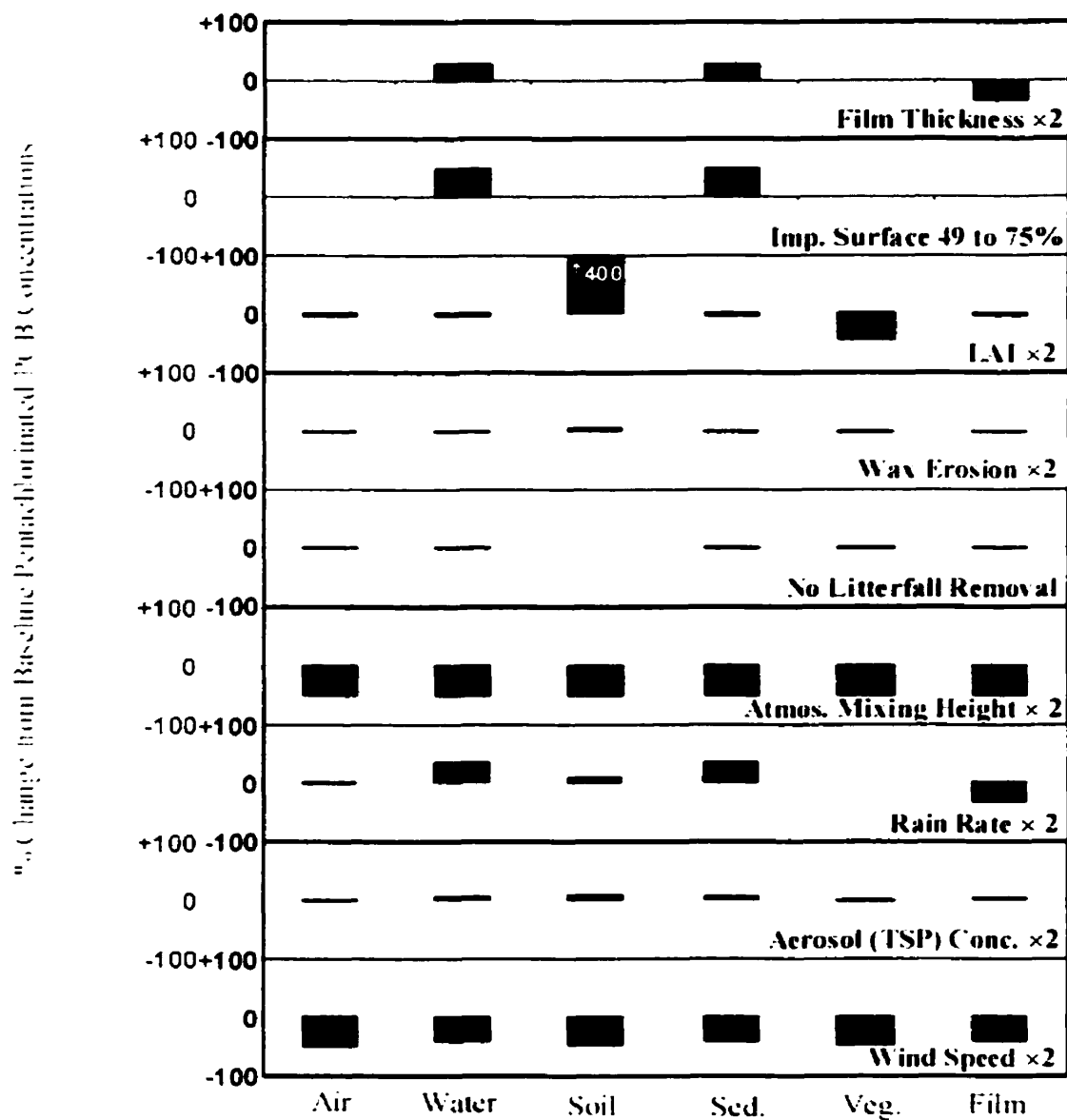


Figure 5.1 Relative change from baseline concentrations in response to changing individual environmental model parameters as indicated.

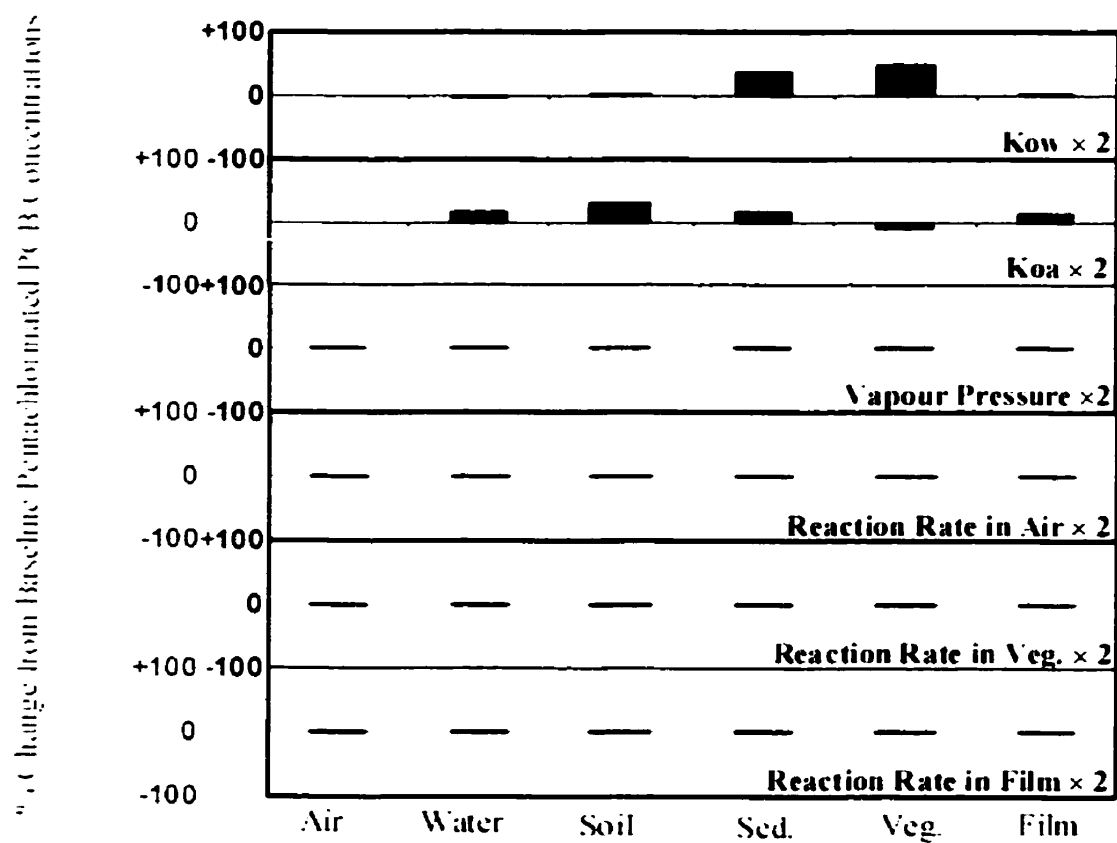


Figure 5.2 Relative change from baseline concentrations in response to changing individual physical/chemical model parameters as indicated.

Doubling the value of K_{OW} increases concentrations in sediment and vegetation by 74 and 95% respectively as chemicals experience increased condensation from the aqueous phase into the organic phases in contact with these media. The concentration in soil increased by 7% due to its smaller aqueous component (30% vs. 80% for sediments and vegetation). On account of this partitioning, the PCB concentration in water decreased by 3%.

Doubling the value of K_{OA} results in increased partitioning from the air to the film. Thus, the concentration in film increased by 31%, and concentrations in surface waters and sediment increased by 32% due to increased chemical washoff from film. Concentration in the soil increased by 65% due to enhanced transfer of chemical from air to vegetation to soil. The total mass of chemical in the system increased by 19 and 58% for the changes in K_{OW} and K_{OA} , respectively, as the increases in hydrophobicity caused chemical to increasingly partition into, and become more tightly bound to, terrestrial media. In reality, the values of K_{OW} and K_{OA} can vary substantially even between congeners of the same homologue group. For example, Harner and Bidleman (1996) found a factor of 50 separating the largest and smallest measured K_{OA} values for 5 different tetrachlorinated PCB congeners, and a factor of 70 separating the largest and smallest values for 6 different pentachlorinated PCB congeners.

Diamond et al. (subm) have found that film thicknesses can range from approximately 25 to 250 nm. Doubling the film thickness translates into a 29% increase in the mass of PCB accumulated by the film and a subsequent 27% increase in both surface water and sediment concentrations and chemical masses. The concentration in the film, however, drops by 35%

on account of dilution, and the pentachlorinated PCB concentration in the atmosphere drops by almost 5% as more chemical is retained by the film.

In order to assess the importance of the film's ubiquity we increased its surface area, on an aerial basis, from 49 to 75%, thereby reducing the aerial surface area of soil and vegetation from 36 to 10%. In reality, the percentage of impervious surface can vary from 5% for low density suburbs to 98% for high density downtown areas (Boyd et al. 1993). The change resulted in a 50% increase in both chemical concentrations and accumulated masses in both surface waters and sediment as a result of the increased contribution from the film washoff mechanism. With the increase in impervious surface coverage and a decrease in the soil and vegetation coverage came a decrease in the amount of chemical immobilized by the soil. As discussed by Simonich & Hites (1995) and McLachlan & Horstmann (1998), forested areas decrease the atmospheric half-lives of a variety of environmental contaminants through transport to soils via interception from the forest canopy. In our analysis, this trend is illustrated by the 71% decrease in the chemical mass in both the vegetation and soil compartments.

Values for the leaf area index are well known and can vary from about 1 to 6 depending on the maturity of the canopy and the variety of vegetation being considered (Müller and Pröhl 1993). By doubling the leaf area index we observed a 15% increase in the mass of pentachlorinated PCB in vegetation, and a four-fold increase in the mass and concentration in the soil; this is evidence of the relative inefficiency with which chemicals are immobilized in urban areas with sparse canopies. Due to the increase in the relative efficiency of the air-

vegetation-soil transport in contrast to the air-film-water transport, concentrations in air, surface waters, sediment, and film decreased by 4% and masses decreased by 4, 18, 18, and 20% respectively. These results indicate the importance of the leaf area index in reducing chemical mobility and suggests the impact of vegetation in urban areas.

Wax erosion, a processes whereby a portion of the leaf surface itself is physically removed, is caused by wind and wind-borne particulate abrasion and/or the rubbing motions of leaves against each other (Van Gardigen et al. 1991, Rogge et al. 1993, Horstmann et al. 1997). Whereas this processes is believed to dislodge contaminant enriched, crystalline-like leaf surface waxes and transport them to soils, the magnitude of this processes is difficult to ascertain (Horstmann and McLachlan, 1996). Our results show that by doubling the rate at which this process occurs increases the pentachlorinated PCB concentration and mass accumulated in soil by only 6%. In the model, wax erosion accounts for about 8% of the total deposition flux to the soil for pentachlorinated homologues. While Horstmann and McLachlan (1996) suggest that this transport mechanism may account for a substantial portion of non-litterfall deposition to forest floors in hot, dry conditions (78-95%), they point out than during periods of precipitation the contribution will be small.

The impact of litterfall removal from urban areas was also considered. Litterfall describes the process by which dead or decaying leaf matter falls from trees to the ground below. In urban centres litterfall is typically collected and disposed of outside the city boundary making it a permanent removal process for chemicals in the system. As Figure 5.1 shows, including litterfall has little effect on chemical concentrations. While researchers have shown litterfall

to be a significant mechanism of contaminant transport to soils in forested areas (8-22%) (Horstmann and McLachlan 1996, Brorström-Lundén and Löfgren 1998), our results indicate that litterfall contributes less than 1% of the total PCB flux to the soil. In contrast, canopy drip, the wet removal of particulates from vegetation due to the impact of rainfall, is responsible for about 90% of the total PCB transport from urban vegetation to soil. In MUM, the steady-state formulation and hence, constant precipitation, favours the *wet* removal of chemicals from vegetation as opposed to litterfall and wax erosion which make larger contributions under dry conditions.

Next, atmospheric parameters were varied. The atmosphere is believed to be the primary source of SOC to the terrestrial media (MacDonald and Metcalfe 1991, Halsall et al. 1997, Cousins and Jones 1998, Lee et al. 1999) and is important to characterize well. Our first variation was a doubling of the atmospheric mixing height. Whereas the mixing height was considered to have a constant value of 1 km, in reality, it is subject to significant seasonal, diurnal, and meteorological variability and can range from about 200 to 2000m (Holton 1992, Hartmann 1994, Stull 1995). In MUM the volume of the air compartment is more than 10,000 times greater than the volume of the 5 remaining compartments combined. Not surprisingly then, increasing the mixing height by 100% decreases chemical concentrations and amounts in all media by 50% with the exception of air. Similarly, halving the mixing height would essentially double chemical concentrations in all media. This is consistent with reports that under certain meteorological conditions, a lowering of the mixing height can cause large concentrations of ozone to be trapped close to the Earth's surface, resulting in ground-level ozone pollution episodes (Chung 1977, Heidorn and Yap 1986).

The rain rate is highly spatially and temporally variable and is important due to its influence on wet deposition and washoff mechanisms. Doubling the rain rate markedly changes PCB concentrations and masses in almost all media. Due to an increase in the magnitude of the chemical washoff from the film, pentachlorinated PCB concentrations and masses in water and sediment increased by 34%. The concentration and mass of PCB in the film decreases by 33% due to a increase in removal, and the concentration of chemical in the soil increases by 10% owing to more wet removal and subsequent transport from vegetation.

Total suspended particulate (TSP) or atmospheric aerosol concentration controls the partitioning of hydrophobic SOC_s to the particulate phase in air and influences processes such as atmospheric deposition and transfer to terrestrial media, as well as the amount of chemical available for transformation via photolysis and reaction with OH radicals (Kaupp and McLachlan 1999). Increasing the TSP concentration from $50\mu\text{g}/\text{m}^3$ to $100\mu\text{g}/\text{m}^3$ increases partitioning to these particles, and consequently, to terrestrial media. A two-fold increase in the TSP concentration results in 6 and 10% increases in chemical concentrations in the sediment and soil respectively, and the concentration and mass of pentachlorinated PCB in the film increased by 4%. Urban TSP levels, however, can be as high as $160\mu\text{g}/\text{m}^3$ (Harner and Bidleman 1998a) and therefore, the consequences of increases in particulate concentrations can be more dramatic.

Finally, wind speed is perhaps one of the most highly variable environmental parameters and one which has the potential to markedly effect regional SOC fate and transport. Since urban

areas can act as point sources for pollutant transport to surrounding areas (Simcik et al. 1997, Cole et al. 1999), the speed with which urban air masses are transported will effect the extent to which this contamination occurs. Doubling the wind speed causes 41 to 49% decreases in chemical concentrations and masses in all media as 46% more chemical is advected from the system.

5.2.4 Summary: Sensitivity Analysis

Chemical transformation rates and have minimal impact on the model output, however, changes in chemical hydrophobicity and the properties of the media can appreciably alter the fate of SOC_s. The model is most sensitive to changes in the parameterization of the media which facilitate chemical transport from air to the organic film and vegetation. Thus, sensitivity is, in part, an artifact of the scenario used to illustrate model sensitivity, namely the emission of chemical to air. Model sensitivity is also a function of the chemical considered, which in this case, has intermediate volatility and hydrophobicity among SOC_s, but is highly persistent.

The properties of urban vegetation and the impervious surface coverage are also important and can vary temporally and spatially. Therefore, careful attention must be paid to the parameterization of these media which is possible using remote sensing methods (Burchfield 1999).

5.2.5 Model Application: Uncertainty Analysis

In addition to conducting a sensitivity analysis in which selected model parameters were varied by a factor of two, an uncertainty analysis was carried out in which natural variations in some of these parameters were examined. As mentioned above, many of the parameters that markedly impact SOC dynamics, vary substantially both temporally and spatially. Therefore, it is helpful to bound the impact of the uncertainty associated with these parameters. For the purposes of this uncertainty analysis we used the same model parameterization given in Table 5.3. In addition, five of the most influential model parameters, as determined by our sensitivity analysis, were examined: the atmospheric mixing height, leaf area index, film thickness, rain rate, and wind speed.

The atmospheric mixing height is subject to geographic, seasonal and diurnal variability and usually ranges from 200 to 2000m depending on the prevailing meteorological conditions (Stull 1995). The leaf area index directly influences the efficiency with which chemicals are removed from the atmosphere and subsequently transported to soils where their mobility is greatly hindered (McLachlan and Horstmann 1998). The value of the leaf area index can vary from about 1 to 6 depending on the maturity of the canopy and the variety of vegetation being considered (Müller and Pröhl 1993).

A change in the thickness of the organic film was also shown to markedly impact contaminant loadings to air, surface waters and sediments via washoff (Figure 5.1). These mechanisms are especially important in urban areas due to the ubiquity of the impervious surfaces on which these films are found. Diamond et al. (subm) have found that these films

can range in thickness from approximately 25 to 250 nm depending on the age of the surface and the atmospheric burden of SOC_s, which contributes to the formation of the film.

The rain rate and wind speed parameters are important in terms their direct impact on the rate at which chemical transport from the atmosphere to the Earth's surface occurs. The rain rate effects the rate at which all "wet" transport mechanisms occur and thus, changes in this parameter will certainly influence SOC dynamics. In order to bound the uncertainty associated with this parameter we have selected as our lower and upper limits, average annual rate rates for Kelowna, British Colombia and St. John's, Newfoundland respectively (Environment Canada 1996). Wind speed can also impact both local and regional chemical dynamics. I have used a Weibull distribution of wind speed probability (Stull 1995), to set lower and upper limits of wind speed.

The model parameters considered in this uncertainty analysis along with their lower and upper limits are shown in Table 5.6

Table 5.6 Upper and lower limits to the natural variability associated with selected model parameters.

Parameter	Lower Limit	Upper Limit	Reference
Mixing Height	200 m	2000 m	Stull 1995
Leaf Area Index	1	6	Müller and Pröhl 1993
Film Thickness	25 nm	250 nm	Diamond et al. (subm.)
Rain Rate	4.2×10^{-5} m/h	1.7×10^{-4} m/h	Environment Canada 1996
Wind Speed	2 km/h	40 km/h	Stull 1995

The model was subsequently used to asses the five scenarios listed in Table 5.7 which makes use of various permutations of the limits listed above. As before the model was run for

illustrative purposes for the pentachlorinated homologue group whose physical/chemical properties are given in Table 5.4. A emission of 1 mol/h into air was used.

Table 5.7 Summary of the parameters used for MUM uncertainty analysis scenarios. *L* indicates that the lower limit was used for that parameter and *U* indicates that the upper limit was used.

Scenario	Mix. Height	LAI	Film Thick.	Rain Rate	Wind Speed
1	L	U	L	U	U
2	U	L	U	L	L
3	U	L	L	L	U
4	L	U	L	U	L
5	L	U	U	U	U

5.2.6 Results and Discussion: Uncertainty Analysis

Multimedia PCB concentrations are given for each scenario (Table 5.8). Changes from baseline concentrations are illustrated in Figure 5.3.

Table 5.8 Multimedia PCB concentrations for each uncertainty scenario (assuming emissions of 1 mol/h into air).

Scenario	Air (ng/m ³)	Water (ng/L)	Soil (ng/g)	Sed. (ng/g)	Veg. (ng/g)	Film (g/m ³)
Base	46	123	500	1400	210	13
1	62	135	17000	1600	130	30
2	167	253	630	2900	810	23
3	10	7	40	81	53	6
4	357	515	35000	5900	260	110
5	61	357	17000	4100	130	9

Scenario 1 represents urban conditions consistent with a coastal locale with little industrial activity and a great deal precipitation, and hence, lush foliage. Low air pollution is indicated by the lower film thickness. The low mixing height implies that airborne contaminants are trapped closer to the Earth's surface. The large leaf area index facilitates the efficient transport these SOC's from the air to the dense vegetative canopy and subsequently, to the soil. The high wind speed decreases the chemical's atmospheric residence time by 78%,

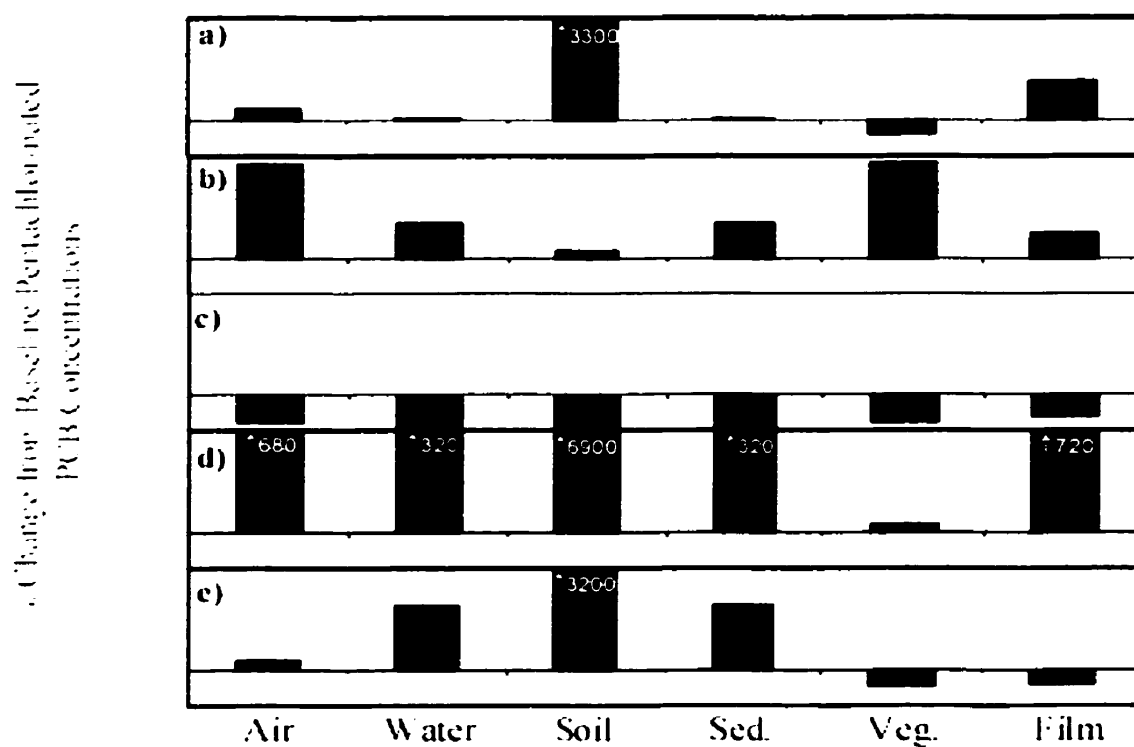


Figure 5.3 Relative change from baseline pentachlorinated PCB concentrations for each uncertainty analysis scenario. Figures a) through e) represent scenarios one through five respectively. A emission of 1 mg/L into air is assumed in each case.

thereby increasing chemical loss due to advection and thus, slightly offsetting the magnitude of this transport. The end result is a 33-fold increase in pentachlorinated PCB concentration in soil. The high rain rate in contrast to the lower film thickness results in little change in loadings to surface waters and sediments due to washoff. The concentration of chemical in the film increases by 120% due to accumulation.

Scenario 2 represents an arid yet more industrial urban location as evident by the low rain rate and leaf area index, and the greater film thickness. Higher air pressures prevail in this scenario, and hence, the greater mixing height. In contrast to the previous scenario, the high mixing height combined with the low wind speed, rain rate, and leaf area index, increases the atmospheric concentration and residence time of pentachlorinated PCB by 276 and 630% respectively. This increased atmospheric chemical burden combined with the decrease in chemical washoff leads to the accumulation of chemical in film and vegetation as evident by the 75 and 280% increases in chemical concentrations in these media respectively (the highest vegetation concentration amongst the 5 scenarios). Despite the low rain rate, chemical concentrations in surface waters and sediment increase by 160% due to the increase in film thickness and periodic washoff. While the changes in the overall multimedia concentrations are marked, these fluctuations are the least dramatic of the 5 scenarios considered.

Scenario 3 is similar to scenario 2 except the urban environment is characterized as having less air pollution and stronger winds (urban/desert type conditions). The large mixing height combined with the high wind speed decreases the atmospheric residence time by 53%,

resulting in chemical loss due to advection. Furthermore, the low leaf area index, film thickness, and rain rate minimize the transport of the remaining chemical from the atmospheric to terrestrial media. Concentrations in all media are therefore, at a minimum for the 5 scenarios considered, decreasing 58 to 94% from their base levels.

In scenario 4 we consider urban conditions similar to those in scenario 1, but with below average wind speeds. In contrast to the first scenario where only a 36% increase in baseline atmospheric pentachlorinated PCB concentration was observed, the lower wind speeds in this scenario result in an almost 8-fold increase in atmospheric PCB levels. This phenomenon dramatically increases the amount of chemical available to the system and increases chemical concentrations in all other media (this scenario represents the maximum concentration of PCBs for all media with the exception of vegetation). The high leaf area index and rain rate result in soil concentrations being 70 times greater than those in the baseline scenario. Despite the high rain rate, the thinner film is able to accumulate twice as much chemical by mass, due to the increased atmospheric burden, with chemical concentrations in the film being over 8 times greater than baseline levels. On account of film washoff, chemical burdens to surface waters and sediment were also 320% as great as in the baseline scenario.

Scenario 5 is also similar to scenario 1, however, a greater amount of air pollution is assumed as indicated by the larger film thickness. Changes from baseline contaminant dynamics are therefore, similar to those observed in the first scenario with the exception of the film, surface waters, and sediment. Chemical burdens to the film are three times as great as in scenario 1 and 61% greater than baseline levels. The increase in the film thickness results in

a 36% decrease in chemical concentration in this compartment due to dilution. The high rain rate combined with the thicker film results in 190% increases in both surface water and sediment PCB concentrations.

With the exception of vegetation, scenarios 3 and 4 elicit the most dramatic changes in environmental SOC dynamics. In scenario 3 the large amount of chemical lost due to advection from the atmosphere combined with the relative inefficiency with which contaminants were transferred to terrestrial media resulted in a 92% decrease in the overall mass of chemical in the system. In scenario 4 we observe the opposite effect: the low boundary layer and wind speed trap airborne PCB close to the Earth's surface where they are efficiently captured by both the vegetation and the film and subsequently transferred to soil and surface waters, respectively. The enhanced rain rate further enhances the rate at which this transport occurs.

5.2.7 Summary: Uncertainty Analysis

The results of this uncertainty analysis confirm the importance of the factors which effect the partitioning of SOC's between the atmosphere and terrestrial media to overall contaminant dynamics in urban areas. PCB levels throughout this uncertainty analysis were shown to fluctuate dramatically with the prevailing environmental conditions. While these results are acceptable for assessing the uncertainty inherent to our deterministic model, they underscore the importance of the accuracy with which these key parameters should be determined for use in decision making or regulatory applications.

In reality, the environment's response to fluctuations in these key parameters would perhaps not be as rapid or dramatic as those suggested by our steady-state or "snap-shot" approach. Nevertheless, the model does give us an indication of the type of trends we might expect to see, consistent with the changes in the environmental framework. The lack of temporal resolution suggests that an unsteady-state formulation might further help in quantifying the environmental response time to fluctuations in these parameters.

5.3 SEASONAL VARIATIONS

Many researchers have measured seasonal as well as diurnal variations of environmental SOC concentrations (e.g.- Hornbuckle and Eisenreich 1996, Wallace and Hites 1996, Lee et al. 1998), and others have sought to parameterize these variations through the application of various mathematical models (Kömp and McLachlan 1997, Wania et al. 1998a). Since the atmosphere is believed to be the primary source of SOC to the terrestrial media (section 5.2.3), variations in a variety of meteorological factors such as precipitation, humidity, as well as wind speed and direction have all been examined in an attempt to explain observed seasonal trends (Lee et al. 1999, Currado and Harrad 2000). While the degree to which specific groups of SOC's respond to meteorological changes varies spatially and with the properties of the contaminants themselves (Scheringer 1997, Wania et al. 1998a, Lee et al. 2000), all of these elements have the ability to effect contaminant dynamics in urban areas. In this section, the Multimedia Urban Model is used to assess the impact of seasonal variations on contaminant dynamics in an urban setting.

5.3.1 Model Application

In order to simulate winter conditions, media temperatures, the leaf area index (LAI), and wind speed were varied. The presence of snow, which effects chemical movement due to atmospheric scavenging and snowpack dynamics (Hoff et al. 1995, Wania et al. 1998b, Wania et al. 1999), was neglected. Reaction rates were not varied because whereas we assume the rates to decrease the values are poorly known and the analysis conducted in section 5.2.3 showed the model was relatively insensitive to these parameters. We have also chosen not to include any seasonal changes in atmospheric stability as long-term seasonal measurements showed these variations to be minimal (Environment Canada 1998).

Temperatures of the air, soil, vegetation, and the organic film were set to 0°C while the water and sediment temperatures were set to +4°C. The leaf area index for vegetation was decreased from 1.2 to 1.0 to account for the presence of coniferous vegetation and short grasses. Wind speed was increased from 12 to 17 km/h (Environment Canada 1998). The temperature dependent parameters that were considered were chemical vapour pressure, solubility, the octanol-air partition coefficient (K_{OA}), and Henry's law constant (Hinckley et al. 1990, Harner and Bidleman 1996, 1998b, Tesconi and Yalkowsky, 1998, Paasivirta et al. 1999). Other parameters such as the octanol-water partition coefficient (K_{OW}), do not vary as substantially with temperature (Bahadur et al. 1997).

The model was parameterized to simulate conditions in the lower Don River watershed in downtown Toronto, Ontario, Canada. The model was run for illustrative purposes for 5 PCB homologue groups (3-Cl to 7-Cl) that range in physical-chemical properties and for which

temperature dependent physical/chemical data are available. As before, we have assumed an emission rate of 1 mol/h into air. Selected physical-chemical properties were taken as averages for the homologue group itself and not one particular congener. Coefficients used in the temperature dependent calculations (for the log-linear relationships of the type $\text{Log}[\text{property}] = A - B/T$) are shown in Table 5.9. All other properties are the same as those listed in Table 4.4.

Table 5.9 Temperature dependent physical/chemical property equation coefficients for the tri- to heptachlorinated PCB homologues.

#Cl / Property	Sol (mol/m ³) ^{a*}	Log[K _{OA}] ^b	H (Pa/m ³ Pa) ^a	V.P. (Pa) ^{a*}	
3	A	0.232	-4.77	11.97	12.2
	B	976	3792	3100	4075
4	A	-0.518	-4.01	13.00	12.5
	B	1104	3813	3283	4386
5	A	-0.723	-5.05	13.59	12.8
	B	1128	4317	3568	4711
6	A	-1.12	-4.88	14.10	12.9
	B	1113	4498	3757	4800
7	A	-1.68	-4.70	14.71	13.03
	B	1132	4535	3910	5042

^a Paasivirta et al. 1999

^b Harner and Bidleman 1996

* Properties of the sub-cooled liquid.

5.3.2 Results and Discussion

Figures 5.4 and 5.5 summarize the impacts of seasonal changes on the dynamics of pentachlorinated PCB in urban areas. Chemical transfer rates reflect the changes in multimedia partitioning between the atmosphere and terrestrial media.

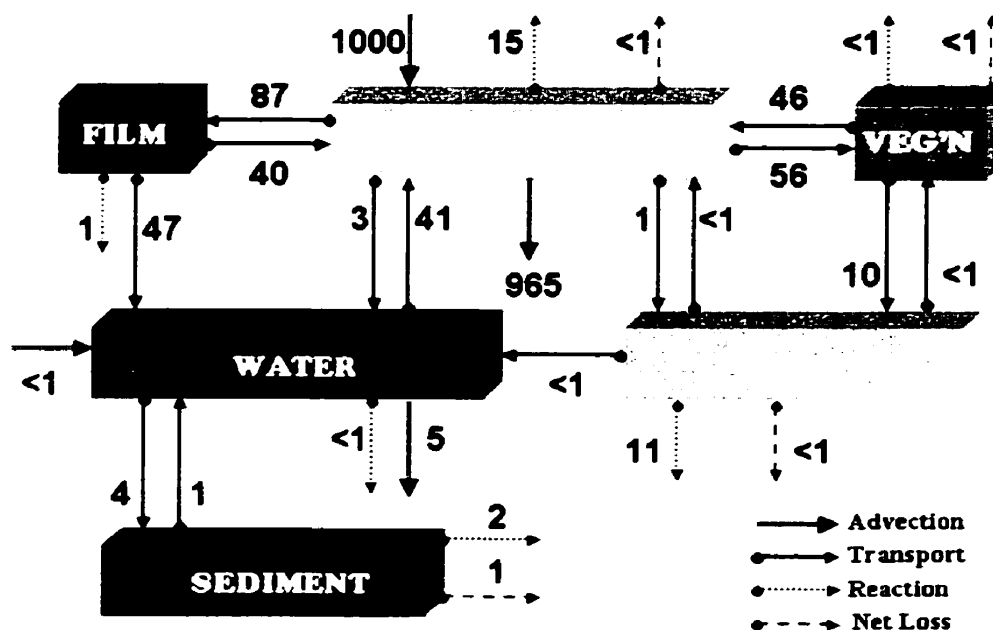


Figure 5.4 Estimated rates of chemical movement and transformation for pentachlorinated PCB under summer conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

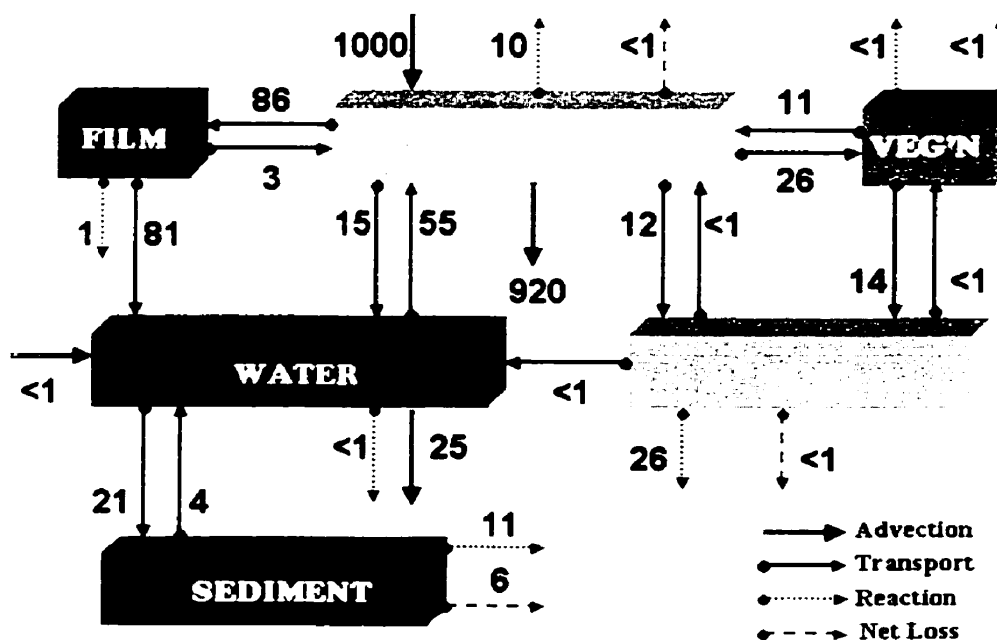


Figure 5.5 Estimated rates of chemical movement and transformation for pentachlorinated PCB under winter conditions. Emission of 1 mol/h into air is assumed. Numbers shown are transport rates in mmol/h.

5.3.2.1 Multimedia Partitioning

The temperature dependent gas-phase partitioning of SOC's between the atmosphere and terrestrial media is critical in altering chemical distribution and dynamics between the seasons (Kaupp et al. 1996, Wallace and Hites 1996, Hillery et al. 1997, Simcik et al. 1999). One of the most important factors determining the rate at which a given SOC can undergo such partitioning is the chemical's particle-bound fraction. Kaupp and McLachlan (1999) point out the decisive influence of this partitioning mechanism on the environmental fate of SOC's as it determines both the manner and speed of atmospheric deposition as well as the availability of the compounds for degradative processes. The seasonal change in the particle-bound fraction of the PCB homologues, then, indicates how these chemicals partition throughout the terrestrial media.

Particle-bound fractions (ϕ) for both winter and summer scenarios (Table 5.10) were calculated using the relationship from Harner and Bidleman (1998a),

$$\phi = K_p(TSP) / [1 + K_p(TSP)] \quad (5.1)$$

where K_p ($\text{m}^3 \cdot \mu\text{g}^{-1}$) is the particle/gas partition coefficient and TSP is the total suspended particle concentration ($\mu\text{g} \cdot \text{m}^{-3}$).

Table 5.10 Particle-bound fractions for PCB homologue groups under summer and winter conditions.

PCB	% Particulate	
	Summer (25°C)	Winter (0°C)
3-Cl	0.1	1.6
4-Cl	0.7	10.0
5-Cl	3.3	41.6
6-Cl	16.8	82.9
7-Cl	28.9	90.9

K_P is then correlated with K_{OA} using the empirical relationship,

$$\log K_P = \log K_{OA} + \log f_{om} - 11.91 \quad (5.2)$$

where f_{om} is the organic matter fraction (Harner and Bidleman 1998a). The octanol-air partition coefficient (K_{OA}), which has been used to describe particle/gas partitioning of atmospheric borne SOC's (Finizio et al. 1997, Harner and Bidleman 1998a), has been shown to increase linearly with reciprocal temperature, illustrating enhanced partitioning to lipid phases as temperatures decrease (Harner and Mackay 1995, Harner and Bidleman 1996). Hence, a decrease in temperature increases K_{OA} , K_P , ϕ , and the particle-bound fraction partitioning to lipid phases. This phenomenon is clearly demonstrated by the seasonal PCB concentrations (Table 5.11) and the relative change between the two scenarios (Figure 5.6).

Table 5.11 PCB concentrations for summer and winter conditions (assuming equal of 1 mol/h into air).

#Cl	Air (ng/m ³)		Water (ng/L)		Soil (ng/g)		Sed. (ng/g)		Veg. (ng/g)		Film (ng/m ²)	
	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.
3	36	26	11	111	20	66	39	406	35	114	95	541
4	41	29	30	178	104	338	203	1211	36	114	445	1455
5	46	31	123	604	501	1258	1416	6956	212	407	1338	2466
6	49	32	204	601	1752	2091	7909	23330	381	280	2661	3447
7	53	35	277	727	2498	2389	10740	28220	264	174	3461	3926

The extent to which PCB partition into lipid phases increases with the colder temperatures, and the relative magnitude of these changes, decreases with increasing hydrophobicity. For this reason the overall residence times and burdens are four times as great under the winter scenario for the tri- and tetrachlorinated homologues, three times as great for the pentachlorinated homologues, and one and a half times as great for the hexa- and heptachlorinated homologues (Table 5.12).

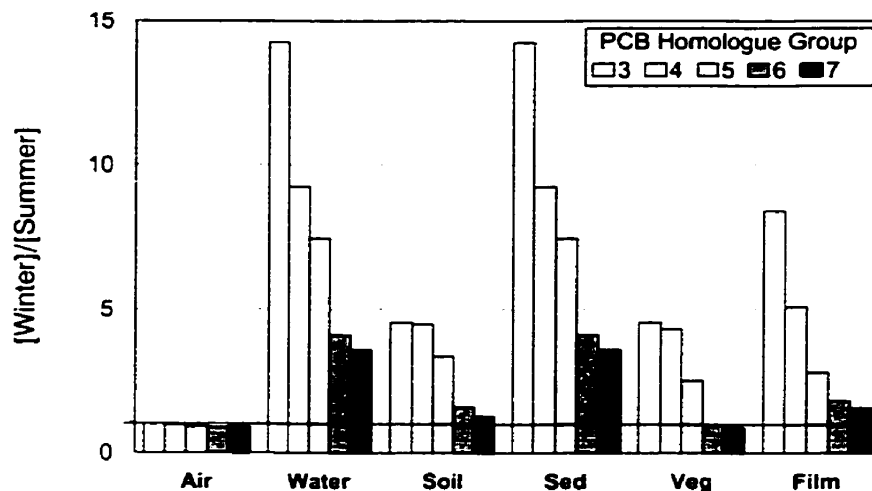


Figure 5.6 Ratio of winter to summer concentrations of tri- to heptachlorinated PCB homologues.

Table 5.12 Mass of PCB in each medium for summer and winter conditions (assuming equal emissions of 1 mol/h into air).

#Cl	Air (kg)		Water ($\times 10^{-3}$ kg)		Soil (kg)		Sed. (kg)		Veg. ($\times 10^{-3}$ kg)		Film ($\times 10^{-3}$ kg)	
	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.
3	1.7	1.2	29	294	11	37	2	17	2	6	4	25
4	2.0	1.4	79	473	58	188	9	51	2	6	20	67
5	2.2	1.4	327	1606	278	699	59	292	14	23	61	113
6	2.3	1.5	542	1600	974	1162	332	980	26	16	122	158
7	2.5	1.7	736	1935	1388	1328	451	1185	18	10	159	180

In contrast to the “condensed” media, however, the change in atmospheric PCB concentrations becomes slightly more pronounced with *increasing* hydrophobicity. This is primarily due to the larger decrease in advective losses for the heavier homologues with colder temperatures (Mackay and Wania 1995). Results show that the summer gas-phase concentrations of tri- and tetrachlorinated homologues are 31 and 37% greater than in winter respectively, but concentrations of the penta-, hexa-, and heptachlorinated homologues are 2, 7, and 12 times greater respectively. These results are consistent with the observations of Halsall et al. (1995) who noted greater summer to winter atmospheric PCB concentration ratios of five for higher chlorinated congeners compared to two for lower chlorinated

congeners in Manchester, England. They cautioned, however, that the ratios can vary markedly with the seasonal temperature variations in different geographic locations.

5.3.2.2 Organic Film and Surface Waters

As previously discussed, most SOC_s in the organic film undergo one of two fates: volatilization to the atmosphere or washoff to surface waters (both of these processes are faster than reaction losses). Results indicate that the winter to summer ratios of the total mass and concentrations of PCBs in waters and sediment are 10 for the trichlorinated homologues, six and five for the tetra- and pentachlorinated homologues respectively, and three for both the hexa- and heptachlorinated homologues. This relative seasonal decrease in PCB mass in water and sediment with increasing chlorination can be explained by examining the fluxes from the air to the film and from the film to surface waters (Table 5.13), and thus, the relative air to water transfer efficiency for each homologue group (Figure 5.7).

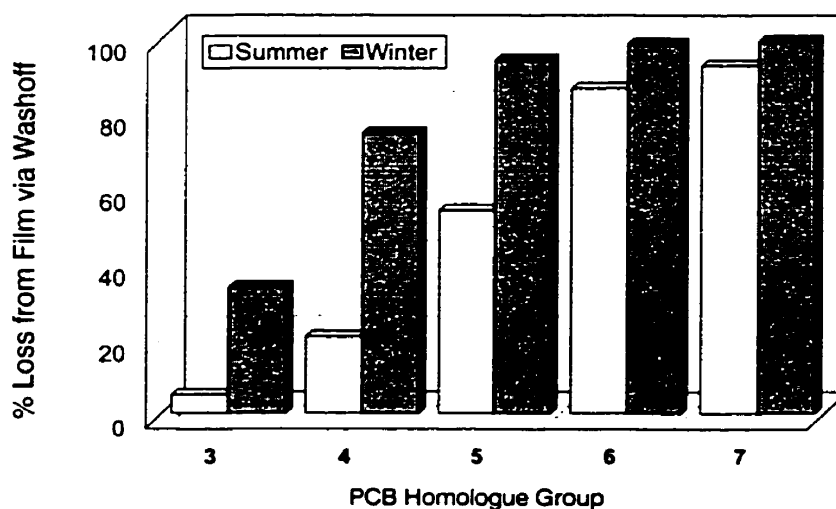


Figure 5.7 Percent of chemical undergoing film washoff expressed in terms of total chemical flux from the atmosphere to the film.

Table 5.13 PCB fluxes (mmol/h) from the air to film and from film to surface waters for summer and winter conditions (emission of 1 mol/h into air is assumed).

# Cl Flux (mmol/h)	Summer		Winter	
	Air to Film	Film to Water	Air to Film	Film to Water
3	84	4	72	24
4	85	17	77	57
5	87	47	92	86
6	98	84	111	109
7	108	100	115	114

Percentage loss through washoff increases during winter when a larger percentage of SOCs is contained in the film. The relative magnitude of the seasonal changes in washoff percentage decreases with increasing chlorination, similarly to temperature and K_{OA} dependent changes in the particle-bound fraction of the SOCs (Table 5.10). Trends in surface water and sediment PCB concentrations (Figure 5.6) also follow the same seasonal pattern as the changes in particle-bound fraction.

5.3.2.3 Vegetation and Soil

Chemical transfer from air to vegetation to soil is important for reducing the mobility of SOCs. In the summer scenario, the film transfers three to five times more tri-, tetra-, and pentachlorinated homologues, and 58 and 31% more hexa- and heptachlorinated homologues to surface waters, respectively, than vegetation transfers to soil (Table 5.14 and Figure 5.8).

Table 5.14 PCB fluxes (mmol/h) from the air to vegetation and from vegetation to soil for summer and winter conditions (emission of 1 mol/h into air is assumed).

# Cl Flux (mmol/h)	Summer		Winter	
	Air to Veg	Veg to Soil	Air to Veg	Veg to Soil
3	57	1	39	1
4	57	2	37	5
5	56	10	29	15
6	51	28	20	18
7	47	33	19	17

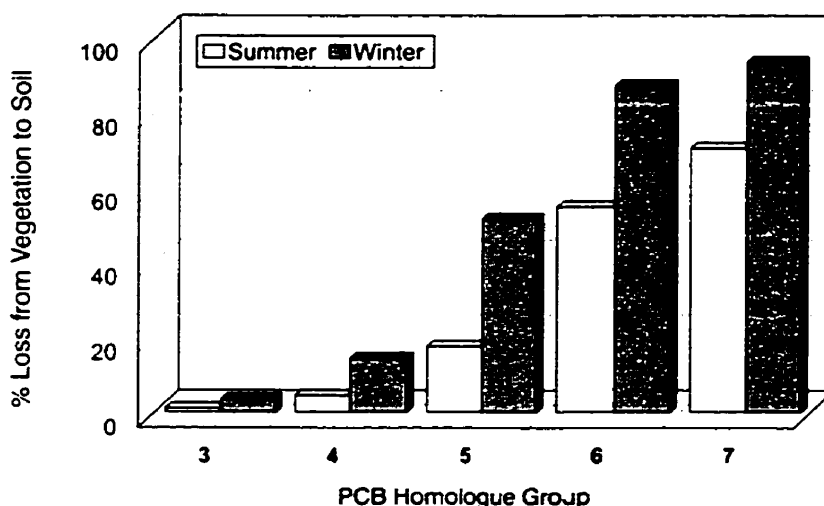


Figure 5.8 Percentage of chemical undergoing transfer to soil expressed in terms of total chemical flux from the atmosphere to vegetation.

The mechanism of the partitioning and accumulation of atmospheric SOC_s in cuticular plant waxes is similar to that which occurs in the organic film (Law and Diamond, 1998). The film, however, has a surface area to volume ratio almost 3000 times greater than that of the vegetation, and hence, is unable to “trap” as much gas-phase chemical as vegetation. Thus, vegetation promotes chemical mobility to a lesser extent than film. While the film provides a greater area for particle deposition, persistence in vegetation is, on average, 3 times greater than in the film for both scenarios for the five homologues. Nevertheless, under both sets of conditions air-vegetation-soil transport remains an important mechanism with respect to reducing SOC mobility in a multimedia system.

5.3.2.4 Chemical Mobility

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, Crunkilton and DeVita 1997, Ashley and Baker 1999). This has led to the recognition

that advective losses from the atmosphere cause urban areas act as point sources for the medium and long-range transport of SOC's (Simcik et al. 1997, Cole et al. 1999). Decreasing temperatures reduced advective losses by 1, 2, and 8% for the tri-, tetra-, and pentachlorinated homologues from the air compartment, respectively, and 11% for the hexa- and heptachlorinated homologues. As temperatures decrease hydrophobic contaminants become more tightly bound to terrestrial media. This pattern is confirmed by comparing the total mass in all compartments in the summer and winter scenarios as show in Figure 5.9.

Results show that the mass of tri-, tetra-, and pentachlorinated homologues is three to four times greater in winter than summer, and only 37 to 64% greater for the hexa- and heptachlorinated homologues. The trend of greatest difference in chemical mass for the lighter homologues is similar to differences seen for chemical dynamics.

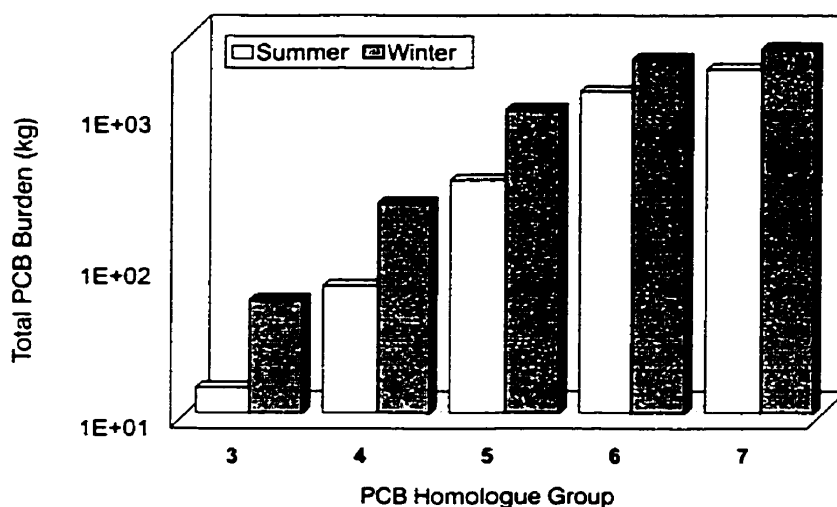


Figure 5.9 Total mass of PCB homologues in all model compartments for summer and winter conditions. Chemical masses are based on a 1 mol/h emission rate into air.

Persistence, expressed as a media residence time, is calculated as the ratio of the chemical mass to rate of removal in a compartment (Table 5.15).

Table 5.15 Persistence of PCB in each medium for summer and winter conditions (assuming equal emissions of 1 mol/h into air).

#Cl	Air (h)		Water (h)		Soil (y)		Sed. (y)		Veg. (h)		Film (h)	
	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.
3	5.8	4.3	19.5	42.2	7.9	8.6	3.6	3.6	0.2	0.6	0.2	1.3
4	5.9	4.2	14.5	25.8	8.0	8.7	4.3	4.3	0.1	0.6	0.8	3.0
5	5.9	4.1	19.7	46.6	8.8	8.9	4.7	4.7	0.8	2.4	2.2	3.8
6	5.8	4.0	15.6	30.6	8.9	9.0	5.0	5.0	1.4	2.2	3.5	3.9
7	5.7	4.0	15.7	32.2	8.9	9.0	5.0	5.0	0.9	1.3	3.7	4.0

Persistence in soil and sediment is on the order of several years, and increases by only 9% for the tri- and tetrachlorinated homologues, 2% for pentachlorinated homologues, and negligibly for the heavier homologues in the soil compartment. Differences in persistence in the organic film and vegetation between summer and winter are more pronounced on account of the transient nature of contaminants in these media. Under winter conditions persistence in the film is seven, four, and two times longer for the tri-, tetra-, and pentachlorinated PCB homologues, respectively, than in the summer. Hexa- and heptachlorinated homologues experience less of a seasonal change, with film residence times in the winter being 14 and 7% greater than in summer. In vegetation the persistence during winter was four times greater for tri- and tetrachlorinated homologues, three times greater for pentachlorinated homologues, and about 40% greater for hexa- and heptachlorinated homologues, than in summer. Overall residence times increase from summer to winter by four times for the tri- and tetrachlorinated homologues, three times for pentachlorinated homologues, and about one and a half times for the hexa and heptachlorinated homologues.

5.3.4 Summary

Increases in the particle-bound fractions of the SOC's themselves determines much of the multimedia partitioning and concentration changes. Increased partitioning to particle and

condensed phases was most pronounced for the lower chlorinated PCBs. The model results illustrate that lower temperatures decrease atmospheric PCB concentrations and reduce chemical mobility as chemicals condense from air and water to soil and sediment. Overall, chemical mobility decreased and persistence increased in the winter versus summer scenario indicating that, given constant loadings, urban areas will be less of a point source for the medium and long-range transport of SOC with colder temperatures. This result is, of course, the same phenomenon described by Mackay and Wania (1995) to explain the global distribution of SOC.

5.4 CONCLUSIONS

In constructing multimedia models of contaminant fate and transport under a variety of conditions and scenarios, various simplifying assumptions and approximations must be made. While many of these approximations are necessary in order to facilitate the model's parameterization and ease of implementation, considerable uncertainty exists with respect to many parameters. The degree to which these uncertainties effect the model output depends on their overall importance to the mechanisms being modeled. In general, changes to environmental properties were found to have a more significant impact on the results than changes in physical/chemical properties. The model was sensitive to changes in the properties of the vegetation and the organic film as these two media represent the primary conduits by which SOC move from the atmosphere to terrestrial media.

Running the model for summer and winter scenarios indicated lower chemical mobility and higher persistence in winter which is consistent with descriptions and theories of temperature induced chemical condensation. This effect is more pronounced for chemicals with moderate hydrophobicity (e.g.- K_{OA} from 8 to 10) that shift from being almost entirely in the gas phase to particle phase as the temperature decreases from 25 °C to 0 °C.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The goal of this research was to develop a multimedia model to estimate chemical dynamics in an urban area. This thesis describes the Multimedia Urban Model (or MUM), and uses the model to illustrate the effect of urbanization, or specifically, impervious surfaces, on the fate of environmental SOC_s. The model is an improvement over previous representations by explicitly taking into account the organic film on impervious surfaces through the parameterization of an additional environmental compartment. The newly defined process of chemical washoff from the film to surface waters was quantified using empirical data. Vegetation, and related hydrological and chemical transfer processes, has also now been explicitly considered within an multimedia, urban framework. The model is also used to contrast chemical dynamics under urban and forested conditions as well as during summer and winter. The model's sensitivity to parameter uncertainty is also explored. From this research the following conclusions can be drawn and recommendations formulated.

6.1 Conclusions for Results and Processes

1. The organic film increases contaminant mobility through volatilization and washoff of SOC_s to surface waters. Volatilization is the dominant process for chemicals with K_{OA} less than 9, whereas washoff predominates for chemicals with K_{OA} greater than 9. The volatilization of air-borne SOC_s from the film increases atmospheric concentrations, persistence and advective losses. This process accounts for the elevated concentrations of some SOC_s in urban air and is hypothesized to contribute to advective loss via atmospheric transport (i.e.- the urban "plume"). Washoff of film-borne contaminants to surface waters

explains, in part, the observed correlation between watershed impervious coverage and chemical burdens in urban streams.

2. Vegetation transfers chemicals from the atmosphere to the soil where they are relatively immobile. The efficiency with which SOC transfer within the air-vegetation-soil system occurs depends primarily on the canopy's leaf area index.

3. Under forested conditions, in the absence of the film, SOC's are efficiently transferred from the atmospheric to soils where they are immobilized. Thus, air concentrations in forested areas are lower than in urban areas.

4. Under winter conditions the decrease in ambient air temperatures leads to increases in the particle-bound fraction of SOC's, and condensation in terrestrial and aquatic phases. Cold temperatures decrease SOC levels in air and overall contaminant mobility as vegetation and the organic film more efficiently capture atmospheric contaminants and transfer them to soils and sediments, respectively, where are relatively immobile.

5. Model output is most sensitive to variations in environmental characteristics (e.g.- boundary layer thickness, film thickness, leaf area index, etc.) and is less sensitive to changes in certain physical/chemical properties (e.g.- vapour pressure, reaction rates).

6.2 Recommendations for Future Work

This research is a first step towards developing a model to describe contaminant dynamics in urban areas. The model includes the organic film on impervious surfaces, that is just now being characterized and investigated for its implications for chemical movement. As well, the model includes vegetation, for which many process rates are currently being quantified. As such, the model contains many approximations and parameter values based on judgment rather than solid data. Stemming from this research a number of recommendations for future work can be made.

1. A comprehensive set of simultaneous, measurements of multimedia SOC concentrations is necessary for model calibration and validation (as opposed to the fragmented and disjointed measurements currently being used). The quantification of chemical-specific environmental emission rates are necessary for testing model accuracy.
2. Research is required to quantify mechanisms that are poorly understood, such as film washoff and wax erosion. The inclusion of additional transport mechanisms such as hydrologic transfer in sewer systems, ground water transport, and compartments such as biota (perhaps humans) would make for an even more comprehensive treatment of urban areas.
3. Geographic segmentation which makes use of Geographical Information System (GIS) data would further highlight the variability in SOC dynamics based on land use.

4. Relationships for the temperature dependence of physical/chemical properties of various hydrophobic contaminants should be better quantified so as to reduce the error associated with modeling seasonal variability.

5. Organic films on the surfaces of other urban media such as vegetation and surface waters should be considered.

Although a first attempt has been made to assess the efficiency with which the model describes contaminant dynamics in urban areas, the model has not been calibrated or validated. Thus, an important contribution of this research is the identification of areas requiring more research.

APPENDIX

MODEL CODE; Main Subroutine

```

For i = 0 To 7      'Initialize these paramters
  Inflow_conc(i) = 0#
  adv_flow(i) = 0#
  adv_restime(i) = 0#
Next i
For i = 2 To 7
  emission_rate(i) = 0#
Next i

If chkTemp.Value = 1 Then
  Call TD_PhysProp(cboChemical.ListIndex) 'Temperature Dependent Properties
Else
  Call PhysProp(cboChemical.ListIndex)    'Properties at 25°C
End If

adv_flow(0) = (area(0) ^ 0.5) * depth(0) * wind_speed * 1000#
adv_restime(0) = volume(0) / adv_flow(0)
adv_flow(6) = adv_flow(0) * vf_aero 'flow rate of aerosols (m3/h)

adv_flow(1) = water_diss * 3600# 'm^3/h
adv_restime(1) = volume(1) / adv_flow(1)
adv_flow(7) = adv_flow(1) * vf_ss 'susp. solid flow rate (m^3/h)

Inflow_conc(0) = (bulk_conc(0) * 0.000001) / mol_mass 'mol/m^3
Inflow_conc(1) = (bulk_conc(1) * 0.000000001) / mol_mass 'mol/m^3
Inflow_conc(6) = Inflow_conc(0) * vf_aero 'mol/m^3
'Included in air advection statement
Inflow_conc(7) = Inflow_conc(1) * vf_ss 'mol/m^3

tot_emiss = 0#
tot_input = 0#

For i = 0 To 7
  Inflow_rate(i) = adv_flow(i) * Inflow_conc(i) 'm3/h * mol/m3 = mol/h
  input_rate(i) = emission_rate(i) + Inflow_rate(i) 'm3/h * mol/m3 = mol/h
  tot_emiss = tot_emiss + emission_rate(i) 'm3/h * mol/m3 = mol/h
  tot_input = tot_input + input_rate(i) 'm3/h * mol/m3 = mol/h
Next i

'-----CALCULATE PURE Z VALUES-----
'all pure Z-values are in: mol/(Pa.m^3)
p_zvalue(0) = (1#) / (R * temp(0)) 'air
p_zvalue(1) = (1#) / (hlc(1)) 'water
If (T_melt > temp(1)) Then 'use sub-cooled prope. if chem. is solid at Temp[x]
  p_zvalue(1) = (1#) / (sub_hlc(1)) 'water (sub-cooled)
End If
p_zvalue(2) = p_zvalue(1) * dens_soil * koc * organic(2) 'soil
p_zvalue(3) = p_zvalue(1) * dens_sed * koc * organic(3) 'sediment
p_zvalue(4) = p_zvalue(1) * kow * organic(4)
p_zvalue(5) = p_zvalue(1) * kow * organic(5)
p_zvalue(6) = p_zvalue(0) * Kp * 1000000000# * (dens_aero ** 1000)
'Factor of 10^9 to convert from ug to kg
p_zvalue(7) = p_zvalue(1) * dens_susp * koc * organic(7) 'suspended solids

'-----CALCULATE BULK Z VALUES-----
'all bulk Z-values are in: mol/(Pa.m^3)
b_zvalue(0) = p_zvalue(0) + (p_zvalue(6) * vf_aero)
'value for air is "air" + "aerosols".
b_zvalue(1) = p_zvalue(1) + (p_zvalue(7) * vf_ss)
'value for water is "water" + "suspended solids".
b_zvalue(2) = 0.2 * p_zvalue(0) + 0.3 * p_zvalue(1) + 0.5 * p_zvalue(2)
'value for soil is 20% air, 30% water, & 50% solids.
b_zvalue(3) = 0.8 * p_zvalue(1) + 0.2 * p_zvalue(3) 'Mackay 1991 Jrnl.
'value for sediment is 80% water & 20% sediments.

```

```

b_zvalue(4) = (0.18 * p_zvalue(0)) + (0.8 * p_zvalue(1)) + (0.02 * p_zvalue(4))
b_zvalue(5) = (p_zvalue(5) * 0.3) + (p_zvalue(6) * 0.7)
'value for film is "film" + "aerosol" fraction of film

b_zvalue(6) = 0# 'initialize dummy variable
b_zvalue(7) = 0# 'initialize dummy variable

'Define the vegetation interception factors
Veg_If_Wet = 1 * lai * (1 - Exp(-1 * Log(2#) / 3#)) 'Log is like Ln in this language
If (Veg_If_Wet > 1#) Then 'Interception fraction can't be greater than 1
    Veg_If_Wet = 1#
End If
Veg_If_Dry = 1 - Exp(-2.8 * dry_mass_inv)

'-----INTERMEDIA D VALUES-----
'All Intermedia, Total, Reaction, & Advection D-Values have units of(mol)/(Pa.h)

Call SpecialInstruct 'subroutine sets certain parameters to "test" values
'The above line calls a special routine which sets certain parameters to
'calibration values...subroutine is contained in "Chemlist" module

'----- Air - Water -----
diff_aw = (1#) / ((1# / (mtc_aw * air_water * p_zvalue(0))) + _
    (1# / (mtc_wv * air_water * p_zvalue(1)))) 'diffusion
rain_aw = air_water * rain_rate * p_zvalue(1) 'rainout
wdep_aw = air_water * rain_rate * scav_ratio * vf_aero * p_zvalue(6)
'wet deposition from atmospheric aerosols
ddep_aw = air_water * dry_dep_h2o * vf_aero * p_zvalue(6)
'dry deposition from atmospheric aerosols

'----- Air - Soil -----
bae = (0.04 * (0.2 ^ (10# / 3#))) / (0.25) 'eq. from Mackay 1991 pg.159
bwe = (0.000004 * (0.3 ^ (10# / 3#))) / (0.25) 'eq. from Mackay 1991 pg.159
'bae, bwe, & bwv are effective diffusivities deduced from molecular
'diffusivities and void fractions, Mackay 1991.

diff_as = (1#) / ((1# / (mtc_as * air_soil * p_zvalue(0))) + _
    (y_soil / (air_soil * (bae * p_zvalue(0) + bwe * p_zvalue(1)))))
rain_as = air_soil * rain_rate * (1 - Veg_If_Wet) * p_zvalue(1)
wdep_as = air_soil * rain_rate * (1 - Veg_If_Wet) * scav_ratio * vf_aero * p_zvalue(6)
ddep_as = air_soil * dry_dep_vel * (1 - Veg_If_Dry) * vf_aero * p_zvalue(6)

'----- Soil - Water -----
runoff_ss = air_soil * runoff_solid * p_zvalue(2) 'soil runoff
runoff_sw = air_soil * runoff_water * p_zvalue(1) 'water runoff

'----- Sediment - Water -----
bwv = (0.000004 * (0.8 ^ (10# / 3#))) / (0.8) 'eq. from Mackay 1991 pg.159
diff_sw = (1#) / ((1# / (mtc_wsed * air_water * p_zvalue(1))) + _
    (y_sed / (bwv * air_water * p_zvalue(1))))
'air_water = sediment_water b/c it's the same area just different depth.
dep_ws = air_water * sed_dep * p_zvalue(7)
'deposition of suspended solids from the water to the sediment
resus = air_water * sed_resus * p_zvalue(3)

'----- Air - Vegetation -----
diff_av = (1#) / ((1# / (mtc_av * air_vege * p_zvalue(0))) + _
    (1# / (mtc_veg * air_vege * p_zvalue(4)))) 'diffusion
rain_av = air_vege * rain_rate * Veg_If_Wet * p_zvalue(1)
'may be taken out b/c contaminated rainwater does not penetrate through
'it just gets washed off to soil below
wdep_av = air_vege * rain_rate * Veg_If_Wet * scav_ratio * vf_aero * p_zvalue(6)
ddep_av = air_vege * dry_dep_vel * Veg_If_Dry * vf_aero * p_zvalue(6)

'----- Air - Film -----
diff_af = (1#) / ((1# / (mtc_af * air_film * p_zvalue(0))) + _
    (1# / (mtc_film * air_film * p_zvalue(5)))) 'diffusion
rain_af = air_film * rain_rate * p_zvalue(1)
wdep_af = air_film * rain_rate * scav_ratio * vf_aero * p_zvalue(6)
ddep_af = air_film * dry_dep_vel * vf_aero * p_zvalue(6)

```

```

'----- Film - Water -----
'Runoff is a bulk film removal process
'0.75 defined as washoff efficiency
runoff_fw = air_film * depth(5) * film_washoff * b_zvalue(5)

'----- Vegetation - Soil -----
'there is a factor in the wq. below used to correct for the aerosol coverage of the
'foliage
wdep_vs = air_vege * (rain_rate / 0.000093) * (Veg_If_Wet - int_loss_frac) * 0.00000008052
* p_zvalue(6)
erosion_vs = air_vege * 0.00000008052 * p_zvalue(4)
'***** Erosion is removal of the plant cuticle + particulate phases *****

If Litt_Removal = 0 Then
    litter_vs = volume(4) * b_zvalue(4) * (1# / (grow_seas * 24))
Else
    litter_vs = 0#
End If

'-----Soil - Vegetation-----
rain_splash = volume(2) * b_zvalue(2) * splash_rate

'Initialize the intermedia d_values
For i = 0 To 5
    For j = 0 To 5
        d_value(i, j) = 0#
    Next j
Next i

d_value(0, 1) = diff_aw + rain_aw + wdep_aw + ddep_aw 'air - water
d_value(1, 0) = diff_aw 'water -air
d_value(0, 2) = diff_as + rain_as + wdep_as + ddep_as 'air - soil
d_value(2, 0) = diff_as 'soil - air
d_value(2, 1) = runoff_ss + runoff_sw 'soil - water
d_value(2, 4) = rain_splash 'soil - vegetation
d_value(1, 3) = diff_sw + dep_ws 'water - sediment
d_value(3, 1) = diff_sw + resus 'sediment - water
d_value(0, 4) = diff_av + rain_av + wdep_av + ddep_av 'air - vegetation
d_value(4, 0) = diff_av 'vegetation - air
d_value(4, 2) = wdep_vs + erosion_vs + litter_vs 'vegetation - soil
d_value(0, 5) = diff_af + rain_af + wdep_af + ddep_af 'air - film
d_value(5, 0) = diff_af 'film -air
d_value(5, 1) = runoff_fw 'film - waters

d_value_strat = strat * area(0) * p_zvalue(0)
'stratospheric transport D-value
d_value_burial = sed_burial * air_water * p_zvalue(3)
'sediment burial D-value
d_value_gw = leach * air_soil * p_zvalue(1)
'ground water leaching D-value

If Litt_Removal = 1 Then
    d_value_litter = volume(4) * b_zvalue(4) * (1# / (grow_seas * 24))
Else
    d_value_litter = 0#
End If

'Vegetation litterfall process... may be treated as a loss since
'in urban areas leaves fall and are removed
'(i.e.-collected and disposed of elsewhere)
'The factor of 24 is used to convert from days to hours

'Chemical Reaction and Advection Loss D-Values:
For i = 0 To 5
    d_reaction(i) = volume(i) * b_zvalue(i) * rate_const(i) 'Mackay Handbook,20
    d_advection(i) = adv_flow(i) * b_zvalue(i)
Next i

```

```

'Total D-Values:
total_dvalue(0) = d_reaction(0) + d_advection(0) + d_value(0, 1) _
                  + d_value(0, 2) + d_value(0, 4) + d_value(0, 5) _
                  + d_value_strat                                     'air
total_dvalue(1) = d_reaction(1) + d_advection(1) + d_value(1, 0) _
                  + d_value(1, 3)                                     'water
total_dvalue(2) = d_reaction(2) + d_value(2, 0) + d_value(2, 1) _
                  + d_value_gw + rain_splash                         'soil
total_dvalue(3) = d_reaction(3) + d_value(3, 1) + d_value_burial    'sediment
total_dvalue(4) = d_reaction(4) + d_value(4, 0) + d_value(4, 2) _
                  + d_value_litter                                   'vegetation
total_dvalue(5) = d_reaction(5) + d_value(5, 0) + d_value(5, 1)    'film

'-----FUGACITY VALUE CALCULATIONS-----
'six equations and six unknowns were solved for by standard algebra
'results are summarized by the equations below.

A1 = d_value(0, 4)
A2 = (d_value(0, 2) * d_value(2, 4)) / (total_dvalue(2))
AA = A1 + A2                                     'simplified parameter #1

B1 = total_dvalue(4)
B2 = (d_value(4, 2) * d_value(2, 4)) / (total_dvalue(2))
BB = B1 - B2                                     'simplified parameter #2

CC = AA / BB                                     'simplified parameter #3

D1 = d_value(0, 2) + (CC * d_value(4, 2))
D2 = total_dvalue(2)
DD = D1 / D2                                     'simplified parameter #4

E1 = DD * d_value(2, 0)
E2 = CC * d_value(4, 0)
E3 = (d_value(0, 5) * d_value(5, 0)) / (total_dvalue(5))
E4 = total_dvalue(0)
EE = E1 + E2 + E3 - E4

F1 = d_value(0, 1)
F2 = DD * d_value(2, 1)
F3 = (d_value(0, 5) * d_value(5, 1)) / (total_dvalue(5))
FF = F1 + F2 + F3

G1 = total_dvalue(1)
G2 = (d_value(1, 3) * d_value(3, 1)) / (total_dvalue(3))
GG = G1 - G2

HH = GG / (-1# * d_value(1, 0))

inp(0) = input_rate(0)      'express as short forms to conserve on space
inp(1) = input_rate(1)

'All Fugacities are in units of Pa
fugacity(0) = (inp(0) * HH - inp(1)) / (FF - (EE * HH))           'air
fugacity(1) = (inp(0) + (fugacity(0) * EE)) / (-1# * d_value(1, 0)) 'water
fugacity(2) = (fugacity(0) * DD)                                  'soil
fugacity(3) = (fugacity(1) * d_value(1, 3)) / total_dvalue(3)    'sediment
fugacity(4) = (fugacity(0) * CC)                                  'vegetation
fugacity(5) = (fugacity(0) * d_value(0, 5)) / total_dvalue(5)    'film

'-----OUTPUT PARAMETER CALCULATIONS-----

'.....
Call SpecialInstruct      'subroutine test values for validity
'.....

'initialize rate parameters
For i = 0 To 5
  For j = 0 To 5
    trans_rate(i, j) = 0#

```

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Next j
Next i

'all rates are in mol/h
trans_rate(0, 1) = d_value(0, 1) * fugacity(0) 'air - water loss rate
trans_rate(1, 0) = d_value(1, 0) * fugacity(1) 'water - air loss rate
trans_rate(0, 2) = d_value(0, 2) * fugacity(0) 'air - soil loss rate
trans_rate(2, 0) = d_value(2, 0) * fugacity(2) 'soil - air loss rate
trans_rate(2, 1) = d_value(2, 1) * fugacity(2) 'soil - water loss rate
trans_rate(2, 4) = d_value(2, 4) * fugacity(2) 'soil - vegetation loss rate
trans_rate(3, 1) = d_value(3, 1) * fugacity(3) 'sediment - water loss rate
trans_rate(1, 3) = d_value(1, 3) * fugacity(1) 'water - sediment loss rate
trans_rate(0, 4) = d_value(0, 4) * fugacity(0) 'air - vegetation loss rate
trans_rate(4, 0) = d_value(4, 0) * fugacity(4) 'vegetation - air loss rate
trans_rate(4, 2) = d_value(4, 2) * fugacity(4) 'vegetation - soil loss rate
trans_rate(0, 5) = d_value(0, 5) * fugacity(0) 'air - film loss rate
trans_rate(5, 0) = d_value(5, 0) * fugacity(5) 'film - air loss rate
trans_rate(5, 1) = d_value(5, 1) * fugacity(5) 'film - water loss rate

rate_strat = d_value_strat * fugacity(0) 'loss rate to stratosphere
rate_burial = d_value_burial * fugacity(3) 'loss rate due to sed. burial
rate_leach = d_value_gw * fugacity(2) 'loss rate due to gw leach f/soil

rate_litter = volume(4) * b_zvalue(4) * (1# / (grow_seas * 24)) * fugacity(4)
'loss rate due to litterfall from veg
'Same weather or not litterfall is a permanent removal mechanism

If Litt_Removal = 1 Then
    SoilFlux = trans_rate(0, 2) + trans_rate(4, 2) + rate_litter
Else
    SoilFlux = trans_rate(0, 2) + trans_rate(4, 2)
End If

If (Veg_If_Wet = 0#) Then 'No vegetative canopy, conditions
    SoilFlux = trans_rate(0, 2)
End If

PerLitt = (rate_litter * 100) / (SoilFlux)
'Litterfall transport as a percentage of total transport to soil
NonLittDep = (erosion_vs * fugacity(4) * 100) / (SoilFlux)

'initialize output parameters
total_moles = 0# 'total number of moles of chemical all media
total_react = 0# 'number of moles per hour reacted over all media
total_advec = 0# 'number of moles per hour advected though all media
total_r_and_a = 0# 'total number of mol/h reacted and advected
total_loss = 0# 'total permanent loss of chemical in all media

For i = 0 To 5
    conc(i) = fugacity(i) * p_zvalue(i) 'conc. in (mol/m^3)
    b_conc(i) = fugacity(i) * b_zvalue(i) 'bulk conc. in (mol/m^3)
    mass_conc(i) = conc(i) * mol_mass 'mass conc. in (g/m^3)
    moles(i) = b_conc(i) * volume(i) '# moles in (mol)
    'Above is using bulk concs...you can switch it to pure conc if you want.
    mass(i) = (moles(i) * mol_mass) / 1000# 'mass in kg
    total_moles = total_moles + moles(i) 'in (mol)
    react(i) = d_reaction(i) * fugacity(i) 'in (mol/h)
    total_react = total_react + react(i) 'in (mol/h)
    advec(i) = d_advection(i) * fugacity(i) 'in (mol/h)
    total_advec = total_advec + advec(i) 'in (mol/h)
Next i

total_mass = mass(0) + mass(1) + mass(2) + mass(3) + mass(4) + mass(5)

removal(0) = react(0) + advec(0) + rate_strat + trans_rate(0, 1) + trans_rate(0, 2) +
    + trans_rate(0, 4) + trans_rate(0, 5)
'from air in (mol/h)
removal(1) = react(1) + advec(1) + trans_rate(1, 0) + trans_rate(1, 3)
'from water in (mol/h)
removal(2) = react(2) + rate_leach + trans_rate(2, 0) + trans_rate(2, 1) _

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        + trans_rate(2, 4)
'from soil in (mol/h)
removal(3) = react(3) + rate_burial + trans_rate(3, 1)
'from sediment in (mol/h)
If Litt_Removal = 1 Then
    removal(4) = react(4) + trans_rate(4, 0) + trans_rate(4, 2) + rate_litter
Else
    removal(4) = react(4) + trans_rate(4, 0) + trans_rate(4, 2)
End If
'from vegetation in (mol/h)
removal(5) = react(5) + trans_rate(5, 0) + trans_rate(5, 1)
'from film in (mol/h)

loss(0) = react(0) + advec(0) + rate_strat      'permanent chemical loss from air
loss(1) = react(1) + advec(1)                  'permanent chemical loss from water
loss(2) = react(2) + rate_leach                 'permanent chemical loss from soil
loss(3) = react(3) + rate_burial                'permanent chemical loss from sediment
If Litt_Removal = 1 Then
    loss(4) = react(4) + rate_litter            'permanent chemical loss from vegetation
Else
    loss(4) = react(4)                        'permanent chemical loss from vegetation
End If
loss(5) = react(5)                            'permanent chemical loss from film

For i = 0 To 5
    res_time(i) = moles(i) / removal(i)        'residence time in hours
    'Above residence time takes into account loss by reaction and advection only
    total_loss = total_loss + loss(i)          'total permanent loss rate
Next i

total_r_and_a = total_react + total_advec      'in (mol/h)
If Litt_Removal = 1 Then
    total_r_and_a = total_r_and_a + rate_strat + rate_leach + rate_burial + rate_litter
    'to take into account the other 4 loss mechanisms
Else
    total_r_and_a = total_r_and_a + rate_strat + rate_leach + rate_burial
End If
tot_in = input_rate(0) + input_rate(1)        'total envir. chemical input rate
tot_rem = total_r_and_a                       'total envir. chemical output rate

conc_aero = fugacity(0) ** p_zvalue(6)        'conc. in (mol/m^3)
conc_susp = fugacity(1) ** p_zvalue(7)        'conc. in (mol/m^3)

'total inputs and outputs from each medium
inpt(0) = input_rate(0) + (fugacity(1) ** d_value(1, 0)) _
        + (fugacity(2) ** d_value(2, 0)) + (fugacity(4) ** d_value(4, 0)) _
        + (fugacity(5) ** d_value(5, 0))      'air
outg(0) = fugacity(0) ** total_dvalue(0)      'air
inpt(1) = input_rate(1) + (fugacity(0) ** d_value(0, 1)) _
        + (fugacity(2) ** d_value(2, 1)) + (fugacity(3) ** d_value(3, 1)) _
        + (fugacity(5) ** d_value(5, 1))      'water
outg(1) = fugacity(1) * total_dvalue(1)        'water
inpt(2) = (fugacity(0) ** d_value(0, 2)) + (fugacity(4) ** d_value(4, 2)) 'soil
outg(2) = fugacity(2) ** total_dvalue(2)      'soil
inpt(3) = fugacity(1) * d_value(1, 3)          'sediment
outg(3) = fugacity(3) * total_dvalue(3)        'sediment
inpt(4) = fugacity(0) * d_value(0, 4) + (fugacity(2) ** d_value(2, 4)) 'vegetation
outg(4) = fugacity(4) ** total_dvalue(4)      'vegetation
inpt(5) = fugacity(0) ** d_value(0, 5)        'film
outg(5) = fugacity(5) ** total_dvalue(5)      'film

total_i = 0#
total_o = 0#
For i = 0 To 5
    total_i = total_i + inpt(i)
    total_o = total_o + outg(i)
Next i

'Input and output from each medium per meter squared
per_m_in(0) = inpt(0) / (air_water + air_film + air_vege) 'air

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per_m_in(1) = inpt(1) / area(1) 'water
per_m_in(2) = inpt(2) / area(2) 'soil
per_m_in(3) = inpt(3) / area(1) 'sediment
per_m_in(4) = inpt(4) / air_vege 'vegetation
per_m_in(5) = inpt(5) / air_film 'film

'Te statements below calculate loss rates per m2 rather than output rates (not outg)
per_m_out(0) = (loss(0)) / (air_water + air_film + air_vege) 'air
per_m_out(1) = (loss(1)) / area(1) 'water
per_m_out(2) = (loss(2)) / area(2) 'soil
per_m_out(3) = (loss(3)) / area(1) 'sediment...area of sediment = area of water
per_m_out(4) = (loss(4)) / air_vege 'vegetation
per_m_out(5) = (loss(5)) / air_film 'film

For i = 0 To 5
    Loss_div_In(i) = per_m_out(i) * 100# / per_m_in(i)
Next i

env_res_time = total_moles / total_loss      'Total environmental residence time

'now convert some of the concentrations into more appropriate units
'I'm using pure concentrations now! Not bulk concentrations
conc_air = b_conc(0) * mol_mass * 1000000000#      'ng/m^3
conc_water = b_conc(1) * mol_mass * 1000000#      'ng/L
conc_soil = (mass_conc(2) / dens_soil) * 1000#      'ng/g
conc_sed = (mass_conc(3) / dens_sed) * 1000#      'ng/g
conc_vege = conc(4) * mol_mass * 1000000000#      'ng/m^3
conc_vege = (mass_conc(4) / 0.82) * 1000#          'ng/g
'Line above used for comparison of veg values with literature.
'Leaf density of 0.82 kg/L taken from Plant Cont. pg 194 (LHS)
conc_film = mass_conc(5) * depth(5) * 1000000000# '10^9 needed for g -->ng
'film concentration in ng/m^2 for an organic film 70nm thick

'calc. everything in ng/m^3 for purpose of comparison with Miriam's model
mir_air = conc(0) * mol_mass * 1000000000#      'ng/m^3
mir_water = conc(1) * mol_mass * 1000000000#      'ng/m^3
mir_soil = conc(2) * mol_mass * 1000000000#      'ng/m^3
mir_sed = conc(3) * mol_mass * 1000000000#      'ng/m^3
mir_vege = conc(4) * mol_mass * 1000000000#      'ng/m^3
mir_film = conc(5) * mol_mass * 1000000000#      'ng/m^3
mir_aero = conc_aero * mol_mass * 1000000000#      'ng/m^3
mir_susp = conc_susp * mol_mass * 1000000000#      'ng/m^3

'calc. everything in BULK ng/m^3 for purpose of comparison with Miriam's model
b_air = b_conc(0) * mol_mass * 1000000000#      'ng/m^3
b_water = b_conc(1) * mol_mass * 1000000000#      'ng/m^3
b_soil = b_conc(2) * mol_mass * 1000000000#      'ng/m^3
b_sed = b_conc(3) * mol_mass * 1000000000#      'ng/m^3
b_vege = b_conc(4) * mol_mass * 1000000000#      'ng/m^3
b_film = b_conc(5) * mol_mass * 1000000000#      'ng/m^3

'now calculate the fraction of chemical in each medium
For i = 0 To 5
    percent(i) = (100# * moles(i)) / (total_moles)
    percent(i) = (100# * mass(i)) / (total_mass)
    perc_react(i) = (100# * react(i)) / (total_react)
    perc_advec(i) = (100# * advec(i)) / (total_advec)
    perc_rem(i) = (100# * loss(i)) / (total_loss)
Next i

'Fraction of chemical in the particulate phase
part_perc = 100 * (Kp * aero_conc) / (1 + (Kp * aero_conc))

```