Estimating Urban Scale Semi-Volatile Organic Compound Emissions and Fate Using a Coupled Multimedia and Atmospheric Transport Model

by

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Abstract

Cities are sources of persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), to surrounding regions and beyond. A spatially resolved, (5×5 km²), dynamic contaminant fate model named Spatially Oriented or SO-MUM was developed by coupling the fugacity based Multimedia Urban Model (MUM) (Diamond et al., 2001; Diamond et al., 2010c) and the Boundary Layer Forecast Model and Air Pollution Prediction System (BLFMAPS) which was developed at Environment Canada (Daggupaty et al., 2006). MUM was updated to contain a revised surface film sub-model which takes into account the dynamic nature of surface films. SO-MUM was illustrated by application to the City of Toronto, Canada. Spatially resolved air emissions of Σ₂₅PCB were estimated to be ~230 (40-480) kg y⁻¹, 280 (50-580) g y⁻¹ km⁻², and 90 (16-190) mg y⁻¹ capita⁻¹ and Σ₂₆PBDE were estimated to be 28 (6-63) kg y⁻¹, 34 (7-77) g y⁻¹ km⁻² and 11 (2-25) mg y⁻¹ capita⁻¹. These emissions were back-calculated from measured air concentrations and spatial chemical mass inventories yielding emission rates per mass inventory of 0.4 (0.05-1.6) and 0.1 (0.01-0.7) g kg⁻¹ inventory y⁻¹, for Σ₂₅PCBs and Σ₂₆PBDEs, respectively. Approximately 30% and 16% of PCB and PBDE emissions emanate from the city’s downtown. Air advection accounted for ~95% (PCB)
and ~70% (PBDE) of total air emission losses with the remaining balance depositing to the city. The metric “Urban Travel Distance” or UTD was introduced for quantifying the extent of an urban plume resulting from spatially heterogeneous emissions. For PCBs and PBDEs the UTDs were ~25 and ~30 km. The updated surface film sub-model indicated that films “bounce” higher vapor pressure semi-volatile organic compounds (SVOCs) back into the air but they act as a transient sink from air for lower vapor pressure SVOCs, thereby facilitating transport to surface waters. Model calculations suggest that if the PCB inventory is reduced, volatilization from near-shore Lake Ontario will become a net source of PCBs to air, but that neither near-shore Lake Ontario nor soil would become a significant volatilization PBDE source to air.
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Chapter 1
Introduction

1 Introduction

Persistent organic pollutants (POPs) are chemicals that have physical-chemical properties such that they are persistent, bioaccumulative, toxic, and undergo long range transport (P, B, T, and LRT). POPs have been found worldwide due to their LRT properties. The Stockholm Convention and the Convention on Long-range Transboundary Air Pollution have suggested source identification as a strategy to control further release and spread of these chemicals (Stockholm Convention, 2009; UNECE, 2012).

POPs originate from anthropogenic activities and it hence follows that urban areas where many people live and work provide a high geographic concentration of these activities (Diamond and Hodge, 2007). Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBDEs), both of which are listed as POPs under the Stockholm Convention, originate from building materials, infrastructure, and consumer products which are harder to locate and control than point source emissions. Furthermore, the architecture of urban areas enhances chemical mobility as cities have relatively higher proportions of impervious surfaces which allows for greater chemical movement during rain events and lower proportions of soils and foliage which provide chemical sinks. High urban POP concentrations have led cities to become significant sources to the greater environment via air and water transport. Despite knowledge about elevated POP concentrations in urban areas, little information is available on the mass of chemical inventories and emission rates from these inventories.

The overall goal of this thesis was to provide a general framework for quantifying emissions of semi-volatile organic compounds (SVOCs) such as POPs, based on chemical inventories in order to guide actions that can be taken to reduce primary emissions from these inventories. PCBs and PBDEs in Canada’s largest city, Toronto, were used as a case study.
### 1.1 Study Chemicals: PCBs and PBDEs

The general method developed to estimate POP emissions will be detailed using two study chemicals: PCBs and PBDEs which have similar physical-chemical properties but have been in-use on different time scales as new-use and import of PCBs was banned in 1977 and the penta- and octa- mixtures of PBDEs have only been recently banned in 2008 in Canada.

PCBs have been produced since the 1930's (McDonald and Tourangeau, 1986). Their main uses were used as dielectric fluids in capacitors and transformers and in various building materials and products such as building sealants, flame retardants in products, and preservatives in outdoor paints (ASTDR, 2000; Diamond et al., 2010c). Import and new use of PCBs was banned in Canada in 1977, however, they are still in-use, for example in building sealants and some may still be in use in capacitors, transformers and light ballasts (Diamond et al., 2010c; Government of Canada, 2012; Robson et al., 2010). PBDEs have been in production since the 1970s (Alcock et al., 2003; ASTDR, 2004). Due to their persistence, ubiquity in the environment, and toxicity, PBDEs have been recently regulated in North America with a voluntary production ban in the U.S. in 2004, and in Canada were declared a CEPA (Canadian Environmental Protection Act) toxic substance in 2008 (Environment Canada, 2010; Government of Canada, 2008; Ward et al., 2008). The deca mixture will be voluntarily phased out of use in consumer products by the three largest North American manufacturers by 2012 (Environment Canada, 2011). PBDEs are used as flame retardants in various products such as electronics, furniture, textiles, and plastics (Ward et al., 2008).

PCBs and PBDEs are both found ubiquitously in the environment, having been measured in media including air, water, soil, films that coat impervious surfaces, humans, and animals (Butt et al., 2004; Gingrich et al., 2001; Hites, 2004; Hornbuckle and Robertson, 2010). The sources of these chemicals originate from products to which these chemicals were added. They can migrate globally as they undergo long range transport and contribute to measurable levels found in remote regions such as the Arctic where there are few primary sources (de Wit et al., 2006; MacDonald et al., 2000).

Exposure to PCBs and PBDEs is of concern because they have been found to be toxic to humans and ecological receptors. Some human health concerns related to PCB exposure include effects on the endocrine system, neurodevelopment, and immune development (e.g. Boucher et
al., 2009; Diamanti-Kandarakis et al., 2009; Schantz et al., 2003; Weisglas-Kuperus et al., 2000). Human health issues related to PBDE exposure include developmental and neurodevelopmental disorders, and thyroid and liver toxicity (inter alia Frederiksen et al., 2009; Lorber, 2008). Environmental concerns include chemical accumulation in environmental media, long range transport, and health effects on wildlife exposed to these chemicals (Darnerud, 2003; Hites, 2004; MacDonald et al., 2000; Zala and Penn, 2004).

Human exposure to PCBs and PBDEs is related to their uses, persistence and how they are transported in the environment. Their persistence and fate are ultimately controlled by their physical-chemical properties. The major human PCB exposure pathways are through diet and indoor dust as PCBs have been found to bioaccumulate in food and partition to dust in indoor air (e.g. Alcock et al., 1998; Fisk et al., 1998; Harrad et al., 2009). The predominant human exposure pathways of PBDEs are through dust and diet; dust has currently been found to be the dominant pathway in North America (e.g. Johnson-Restrepo and Kannan, 2009; Johnson et al., 2010; Jones-Otazo et al., 2005; Voorspoels et al., 2007). Diet may become a more important exposure route as PBDEs move from an indoor contaminant to an outdoor one where they can subsequently accumulate in the food chain (Fraser et al., 2009; Harrad and Diamond, 2006). Exposure through dust likely occurs in areas which are in close proximity to a chemical source whereas exposure through diet occurs via chemicals that have been transported away from the source. Dietary exposure occurs when a chemical has been transported from a source area and persists long enough to be transferred into the food chain (Arnot et al., 2010). PCBs and PBDEs can be transferred into aquatic media and are hence measured in water bodies. Both compound groups have been found to bioaccumulate in fish, thereby providing a dietary exposure pathway (Sjodin et al., 2003; Turyk et al., 2012). Furthermore, PCBs and PBDEs can be transported from source areas and accumulate in the terrestrial food web, for example, PCBs and PBDEs have both been found in animal based food products such as meat and dairy products (ASTDR, 2000; Frederiksen et al., 2009; Schecter et al., 2001). Therefore, human exposure to PCBs and PBDEs originate from two modes: near-source exposure from indoor dust (i.e. direct) and a recycling of transported chemical via the food web (indirect). Identifying sources in order to inform removal strategies and understanding chemical fate can both aid in reducing direct and indirect human exposure to these chemicals.
1.2 Urban Areas: PCB and PBDE Sources

As cities contain large amounts of infrastructure, consumer products, and materials, it follows that cities, compared to rural locations, have elevated PCB and PBDE concentrations in various media such as air (Jaward et al., 2004; Pozo et al., 2006; Strandberg et al., 2001), soils (Harrad and Hunter, 2006; Wong et al., 2009), rivers (Robson et al., 2008; Rodenburg et al., 2011), and films that cover impervious surfaces (Butt et al., 2004; Gingrich et al., 2001). These elevated urban POP concentrations turn cities into sources of POPs to the greater environment. In the Great Lakes region, for example, cities have been found to contribute to neighboring lake water concentrations and downwind air concentrations (e.g. Blanchard et al., 2008; Hafner and Hites, 2003; Offenberg et al., 2005; Simcik et al., 1997). Air transport is the dominant removal pathway of urban PCB and PBDE air emissions (Diamond et al., 2010c; Gasic et al., 2010; Jones-Otazo et al., 2005; Priemer and Diamond, 2002) and hence provides a pathway of chemical transport to other regions. Furthermore, cities have high percentages of impervious surfaces where surface films develop and can act as temporary chemical sinks from air which allows mobilization of chemicals during rain events into surface waters and soils. This provides another urban contamination pathway via storm water and soil run-off which feed urban water bodies (Rodenburg et al., 2011) and ultimately contaminate the aquatic food web. In order to control migration of these emissions, which drives far field human exposure and exposure to the ecosystem, it is necessary to identify and remove urban chemical primary sources such as PCB-containing electrical equipment and PBDE-containing consumer products. As humans are also exposed to PCBs and PBDEs through indoor house dust, removing sources would also reduce near field exposure to these chemicals. In Canada, for example, in-use PCB inventories (askerels and mineral oils) have decreased over time (Environment Canada, 2006b) and most PCB wastes in Canada are sent to PCB destruction facilities (Environment Canada, 2006a). The export of PCB waste to foreign countries (other than to authorized destruction facilities in the United States) is prohibited in Canada (Government of Canada, 1996). Breivik et al. (2011), however, reported that PCB waste and old products are being exported to Asia and Africa from industrialized nations such that PCB removal regulations should take end of life-cycle factors into account. As PBDEs are contained in consumer products they are often exported out of urban areas into landfills or e-waste facilities (Ward et al., 2008). E-waste is extensively exported to Africa and Asia as waste or within old products (Breivik et al., 2011).
Since PCBs and PBDEs have many different uses, it follows that their applications are likely to spread heterogeneously throughout a city. This makes it difficult to identify sources and emissions as they do not emanate from specific source areas (Breivik et al., 2004). Moreover, due to their persistence, they may also originate from secondary sources, i.e. media in which chemicals have accumulated and may be re-emitted to air. The notion that sources to air are heterogeneous is supported by measured intra-urban concentration gradients (e.g. in air, soil, surface films) that have been observed in many cities (e.g. Du et al., 2009; Harrad and Hunter, 2006; Hu et al., 2010; Jamshidi et al., 2007; Melymuk et al., 2012). Within Canada’s largest city, Toronto, PCB concentrations measured in the early 2000s varied ~5 and ~7 times in air and films, respectively, (Gingrich et al., 2001; Harner et al., 2004) and ~3 and ~2-13 times in air and film, respectively, for PBDEs (Butt et al., 2004; Harner et al., 2006). Furthermore, Gouin et al. (2005) found that PCB and PBDE air concentrations exhibited an urban-rural gradient of ~5 times in Toronto. Recently, Melymuk et al. (2012) found that air concentrations can vary 7 and 8 times in Toronto for PCBs and PBDEs, respectively, at urban sites within 1 km of each other. Soil PCB concentrations in Toronto can vary spatially over an order of magnitude (Wong et al., 2009).

1.3 PCB and PBDE Emissions

The link between chemical sources and air concentrations are the emissions emanating from sources. Despite much information on PCB and PBDE concentrations, emissions have been difficult to quantify as they could originate from a wide range of products and materials. One method to estimate anthropogenic chemical emissions uses emission factors (EF) in which emissions are estimated based on activities involving a chemical, for example, mass of PAH emitted per tonne of municipal solid waste incinerated or wood burned (Dyke et al., 2003; Gullett et al., 2003). This method has been widely applied to chemicals such as polychlorinated dibenzodioxins and furans (PCDD/F), polycyclic aromatic hydrocarbons (PAH) and mercury (e.g. Gullett et al., 2003; Marr et al., 1999; Pirrone et al., 1996), however, it has been applied less frequently to PCBs and PBDEs (Breivik et al., 2002; Prevedouros et al., 2004a) as emission factors for these chemicals could vary significantly over different chemical usages (e.g. closed vs. open PCB sources) (Breivik et al., 2002).
Chemical emissions can also be estimated using measured concentrations by back-calculating what emission is needed to sustain the observed concentrations. This method has been applied to PCBs on an urban scale (Diamond et al., 2010c; Gasic et al., 2010; Gasic et al., 2009; Jones-Otazo et al., 2005) but few studies have focused on identifying emissions at site scale (i.e. within an urban area) (Totten et al., 2006). Few emission estimates are available for PBDEs, however they have been recently estimated on national (Batterman et al., 2009) and urban scales (Jones-Otazo et al., 2005; Moeckel et al., 2010) using measured air concentrations. PCB emissions have been scaled regionally to population density (Meng et al., 2007), however, this does not allow for quantifying emissions from PCB stocks and contaminated sites nor does it account for the spatial heterogeneity of PCB usage patterns and concentrations in cities (Du et al., 2009; Hu et al., 2010; Melymuk et al., 2012).

In order to better understand the relationship between PCB and PBDE sources and emissions it is necessary to quantify intra-urban emissions and relate these to chemical stocks as well as sources of secondary emissions. Multimedia fugacity models have been used to predict urban chemical emissions from a city as a whole (e.g. Diamond et al., 2010c; Gasic et al., 2009; Jones-Otazo et al., 2005; Morselli et al., 2011); however these models average properties over entire urban areas and do not take into account the spatial heterogeneity of chemical concentrations (Gasic et al., 2010), sources, and geographic characteristics. With the recent availability of measured intra-urban PCB and PBDE concentrations (Du et al., 2009; Hu et al., 2010; Melymuk et al., 2012), fugacity models can be used to estimate intra-urban air emissions and further reduce the spatial scale of emission estimates. Furthermore, intra-urban emission estimates can be combined with mass inventories to yield emission rates per mass of chemical for PCBs and PBDEs which is similar to that of an aggregate emission factor. This can provide a novel method to relate chemical emissions to sources on an intra-urban spatial scale such that significant sources can be identified and removed to prevent further emissions. Spatially resolved PCB mass inventories have been estimated in Toronto by Diamond et al. (2010c) and Robson et al. (2010) and PBDE mass inventories are presented in this thesis. The estimated emission rates per inventory can be used to predict effects of reducing chemical sources on air emissions and to inform policy decisions.
1.4 Multimedia Fugacity Modeling

Multimedia fugacity modeling has been widely used in order to understand fate and transport processes of POPs. The concept of using fugacity for environmental modeling was introduced by Don Mackay about 30 years ago (e.g. Mackay and Paterson, 1981) and has become a popular method used to study the fate of environmental contaminants (MacLeod et al., 2010) on scales ranging from indoors, to urban, regional, and global (e.g. MacLeod et al., 2001; Priemer and Diamond, 2002; Wania and Mackay, 1995; Zhang et al., 2009). Environmental fugacity models divide the environment into various compartments (such as air, water, and soil) in order to estimate the fugacity of a given chemical in all media as well as fluxes between compartments and in and out of the system given compartmental emissions and inputs. The models estimate concentrations by calculating compartmental fugacities, $f$ (Pa), which are linearly related to concentration through the fugacity capacity, $Z$ (mol m$^{-3}$ Pa$^{-1}$). Fugacity models can be applied to chemicals with non-negligible vapor pressures such as semi-volatile organic compounds (Mackay, 1991). Chemical transport between media is calculated based on parameters such as partition coefficients, $K$ (which is defined as the ratio of concentrations of a chemical between two media at equilibrium) and mass transfer velocities. Chemical loss processes from the system include transport processes such as advection and degradation/transformation pathways. Chemical mass in each compartment is governed by a mass balance equation and hence the entire system of $n$ compartments is governed by $n$ mass balance equations which are solved simultaneously. The models are solved under steady-state or unsteady conditions where the mass of chemical in each compartment remains constant or varies in time, respectively.

Geographic areas are represented by multimedia models either as one-box or multi-box systems where the entire model area is either represented as one area or divided into multiple areas on varying scales, respectively. Multi-box systems have been applied on a global scale (e.g. Globo-POP (Wania and Mackay, 1995) and CliMoChem (Scheringer et al., 2000)) and have been coupled to atmospheric transport models to assess long range transport (Scheringer, 2009). These strategies have also been used on regional scales, for example BETR in North America and Europe (MacLeod et al., 2001; Prevedouros et al., 2004b). Recently, Hollander et al. (2012) determined that spatial differences in emission rates in multi-box models generally account for spatial differences in environmental concentrations.
On an urban scale, however, generally one box models have been used to study an entire city (e.g. Gasic et al., 2009; Priemer and Diamond, 2002). Diamond and co-workers (2001) developed the multimedia urban model (MUM) in order to estimate the emissions, fate, and transport of SVOCs in areas with impervious surface coverage. Their initial application assumed a one-box representation of the city, using Toronto as a case study. However, urban areas vary in their built form from downtown to suburban areas, in particular in terms of impervious surface coverage. Furthermore, as discussed previously, chemicals vary geographically in their sources, emissions, and concentrations within an urban area.

Subsequently, the next step in urban SVOC modeling is to incorporate more spatial refinement accounting for heterogeneities within urban areas. Multi-box fugacity models on smaller scales, such as 5 km and 0.5 km, have been used to study Lindane in the Great Lakes Region (Ma et al., 2003); dioxins, benzene, 1,3-butadiene, and di-(2-ethylhexyl)phthalate in Japan (Suzuki et al., 2004); and benzene, toluene, xylene, and styrene in Seoul, North Korea (Kim et al., 2011). In this project, PCBs and PBDEs were studied using a dynamic multi-box fugacity model on a 5 km scale applied to the city of Toronto.

The one-box steady-state version of MUM was applied to the city of Toronto to estimate PCB and PBDE emissions emanating from the city and to quantify the fate and transport of these emissions (Diamond et al., 2010c; Jones-Otazo et al., 2005). In order to extend the one-box MUM model into a multi-box model, MUM was coupled to an air transport model to simulate air transport between boxes. The one-box model estimated that the dominant removal pathway for both chemicals was via air transport and hence the addition of a more detailed air transport model could provide further information about chemical air transport processes. More specifically, extending the model area beyond the borders of Toronto would allow estimation of the travel distance of the chemical plume emanating out of the city. Furthermore, as Toronto sits on Lake Ontario, air transport and air-lake exchange over the lake could also be studied. This would give further insight into how chemical is transported out of urban areas in the air compartment which allows for potential human and environmental exposure outside of the city resulting from urban sources.

The one-box steady-state version of MUM also estimated the fate of PCBs within Toronto where it was found that chemical that was not subject to advective loss was deposited to surface films (covering impervious surfaces) under average yearly conditions (Diamond et al., 2010c).
The net deposition to films was found to almost entirely be mobilized further to surface waters during rain wash-off which provides another pathway for chemicals to enter Lake Ontario and enter the aquatic food web. As film wash-off may be an important route for chemical mobilization out of urban areas, it is important to account for the dynamic nature of film growth and wash-off. This was further facilitated by coupling MUM to an air transport model as dynamic atmospheric conditions such as wind speed and temperature could also be taken into account in the film sub-model.

1.5 Project Summary

The overarching goal of my research was to develop a general method to estimate spatially resolved emissions and fate of SVOCs in an urban area. This was accomplished by coupling the Multimedia Urban Model, MUM developed by Diamond and co-workers, with the regional air transport model, BLFMAPS of Daggupaty and co-workers. To evaluate the use of the new model and to shine light on two POPs that are of continuing concern, the coupled model, Spatially Oriented or SO-MUM, was applied to study the sources, fate, and transport of PCBs and PBDEs. This thesis presents the general method to estimate SVOC emissions on an intra-urban scale using measured air concentrations and mass inventories, using PCBs and PBDEs as a case study. The method can then be further applied to other SVOCs of concern. The information gained from this project will improve our understanding of the role of cities as sources of POPs, estimate urban PCB and PBDE emissions from these sources, and quantify chemical transport out of urban areas into the surrounding environment.

The chemicals were studied by coupling two models: the mass balance Multimedia Urban Model (MUM) developed in the Diamond Lab (Diamond et al., 2010c; Priemer and Diamond, 2002) and a meteorological and air transport model, the Boundary Layer Forecast Model and Air Prediction Pollution System (BLFMAPS) developed at Environment Canada (Daggupaty et al., 2006; Daggupaty et al., 1994). The coupled model, SO-MUM has been parameterized to examine the city of Toronto and to estimate the multimedia fate and atmospheric transport of these POPs. MUM was used to estimate air emissions by 'back-calculating' emissions needed to sustain measured air concentrations (Diamond et al., 2010c; Jones-Otazo et al., 2005).

Before coupling the models, the steady-state version of MUM was updated into an unsteady-state version taking into account the dynamic nature of surface films and recent advances in the
understanding of SVOC interactions with films. As urban areas can contain high percentages of impervious surface coverage, chemical build-up in film and subsequent wash-off during rain events provide a critical pathway for contamination of receiving waters (e.g. urban lakes and tributaries). An unsteady-state model is better suited to study urban chemical fate in films as their properties change over time, for example via film growth and wash off. Furthermore, air-film exchange processes depend on temperature and wind speed which can vary substantially in time. Thus, the film sub-model within MUM was updated to allow for film growth and wash-off, dynamic change in air-film mass transfer coefficients, and account for new empirical data on air-film partitioning. The updated model was used to study the source/sink nature of films and was coupled to BLFMAPS to further this investigation.

The Boundary Layer Meso-scale Forecast Model, BLFM interpolates wind velocities and air temperatures between 12 hour data input intervals (the data is from Environment Canada's weather prediction model, Global Environmental Multi-scale Model (GEM)) (Daggupaty et al., 1994). BLFM was extended into an air transport model by Daggupaty et al. (2006) to estimate chemical concentrations in air based on transport via air advection and diffusion; this latter usage is referred to as BLFMAPS. BLFMAPS divides the model area into 5km×5km cells. The dynamic version of MUM (with the updated film sub-model) was coupled into each BLFMAPS cell. The models were coupled by using BLFMAPS to predict meteorological data and chemical transport in air between cells and MUM was used for all other processes including atmospheric deposition. Tributary transport within the city was modeled in MUM by connecting cells with tributaries flowing through them and applying the standard fugacity formulation for river transport (Mackay, 1991).

Steady-state MUM was used to back-calculate spatially resolved PCB and PBDE intra-urban emissions in Toronto on a 5×5 km² resolution using spatial PCB and PBDE mass inventories and measured air concentrations (using passive air samplers) of Melymuk et al. (2012) in 2008 with sampling sites spaced 1-20 km apart across the city. The PCB mass inventory was developed by Diamond et al. (2010b) and Robson et al. (2010) and the PBDE inventory was developed in the Diamond lab (with the aid of A. Giang and S. Verkoeyen) following the methods of Diamond et al. (2010c).
SO-MUM was run for the spring of 2008 corresponding to one of the deployment periods of the passive air samplers (Melymuk et al., 2012). The model was assessed by comparing modeled and measured concentrations in air, surface films, precipitation, and tributaries (Diamond et al., 2010a; Gingrich et al., 2001; Melymuk et al., 2011; Melymuk et al., 2012; Wong et al., 2009) at various locations in the city. The model was used to quantify the emission rates per mass inventory for PCBs and PBDEs and the relative contributions of these emissions and air transport to urban air concentrations. SO-MUM was also used to estimate the multimedia urban fate of the emissions as well as transport to neighboring regions via air transport and surface waters. The model was also run under various inventory scenarios in order to assess the implications of removing primary chemical sources.

In summary, the one-box steady-state version of MUM was coupled to an air transport model which facilitated the extension of the model into a multi-box unsteady-state model. This resulted in a model that was used to estimate intra-urban scale PCB and PBDE emissions, relate emissions to spatially resolved mass inventories, estimate the travel distance of these chemicals outside of the city, and estimate effects of the urban area on Lake Ontario via air-lake exchange and surface water run-off. This application of a multi-box urban fugacity model enabled estimates of intra-urban PCB and PBDE emissions per chemical inventory and to pave the way for further studies relating chemical sources to chemical emissions.

1.6 Research Objectives

The following is a list of research objectives addressed in this thesis:

- Develop a general modeling method for use in estimating spatially resolved SVOC emissions from sources in urban areas.

- Use this modeling method to estimate PCB and PBDE emissions emanating from chemical inventories on a 5km scale in Toronto and investigate the contribution of primary versus secondary sources to total urban air emissions.

- Use the relationship between sources and emissions to investigate effects of inventory reduction removal strategies.

- Quantify the travel distance of the chemical plume traveling out of Toronto in terms of air concentration.
- Quantify the contribution of Toronto to PCB and PBDE loadings to Lake Ontario.

- Investigate how films and surface waters mediate non-air chemical transport from urban areas.

### 1.7 Thesis Outline

The bulk of this thesis consists of chapters taken from journal articles: one is published, one is submitted, and one is in preparation for submission.

- **Chapter 2: Modeling Urban Films Using a Dynamic Multimedia Fugacity Model**

  This chapter describes the extension of the steady-state version of MUM into an unsteady-state version and inclusion of recent developments in film and SVOC interactions with application to PCBs. It includes minor modifications from the original published document.


- **Chapter 3: SO-MUM: A coupled atmospheric transport and multimedia model used to predict intra-urban scale PCB and PBDE emissions and fate**

  This chapter outlines the modeling details of SO-MUM, the methods used to estimate spatially resolved intra-urban emissions, and an assessment of the model using both PCBs and PBDEs. The model is used to estimate the magnitude of primary emissions of PCBs and PBDEs from Toronto per unit inventory, per unit land area, and per capita.


- **Chapter 4: Modeling the influence of urban SVOC emissions on neighboring regions using a coupled multimedia and air transport model**
This chapter presents an analysis of urban fate, and contribution of urban emissions to surrounding regions including loadings to Lake Ontario. The model is used to compare primary and secondary emissions and to evaluate the effects of reducing PCB and PBDE inventories on total emissions.


- Chapter 5: Conclusions and Research Outlook

This chapter summarizes the main findings and scientific contributions and suggests research pathways for future work.

1.8 References


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Chapter 2
Modeling Urban Films Using a Dynamic Multimedia Fugacity Model

Co-authors: Miriam L. Diamond (University of Toronto), Louis J. Thibodeaux (Louisiana State University)

Contribution: S. Csiszar developed the film sub-model, coded it, produced and analyzed all the data, and wrote the manuscript. The research and manuscript were prepared under the supervision of M. Diamond; L. Thibodeaux provided feedback on the manuscript.

2 Abstract

A thin film coats impervious urban surfaces that can act as a source or sink of organic pollutants to the greater environment. We review recent developments in the understanding of film and film-associated pollutant behavior and incorporate them into an unsteady-state version of the fugacity based Multimedia Urban Model (MUM), focusing on detailed considerations of surface film dynamics. The model is used to explore the conditions under which these atmospherically-derived films act as a temporary source of chemicals to the air and/or storm water. Assuming film growth of 2.1 nm/d (Wu et al., 2008a), PCB congeners 28 and 180 reach air-film equilibrium within hours and days, respectively. The model results suggest that the film acts as a temporary sink of chemicals from air during dry and cool weather, as a source to air in warmer weather, and as a source to storm water and soil during rain events. Using the downtown area of the City of Toronto Canada, as a case study, the model estimates that nearly 1 g/d of $\sum_3$PCBs are transferred from air to film to storm water.

2.1 Introduction

Diamond and co-workers found that a thin film accumulates on impervious surfaces in urban and rural areas which is derived from atmospherically deposited and condensed species (Diamond et al., 2000a; Law and Diamond, 1998). Semi-volatile organic compounds (SVOCs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) have all been detected in films (Butt et al., 2004;
Gingrich et al., 2001; Unger and Gustafsson, 2008). The film is significant as it alters the surface characteristics of impervious surfaces and as a consequence it can mediate contaminant dynamics (e.g. Lam et al., 2005). This phenomena is especially important in urban areas where chemical emissions are numerous and impervious surfaces can cover up to 98% of dense urban areas with an even larger area on a 3-dimensional basis (Diamond and Hodge, 2007; Diamond et al., 2001).

The Multimedia Urban Model (MUM) of Diamond et al. (2001) and the models of Foster et al. (2006), Prevedouros et al. (2008), and Ashley et al. (2009) have included surface films. These models considered the film as a static compartment whereas the research of Wu et al. (2008a) has shown that films are dynamic as they grow thicker during dry periods and are washed off during rain events. In this paper, we review empirical information gathered on the nature and dynamics of films and chemicals associated with films. This information is incorporated into an unsteady-state extension of MUM (Diamond et al, 2010a) to investigate the source/sink nature of films in an urban area using PCBs in downtown Toronto, Canada as a case study.

2.1.1 Film Properties and Processes

Film thicknesses and growth rates are ~5 to ~12-20 times greater in urban than rural areas, respectively. Film thickness is on the order of nanometers on urban glass windows and growth rates on glass beads deployed at an urban site in Toronto were on the order of a few nm/day (Diamond et al., 2000b; Gingrich et al., 2001; Wu et al., 2008a). Film mass is dynamic as it grows with time but it also decreases during rain events via wash-off. The mechanism of film wash-off is presumed to be physical detachment of particles by the mechanical action of raindrops and secondarily by solubilization (Diamond et al., 2000b; Wu et al., 2008a). For example, Vaze and Chiew (2003) noted that rain intensity plays a larger factor in pollutant wash-off loads than total rain volume as the impact energy of rain drops is responsible for the amount of particles that can be dislodged from a surface. Furthermore, particle wash-off from urban surfaces is greatest during initial rainfall (Egodawatta et al., 2009; Vaze and Chiew, 2003). This is consistent with the findings of Eckley et al. (2008) who found that 52% of particle associated mercury was washed off within a 2 mm simulated rain event, Labencki et al. (In Prep.) who reported that average wash-off rates for PAHs were 59% based on a 0.75 mm
simulated rain event, and Diamond et al. (2000b) who reported that 72% of PCBs were washed off based on a simulated rain event of 0.45 mm.

The chemical composition of films reflects that of the atmosphere. Semi-volatile organic compounds such as PCBs, PBDEs, PAHs, OC pesticides, and PFCs have been measured in urban window films in North America, Europe, and Australia (Butt et al., 2004; Duigu et al., 2009; Gewurtz et al., 2009; Gingrich et al., 2001; Unger and Gustafsson, 2008). Following an urban-rural trend, PCB, PAH, and OC pesticide concentrations were 50, 30, and 11 times higher, respectively, in urban compared to rural films (Gingrich et al., 2001). The congener profiles of each compound class closely resembled that of atmospheric particles from which the film is derived.

Semi-volatile organic compounds, however, contribute to a minor fraction of the total organic composition of the film. Lam et al. (2005) and Simpson et al. (2006) studied the composition of films in Toronto and found them to contain ~5% organic carbon which, in turn, was comprised of 35%, 35%, 20%, and 10% carbohydrates, aliphatics, aromatics, and carbonyls, respectively. This is significant for film modeling as the organic carbon content of a material provides the sorptive capacity for partitioning characteristics with gas-phase compounds in air. These compounds are also “stickier” than inorganic compounds and as such could increase film growth due to the dry deposition of particles (by minimizing particle rebound). Lam et al. (2005) found that the non-organic constituents were 8%, 7%, and 18% sulfate, nitrate, and metals, respectively, and Duigu et al. (2009) also found that metals accounted for a significant mass of film in Brisbane, Australia. Urban surface films may be also contain black carbon which would increase the films’ sorptive capacity of chemicals which readily associate with black carbon, for example polycyclic aromatic hydrocarbons (Unger and Gustafsson, 2008).

Assuming that all organic compounds are available to partition between gas and condensed phases such as particles and film, we can then assume that chemical concentrations in films can be described by equilibrium partitioning between the gas phase in air and the organic fraction of the film (Diamond et al., 2001), similarly to that assumed for particulate matter (Harner and Bidleman, 1998). Wu et al. (2008b) derived an empirical relationship for the bulk film-air partition coefficient, $K_{fa}$ based on empirical studies with PCBs, as

$$\log(K_{fa}) = 1.1\log(K_{EVA-air}) - 1.2$$

where $K_{EVA-air}$ is the EVA-air partition coefficient (EVA
represents an ethylene vinyl acetate film). Using the average relationship based on four studies (as reported in (Wu et al., 2008b)) between the octanol-air partition coefficient, $K_{oa}$, and $K_{EVA-air}$ yields the following relationship between $K_{fa}$ and $K_{oa}$

$$\log(K_{fa}) = 1.1\log(K_{oa}) - 0.54.$$  \hspace{1cm} (2.1)

The partition coefficient between the film organic fraction and air is equal to $K_{fa}$ divided by the organic matter fraction of film ($f_{OM}$) (Wu et al., 2008b).

Limited information is available on chemical reaction rate constants on or in film, however, several studies have examined reactions on surrogate surface films (e.g. Finlayson-Pitts, 2009; Isidorov et al., 1997; Kwamena et al., 2007b; Shiraiwa et al., 2009). Donaldson et al. (2005) and Kahan et al. (2006) found that reactions of PAH with ozone in pure films made of oleic acid and squalene; and octanol or decanol on grease coated glass slides, respectively, can be a significant loss process, however film-associated reaction rate constants of PAH can be slower than on particles (Kahan et al., 2006; Kwamena et al., 2007a; Kwamena et al., 2004). Using measured rates, Kwamena et al. (2007a) modeled PAHs in order to explore the significance of degradation in film as a loss process compared to air advection and particle-associated degradation. They found that air advection was by far the dominant removal process from a highly urbanized (high impervious surface coverage) environment. However, reaction losses from films exceeded that from particles for higher mass, lower volatility PAHs by virtue of the chemical mass that partitioned into the film and because of the higher surface area of the film compartment compared to particle surfaces. Minimal information is available on reaction rate constants of PCBs associated with surface film. Atkinson (1996) reported that particle-phase PCB reaction rates were not significant compared to gas-phase reaction with OH radicals.

Further details about film properties and processes can be found in Diamond and Thibodeaux (2010).

2.2 Model Development

MUM (Diamond et al., 2010a; Diamond et al., 2001) is a steady-state version of a fugacity based model which divides the environment into seven compartments (upper and lower air, water, soil, sediment, vegetation, and surface film). The film compartment was previously
represented in MUM as a 100 nm thick layer that coats the 3-dimensional impervious surface area of the system. Film growth was not taken into account and rain wash-off was considered to be constant. Chemical that was washed off with the film was entirely transferred to the water compartment with no transfer to storm water or soil. These latter issues are addressed in the updated unsteady-state version of MUM that is presented here.

2.2.1 Film inter-compartmental interactions

The film compartment interacts with the air (bi-directional gas diffusion and wet and dry particle-phase deposition) and soil (one-way chemical transfer via film wash-off) compartments; and with storm water (one-way chemical transfer via film wash-off).

The transport processes between film and air are described by Diamond et al. (2001) as wet and dry particle deposition, wet gas deposition, and gas diffusion. The D-value for gas diffusion is given by

\[ D_v = \left[ \frac{1}{k_{af} A_f Z_a} + \frac{1}{k_{ff} A_f Z_f} \right]^{-1} \]  

where \( k_{af} \) and \( k_{ff} \) are the air- and film-side mass transfer coefficients (m h\(^{-1}\)), respectively, \( A_f \) (m\(^2\)) is the film area, and \( Z_a \) and \( Z_f \) are the Z-values (mol m\(^{-3}\) Pa\(^{-1}\)) for air and dissolved phase of the film, respectively. Premier and Diamond (2002) expressed \( k_{af} \) as the ratio of the diffusivity and boundary layer thickness, \( \delta^{bl} \) (m), which depends on wind speed, as such

\[ \delta^{bl} = \beta \sqrt{\frac{l}{v}} \]  

where \( v \) is wind speed (m/s), \( l \) (m) is the mean surface length in the wind direction, and \( \beta \) is given a value of 0.006 m s\(^{-1/2}\).

As discussed above, chemical wash-off is a bulk removal process. Wash-off studies suggest that the process can be modeled using a simple wash-off efficiency, \( W_E \), such that \( W_E \)% of chemical and film are washed-off for any given rain event (see Equation (2.11) below). The next factor to consider is the fraction of rain water delivered to storm water which has been well studied for the purpose of municipal hydrological planning (e.g. Chen and Adams, 2007; Goldshleger et al., 2009; Mueller and Thompson, 2009). Goldshleger et al. (2009) studied 800 rain events on three
continents to derive a relationship to describe the runoff ratio, $R$, which is defined as the ratio of the volume of urban runoff to the water volume of the rain event. The relationship is based on fraction of two-dimensional impervious surface area, $x$, such that

\[
R = \begin{cases} 
0; x < 0.2 \\
2x - 0.4; 0.2 \leq x \leq 0.4 \\
x; x > 0.4
\end{cases}
\]

(2.4)

This relationship is simple and should provide a reasonable approximation although it does not account for factors such as depression storage and soil type (Chen and Adams, 2007; Dayaratne and Perera, 2004). We apply $R$ and $(1-R)$ to represent the fraction of film that is transferred to storm water and to soil, respectively. This formulation is an approximation as it neglects the fraction of rain water that evaporates or is subject to surface storage (Chen and Adams, 2007; Dayaratne and Perera, 2004; Mueller and Thompson, 2009).

### 2.2.2 Model Equations

Incorporating the information described above, the pertinent model equations are updated from Diamond et al. (2010a; 2001) as follows. The general mass balance fugacity equations for air (a), upper air (ua), water (w), soil (s), sediment (se), vegetation (v), and film (f) are

\[
\frac{dm_i}{dt} = \frac{d(Z_i V_i f_i)}{dt} = E_i + \sum_{i \neq j} (D_{ji} f_j) - D_{ii} f_i \quad i = a, ua, w, s, se, v, f
\]

(2.5)

where $m_i$, $V_i$, $Z_i$, $f_i$, $E_i$, and $D_{ii}$ are the mass, volume, bulk Z-value (mol m$^{-3}$ Pa$^{-1}$), fugacity (Pa), emission source or sink (mol h$^{-1}$), and total loss D-values (mol h$^{-1}$ Pa$^{-1}$) respectively, for compartment $i$; and $D_{ji}$ is the D-value for chemical transfer from compartment $j$ to $i$ by gas- and particle-phase transport. These equations can be generalized into matrix form by defining a mass vector, $\overline{M}$ as

\[
\overline{M} = (V_a Z_a f_a, V_{ua} Z_{ua} f_{ua}, \ldots, V_f Z_f f_f) \text{ T}
\]

(2.6)

and by expressing the mass balance equations as

\[
\frac{d\overline{M}}{dt} = \overline{AM} + \overline{E}
\]

(2.7)
where $\mathbf{A}$ is a $7 \times 7$ matrix consisting of the $-D_{ij}$ values on the diagonal and the $D_{ji}$ values on the off-diagonal; and $\overline{E}$ is the vector of sources and sinks. We solved Equation (2.7) by discretizing it using the implicit Euler approach with $t_n = n \Delta t$, where $n$ and $\Delta t$ represent the time step number and length of a time step (set to a constant 5 min.), respectively. We use the convention where $t_n$ represents the current time and $t_{n+1}$ represents one time step into the future. Applying the implicit Euler approximation to Eqn. (2.7) results in the following relationship

$$
\frac{\bar{M}^{n+1} - \bar{M}^n}{\Delta t} = \mathbf{A}^{n+1} \bar{M}^{n+1} + \bar{E}^{n+1} + \bar{S}^n
$$

(2.8)

where we have added an additional source/sink vector, $\bar{S}$ to represent processes that are modeled to occur at the beginning of the time step. Implicit Euler would require evaluation of all sources/sinks at the future time step, $t_{n+1}$, however, due to the nature of film wash-off, it is necessary to evaluate this process at the present time step, hence the source/sink term evaluated at $t=t_n$ was introduced and will be discussed in further detail below. The vector, $\bar{E}$ is given by

$$
\bar{E} = (E_a, E_{ua}, E_w, E_s, E_{sc}, E_r, E_f)^T
$$

(2.9)

where $E_i$ represents the emission source to compartment $i$ and was non-zero only for the air and upper air compartments in the current application. The implicit solution to Eqn. (2.8) is then

$$
\left[ \frac{\mathbf{I}}{\Delta t} - \mathbf{A}^{n+1} \right] \bar{M}^{n+1} = \frac{\bar{M}^n}{\Delta t} + \bar{E}^{n+1} + \bar{S}^n
$$

(2.10)

where $\mathbf{I}$ is the identity matrix and the matrix $\mathbf{A}^{n+1}$ is known as it contains the model D-values which can be calculated at any time step, hence the only unknown in Equation (2.10) is $\bar{M}^{n+1}$.

The vector, $\bar{S}$, is necessary to model the film wash-off process which is described as follows. The volume of the film compartment, $V_f$ (m$^3$) is dynamic and can be expressed as

$$
V_f(t) = A_f \left( 1 - W_E \right) (\theta_0 + at)
$$

(2.11)
where $A_f$ ($m^2$) is the film area, $W_f$ is the wash-off efficiency, $\theta_0$ (m) is the initial film thickness, and $a$ (m h$^{-1}$) is the film growth rate. The change in chemical mass in film over time under dry conditions of film growth is given by

$$\frac{d(Z_f V_f f_f)}{dt} = -(D_{ja} + D_{rf}) f_f + D_{af} f_a$$

(2.12)

as described in Eqn. (2.5). At the beginning of a rain event, however, there is an explicit, instantaneous loss of film and film-associated chemical. As the film (and associated chemical) loss process is assumed to occur via instantaneous wash-off, it does not follow the traditional D-value process used in fugacity models. In order to model this process, we assume that the wash-off occurs at the beginning of the time step and, hence is a function of the initial (i.e. at $t=t_0$) chemical fugacity in film and film volume. We can then represent the change in chemical mass in film due to wash-off as a rate, $W_m$ (mol h$^{-1}$) by assuming that the process occurs over the model time step, $\Delta t$, as

$$W_m = \frac{Z_f V_f f_f}{\Delta t}$$

(2.13)

where $V_{fw}^n$ is the volume of film washed-off at $t=t_n$, $V_{fw}^n = W_f V_f^n$. The discretized mass balance for film during a rain event then becomes

$$\frac{(m_{f}^{n+1} - m_{f}^{n})}{\Delta t} = -(D_{ja} + D_{rf}) f_{f}^{n+1} + D_{af} f_{a}^{n+1} - W_{m}^{n}.$$  

(2.14)

Similarly, the discretized mass balance for soil is updated to receive chemical from film during a rain event as follows

$$\frac{(m_{s}^{n+1} - m_{s}^{n})}{\Delta t} = -(D_{sa} + D_{sw} + D_{sv} + D_{sg} + D_{Rs}) f_{s}^{n+1} + D_{as} f_{a}^{n+1} + D_{vs} f_{v}^{n+1} + (1 - R) W_{m}^{n}$$

(2.15)

where R is the runoff ratio as described in Equation (2.4) and $D_{sg}$ refers to the movement of dissolved-phase chemical from soil to groundwater due to leaching. The vector, $\overline{S}^n$, in Eqn. (2.10) at the beginning of a rain event is therefore given by

$$\overline{S}^n = (0,0,0,(1 - R) W_{m}^{n},0,0,-W_{m}^{n})^T$$

(2.16)
and is zero otherwise.

As mentioned above, air-to-film exchange processes in the previous model version included wet and dry particle deposition, wet gas deposition, and gas diffusion. However, during the unsteady-state simulation when the air concentration is depleted via atmospheric wash-out processes and film concentrations increase due to receiving the wash-out, a net film-to-air transfer results. In reality it is more likely that chemical deposited on film due to rain is transferred immediately to storm water and as such, has been incorporated into the model as an air-film-storm water D-value, $D_{a,sw}$ as follows

$$D_{a,sw} = R(D_{wf} + D_{qf})$$

where $D_{wf}$ and $D_{qf}$ are the wet gas and particle deposition D-values to film, respectively, and $R$ is the runoff ratio. Air-to-vegetation transfer during rain events is also modeled using a similar process (Prevedouros et al., 2008) (equations are in Tables A1.1 and A1.2).

Finally, we added storm water as a chemical sink since it receives chemical from film. The chemical mass transferred from film to storm water at the beginning of a rain event at $t=t_n$ is given by $RW_m^n \Delta t$. The chemical that is transferred to storm water then becomes available for transport into sanitary and/or storm water collection systems, and from there into surface water bodies. Complete model equations can be found in Appendix 1 (i.e. mass balance equations, D-values, and Z-values).

### 2.2.3 Model Parameterization

The unsteady-state model was parameterized to reflect downtown Toronto (~3% of City of Toronto area) as described by Diamond et al. (2010a) where the area is comprised of 61% impervious surface, 38% soil and vegetation, and 1% water, and was run under summer-fall conditions (18°C). Environmental parameter values such as compartmental areas and depths are described in Table A1.6.

A film growth rate of 2.1 nm/day was assumed which is the median value for urban areas reported by Wu et al. (2008a). Wash-off efficiency, $W_E$, was set to 60% which is the average value from empirical wash-off data (Diamond et al., 2000b; Eckley et al., 2008; Labencki et al.,
However, applying a single wash-off efficiency results in the film thickness never reaching zero and therefore the film can grow infinitely in the model. In order to resolve this issue we assumed that during high rain intensity events the film thickness is reduced to ~0, as observed by Wu et al. (2008a). We defined storm or high rain intensities to be greater than or equal to 10 mm/h (American Meteorological Society, 2000; United Kingdom Met Office, 2007). We assumed that the reaction rate constant in the film compartment was 10% of the gas-phase reaction rate constant and also set the reaction rate constant on vegetation to that of the film compartment as done by Prevedouros et al. (2008) due to lack of data available on vegetation reaction rate constants. The $K_{fa}$ and $K_{oa}$ relationship in Equation (2.1) was applied assuming a film organic matter content of 7.5% (Liu et al., 2003). Additional parameters used in the model are listed in Appendix 1.

As the model is unsteady-state, the fugacities in all compartments must be initialized which was done using results from the steady-state version of MUM. We did this according to the parameterization described by Diamond et al. (2010a) for summer conditions. The model was run for 10 d to allow values to stabilize. Back-calculated emissions (rounded to the nearest unit emission) from the steady-state version of MUM were used as emissions for the dynamic simulation. Initial concentrations and unit emissions can be found in Table A1.7.

### 2.2.4 Model Application

We investigated various characteristics and applications of the model including film dynamics, the source/sink nature of films, and multimedia dynamics using PCBs as test chemicals. We first explored the model's ability to reproduce film growth and wash-off processes. The model was run for 80 d with various rain intensities starting with an initial zero film thickness. The rain intensities were adapted from Wu et al. (2008a) who measured film thickness over time as a function of total rain. Next, we used the model to calculate the time required for PCB concentrations to reach steady state as a function of wind speed. We used an initial film thickness of 100 nm, a starting film concentration of zero, and initial lower air concentrations of 28 and 4 pg m$^{-3}$ (CB-28 and -180, respectively), and varied wind speed ($v$ in Eqn. 2.3) between 0.0125 (low) to 4 (high) m s$^{-1}$.

We also investigated the source/sink nature of films. The importance of film as a source to air or as a sink from air was investigated by running the model over a 5 d dry period at
temperatures ranging from 0 to 45 °C and summing the net air-to-film exchange rate. Two scenarios were investigated: one in which the initial film concentration was set to zero and the other in which the initial concentration was non-zero (Table A1.7). The effect of a rain event on net air-to-film exchange was also investigated. We ran a 5 d simulation with an initial non-zero film concentration and specified a light (<10 mm/h) or heavy (>10 mm/h) rain event lasting 2 h beginning at the 12th hour of the simulation. The simulation was under dry conditions at all other time steps. The net air-film exchange was then summed over a 5 d period to assess the overall effect of the rain event over this period of time.

Various factors affect the amount of chemical washed off with film such as impervious surface area and antecedent dry time. We investigated the effects of these factors by individually varying these parameters and analyzing the amount of chemical transferred to soil and storm water during a rain event. We also tested the effect of film growth rate on chemical accumulation (over 30 d) by varying the rate from 0.5 to 4 nm/day based on experiments conducted by Wu et al. (2008a) in urban and rural areas. The same initial compartmental concentrations and lower air emission rate (1 mmol h⁻¹) were used for both congers.

Finally, the model was applied to downtown Toronto as a case study in order to estimate chemical loadings to Lake Ontario (on which Toronto is situated) via film runoff into storm water. The simulation was run for the month of September. In order to isolate the effect of intermittent precipitation on film growth rate and chemical dynamics in the film, the following parameter values were kept constant: wind speed, temperature, and particulate matter concentrations. Inflow and urban PCB air concentrations reported by Motelay-Mossei et al. (2005) were used to initialize the model. All other parameters are described by Diamond et al. (2010a) for downtown Toronto (Table A1.5) in the fall. Total daily precipitation data (Environment Canada, 2010) for September 2000 (Fig. A1.4) was converted to daily rain rates by assuming that rain events were of 2 h duration (Fig. A1.5). Chemical transfer was summed over every time step of 5 min. for the month for five PCB congers: 28, 52, 101, 153, and 180 (Fig. 2.4).
2.3 Results and Discussion

2.3.1 Film Dynamics

The model reproduced the phenomena of linear growth during dry periods and thickness reduction during rain events (Figure 2.1). During light to medium rain events of <10 mm/h, the film thickness decreased by 60%, whereas during heavy rain events of >10 mm/h the film volume went to nearly zero. The model estimated a final film thickness of ~45 nm after nine rain events in comparison to 10 nm after 12 rain events, as reported by Wu et al. (2008a) which is reasonable given the lack of detailed information on daily film growth rates.

The model predicted that CB-28 and -180 reached equilibrium between air and film within hours and days, respectively for the range of modeled wind speeds and initial film thickness of 100 nm (Figure 2.2). CB-28 reached 95% equilibrium within ~34 and ~2 h at the low and high wind speeds, respectively. CB-180 failed to reach equilibrium within 80 d at the low wind speed and 95% of equilibrium was reached within ~40 d at 4 m/s. The results are consistent with those of Harner et al. (2003) who found that CB-28 took longer to equilibrate between the gas phase and 570 nm thick EVA-coated glass cylinders under a 'no wind' scenario than at a wind speed of 4 m/s and that CB-153 failed to reach equilibrium within 21 d under both wind scenarios.

2.3.2 Films as a source or sink

Model results showed that the direction of air-film exchange is controlled by environmental conditions. Over a 5 d period, when the initial PCB concentration in film was set to zero net air-to-film exchange prevailed (results not shown) as the PCBs in film increased in fugacity and either reached equilibrium with air (CB-28) or strove to reach equilibrium (CB-180), regardless of temperature. However, when the initial PCB concentration in film was non-zero (see Table A1.7), the film acted as a source to air at temperatures above 20 °C and 25 °C (Figure A1.1a,b) for CB-28 and -180, respectively. A situation where an initial PCB film fugacity may be high enough to cause film-to-air volatilization may occur after cool and dry conditions during which SVOCs can accumulate in film, followed by warmer conditions. This is analogous to the findings of Hornbuckle and Eisenreich (1996) who measured a diurnal pattern in PCB air concentrations over a remote bog where the concentrations where found to be higher in the early
morning compared to those in the afternoon. They attributed this to warm daytime temperatures causing vegetation-to-air transfer of PCBs that had deposited during the previous cool night.

Contrary to the results found under dry conditions, net chemical transfer from air to film was predicted for CB-28 at all temperatures because its fugacity in air decreased during the rain event and this congener equilibrates quickly between air and film. Conversely, at >35 °C net exchange of CB-180 was still from film to air which was likely due to its slower equilibration time with air (Fig. A1.1a,b). We therefore conclude that, in general, film will most likely act as a source of chemical to air under warm and dry conditions and as a sink at lower temperatures and during and after rain events.

The model predicted that increasing impervious surface area or antecedent dry time increased the amount of chemical washed off from films. Because of the linearity of the model, increasing impervious surface area of the model domain resulted in a linear increase in wash-off of CB-28 and -180, i.e., an impervious surface area of 90% resulted in ~9 times more chemical wash-off than an impervious surface area of 10% (Figure A1.2 a,b). The consequence of impervious surface coverage is that the greater the coverage, the greater the loadings to storm water. As expected, antecedent dry time also increased the amount of chemical transferred from film during a rain event (Fig. A1.2) due to the time available for film growth and chemical accumulation.

Increasing film growth rate increased the mass of PCB in the film. The mass accumulation rate as a function of film growth rate was 0.006 and 0.5 mmol nm⁻¹ d⁻¹ for CB-28 and -180 during a 30 d dry simulation, respectively (Figure A1.3). More mass of CB-180 accumulates in film than CB-28 because of the former’s higher K_{oa}. We further investigated the effect of K_{oa} and film growth rates by running a 90 d dry simulation at 5 and 25°C (Figure 2.3). Similarly to relationships of gas-particle partitioning, at values of LogK_{oa} <7.5-8.5 (depending on temperature) the accumulated mass was independent of K_{oa} values because virtually all chemical is in the gas phase in air, not in film. At larger values of K_{oa} the mass accumulated rose sharply until an asymptote was reached at K_{oa} of ~11.5-12 at which point virtually all chemical enters the film sorbed to particles (via the particle deposition D-value and is assumed to be henceforward in equilibrium with the dissolved phase of the film). Thus, not surprisingly, K_{oa} controls chemical loadings to film and hence storm water. In reality, chemicals with high
Koa’s will accumulate in the film due to particle deposition rather than diffusion, but air-particle exchange is governed by the same slow phase exchange kinetics (Pankow and Bidleman, 1992).

### 2.3.3 Multimedia Dynamics

The model can be used to estimate chemical loadings to neighboring water bodies via film runoff into storm water as we demonstrated here using downtown Toronto as a case study. Most PCBs entering the city via upwind advection and direct emission from the city were advected out of the system by air (in this case 98%). The remainder was lost via transfer to the city (~2%) or reaction (~0.1%). Of the compartments that received chemical from the air, film received the largest amount (~64%) followed by vegetation (~22%) and only ~1% was directly deposited to urban rivers. Of the chemical that was transferred to film, ~23 g and ~16 g were transferred to storm water and soil, respectively, in the 1 month period. The PCB concentration in the film at the final step of the simulation after ~6 dry days was ~6 ng/m² for Σ₃PCB which can be approximately scaled to 35 ng/m² for Σ₆₈PCB based on PCB film profiles (Gingrich et al., 2001). This compares to film concentrations measured by Gingrich et al. (2001) with a geometric mean of 95 ng/m² for Σ₁₀³PCB, noting that the model concentration was reported ~6 d after a rain event (Figure A1.5) in comparison to Gingrich et al. (2001) for which film accumulation was measured after weeks to months of accumulation. The film concentrations for the entire model period can be found in Figure A1.5.

We compared the unsteady-state results to those of the steady-state version of MUM in order to understand the implications of the time-dependent behavior of films described here. The steady-state version was run for the same 5 PCB congeners over the same conditions as described above with a constant film thickness of 100 nm and a rain rate of 0.1 mm/h corresponding to the average rate used in the model. The overall pattern of chemical fate was very similar to that of the steady-state version. Finally, approximately scaling the unsteady-state downtown monthly storm water transfer to Σ₆₈PCBs yields a loading of ~5 g/d which compares to ~22 g/d for Σ₈₁PCBs found by Diamond et al. (2010b) in the City of Toronto, indicating that film wash-off is a likely contributor to urban surface water loadings.
2.4 Conclusions

The Multimedia Urban Model was revised to simulate unsteady-state conditions of the growth and wash-off of films on impervious surfaces. The film mediates chemical movement between air and storm water. Model results suggested that the time to reach air-film equilibrium for PCB-28 and 180 varies from hours to days at wind speeds of 0.01 to 4 m/s assuming an air temperature of 18°C. Films accumulate chemicals with Log\(K_{oa}\) > 7.5, especially at high film growth rates. Thus, films act as a sink for atmospheric chemicals at low to medium temperatures, and acts as a source to air at higher temperatures. Film wash-off converts the film into a source to storm water, particularly following dry periods during which the film grows and accumulates chemical, where growth rates are highest in densely urbanized areas. Model simulations show that a chemical’s \(K_{oa}\) controls film accumulation even though the time to equilibration increases as a function of \(K_{oa}\). Introducing the unsteady-state treatment of film growth and wash off adds to our ability to consider urban contaminant dynamics.

Acknowledgements

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2.5 Figures

Figure 2.1 Modeled film thickness versus rain intensity using a hydrograph similar to the one presented in Wu et al. 2008a.
Figure 2.2 Modeled film concentration versus time for (a) CB-28 and (b) CB-180 over varying wind speeds used to calculate the air-side air-film mass transfer coefficient, $k_{af}$. 
Figure 2.3 Modeled mass accumulated in film at varying values of $\log K_{oa}$ over a 90 dry day simulation at various film growth rates (nm/d) at (a) 5 °C and (b) 25 °C.

Figure 2.4 Fate of $\sum_5$PCB (28, 52, 101, 153, 180) over a one month period in September; units are in grams.
2.6 References


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2.7 Addendum

After publication of this manuscript it came to our attention that the vertical wind velocity used
in the case study calculation was unrealistic. We thus re-ran the simulation using the average
vertical wind speed calculated by BLFM for the City of Toronto. These are the corrected results
and figures.

2.3.3 Multimedia Dynamics

The model can be used to estimate chemical loadings to neighboring water bodies via film
runoff into storm water as we demonstrated here using downtown Toronto as a case study.
Most PCBs entering the city via upwind advection and direct emission from the city were
advected out of the system by air (in this case 98%). The remainder was lost via transfer to the
city (~2%) or reaction (~0.1%). Of the compartments that received chemical from the air, film
received the largest amount (~67%) followed by vegetation (~30%) and only ~0.4% was
directly deposited to urban rivers. Of the chemical that was transferred to film, ~5 g and ~4 g
were transferred to storm water and soil, respectively, in the one month period. The PCB
concentration in the film at the final step of the simulation after ~6 dry days was ~7 ng/m² for
$\Sigma_{5}$PCB which can be approximately scaled to 27 ng/m$^2$ for $\Sigma_{68}$PCB based on PCB film profiles (Gingrich et al., 2001) with a range in modeled film $\Sigma_{68}$PCB concentrations of ~2-120 ng/m$^2$. This falls within the range of film concentrations measured by Gingrich et al. (2001) with a geometric mean of 95 ng/m$^2$ (4-5800 ng/m$^2$) for $\Sigma_{103}$PCB, noting that the final modeled concentration was reported ~6 days after a rain event (Figure S5) in comparison to Gingrich et al. (2001) for which film accumulation was measured after weeks to months of accumulation. The film concentrations for the entire model period can be found in Figure S5.

We compared the unsteady-state results to those of the steady-state version of MUM in order to understand the implications of the time-dependent behavior of films described here. The steady-state version was run for the same 5 PCB congeners over the same conditions as described above with a constant film thickness of 100 nm and a rain rate of 0.1 mm/h corresponding to the average rate used in the model. The overall pattern of chemical fate was very similar to that of the steady-state version. Finally, approximately scaling the unsteady-state downtown monthly storm water transfer to $\Sigma_{68}$PCBs yields a loading of ~1 g/d compared to ~22 g/d for $\Sigma_{81}$PCBs tributary input found by Diamond et al. (2010b) in the City of Toronto, indicating that film wash-off likely contributes to urban surface water loadings.

Figure 2.5 Fate of $\Sigma_{5}$PCB (28, 52, 101, 153, 180) over a one month period in September. Units are in g/d; solid lines refer to transport, dotted lines refer to transformation, and the
curved arrow refers to emission. As the model is unsteady-state, the change in mass in each compartment is indicated in brackets.
Chapter 3

SO-MUM: A coupled atmospheric transport and multimedia model used to predict intra-urban scale PCB and PBDE emissions and fate

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Contributions: S. Csiszar developed the method to couple the models and adapted MUM for coupling to BLFMAPS and provided all the coding for this. She ran the model to produce and analyze all the computational data. The PCB inventory was provided by Diamond et al. (2010) and the PBDE inventory calculations were mainly performed by S. Verkoeyen and A. Giang (under the supervision of S. Csiszar) with some additional calculations by S. Csiszar. S. Csiszar wrote the manuscript. The research and manuscript were prepared under the supervision of M. Diamond; S. Daggupaty provided the code for BLFMAPS and editorial comments for the manuscript.

3 Abstract

A spatially resolved, dynamic version of the Multimedia Urban Model (MUM) and the boundary layer forecast and air pollution transport model BLFMAPS, were coupled to build Spatially Oriented MUM (SO-MUM), to estimate emissions and fate of POPs in an urban area on a 5×5 km^2 cell resolution. SO-MUM was used to back-calculate emissions from spatially resolved measured air concentrations of PCBs and PBDEs (Melymuk et al., 2012) in Toronto, Canada. Estimated emissions of Σ_52 PCB were ~230 (40-480) kg y^{-1}, 280 (50-580) g y^{-1} km^{-2}, or 90 (16-190) mg y^{-1} capita^{-1} and Σ_{26} PBDE were 28 (6-63) kg y^{-1}, 34 (7-77) g y^{-1} km^{-2} or 11 (2-25) mg y^{-1} capita^{-1}. A mass inventory of penta- and octa-BDEs in Toronto was estimated to be ~200 tonnes (90-1000 tonnes) or ~80 (40-400) g capita^{-1}. Using this estimate and that of 437 (282-796) tonnes for PCBs (Diamond et al., 2010), estimated emissions of Σ_{98} PCB and Σ_{26} PBDE were 0.4 (0.05-1.6) and 0.1 (0.01-0.7) g kg^{-1} inventory y^{-1}, respectively. The results suggest annual emission rates of 0.04% and 0.01% from the inventory with downtown accounting for ~30% and ~16% of Toronto’s inventory and emissions for PCBs and PBDEs, respectively. Per inventory emission rates were negatively related to vapor pressure within a compound class, but not consistently when considering all compound congeners.

3.1 Introduction

As laid out by the Stockholm Convention on Persistent Organic Pollutants (POPs) and the Convention on Long-Range Transboundary Air Pollution (UNECE CLRTAP), a necessary step
towards controlling POPs in the environment is identifying emission sources (Stockholm Convention, 2009; UNECE, 2012). Emission sources have been calculated using two main methods. The first method uses activity-specific emission factors and the second uses an aggregate estimate such as emissions on a per capita basis. The advantage of developing emission estimates based on activity-specific emission factors is the ability to clearly identify the activity or sector contributing most to emissions. Perhaps the best examples of emission estimates that use emission factors are those for polychlorinated dibenzodioxins and furans (PCDD/F), polycyclic aromatic hydrocarbons (PAH) and mercury (Pirrone et al., 1996; Marr et al., 1999; Gullett et al., 2003). Extensive measurement programs have produced series of well vetted emission factors, e.g., mass of PAH emitted per tonne of municipal solid waste incinerated or wood burned (Dyke et al., 2003; Gullett et al., 2003). Emission factors for other POPs such as PCBs and PBDEs are less well studied and more uncertain (Breivik et al., 2002; Alcock et al., 2003; Prevedouros et al., 2004; Breivik et al., 2006; Moeckel et al., 2010).

Several studies have developed aggregate urban emission estimates for PCBs (Gasic et al., 2009; Diamond et al., 2010; Gasic et al., 2010; Morselli et al., 2011) and PBDEs (Jones-Otazo et al., 2005; Moeckel et al., 2010) at specific locations, expressed on an aerial and/or per capita basis. This approach has typically relied on inverse mass balance modeling and air measurements to derive their estimates. While this method is arguably less data intensive than using emission factors, it has not been specifically connected to chemical inventories or activities and, as such, is less useful for focusing source reduction efforts than using activity-specific emission factors. Furthermore, Breivik et al. (2002) suggested that combining inverse modeling and mass inventories could be used to connect emissions and usage.

Elevated urban air concentrations of PCBs persist despite bans on new production passed some 40 years ago in the late 1970s in many western countries, and global agreements to ban production, new uses, and promotion of efforts to eliminate stocks (Jaward et al., 2004; Diamond et al., 2010). PBDEs have been controlled recently, with complete bans of penta and octa mixtures by 2004 in Europe and 2008 in Canada (Ward et al., 2008). Salamova and Hites (2011) estimated that PBDE air concentrations are decreasing in Great Lakes air with a halving time of 5-7 years.
Several lines of evidence suggest that primary, rather than secondary emissions dominate PCB air concentrations, at least in urban and industrial areas where concentrations are highest (Robson and Harrad, 2004; Hung et al., 2005; Gioia et al., 2006). Primary PCB emissions can originate from open sources such as building sealants, light ballasts, paint and floor coatings, and inadvertent releases from closed sources (Breivik et al., 2002; Diamond et al., 2010). For PBDEs, elevated air concentrations have been related to releases from indoors that have PBDE-containing consumer products such as electronics, furniture, textiles, and plastics (Hazrati and Harrad, 2006; Allen et al., 2008; Batterman et al., 2009; Zhang et al., 2011; Björklund et al., 2012). Furthermore, Melymuk et al. (Submitted) have shown a link between outdoor PBDE air concentrations and building volumes and dwelling counts as surrogates for the inventory of PBDE-containing products.

Diamond et al. (2010) reported a PCB stock of 437 (282-796) tonnes in Toronto, Canada and used the one-box, steady-state (SS) version of the Multimedia Urban Model (MUM), to estimate emissions of 90-880 kg y^{-1} originating from the city; the emissions were back-calculated from measured outdoor air concentrations. The weakness of the one-box model is that spatial heterogeneity cannot be captured (Gasic et al., 2010; Hollander et al., 2012) nor can emissions be linked to a spatially variant inventory. Hence, we have extended this relatively simple version of MUM into a multi-box, unsteady-state (USS) version of MUM and coupled it to BLFMAPS (Boundary Layer Forecast Model and Air Pollution Prediction System) (Daggupaty et al., 2006), which is a chemical air transport model. We call the coupled model Spatially-Oriented MUM or SO-MUM.

We illustrate the use of SO-MUM with PCBs and penta- and octa-BDEs, using measured outdoor air concentrations from Melymuk et al. (2012) to back-calculate air emissions (Jones-Otazo et al., 2005; Gasic et al., 2009; Diamond et al., 2010; Morselli et al., 2011). The goal of this application is to estimate aggregate emissions of these two compound groups, expressed on a city-wide, aerial, inventory and per capita basis. The advantage of this method is the ability to estimate inventory-based intra-urban emissions and to account for spatially variable fate and concentrations. Furthermore, SO-MUM sets up a framework to further understand how emissions are transported within and from urban areas where chemicals can be further mobilized to the surrounding environment (Csiszar et al., In Prep.).
3.2 Methods

3.2.1 Model Descriptions

MUM is a single-box 7-compartment (air, upper air, water, soil, sediment, vegetation, and film) fugacity mass balance model (Diamond et al., 2001; Diamond et al., 2010). Csiszar et al. (2012) extended MUM into an unsteady-state version which takes into account the dynamic nature of films that develop on impervious surfaces. The general unsteady-state mass balance equation for each compartment is

\[
\frac{dm_i}{dt} = \frac{d(Z_iV_if_i)}{dt} = E_i + \sum_{i,j} (D_{ji}f_j) - D_{Ti}f_i \quad i = a, ua, w, s, se, v, f
\]

where \(m_i\) (mol), \(V_i\) (m\(^3\)), \(Z_i\) (mol m\(^{-3}\) Pa\(^{-1}\)), \(f_i\) (Pa), \(E_i\) (mol h\(^{-1}\)), and \(D_{Ti}\) (mol h\(^{-1}\) Pa\(^{-1}\)) are the mass, volume, bulk Z-value, fugacity, specified emission source or sink, and total loss D-value (transport and transformation), respectively, for compartment \(i\); and \(D_{ji}\) (mol h\(^{-1}\) Pa\(^{-1}\)) is the inter-compartmental transfer D-value of chemicals from compartment \(j\) to \(i\) (see Csiszar et al. (2012) for further details). Equation 3.1 was solved simultaneously for each compartment using the Implicit Euler approximation as follows

\[
Z_i^{n+1}V_i^{n+1}f_i^{n+1} - Z_i^nV_i^nf_i^n = E_i^{n+1} + \sum_{i,j} (D_{ji}^{n+1}f_j^{n+1}) - D_{Ti}^{n+1}f_i^{n+1}
\]

with \(t_n = n\Delta t\), where \(\Delta t\) is the time step, which was set to 5 minutes to match the time step of BLFMAPS. We used the convention whereby \(t_n\) represents the current time and \(t_{n+1}\) represents one time step into the future. In order to couple the model to BLFMAPS, the upper air compartment of MUM was removed and, accordingly, the number of mass balance equations was reduced from seven to six. BLFMAPS (Daggupaty et al., 2006) is a modified version of the Boundary Layer Forecast Model (BLFM) (Daggupaty et al., 1994) which is a meteorological prediction model. BLFM was extended from its first version (Daggupaty et al., 1994) to form the air pollution prediction system, BLFMAPS, by including atmospheric transport, diffusion, and deposition for atmospheric pollutants such as particulate metals and trace substances (Daggupaty et al., 2006). Ma et al. (2003) used BLFMAPS to study Lindane transport from the Canadian Prairies in order to assess the effects of Lindane on the Great Lakes.
As a mesoscale atmospheric model used to simulate boundary layer flow over heterogeneous terrain, BLFM predicts three-dimensional land and water induced air circulation, temperature, and turbulence parameters in the model domain that includes a 5×5 km² horizontal grid resolution over Southern Ontario. In the vertical, it has 10 non-uniformly distributed levels at 0, 1.5, 3.9, 10, 100, 350, 700, 1200, and 2000 m above ground with the top level at 3000 m above ground. The model considers 37 land use categories from the United States Geological Survey (Daggupaty, 2001). BLFM uses twice daily objectively analyzed weather data from Environment Canada’s Global Environmental Multi-scale Model (GEM). The model’s meteorological data are updated and initialized on every 12th hour from which BLFM predicts wind velocities, temperatures, and other meteorological variables as a function of the three dimensional space of the model domain for the next 12 hour period, with a time integration step of 5 minutes.

In BLFMAPS chemical transport is modeled by the following equation

\[
\frac{\partial C_a}{\partial t} = -\vec{v} \nabla C_a - w_z \frac{\partial C_a}{\partial z} + k_h \nabla^2 C_a + \frac{d}{dz} \left( k_z \frac{\partial C_a}{\partial z} \right) + (E - S) - \eta C_a \tag{3.3}
\]

where \( C_a \) is the air concentration; \( t \) is time; \( w_z \) is the vertical velocity in terrain following coordinates; \( z_z = z - h(x,y) \) (where \( z \) is height and \( h(x,y) \) is surface elevation); \( k_h \) and \( k_z \) are the horizontal and vertical eddy diffusivities, respectively; \( E \) and \( S \) are concentration fluxes due to emission and deposition, respectively; and \( \eta \) is the degradation rate of the chemical in air. This equation is solved with a 5 minute time-step using a finite-difference approximation (Ma et al., 2003; Daggupaty et al., 2006).

### 3.2.2 Coupled Model: SO-MUM

In order to couple the models, the one-box version of MUM was extended into a multi-box model with cells corresponding to the size (5×5 km²) and locations of the cells in BLFMAPS. The upper air compartment in MUM was replaced by BLFMAPS and inter-cell air transport was modeled by BLFMAPS. Equation 3.3 was modified so that BLFMAPS modeled bulk air advection and diffusion in the horizontal and vertical directions, as well as chemical input via emission, as follows.
\[ \frac{\partial \mathcal{C}_a}{\partial t} = -\mathbf{v} \nabla \mathcal{C}_a - w_s \frac{\partial \mathcal{C}_a}{\partial z_s} + k_h \nabla^2 \mathcal{C}_a + \frac{d}{dz_s} \left( k_z \frac{\partial \mathcal{C}_a}{\partial z_s} \right) + E. \quad (3.4) \]

All other air processes, such as chemical deposition (gas, particle-associated, and wet) and reactive loss, were modeled in MUM, in addition to processes concerning the other urban compartments (water, soil, sediment, vegetation, and film).

MUM was also extended to include tributary transport between cells in Toronto. The chemical input, \( I_{r,i} \) and output, \( O_{r,i} \) terms via rivers for a given cell, \( i \), follow the standard fugacity mass balance formulation of

\[ I_{r,i} = D_{A,i} f_{r,j} \quad \text{and} \quad O_{r,i} = D_{A,i} f_{r,i} \quad (3.5) \]

where \( D_{A,i} \) is the water advection D-value (mol h\(^{-1}\) Pa) for cell \( i \), \( f_{r,i} \) (Pa) is the water fugacity in cell \( i \), and the subscript \( j \) refers to the cell directly upstream of cell \( i \). Other minor tributaries in the city were not connected cell-to-cell and were giving constant water outflow rates in order to prevent anomalous chemical build-up such that water outflow in these cells represented a loss route rather than a transport route to another cell or compartment.

MUM and BLFMAPS were loosely coupled into SO-MUM by moving them forward separately for a given time step as follows: BLFMAPS receives a chemical emission into air and MUM is then moved forward by \( \Delta t \), the resulting air concentration is inputted into BLFMAPS which is then moved forward by \( \Delta t \). This process is repeated for the entire simulation period. In order to pass concentrations between the two models a volume weighted average of the air concentrations from the first 4 BLFMAPS air layers (i.e. up to 100m) were used as input into MUM’s single, vertical air compartment which was set to a 100 m height. We chose to set the MUM vertical air height to be 100 m as this corresponded to the BLFM height which would most closely represent the 50 m air height of the one-box version of MUM (Diamond et al., 2001), in addition to being within the average boundary layer height as predicted by BLFM (~250 m). Selecting this height errs on the side of larger advective losses as horizontal wind speeds increase with height as the model assumes a well-mixed 100 m air compartment rather than decreasing concentration with height. The resulting MUM calculated air concentrations were then used as input to the first 4 layers of BLFMAPS such that these levels have the same air concentrations at the beginning of each time step; chemicals in these layers are subsequently
mixed vertically during BLFMAPS calculations. BLFMAPS was written in Fortran and for ease of compatibility MUM was also written in Fortran and added as a subroutine within the framework of BLFMAPS.

The model domain of SO-MUM contains 494 cells making up an area of 12350 km² (19×26 cells or 95km×130km) and is centered around the City of Toronto which is made up of 39 cells with a land area of 820 km² (Figure 3.1). Details of the model parameterization including physical-chemical properties as well as environmental data can be found in the Appendix 2.

3.2.3 Estimating Emissions

Chemical emissions for cells within Toronto were estimated using a two-step process where first, emissions to air were back-calculated by deriving the emission rate that resulted in a match between measured and modeled air concentrations, and second, those rates were scaled to estimated chemical inventories. We assumed one bulk emission into the lower air compartment of each cell (100 m height). Air concentrations were those measured by Melymuk et al. (2012) using PUF (polyurethane foam) passive samplers deployed in 2008 for 3-month periods throughout the city. These concentrations were treated as bulk-phase (rather than gas-phase) as Melymuk et al. (2011b) found that PAS-measured concentrations represented bulk, rather than gas-phase air concentrations most accurately. See Melymuk et al. (2012) for details of the measurement campaign.

Step 1: Back-calculate emissions. Air measurements were available for 9 cells (corresponding to sites W10, W5, W1/0KM/N1, 0KM/E1, E1/E5, E10, E20, N5, and N10, Figure 3.1b) within the city. Chemical emission rates from within these 9 cells were back-calculated assuming chemical inputs from air advected from adjacent cells at a concentration equal to that in the said cell in the lower air compartment and one quarter that concentration in the upper air compartment, as air concentrations have been found to be lower at higher air levels (Farrar et al., 2005). For cells with more than one air sampling site (e.g. sites E1 and E5 in cell (5,3)), we averaged measured values. For the downtown cell (5,2; referred to as DT) we took the average of the 0KM and E1 sites which fell in cells adjacent to the DT cell as air concentrations at site S5 in cell DT were representative of those over Lake Ontario rather than the downtown core (Figure 3.1b) (Melymuk et al., 2012). For cell DT we assumed an inflow air concentration equal to one half in the lower air compartment of that measured concentration because of the
higher concentrations measured in downtown (see Melymuk et al. (2012)) relative to the rest of the city.

Step 2: Normalize back-calculated emissions per unit inventory. The mass of chemical stock in each cell was estimated for PCBs using the 2006 inventories presented by Diamond et al. (2010) and Robson et al. (2010); the PBDE mass inventory is described in Section 3.2.4. For the 9 cells with back-calculated emissions we calculated an emission per unit inventory, \( EI \) (g h\(^{-1}\) kg\(^{-1}\)) and then averaged the 9 values

\[
EI = \frac{1}{n} \sum_{j=1}^{n} \frac{E_j}{m_j}
\]

where \( E_j \) is the back-calculated emission and \( m_j \) is the chemical mass in cell \( j \), where \( j \) refers to one of the \( n \) cells.

Next, the process was extended to the 30 cells lacking measured air concentrations. For these cells we multiplied \( EI \) by the mass inventory in each cell to estimate the cell-specific chemical emission rate. Thus, emissions for all cells were set as the product of \( EI \), as determined in Equation 3.6 and the mass of total inventory in that cell.

As SO-MUM is time-dependent we initialized the compartmental (water, soil, sediment, vegetation, and film) concentrations in each cell by setting the values to those calculated by the steady-state (SS) version of MUM with further details in Appendix 2. Initial SO-MUM air concentrations were set to zero in all cells. SO-MUM had a run-up time of two weeks before recording data.

### 3.2.4 Mass Inventories

Diamond et al. (2010) and Robson et al. (2010) reported a spatially resolved PCB stock of 437 (282-796) tonnes in Toronto which included PCBs in-use, in-storage, and contained within building sealants. This inventory was used in the emission calculations by assigning the data to each SO-MUM cell.

The spatial mass inventory for penta- and octa-BDE mixtures was developed for Toronto by first estimating the amount of penta- and octa- containing products including computers,
printers, televisions, furniture (chairs, sofas, beds, and pillows), and cars and secondly, converting to the mass of penta and octa based on concentrations in these media (we excluded deca as we did not have measured air concentrations for BDE-209). We used PBDE product concentrations of Morf et al. (2002; 2005) for computers, printers, televisions, Allen et al. (2008) for furniture, and Morf et al. (2002) and Imm et al. (2009) for cars. Further details of the inventory calculations can be found in Appendix 2 and Tables A2.9-10.

3.2.5 Model Runs

SO-MUM was run over spring (April - June) 2008 for 5 PCB congeners (28, 52, 101, 153, 180) and 5 PBDE congeners (28, 47, 100, 154, 183) which range in physical-chemical properties and generally had higher measured concentrations within their respective homologue groups (Melymuk et al., 2012). We ran various sensitivity analyses to assess the effects of wind speeds and dry deposition velocity on various model outcomes. Details and results are presented in Appendix 2.

3.3 Results and Discussion

3.3.1 Model Assessment

As with most environmental models, SO-MUM cannot be independently evaluated as we used measured PCB and PBDE air concentrations (Melymuk et al., 2012) to initialize the model and to calculate emissions. However, we can assess the model’s ability to reproduce those measured air concentrations (at a height of 10m corresponding to the approximate PAS height) by comparing measured and modeled concentrations in 16 cells (9 within and 7 outside the city) averaged over the simulation period. We also compared the modeled concentrations in the DT cell to urban concentrations reported for Toronto in previous years (Gouin et al., 2005; Motelay-Massei et al., 2005; Harner et al., 2006; Shen et al., 2006). Finally, we compared measured and modeled concentrations of PCBs and PBDEs in surfaces films, precipitation, and tributaries.

Modeled $\Sigma_5$PCBs air concentrations fell within an order of magnitude of measured values with a best fit slope (BFS) of modeled vs. measured values of 0.6 ($r^2=0.7$) (Figure A2.1a,c). The regression excluded the outlier of site W20 which had unexplained, high measured concentrations of only tri- and tetra-PCBs but not higher chlorinated congeners (Melymuk et al., 2012). The measured (average of sites 0KM and E1, Figure 3.1b) and modeled $\Sigma_5$PCBs
concentration in the DT cell were 146 and ~86 pg m\(^{-3}\), respectively, and were within an order of magnitude but lower than previously measured values in downtown Toronto of 345 pg m\(^{-3}\) (\(\Sigma\_5\)PCBs) in spring 2001 (Motelay-Massei et al., 2005), 212 pg m\(^{-3}\) (\(\Sigma\_2\)PCBs) annual 2000-2001 (Shen et al., 2006), and 360 pg m\(^{-3}\) (\(\Sigma\_10\)PCBs) in spring 2002 (Gouin et al., 2005) which, hopefully, reflects a diminishing PCB inventory over time (Diamond et al., 2010). In Canada, the federally estimated in-use PCB askarel and mineral oil mass inventory consistently decreased annually between 1998 and 2005 (Environment Canada, 2006).

Modeled \(\Sigma\_5\)PBDE air concentrations were within an order of magnitude of measured values (except for site W60 outside the city, Figure A2.1b,d) with a BFS of measured vs. modeled concentrations of 0.5 \((r^2=0.1)\) where the low \(r^2\) indicates a lack of bias in model predictions. The BFS rose to 0.7 \((r^2=0.4)\) when DT was excluded since the model underestimated the air concentration here by ~3 times. The measured (average of sites 0KM and E1, Figure 3.1b) and modeled concentrations of BDE-47 in the DT cell were 50 and ~14 pg m\(^{-3}\) which were within an order of magnitude of previously measured values in downtown Toronto of 15 pg m\(^{-3}\) in spring/summer 2001 (Harner et al., 2006), 22 pg m\(^{-3}\) annual 2000-2001 (Shen et al., 2006), and 55 pg m\(^{-3}\) in spring 2002 (Gouin et al., 2005).

The model reproduced the urban-suburban gradient in PCB concentrations in Toronto of ~12-fold (~7-86 pg m\(^{-3}\)) between DT and a suburban cell, (1,3). Similar urban-rural gradients were reported for Toronto, Chicago, Philadelphia, and Cleveland (Du et al., 2009; Hu et al., 2010; Persoon et al., 2010; Melymuk et al., 2012). Modeled PBDE concentrations reproduced the urban-suburban gradient of ~4 fold (cells (1,3) and (5,3)), respectively, or ~7-28 pg m\(^{-3}\) which is similar to that reported by Harner et al. (2006) and Melymuk et al. (2012) for Toronto.

In general, DT air concentrations of PCBs and PBDEs were underestimated compared to measured values. Reasons for this discrepancy include an error in the model, that measured values were not representative of the 5\(\times\)5 km\(^2\) area of downtown which could be due to fine scale spatial heterogeneity (e.g. 1 km) (Melymuk et al., 2012), an underestimate of the inventories in DT, or that the PCB and PBDE emission rates per inventory in DT were higher than in other cells. As downtown has the highest geographic density of PCBs and PBDEs, an air sampling location could have a higher probability of being nearby an high emission source compared to a suburban or rural sampling location. Higher emission rates in DT could be
related to higher ventilation rates of office buildings than residential structures (Björklund et al., 2012).

Air concentrations of both compound classes were also underestimated at sites outside of the city, especially to the west of the city which is upwind of Toronto since the prevailing winds are from the southwest during spring (maximum underestimate was in cell W60 by ~12 times and ~30 times for PCBs and PBDEs, respectively). The upwind underestimation is consistent with our neglect of upwind emission sources from the neighboring cities of Hamilton and Burlington at the western end of Lake Ontario. Alternatively, the model is not adequately accounting for chemical transport. To explore these possibilities, we back-calculated PCB emissions based on the average measured concentrations at sites outside of the city (W40, W60, N40, and N80) and ran the model with these emissions originating from each cell outside the city. Adding these emissions beyond the border of Toronto did not significantly change modeled concentrations within Toronto (with background vs. without background had a BFS of 1.0, r²=1.0), however concentrations in cells outside of Toronto increased by 1.6 (W40) to 6 (N80) times. As we are focusing on urban emissions, we present results assuming no emissions from cells outside Toronto.

Modeled concentrations were also compared to air measurements from an high-volume air sampler located in the DT cell in order to assess dynamic model estimates. Melymuk et al. (2011b) took these measurements at the 0KM site at 12 day intervals for a 24 hour sampling period (9am to 9am) during the same time period that passive air samplers were deployed. Hourly modeled concentrations were averaged over the same 24 hour period as the high volume sampler data for ease of comparison. Measured and modeled concentrations were within an order of magnitude agreement where the model underestimated concentrations on average by ~3 times for PCBs and overestimated by ~2 times and underestimated by ~4 times for PBDEs, before and after ~June 1st, respectively) (Figure A2.2). The model reproduced measured temporal trends, with concentrations generally increasing starting in June.

We compared modeled and measured concentrations in media other than air including surface films, precipitation, and tributaries (Gingrich et al., 2001; Butt et al., 2004; Robson et al., 2008; Melymuk et al., 2011a; Melymuk et al., In Prep.). For both $\sum_5$PCBs and $\sum_5$PBDEs, modeled concentrations in surface films, tributaries, and precipitation were all within an order of
magnitude of measured concentration ranges (Tables A2.11-13). Further details on the comparison in these media can be found in Appendix 2.

3.3.2 PBDE Inventory

The mass of PBDEs (penta- and octa-mixtures) including vehicles in Toronto was estimated to be ~200 tonnes (90-1000 tonnes) or ~80 (40-400) g capita\(^{-1}\) with penta- and octa- making up 60% and 40% of the inventory, respectively (Figure A2.3, excluding cars). The PCB mass inventory in 2006 was estimated to be ~180 (110-320) g capita\(^{-1}\) (Diamond et al., 2010) which reflects the higher measured outdoor air concentrations of PCBs in comparison to PBDEs in Toronto (Melymuk et al., 2012). The mass inventories per capita, however, do not reflect the higher estimated body burdens of PBDEs in comparison to PCBs in North America (Schecter et al., 2005) which may be due to differences in relative exposure contributions of dust versus diet (Harrad and Diamond, 2006). The large range in the PBDE inventory estimate was due to the range in concentrations of penta in furniture and vehicle textiles (Allen et al., 2008; Imm et al., 2009) (Table A2.10). The higher mass of penta agrees with higher market demand for penta than octa in North America in 2005 (Ward et al., 2008), however, our inventory likely underestimates the true values for both mixtures as we did not account for all sources (e.g., carpets and other furniture types; and electronics such as entertainment systems and appliances (Morf et al., 2005; Allen et al., 2008).

3.3.3 Emission Rate Estimates

Spatially resolved estimates

Total means and ranges of \(\Sigma_5\)PCBs and \(\Sigma_5\)PBDEs emissions estimated to emanate from Toronto were ~19 (2-41) kg y\(^{-1}\) and 18 (3-42) kg y\(^{-1}\), respectively. A clear spatial trend in values of \(EI\) was not apparent. The mean and ranges were derived from the mean emission rates per inventory, \(EI\) (Equation 3.6), plus/minus the standard deviation of the \(EIs\) (or set to the minimum \(EI\) when the standard deviation was larger than the mean Table A2.15). The low ends of the emission ranges seemed to be unreasonable as they underestimated modeled air concentrations by ~20 and ~8 times on average for PCBs and PBDEs, respectively, assuming a linear relationship between emissions and concentrations. However, the annual means were likely biased high since they were based on measured spring air concentrations which were ~3-4
and 5 times higher on average for PCBs and PBDEs, respectively than those measured in fall and winter (Melymuk et al., 2012).

Scaling up from $\Sigma_5$PCBs to $\Sigma_{88}$PCBs using a $\Sigma_{88}$PCB profile of air concentrations (Melymuk et al., 2012) yielded a city-wide emission rate of $\sim$230 (40-480) kg y$^{-1}$, or 280 (50-580) g y$^{-1}$ km$^{-2}$, or 90 (16-190) mg y$^{-1}$ capita$^{-1}$. The city-wide estimate was on the same order of magnitude as modeled estimates for New York City (300 kg y$^{-1}$ or 400 g y$^{-1}$ km$^{-2}$, $\Sigma_{93}$PCBs) (Totten et al., 2006) and Canada (8-300 mg y$^{-1}$ capita$^{-1}$, based on the default and maximum values of Breivik et al.(2002). The multi-box emission estimate was within the range of the one-box MUM estimate for Toronto of $\sim$90-880 kg y$^{-1}$ ($\Sigma_{70}$PCBs) (Diamond et al., 2010).

Scaling $\Sigma_5$PBDEs emissions to $\Sigma_{26}$PBDEs yielded a city-wide emission rate of 28 (6-63) kg y$^{-1}$, 34 (7-77) g y$^{-1}$ km$^{-2}$ and 11 (2-25) mg y$^{-1}$ capita$^{-1}$. Jones-Otazo et al. (2005) estimated $\Sigma_{12}$PBDE emissions in Toronto of 37-154 kg y$^{-1}$ using the one-box version of MUM, compared to 28 (5-60) kg y$^{-1}$ using SO-MUM for the same 12 congeners. The lower values estimated here could have been due to the 7-8 year span between the years modeled (e.g. air concentrations used by Jones-Otazo et al. (2005) were 45-109 pg m$^{-3}$ compared to average measured urban concentration of $\sim$37 pg m$^{-3}$ used here) or the difference in spatial resolution. We explore this below. Moeckel et al. (2010), also using a multimedia model (without spatial resolution), estimated urban emissions of $\Sigma_3$PBDE (28, 47, 100) emissions for Zurich, Switzerland of 19 mg y$^{-1}$ capita$^{-1}$ which was $\sim$triple that of our mean estimate for these congeners (6 mg y$^{-1}$ capita$^{-1}$). Our estimated range captured the estimate of Batterman et al. (2009) of 5.5 mg y$^{-1}$ capita$^{-1}$ for $\Sigma_3$PBDE (28, 47, 100) for U.S. household emissions.

The estimated $\Sigma_{88}$PCB and $\Sigma_3$PBDE emission rates per mass inventory were $\sim$0.5 g y$^{-1}$ kg$^{-1}$ (0.1-1 g y$^{-1}$ kg$^{-1}$) and $\sim$0.1 g y$^{-1}$ kg$^{-1}$ (0.03-0.3 g y$^{-1}$ kg$^{-1}$), respectively, which equals an emission of $\sim$0.05% (0.01-0.1%) and $\sim$0.01% (0.006-0.07%) of the inventory mass per year, respectively. The ranges in emission rate per mass inventory represent the ranges in estimated emissions divided by the 'best estimate' mass inventories. Using the ranges in inventory as well as emission rates results in $\Sigma_{88}$PCB and $\Sigma_{26}$PBDE emission rates per inventory of 0.05-1.6 and 0.01-0.7 g y$^{-1}$ kg$^{-1}$, respectively. The emission rates per inventory were surprisingly similar for the two chemical classes despite the dissimilarity in their usage profiles and time spans of use. These rates imply that if the inventory of each compound class is not removed from the city it
will take thousands of years for the inventory to be released, assuming a constant emission rate over time.

We calculated congener-specific values of $E_I$ or $E_I_i$ using the congener-specific emissions per total inventory normalized to the composition of Aroclor (weighted average of 1242, 1254, 1260) and DE-71 (Christensen and Lo, 1986; Frame et al., 1996; La Guardia et al., 2006) (Table A2.16). When expressed on a percentage basis, the annual value of $E_I_i$ for BDE-47 of ~0.03 (0.003-0.2)% was within the range predicted by Alcock et al. (2003) of 0.01-0.7%. Within a chemical class, $E_I_i$ generally increased with volatility or decreased with increasing $K_{oa}$ (Figure 3.2), supporting the assumptions made by Breivik et al. (2002) and Prevedouros et al. (2004). Although values of $E_I_i$ for PCBs and PBDEs were very similar, they did not follow a consistent trend according to $K_{oa}$ when considered together. This dissimilar pattern may be due to uncertainties in model estimates and/or the use of PBDEs indoors in comparison to PCBs that have more outside uses in capacitors and transformers, building sealants, and paints (Batterman et al., 2009; Björklund et al., 2012; Melymuk et al., 2012). We anticipate that as the mass of the less volatile chemicals is depleted at a greater rate (i.e. they have a higher emission rate per mass chemical), the congener-specific $E_I$s will gradually lose their relationship to $K_{oa}$ over time (Alcock et al., 2003; Robson et al., 2010). This trend can be seen in Figure 3.2 where the PCB $E_I$s differ by ~2 times (between CB-28 and 180) in comparison to PBDEs which differ ~20 times (between BDE-28 and -183) relative to the difference in Log $K_{oa}$ of ~1.3 times and ~1.4 times.

Σ$_5$PCB emission rates ranged from 0.04-430 g y$^{-1}$ km$^{-2}$ in the (8,7) and DT cells, respectively, a span of 4 orders of magnitude (Figure 3.3a). Cell (8,7) had no known in-use or in-storage PCB inventory versus 36 sites in the DT cell (Diamond et al., 2010). Conversely, Σ$_5$PBDE emission rates ranged from 2 to 60 g y$^{-1}$ km$^{-2}$ in (8,7) and (5,3) DT cells (Figure 3.3b). Thus, considering the city as a whole, PCBs act more as a point source in Toronto where 34% of the emissions originated from the DT cell. In comparison, PBDE emissions are spread more evenly throughout the city with near-downtown cells (4,3) and (5,3) accounting for 16% of the total emissions. The point source nature of PCBs stems from the intense electricity usage in the 1960s and 1970s in downtown office towers, hospitals and public buildings that dominated the 2006 PCB inventory; PCBs were not used in newer areas of the city built after the 1977 ban on new uses (Diamond et al., 2010). PBDE-containing products also have high usage intensities in the
downtown, but are also used in virtually all buildings in Toronto (except perhaps those constructed since 2005) and hence act more as a diffuse source throughout the city. The inventory and emission patterns explain the lower urban-rural gradient of PBDEs versus PCBs seen in air and soil (Harner et al., 2006; Melymuk et al., 2012).

As will be discussed in greater detail by Csiszar et al. (In Prep.), SO-MUM estimated that primary emissions clearly dominate total emissions. Urban media (soil, vegetation, films, and tributaries) transferred ~7 and ~1 g d⁻¹ to air via volatilization compared to estimated primary emissions of ~52 and ~49 g d⁻¹ for Σ₅PCBs and Σ₅PBDEs, respectively. Thus, our analysis of multimedia exchange confirms previous conclusions that ‘fresh’ emissions from PCB and PBDE stocks are by far the main contributors to urban air concentrations (Basu et al., 2004; Prevedouros et al., 2004; Robson and Harrad, 2004; Kohler et al., 2005; Moeckel et al., 2010).

One-box emission estimates

As mentioned above, emission estimates for PBDEs using SO-MUM were lower than those using a single-box model for Toronto but similar for PCBs. These previous estimates, however, were made with concentrations measured in 2000-2001 and with fewer measured locations. To explore whether the increased spatial resolution in SO-MUM provided an improved estimate of emissions that would merit the additional complexity of this model, we estimated emissions using the one-box steady-state version of MUM (with geographical properties averaged across the city) using the 2008 data set of Melymuk et al. (2012) that we used to estimate the spatially resolved emissions. We calculated emissions in two ways, one in which we averaged the air concentrations in the 9 cells used to calculate the emission rates per inventory, and secondly we averaged the 0KM and N10 sampling sites to represent high urban concentrations, following the method of Diamond et al. (2010). A range in emission rates was obtained by setting congener-specific inflow air concentrations to the average of the sampling sites outside of the city for a 'high' emission scenario and to the same as the urban concentration for a 'low' emission scenario (Diamond et al., 2010).

Using both methods, one-box MUM provided emission estimates within the range estimated using the multi-box MUM (Table A2.17). Using the average of all measured air concentrations (22 and 19 kg y⁻¹ for PCBs and PBDEs, respectively) gave results most similar to those of multi-box MUM (19 (2-41) and 18 (3-42) kg y⁻¹ for PCBs and PBDEs, respectively) rather than
using the highest measured concentrations from 0KM and N10. These results suggest that the one-box model can be used with a spatially representative average urban air concentration to estimate aggregate emissions similar to those made using the multi-box model. The advantage of the multi-box model is presumably more accurate emission estimates and use of the model to relate emissions to local air concentrations and to emissions from the city as a whole. However, these advantages come with considerably greater data requirements, model complexity, and computational demands relative to the one-box version.

3.3.4 Sensitivity Analysis

Emission rates were positively linearly correlated with horizontal wind speed $v_h$, vertical wind speed between the upper and lower air compartments $v_v$, and dry deposition velocity $v_d$ ($r^2=1.0$) for the ranges scanned which were 0.1-10 m s$^{-1}$, 0.01-0.1 m s$^{-1}$, and 0.1 to 10 cm s$^{-1}$ for $v_h$, $v_v$, and $v_d$ respectively. The ranges for the wind speeds were based on the high and low hourly values calculated by BLFM for the spring 2008 simulation period and thus have a relatively high degree of certainty. Emissions varied the most over the range of horizontal wind speeds with PCB emissions varying more than those of PBDEs. The emission rates varied ~14, 2, and 1.1 times over the $v_h$, $v_v$, and $v_d$ ranges, respectively for $\sum$PCBs and ~5, 2, and 2 times for $\sum$PBDEs, respectively (Table A2.18).

Varying $v_d$ from 0.1 to 10 cm s$^{-1}$ resulted in the advective losses of PCBs ranging from ~100-97% of emissions; net air deposition ranging from ~1%-3% of emissions; and air concentrations ranging from 67-65 pg m$^{-3}$ indicating that model results for PCBs are not particularly sensitive to changes in $v_d$ (Table A2.19), since they are mainly in the gas-phase. For PBDEs, varying $v_d$ over the same range resulted in advective losses ranging from ~93-49% of emissions; net air deposition ranging from ~6-50% of emissions; and air concentrations ranging from ~60-30 pg m$^{-3}$. PBDE results were clearly more sensitive to changes in $v_d$ due to their higher particle association than PCBs (Table A2.20). The relationships between $v_d$ and the various model outputs were all linear or near-linear ($r^2=0.93-1.0$). Full details of the sensitivity analysis are presented in Appendix 2.
3.4 Conclusions and Further Directions

A local scale, spatially resolved, coupled multimedia and air transport model, SO-MUM, was developed to estimate emissions, as related to a chemical inventory, and to predict transport and fate of urban POPs. This method of estimating emissions based on chemical inventories allows for a direct connection between source locations and the magnitude of chemical emanating from these sources which can be used to inform chemical removal strategies.

The model predicted concentrations in air, tributary water, surface films, and precipitation within an order of magnitude of measured values. As the model can estimate urban concentrations reasonably well, the model sets up a framework to further understand how air mediates transport out of and within urban areas where chemical can be further mobilized to the surrounding environment for example via tributary and storm water loadings; this usage will be presented in Csiszar et al. (In Prep.).
3.5 Figures

Figure 3.1 (a) SO-MUM model domain and (b) zoomed in view of City of Toronto with labeled sample sites. The Toronto cells are identified based on coordinates as indicated in (b).
Figure 3.2 Congener specific emission rates per mass inventory, $E_{i}$ (g y$^{-1}$ kg$^{-1}$) for (a) PCBs and (b) PBDEs.
3.6 References


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Chapter 4
Modeling the influence of urban SVOC emissions on neighboring regions using a coupled multimedia and air transport model

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Contribution: S. Csiszar ran the model to produce and analyze all the data. S. Csiszar wrote the manuscript. The research and manuscript were prepared under the supervision of M. Diamond; S. Daggupaty provided the code for BLFMAPS.

4 Abstract

SO-MUM, a coupled atmospheric transport and multimedia urban model, was used to estimate spatially resolved (5×5 km²) air emissions and chemical fate based on measured air concentrations and chemical mass inventories within Toronto, Canada. Approximately 95% and 70% of total PCB and PBDE emissions, respectively, undergo atmospheric transport from the city, which is partly over Lake Ontario. “Urban travel distance” or UTD, the distance at which concentrations fall to 1/e of an urban reference concentration, was introduced to quantify regional transport of SVOCs from a city. The UTDs of PCBs and PBDEs were ~25 km and ~30 km, respectively in the direction of prevailing winds. Soil wash-off of historically accumulated Σ₃PCBs to surface water contributed ~0.4 kg y⁻¹ (of predominantly higher congeners) to near-shore Lake Ontario which was lower than volatilization of ~6 kg y⁻¹ which was of predominantly lighter congeners. Atmospheric emissions from primary sources followed by deposition to surface films and subsequently wash-off to surface waters both contributed ~1 kg y⁻¹ and were the main route of Σ₃PBDE loadings to near-shore Lake Ontario which was a net PBDE sink. Secondary emissions of PCBs and PBDEs from at least a ~900,000 km² rural land area would be needed produce the equivalent primary emissions as Toronto (~640 km²).

Reducing primary emissions would result in volatilization of PCBs but not PBDEs from near-shore Lake Ontario. These results provide clear support for reducing inventories of these POPs.

4.1 Introduction

It is generally accepted that urban areas are primary sources of persistent organic pollutants (POPs) such as PCBs and PBDEs, and semi-volatile organic compounds (SVOCs) such as PAHs. These compounds originate from anthropogenic sources, for example, from building
materials, consumer products, and vehicle exhaust, respectively (Robson and Harrad, 2004; Hung et al., 2005; Gioia et al., 2006; Melymuk et al., 2012). Hence, chemical use within and release from urban areas leads to an “urban plume” that atmospherically transports chemicals to surrounding regions (e.g. Green et al., 2000; Diamond and Hodge, 2007). This phenomenon has been well documented in the Great Lakes region (e.g. Simeik et al., 1997; Hafner and Hites, 2003; Offenberg et al., 2005; Blanchard et al., 2008). The extent of the urban plume or a chemical's spatial range has been generally quantified based on a point source or single urban measurement (Green et al., 2000; Blanchard et al., 2008), however, intra-urban measurement campaigns have shown that SVOC concentrations and hence source strengths can vary significantly within a city (e.g. Du et al., 2009; Hu et al., 2010; Melymuk et al., 2012). A diffuse geographic distribution of emissions would presumably extend the distance of the urban plume and as cities grow in spatial extent (Jaeger et al., 2010) they will no longer act as point source emitters of certain SVOCs.

This paper is part of a series reporting on a multi-agency program to estimate emissions from an urban area and loadings to an adjacent water body, using Toronto, Canada and Lake Ontario as a case study (Robson et al., 2008; Melymuk et al., 2011; Melymuk et al., 2012; Csiszar et al., Submitted). In a companion paper, Csiszar et al. (Submitted), we developed and applied a method to estimate spatially resolved emissions (on a 5 km scale) of SVOCs from an urban area. These emissions express and can be viewed as an aggregate emission factor for activities in an urban area contributing to a chemical’s release. In terms of controlling chemical emissions, these emission factors, when expressed per unit of chemical inventory can guide our expectations for changes in primary emissions as a function of changes in a city’s chemical inventory. A next question is at what point and to what extent will secondary emissions “cancel” or negate the effects of controlling primary emissions.

In this study we quantify and assess the magnitude of urban emissions and the resulting plume to a surrounding region via air transport and surface waters. Borrowing from the work of Scheringer (1996), Bennett et al. (1998), and Beyer et al. (2000), who developed metrics to quantify a chemical's spatial range, notably the Characteristic Travel Distance, CTD, as an estimate of potential atmospheric travel distance of a chemical from a point location, we introduce the concept of a chemical’s Urban Travel Distance or UTD. Analogously to CTD, the UTD quantifies the potential of a chemical to travel from an urban reference location to reach a
concentration of \(1/e\) of that reference location. We use the coupled model, spatially oriented MUM, or SO-MUM (Csiszar et al., Submitted) to accomplish this numerical analysis. SO-MUM is built from the Boundary Layer Forecast and Air Pollution Prediction System, BLFMAPS (Daggupaty et al., 2006) and the multimedia urban model, MUM (Csiszar et al., 2012). We next used SO-MUM with estimates of the inventories of PCBs and PBDEs (penta- and octa-BDEs) in Toronto, Canada, to explore the implications of reducing these inventories on primary versus secondary emissions.

PCBs have been in use since the 1930s. In 1977, Canada banned production (which never occurred in the country) and importation (McDonald and Tourangeau, 1986; Diamond et al., 2010b). New PCB regulations that passed into law in 2008 and most recently amended in December 2011, specify that equipment may not be used past December 31, 2009 if it contains PCBs at concentrations greater than 500 mg kg\(^{-1}\) or between 50 and 500 mg kg\(^{-1}\) if the equipment is located in a “sensitive” location such as nearby a drinking water treatment facility, child care facility, school or hospital. Equipment containing PCBs between 50 and 500 mg kg\(^{-1}\) that is not in a sensitive location, and PCBs in light ballasts or pole top transformers can be used until 2025 (Government of Canada, 2012). As of 2006, an estimated 437 tonnes of PCBs were in use and storage in Toronto (Diamond et al., 2010b). PCB emissions could temporarily increase during equipment removal due to accidental spills and releases (Füll, 2001; Breivik et al., 2002).

The penta-, octa-BDE flame retardant mixtures were declared toxic in 2008 in Canada under the Canadian Environmental Protection Act after its draft risk assessment was released in 2006 (Government of Canada, 2008). North American manufactures voluntarily ceased production of the penta- and octa- mixtures in 2004. Production (which never occurred in Canada) and importation were banned in Canada in 2008 (Government of Canada, 2008; Environment Canada, 2010). Csiszar et al. (Submitted) have estimated an inventory of \(~200 (90-1000)\) tonnes of penta- and octa-BDEs in computers, printers, televisions, furniture, and cars in Toronto.

Below we briefly present SO-MUM and its application to PCBs and penta- and octa-BDEs using Toronto, Canada as a case study. Full details of the model and application are provided by Csiszar et al. (Submitted). We introduce the concept of UTD and illustrate its utility within
the case study. We then discuss model estimates of the fate of these compounds which leads to estimates of the magnitude of emissions leaving the city and, since Toronto is on the shores of Lake Ontario, loadings to Lake Ontario from the city. Finally, we use the model to investigate the magnitude of primary emissions from the city’s chemical inventories versus secondary emissions as those inventories might decrease.

4.2 Methods

4.2.1 Model Description

The unsteady-state version of MUM and SO-MUM model frameworks are described in detail by Csiszar et al. (2012) and (Submitted), respectively. Briefly, the model’s geographic domain was divided into 5×5 km² cells where interactions between air and other media as well as multimedia transport were modeled in MUM. Air transport (in 10 vertical layers) between cells was modeled using BLFMAPS (Daggupaty et al., 2006). The fugacity-based MUM divides the urban environment into 6 compartments (air, water, soil, sediment, vegetation, and surface film) with the following mass balance (MB) equations

\[
\frac{dm_i}{dt} = \frac{d(Z_i V_i f_i)}{dt} = E_i + \sum_{j \neq i} (D_{ji} f_j) - D_{ti} f_i \quad i = a, r, s, se, v, f
\]  

(4.1)

where \(m_i, V_i, Z_i, f_i, E_i,\) and \(D_{ti}\) are the mass (mol), volume (m³), bulk Z-value (mol m⁻³ Pa⁻¹), fugacity (Pa), specified emission source or sink (mol h⁻¹), and total loss D-value (mol h⁻¹ Pa⁻¹) (transport and transformation), respectively, for compartment \(i; \ D_{ji}\) is the inter-compartmental transfer D-value from compartment \(j\) to \(i\) (Csiszar et al., 2012). The unsteady-state equations are solved using the implicit Euler approximation using a 5 minute time-step corresponding to the time-step used in BLFMAPS. BLFMAPS, given a chemical emission, \(E\), solves for air concentration, \(C_a\), using the following air chemical transport equation

\[
\frac{\partial C_a}{\partial t} = -\vec{v} \nabla C_a - w^* \frac{\partial C_a}{\partial z^*} + k_h \nabla^2 C_a + \frac{d}{dz^*} \left( k_z \frac{\partial C_a}{\partial z^*} \right) + E
\]  

(4.2)

where \(t\) is time; \(w^*\) is the vertical velocity in terrain following coordinates; \(z^* = z - h(x,y)\) (where \(z\) is height and \(h(x,y)\) is surface elevation); and \(k_h\) and \(k_z\) are the horizontal and vertical eddy diffusivities (m² s⁻¹), respectively (Ma et al., 2003; Daggupaty et al., 2006). Tributary transport
was modeled by linking river inflow and outflow rates between cells as described in Csiszar et al. (Submitted) with final river outputs in cells (2,1), (3,2), DT, (8,5), and (9,6) (the cell labeling system is defined in Figure A3.1).

Toronto is on the shores of Lake Ontario and has five tributaries running from north to south where they discharge into the lake. In cells that included Lake Ontario the model was used to estimate air-water exchange fluxes. This was accomplished by reducing Equation (4.1) to include only the air and water compartments. In cells that border Lake Ontario, fugacities were solved using two sets of MB equations: those of Equation (4.1) for the land area (excluding tributaries) and the reduced air-water mass balance for the lake area. Finally, for cells that had tributary discharges into Lake Ontario we used two sets of MB equations: those of Equation (4.1) based on the land, tributary, and lake areas within the cell and the two-compartment air-water mass balance over Lake Ontario. Estimating air-water exchange required calculation of air-side, $k_{a,P}$ and water-side, $k_{w,P}$ air-water mass transfer coefficients, MTCs (m h$^{-1}$) for chemical $P$ (either a PCB or PBDE congener) which were calculated at each time step using the formulations of Scharwenzbach et al. (1993)

$$k_{a,P} = k_{aw} \left( \frac{B_{P,a}}{B_{wa}} \right)^{0.67} \quad \text{and} \quad k_{w,P} = k_{w,CO2} \left( \frac{B_{P,w}}{B_{CO2,w}} \right)^{-a}$$

(4.3)

where $B_{P,a}$, $B_{wa}$, $B_{P,w}$, and $B_{CO2,w}$ are diffusion coefficients (m$^2$ h$^{-1}$) of $P$ and water in air, and $P$ and $CO2$ in water, respectively; $k_{aw}$ is the air-side air-water MTC of water vapor; $k_{w,CO2}$ is the water-side air-water MTC of $CO2$, and $a$ is a constant that depends on the wind speed at a 10m height. Further details on the calculation of $k_{a,P}$ and $k_{w,P}$ are described by Csiszar et al. (Submitted). These MTCs were updated at each time step as they depend on temperature (in both water and air) and wind speed which were provided by the BLFMAPS part of the model.

### 4.2.2 Model Parameterization

Toronto is Canada’s largest city with 2.5 million people covering $\sim$640 km$^2$. Bulk air emissions were estimated using the method described by Csiszar et al. (Submitted). Briefly, chemical concentrations in air measured across Toronto by Melymuk et al. (2012) by means of passive air samplers (PAS) were used as inputs to a steady-state (SS) version of MUM in order to back-calculate emissions necessary to support those concentrations. These emissions were converted
into an emission rate per unit inventory in each of nine cells having a measured air concentration out of 39 cells constituting Toronto. These nine emission rates per unit inventory were then averaged and the average was multiplied by the mass inventory in each of the 39 cells in Toronto to produce cell-specific aggregate emission rates (e.g., g chemical y\(^{-1}\)) for all cells in the city. We set the emission rate to zero outside of Toronto in order to assess the effects of only Toronto on surrounding regions. This assumption was tested for PCBs by running SO-MUM with an emission rate necessary to support measured rural air concentrations in all cells outside of the city. The results of this model run with rural emissions did not differ significantly from the run in which rural emissions were neglected (Csiszar et al., Submitted). We used the PCB mass inventory of Diamond et al. (2010b) and Robson et al. (2010) and the PBDE mass inventory of Csiszar et al. (Submitted) to scale emissions.

The model was initialized as follows. Initial air concentrations were set to zero. In order to initialize the concentrations in other media (tributaries, soil, sediment, vegetation, and film) we ran the SS version of MUM using average environmental properties of the simulation period, the estimated emissions, as well as inflow air concentrations calculated in a manner similar to the emissions. The initial soil concentrations were adjusted so that they were close to measured surface soil concentrations in Toronto (Wong et al., 2009; Diamond et al., 2010a). The model was given a run-up time of 2 weeks before recording data.

Physical-chemical properties used in the model for PCBs and PBDEs are listed in Csiszar et al. (2012) and (Submitted) with partition coefficients from Schenker et al. (2005) and (2008). Meteorological data were provided by BLFMAPS (which was initialized using data from the Global Environmental Multi-scale Model, GEM), as well as surface water and soil temperatures. Values of OH radical concentrations, solar irradiance, total suspended particulate concentrations were described by Csiszar et al. (Submitted). Based on the results of a sensitivity analysis (Csiszar et al., Submitted), we use mid-point values of dry deposition velocities between 0.2 cm s\(^{-1}\) to \(\sim 4.2\) and \(\sim 5.8\) cm s\(^{-1}\) for PCBs and PBDEs, respectively, that were used by others (Cetin and Odabasi, 2007b; Raff and Hites, 2007; Tasdemir et al., 2007; Venier and Hites, 2008; Moeckel et al., 2010) (Table A3.1). Land use was extrapolated from land-use base maps (DMTI Spatial Inc., 2008) using GIS. Tributary flow rates and depths, and inflow water concentrations into Toronto were described by Csiszar et al. (Submitted).
Surface lake water concentrations of PCBs and PBDEs at various locations (5 locations for PCBs and 2 for PBDEs in Lake Ontario nearby Toronto were obtained from Alice Dove (personal communication) (Dove, 2011) and Ueno et al. (2008), respectively (Table A3.2, Figures A3.2 and A3.3). These values were used to interpolate concentrations using an exponential function to 3700 km$^2$ of Lake Ontario extending out from the downtown cell, DT (5,2) (Figure A3.1). Due to the limited availability of water concentration data and since modeling Lake Ontario water concentrations were beyond the study’s scope, water concentrations were kept constant over time.

4.2.3 Model Runs

The model was run for spring (91 days) in 2008 corresponding to the spring PAS deployment period of Melymuk et al. (2012). The following congeners were modeled individually: the five PCB congeners CB-28, -52, -101, -153, and -180 and the five PBDE congeners BDE-28, -47, -100, -154 and -183. The model was run with emission to all Toronto cells and from the cells with the highest emission only (DT for PCBs and (5,3) for PBDEs, Figure A3.1) in order to compare spatially resolved urban emissions from the entire city to “point source” emissions. The model was also run under various inventory reduction scenarios in order to predict the results of reducing these inventories.

4.3 Results and Discussion

Emissions of $\Sigma_5$PCBs and $\Sigma_5$PBDEs from Toronto of 17 (2-36) kg y$^{-1}$ and 18 (3-42) kg y$^{-1}$ where estimated using SO-MUM. The emission ranges were based on the standard deviations of emission rates per inventory calculated in the nine cells for which we had measured air concentrations (see Section 4.2.2 and Csiszar et al. (Submitted)). These emission estimates were similar to those estimated using a one-box version of MUM and those of others using other methods (Jones-Otazo et al., 2005; Totten et al., 2006; Gasic et al., 2009; Diamond et al., 2010b; Moeckel et al., 2010).

4.3.1 Urban Travel Distances

The model estimated that for $\Sigma_5$PCBs, of which ~84% were in the gas phase, ~95% of emissions to air were advected out of the city with the remainder depositing to vegetation, soil, and film within the city (Figure 4.1a). In contrast, ~72% of emissions to air of $\Sigma_5$PBDEs, of which ~73%
were in the particle phase in air, were advected beyond the city (Figure 4.1b). The urban plumes of both chemicals extended over the lake to the east of the city for this spring simulation since the prevailing winds were from the south-west (Figure 4.2).

The Characteristic Travel Distance, CTD, of a chemical is the distance at which its air concentration is reduced to $1/e$ (i.e., 63%) from a point source (e.g. Bennett et al., 1998; Beyer et al., 2000). Here we introduce the Urban Transport Distance, UTD, as the distance traveled by a chemical from its location of greatest emission (referred to as the reference location) in an urban area to a location where the concentrations is at $1/e$ of the concentration of the reference location. The UTD differs from the CTD as it takes into account the spatial heterogeneity arising from spatially distributed urban emissions rather than treating the emissions from an urban area as a single geographic point. We also analyzed the distance at which concentrations dropped to $1/10$ of the urban reference location. We estimated the UTD in two ways. First, we identified the distances from the reference cell at which modeled concentrations were below $1/e$ of that reference cell; this method accounts for prevailing wind velocities. Second, we fit all the modeled concentrations (regardless of direction) to an exponential as a function of distance from the reference cell, which is analogous to fitting a radial dilution model (McDonald and Hites, 2003). This latter calculation yields average travel distances as it does not account for wind velocities. Additionally, in order to assess the differences between the UTD from spatially heterogeneous urban emissions, as described above, versus the UTD from a geographical point source, we ran SO-MUM with emissions emanating from the reference cell only (DT for PCBs and cell (5,3) for PBDEs).

The UTD and $1/10$ travel distance were ~25 and ~60 km for $\Sigma_3$PCBs and ~30 and ~50 km for $\Sigma_3$PBDEs, respectively, when accounting for the prevailing wind velocity. In contrast, using concentrations from all cells and an exponential fit to these data, the UTD and $1/10$ travel distance were ~15 and ~34 km for $\Sigma_3$PCBs and ~13 and ~31 km for $\Sigma_3$PBDEs (Table 4.1), or nearly half the wind-dependent UTD and $1/10$ distance (Figure 4.3). The drop off in air concentrations over Lake Ontario followed similar patterns to those found over the entire model area. These estimates contain considerable uncertainties along all points in the calculation from estimated emissions in each cell to fate calculations. Csiszar et al. (Submitted) evaluated SO-MUM’s performance and discussed uncertainties and model sensitivities.
Green et al. (2000) estimated, by means of an interpolation model supported by over-water air measurements in Lake Michigan, that PCBs originating from Chicago dropped to background levels at ~40-50 km into the lake from the city. This estimated distance is similar to our results determined for the wind-dependent travel distance. Fitting a directionally independent radial dilution model to Toronto air concentrations, Melymuk et al. (2012) estimated that PCB and PBDE concentrations dropped to 94% and 90% the downtown levels at 20 km from downtown, respectively. This distance is similar to the 1/10 distances of ~30 km for both compound classes obtained here by fitting wind-independent modeled concentrations to an exponential function (Table 4.1). Hearn et al. (2012) estimated that over an urban to rural land area in Brisbane, Australia, PBDE concentrations (not including BDE-209) reached a plateau at 30 km from the central business district which is very similar to the values calculated here using the wind-independent exponential fit.

Table A3.4 summarizes the 1/e and 1/10 travel distances of PCBs and PBDEs for dry particle deposition, wet deposition, and film concentrations.

The comparison of travel distances between PCBs and PBDEs shows a subtle difference consistent with their properties and inventories. Although the values for PCBs and PBDEs are similar, we see that PCB concentrations drop off more quickly at the 1/e distance but have a longer 1/10 distance whereas PBDEs show the opposite pattern (Figure 4.2, Table 4.1). These results can be explained by the PCB inventory which is more geographically concentrated in the downtown area versus the PBDE inventory that is spread more evenly throughout the city (Diamond et al., 2010b; Csiszar et al., Submitted), despite the ability of PCBs to travel farther than PBDEs from a point source due to PCBs being more in the gas-phase in comparison to PBDEs. We tested this explanation by running the model with emissions from downtown only, the results of which where shorter 1/e and 1/10 distances for PBDEs than those using emissions from all Toronto cells (Table 4.1, Figure 4.3). Thus, the UTD is affected by chemical mobility due to the prevailing wind velocity, the geographic distribution of the inventory, and gas-particle partitioning.

4.3.2 Urban Chemical Pathways

Of the 5% of $\Sigma_3$PCBs not advected from the city, 30, 52, 16 and 1% were transferred to soil, vegetation, films, and tributaries, respectively. For $\Sigma_5$PBDEs, of the 28% not advected from the
city, the comparable percentages were 40, 27, 32, and 0.6%, respectively. These values refer to net transfer (deposition minus volatilization) from air.

In more detail, the model estimated that ~0.6 g d⁻¹ Σ₃PCBs was deposited to soil with only ~0.1 g d⁻¹ returning via volatilization. The comparable values for Σ₃PBDEs were ~5 g d⁻¹ and <0.001 g d⁻¹. This agrees with previous studies that found that soil is currently not an appreciable source of PCBs or PBDEs to air in urban areas studied (e.g. Robson and Harrad, 2004; Cetin and Odabasi, 2007b; Bozlaker et al., 2008). On a daily scale, the model predicted net air-to-soil transfer for both chemicals (Figure A3.4). The model also estimated net transfer from air to vegetation and to tributaries over the model simulation.

Modeling and measurements have shown that urban surface films mediate contaminant transport (Diamond et al., 2000; Diamond et al., 2001; Priemer and Diamond, 2002; Csiszar et al., 2012). Results from SO-MUM showed that for predominantly gas-phase chemicals, such as PCBs, chemical in air and film were close to equilibrium such that most chemical deposited to film was re-emitted back to air, i.e., air-to-film deposition and volatilization were ~3.6 and ~3.4 g d⁻¹, respectively. On a daily basis, PCB concentrations in film tracked air concentrations due to fast mass transfer between film and air (Harner et al., 2003; Csiszar et al., 2012) (Figure A3.5a). For Σ₃PBDEs, film acted as a net sink from air with modeled air-to-film deposition and film volatilization of ~4.8 and ~0.9 g d⁻¹, respectively. PBDE concentrations in film did not track air concentrations as closely as PCBs on a daily basis (Figure A3.5b) presumably due to slower mass transfer (Harner et al., 2003; Wu et al., 2008). The net direction of exchange was from air-to-film on all days over the entire simulation period (Figure A3.4).

From these results we hypothesize that surface films mediate urban contaminant transport in two ways. First, in the case of less particle-sorbed compounds such as PCBs, films “bounce” chemicals back into the air. Hence, cities with high impervious surface coverage sequester less chemical than forested areas which are more efficient at conveying chemical to soils and which are more effective chemical sinks than films (Wania and McLachlan, 2001; Priemer and Diamond, 2002; Su et al., 2007). Second, surface films act as a more efficient but transient sink of more particle-sorbed chemicals such as PBDEs whereby chemical accumulated during dry periods is transported to soils or surface waters during rain events. Hence, urban surface films
increase chemical mobility by increasing the proportion of chemical subject to either advective air or surface water transport, depending on a chemical’s physical-chemical properties.

4.3.3 Loadings to Lake Ontario

One of the key goals of the research was to estimate loadings from Toronto to Lake Ontario via urban pathways and atmospheric deposition. Atmospheric deposition has received considerable attention and is considered to drive loadings to the Great Lakes (e.g. Zhang et al., 1999; Blanchard et al., 2008; Venier and Hites, 2008). Urban pathways such as tributaries and storm water have received less attention (e.g. Samara et al., 2006; Robson et al., 2008; Howell et al., 2011).

According to SO-MUM calculations, the major urban input routes to tributaries were soil and film wash off (Figure 4.1, Figure A3.6). Since we were unable to distinguish the distribution between soil wash-off going to tributaries versus storm water because of the complicated sewer system in Toronto, we focused on the total masses of chemical transported from soil and films to surface waters by both pathways. Total soil and film wash-off contributed ~0.4 and ~0.8 kg y\(^{-1}\) for \(\Sigma_3\)PCBs and \(\Sigma_5\)PBDEs, respectively, to surface water which is within an order of magnitude agreement of tributary loadings to near-shore Lake Ontario of ~1.7 and ~1.4 kg y\(^{-1}\) estimated from year-round measured values (Diamond et al., 2010a; Melymuk et al., In Prep.). SO-MUM estimated that ~0.1 g d\(^{-1}\) (0.04 kg y\(^{-1}\)) and ~1.8 g d\(^{-1}\) (0.7 kg y\(^{-1}\)) were transferred from film to surface waters of \(\Sigma_5\)PCBs and \(\Sigma_5\)PBDEs, respectively. Film-to-surface water transfer of PBDEs exceeded that of PCBs due to the lower volatility of PBDEs, as mentioned above. Soil wash-off contributed 1.1 g d\(^{-1}\) (0.4 kg y\(^{-1}\)) and 0.4 g d\(^{-1}\) (0.1 kg y\(^{-1}\)) of \(\Sigma_5\)PCBs and \(\Sigma_5\)PBDEs to surface waters, respectively. Greater soil wash-off of PCBs, dominated by higher chlorinated congeners, was related to their higher soil concentrations due to a longer history of release and accumulation compared to PBDEs. Soils were thus found to be a secondary source of PCBs to near-shore Lake Ontario via wash-off.

Atmospheric contributions from Toronto to near shore Lake Ontario accounted for bi-directional air-water gas exchange, as well as wet and dry particle deposition (Figure A3.7). Volatilization of \(\Sigma_3\)PCBs (but dominated by lower chlorinated congeners) exceeded total atmospheric deposition and gas absorption of PCBs in cells within 20 km of DT (based on the UTD over the lake) and constituted ~46% of air-to-lake exchange within the model boundary (3700 km\(^2\) of the
total 18,960 km² lake area). For PBDEs, cells within 20 km of DT accounted for ~44% of total net atmospheric deposition (air deposition minus volatilization) to the lake within the model boundary. Hence, the model predicted that near-shore Lake Ontario is a net source to air and a net sink from air of PCBs and PBDEs, respectively. We note that this analysis is predicated on a few water concentration measurements (Figures A3.2-3) and during spring conditions such that annual conclusions cannot be made from these results. Whereas the magnitude of the exchange contains considerable uncertainty, the direction of the exchange is consistent with the physical-chemical properties of the two compound classes and their status in Lake Ontario and other lower Great Lakes (Blanchard et al., 2008; Meng et al., 2008; Venier and Hites, 2008).

In this spring simulation, net volatilization of $\Sigma_3$PCBs from the lake cells within 20 km of DT contributed ~6 (~4-8) kg y$^{-1}$, or ~16 (10-20) g d$^{-1}$, or ~23 (14-31) ng m$^{-2}$ d$^{-1}$ to air and may be overestimated on an annual basis due to warmer water temperatures in the spring (the range in volatilization rates was based on the range in estimated emissions). This volatilization is equivalent to ~35% of the primary emissions from the city (~17 or 2-36 kg y$^{-1}$) and much greater than the ~0.4 and 1.7 kg y$^{-1}$ delivered by surface waters (modeled and measurement estimated values, respectively). Recent studies have reported that Lake Ontario is a net source of PCBs to air (Blanchard et al., 2008; Meng et al., 2008) and other studies have found similar results in urban areas (Rowe et al., 2007; Yan et al., 2008; Martinez et al., 2010). Studies conducted 8-10 years ago when PCB air concentrations were higher found that Lake Michigan was a net PCB sink near Chicago and Milwaukee (Zhang et al., 1999; Miller et al., 2001; Offenberg et al., 2005; Wethington and Hornbuckle, 2005). These calculations support the interpretation proposed by Mackay and Bentzen (1997) that PCBs accumulated in the lower Great Lakes over the decades before their ban when air concentrations were high were followed by PCB release from the lakes in response to falling air concentrations as inventories were removed. They also note, however, that the direction of air-lake exchange can undergo seasonal changes indicating that our spring calculations should not be extrapolated to yearly exchange rates.

For $\Sigma_3$PBDEs net deposition to the lake within 20 km of DT was ~1 (~0.5 to 4) kg y$^{-1}$, or ~3 (~1 to 11) g d$^{-1}$, which was ~7% of primary emissions of 18 (3-42) kg y$^{-1}$. Again, the range was based on the range in estimated emissions with the lower end unrealistically underestimating measured air concentrations (Csizsar et al., Submitted). The modeled estimate of atmospheric
deposition is comparable to loadings from surface waters of ~0.8 and ~1.4 kg y\(^{-1}\) (modeled and measurement estimated values, respectively). Others have also reported that water bodies near urban areas are sinks for PBDEs (Cetin and Odabasi, 2007a; Venier and Hites, 2008; Wang et al., 2012). Our modeled estimate of ~1 kg y\(^{-1}\) net BDE-47 net deposition within 20 km of DT compares to ~7 kg y\(^{-1}\) estimated by Venier and Hites (2008) for the urban influence of Chicago on Lake Michigan (they estimated that the urban area contributed 5% to the total lake loading of 138 kg y\(^{-1}\)).

Overall, soil wash-off of higher chlorinated congeners to surface waters was the dominant loading pathway of PCBs to near-shore Lake Ontario. In comparison and consistent with the lower vapor pressure of PBDEs, air deposition and film wash-off to surface waters were the dominant pathways to near-shore Lake Ontario. Thus, near-shore Lake Ontario was unambiguously a net sink for PBDEs whereas it appears that the lake is a net source to air due to volatilization of lower chlorinated PCBs originating from primary emissions plus, it would appear, storage in the lake (Figure A3.6).

### 4.3.4 Primary versus Secondary Emissions

Model calculations indicate that Toronto is net source of primary emissions of PCBs and PBDEs to the region. In comparison, we estimated that at least ~900,000 km\(^2\) (approximately the area of Ontario) would be required to supply an equivalent secondary emission of PCBs and PBDEs from background soils as the primary emissions emanating from Toronto. This calculation was based on measured PCB and PBDE soil concentrations at background sites outside of Toronto (see Appendix 3 for more details).

We explored the effects of reducing the PCB and PBDE inventories on the magnitude of primary and secondary emissions (Figure 4.4). For \(\Sigma_5\) PCBs, primary emissions dominate unless the inventory drops to 1/10 or below current levels, at which point volatilization from near-shore Lake Ontario dominates (i.e. ~2 kg y\(^{-1}\) primary vs. ~6 kg y\(^{-1}\) lake volatilization). However, this calculation is illustrative since we assumed a constant PCB water concentration rather than assuming that near-shore lake concentrations would decrease together with the PCB inventory. Alternatively, these calculations can be viewed as predictions based on an instantaneous removal of the inventory. Volatilization from soil did not contribute substantially to air
emissions even at low levels of primary emissions (<0.01 kg y\(^{-1}\)) but continue to be a source to
the lake via soil wash-off.

For \(\Sigma_5\) PBDEs, reducing the inventory by 1000 times did not yield a net soil-to-air transfer.
Reducing the inventory by 100 times, however, did yield net lake-to-air transfer, but at levels 10
times lower than primary emissions (i.e. 0.2 kg y\(^{-1}\) primary and 0.02 kg y\(^{-1}\) lake volatilization).
Again, these estimates are illustrative because they are constrained by the assumption of
constant water concentrations. Reducing primary emissions would also reduce tributary and
storm water loadings of PBDEs since these are supported by primary atmospheric emissions via
wash-off of deposition to surface films.

These results provide a strong incentive to reduce primary emissions and hence the inventory of
these banned compounds.

4.4 Conclusions

SO-MUM was used to estimate the effects of urban air emissions from the City of Toronto on
the surrounding region where it predicted that \(~95\%\) and \(~70\%\) of PCB and PBDE air
emissions, respectively were advected out of the city. At current air concentrations primary
emissions dominate sources to air as opposed to secondary sources such as soil and lake water
volatilization. Furthermore, surface films were found to act as an effective sink from air for
PBDEs and mediated further chemical mobilization to surface waters. Surface films re-
volatileized the majority of deposited PCBs such that impervious surfaces increase the amount of
chemical advected out of the city compared to less urbanized areas with more vegetative cover.
Surface films thus mediate urban contaminant transport in different ways based on physical-
chemical properties.

On a local scale PBDE concentrations decreased at similar distances from the urban centre in
comparison to PCBs due to the former’s broader geographic distribution of inventory.
However, on a regional scale PBDE concentrations dropped off more quickly than PCBs due
their lower tendency for atmospheric transport. This phenomena resulted in PBDEs having a
longer UTD than PCBs while having a shorter 1/10 travel distance. Thus, when assessing the
travel distance from an urban area on a local scale the spatial distribution of emissions may be
an important factor in addition to the relative particle association of a chemical. Urban travel
distances that account for wind velocity can be up to double those calculated using the radial distribution model independent of wind velocities.

Near-shore Lake Ontario is currently a net PCB source, however at a level ~3 times lower than estimated primary urban emissions. Near-shore Lake Ontario receives PBDEs from surface waters via film wash-off whereas soil wash-off was more important than films for PCBs. In a model scenario of reducing primary emissions by reducing the PCB inventory 10 times below its 2006 mass was counteracted by volatilization from near-shore Lake Ontario. Negligible volatilization of PBDEs from the near-shore lake may occur even with an inventory reduction of 1000 times. These two chemicals demonstrate a contrast in usage timelines as PCBs have had longer time to build-up in the outdoor environment (e.g. in soils and lake water). If PBDEs continue to build-up in the urban environment, re-emission may contribute a larger percentage to total air emissions or the lake may be their ultimate sink.

4.5 Tables

<table>
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<tr>
<th>Fraction of urban reference concentration</th>
<th>Travel distance (km) PCB</th>
<th>Travel distance (km) PBDE</th>
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Table 4.1 Travel distances indicating the distance at which air concentrations of PCBs and PBDEs drop to less than 1/e or 1/10 concentrations of the urban reference site, as predicted by SO-MUM and published studies. SO-MUM prevailing wind refers to the maximum distance along the prevailing wind direction; and the exponential fit refers to all data from all model cells regardless of wind direction. The downtown emission only values refer to SO-MUM simulations with emissions emanating from the DT cell (PCBs) or (5,3) cell (PBDEs) only.
4.6 Figures

a. PCB

Figure 4.1 Mass balance diagrams for the sum of 39 Toronto cells for a) $\Sigma_3$PCBs and b) $\Sigma_3$PBDEs. Units are in g d$^{-1}$; solid lines refer to transport, dotted lines refer to transformation, and the curved arrow refers to emission. Rates represent averages over the 91 day simulation period of spring 2008. Values in brackets in each compartment represent the change in mass over the simulation period.
Figure 4.2 Modeled air concentrations in the 5×5 km² cells that span the model domain, averaged over the spring 2008 simulation period (91 days) for a) $\Sigma_5$PCBs and b) $\Sigma_5$PBDEs.
Figure 4.3 Modeled air concentrations averaged over the 91 day spring simulation period considering primary emissions in all Toronto cells versus distance (•) and the exponential fit for this data (-). 0 km is the cell with the highest concentration and (●) is the exponential fit of air concentration vs. distance for the model run with a single point source emission from the highest emission cell a) ΣPCBs in cell DT and b) ΣPBDEs in cell (5,3). (•) and (●) indicate the points at which the exponential fit drops to 1/e and 1/10 the reference concentration, respectively.
Figure 4.4 Comparison of net flux to air from soil and near-shore Lake Ontario (within 20 km of the DT cell) under various emission scenarios achieved by reducing chemical inventories for a) $\Sigma_3$PCBs and b) PBDE-47.

4.7 References


Daggupaty, S.M., Banic, C.M., Cheung, P., Ma, J.M., 2006. Numerical simulation of air concentration and deposition of particulate metals around a copper smelter in northern Quebec, Canada. Geochemistry-Exploration Environment Analysis 6, 139-146.


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Chapter 5
Conclusions

5 Conclusions

5.1 Research Summary

The overarching goal of this research was to estimate spatially resolved urban sources, fate, and transport of semi-volatile organic compounds, SVOCs. This was accomplished by first improving the Multimedia Urban Model, MUM, and second, coupling MUM to an air transport model, BLFMAPS to form spatially-oriented MUM, SO-MUM, and finally applying the coupled model to a detailed study of PCBs and PBDEs in Toronto, Canada.

The one-box steady-state version of MUM predicted \( \Sigma_{88\text{PCB}} \) and \( \Sigma_{26\text{PBDE}} \) emissions to be 180-300 kg y\(^{-1}\) and 26-33 kg y\(^{-1}\), respectively from Toronto which is in order of magnitude agreement with other urban PCB emission estimates on a per capita and per area basis (e.g. Breivik et al., 2002; Gasic et al., 2009; Moeckel et al., 2010; Totten et al., 2006).

The steady-state one-box version of MUM was extended into a dynamic model incorporating recent findings on film properties and their interactions with semi-volatile organic compounds (SVOCs). The model was able to reasonably reproduce film growth and wash-off processes as well as air-film pollutant dynamics. The source/sink nature of films was investigated where it was found that films act as a temporary chemical sink at cooler temperatures, especially for higher \( K_{oa} \) chemicals, and as a source to air via re-volatilization at higher temperatures. Furthermore, films can become a source to surface water during rain events as accumulated chemicals are washed off with the film. This updated model paved the way for furthering our understanding of chemical dynamics in urban areas as the model can temporally resolve varying environmental conditions such as changes in temperature and wind velocities and it can also be applied to different chemicals to assess the effects of differing physical-chemical properties.

The dynamic version of MUM was further extended from a one-box into a multi-box model on a 5km scale by coupling it with an air transport model, BLFMAPS to form SO-MUM. The model domain covered a part of Southern Ontario (12350 km\(^2\)) and was centered over Toronto which was made up of 39 model cells (821 km\(^2\) land area). Tributary transport was added to estimate
spatially resolved emissions and fate of SVOCs as the final extension of SO-MUM. SO-MUM was applied to PCBs and PBDEs which provide a contrast in usage timelines as well as physical-chemical properties.

Spatially resolved PCB and PBDE emissions were estimated in Toronto by calculating average air emission rates per inventory based on back-calculated emissions from available measured concentrations and mass inventories in each cell. The model was run for spring 2008 and reproduced measured concentrations in air, tributaries, surface films, and precipitation within an order of magnitude of measured values. \( \Sigma_{88} \) PCB emissions from Toronto were estimated to be 230 (40-480) kg y\(^{-1} \) with a spatial range spanning four orders of magnitude within the city reflecting the range in inventory. \( \Sigma_{28} \) PBDE emissions from Toronto were estimated to be 28 (6-63) kg y\(^{-1} \) with a spatial range spanning an order of magnitude (~30 times) which is a much smaller range compared to PCBs and reflects the broader geographic distribution of inventory of PBDEs in comparison to PCBs. Emission estimates were most sensitive to horizontal and then vertical wind speeds, both of which were relatively certain as they were taken from the evaluated model BLFMAPS. Estimates for PBDEs were also sensitive to dry particle deposition velocities for PBDEs and horizontal and vertical wind speeds for both chemical classes.

Estimated city-wide emissions were in agreement, however they were on the lower end than those previously estimated using the one-box version of MUM (Diamond et al., 2010; Jones-Otazo et al., 2005) and they were also lower than estimated urban emissions from Zurich, Switzerland (Gasic et al., 2009; Moeckel et al., 2010); both estimation methods were based on measured air concentrations at only one or a few urban sites. Back-calculated emissions using the one-box model with averaged spatial urban air concentrations (nine sites) yielded an aggregate emission range similar to the estimate made using the multi-box model. Thus, one may conclude that using a one-box urban model is sufficient for back-calculating emissions if a spatially representative average SVOC concentration is available, given the high degree of spatial heterogeneity in air concentrations (Melymuk et al. 2012).

Emission rates per inventory were \(~0.5 (0.05-1.6) \) g y\(^{-1} \) kg\(^{-1} \) and \(~0.1 (0.01-0.7) \) g y\(^{-1} \) kg\(^{-1} \) for \( \Sigma_{88} \) PCBs and \( \Sigma_{28} \) PBDEs, respectively. For both chemicals this implies that it would take on the order of a thousand years for the chemicals to be emitted from the stock to the outdoors assuming no changes in emission rates or stock. PBDEs had a lower emission rate per inventory
which may be due to their lower volatility (Prevedouros et al., 2004) and the nature of PBDEs as indoor contaminants (e.g. Batterman et al., 2009; Björklund et al., 2012; Melymuk et al., 2012; Zhang et al., 2009).

Once the emission estimates and SO-MUM were assessed, SO-MUM was used to investigate the interactions between air and urban media (soil, vegetation, surface films, and rivers) as well as the consequences of urban emissions on the surrounding region. For both chemicals, the model predicted net air deposition (wet and dry deposition plus gas absorption minus volatilization) to urban media (soil, vegetation, surface films, and rivers) with films being a more efficient sink from air for PBDEs than for PCBs. As the model predicted net air-to-urban area transfer, it follows that air emissions are dominated by 'fresh' or primary emissions from the inventory rather than secondary emissions from soil.

SO-MUM predicted that ~95% ($\Sigma_3$PCBs) and ~72% ($\Sigma_3$PBDEs) of emissions were advected out of the city. The term “Urban Travel Distance” or UTD was introduced to quantify the distance traveled by an urban (rather than point source) atmospheric plume. The UTD, or the distance for atmospheric concentrations to drop to 1/e the urban reference concentration, were 25 and 30 km for PCBs and PBDEs, respectively when taking into account wind velocities. However, the distance for concentrations to drop to one tenth of the urban reference concentration were 60 and 50 km from the urban reference location for PCBs and PBDEs, respectively, such that PCBs travel a longer distance on this scale. These contrary results can be explained by the geographically broader distribution of the PBDE in comparison to PCB inventory balanced by the faster attenuation rate for more particle-sorbed PBDEs. Furthermore, when wind velocities are not taken into account, travel distances can be half the distance when winds are included in the analysis. Thus, travel distances are controlled by the geographic distribution of the inventory, prevailing wind directions, and physical-chemical properties.

The model predicted that Lake Ontario (within 20 km of downtown) is a net source to air for $\Sigma_3$PCBs (~4 to 8 kg y$^{-1}$) and a net sink from air for $\Sigma_3$PBDEs (~0.5 to 4 kg y$^{-1}$) resulting from differing physical-chemical properties as PCBs are more volatile than PBDEs. In terms of loading pathways to Lake Ontario soil wash-off to surface waters (~0.4 kg y$^{-1}$) was the most significant route for PCBs suggesting the soils act as a secondary source to near-shore Lake Ontario via wash-off; film wash-off to surface waters was an order of magnitude lower than for
soil (~0.04 kg y\(^{-1}\)). Conversely, for PBDEs air deposition to the lake and film wash-off both contributed more significantly to Lake Ontario loadings (~1 kg y\(^{-1}\) and ~0.7 kg y\(^{-1}\), respectively) in comparison to soil wash-off (~0.1 kg y\(^{-1}\)). The increased importance of film wash-off for PBDEs follows from films being a more efficient, but transient sink of the more particle associated PBDEs in comparison to PCBs.

When the inventory of PCBs in Toronto is reduced, Lake Ontario would become a source to air for PCBs, however at levels ~third of current primary emissions. This is driven by primary emissions plus the burden of lower chlorinated congeners in the lake, and less so by soil wash off of higher chlorinated congeners. However, as Lake Ontario is a sink for PBDEs, reducing primary emissions has a more pronounced effect on reducing total emissions to air as Lake Ontario does not become a substantial source.

In summary, this thesis presents a novel method to estimate spatially resolved urban POP emissions based on mass inventories. Furthermore, a dynamic one-box surface film module was developed to better understand the role of films in mediating urban contaminant fate. This model was extended into a multi-box coupled multimedia and air transport model, SO-MUM which was used to quantify the fate of emissions and the magnitude of the urban plume which provided further insight into urban SVOC emissions, dynamics, and fate.

5.2 Scientific Contributions

The following is a list of scientific contributions and major conclusions from this thesis:

- Advanced our understanding of urban SVOC emissions and fate.
- Developed a dynamic surface film module and updated the multimedia urban model (MUM) based on theoretical considerations and empirical data. This model was used to better understand air-film-surface water dynamics as a function of meteorological conditions and physical-chemical properties of SVOCs.
- Developed the SO-MUM model by coupling the dynamic film module version of MUM with BLFMAPS (Daggupaty et al., 2006), an air transport model. This model was used to predict intra-urban SVOC fate as well as to assess the contribution of various urban source pathways to the surrounding regions.
Developed a novel method to estimate intra-urban SVOC emissions based on measured concentrations and spatial mass inventories. This provides a method to scale emissions based on chemical stock which can be used to inform chemical removal strategies.

$\Sigma_{88}$PCB and $\Sigma_{26}$PBDE emission rates were estimated to be 0.4 (0.05-1.6) and 0.1 (0.01-0.7) g y$^{-1}$ kg$^{-1}$ of inventory, respectively. Emissions varied spatially over four orders of magnitude for PCBs and ~30 times for PBDEs due to variations in the mass inventory.

For both chemicals, deposition to soil from air is larger than soil volatilization such that it does not contribute significantly to urban air concentrations even as inventories drop. The results unambiguously show that air emissions are dominated by primary sources that are emanating from the chemical stock in the city. Chemical that deposits to soil can be further mobilized into surface waters via wash-off.

Volatilization from at least an area of $\sim$900,000 km$^2$ of rural soil would be required to reach levels of primary emissions from Toronto.

For chemicals with higher vapor pressures, such as PCBs, deposition to surface films is followed by re-volatilization. For lower vapor pressure chemicals, such as PBDEs, films act as an effective sink from air allowing for chemical build-up and subsequent wash-off to surface waters.

UTDs for PCBs and PBDEs were ~25 and 30 km, however, the 1/10 travel distances were ~60 and 50 km, respectively. Thus, PCBs travel further from the city than PBDEs owing to the mostly gas-phase nature of PCBs versus the more particle-bound nature of PBDEs.

On a local scale, PCB concentrations drop more quickly than those of PBDEs due to the restricted geographic distribution of PCBs and the geographically disbursed inventory of PBDEs as PCBs act more as a point source from downtown in Toronto.

When taking wind velocities into account, chemical travel distances can be up to double those when wind is not included in the analysis. Hence chemical travel distances depend on the distribution of inventory, wind velocities, and physical-chemical properties.

Lake Ontario is currently a net source to air for PCBs and sink from air for PBDEs.

Surface water loadings are dominated by soil wash-off for PCBs and film wash-off for PBDEs resulting from higher PCB soil concentrations and films being a more efficient sink for PBDEs.
- Reducing primary PCB emissions ten times results in secondary emissions from Lake Ontario becoming the dominant emission source. Further reducing primary emissions results in a ~3 times reduction in total emissions (primary plus lake). However, this analysis assumes constant water concentrations which would be unlikely if primary emissions were reduced.

- Reducing PBDE inventories does not result in significant secondary emissions from soil or Lake Ontario to air.

5.3 Research Outlook

This thesis provided insight into urban contaminant emissions and dynamics within and beyond the urban boundary. This was accomplished by developing a novel method to estimate intra-urban POPs concentrations using measured concentrations, mass inventories, and multimedia modeling and can be used to relate emissions back to primary sources. The method was assessed using PCBs and PBDEs, however, it can also be applied to other SVOCs in order to identify emissions emanating from their sources. The method of relating emissions to estimated stocks can be used for other SVOCs that have been measured at an intra-urban scale, such as polycyclic aromatic hydrocarbons and polycyclic musks (Melymuk et al., 2012). Emission rates per mass inventory can also be calculated using only a few measured air concentrations and can be spatially scaled to an urban area or region based on mass inventories. This may provide useful for emerging contaminants, for example as new flame retardants replace PBDEs (Venier and Hites, 2008b). The method could also be used to estimate intra-urban BDE-209 emissions as it is more difficult to measure these with passive air samplers due their particle-associated nature (Melymuk et al., 2011). With these emission estimates SO-MUM can be used to estimate the contribution of BDE-degradation into tetra- and penta-BDE emissions (Schenker et al., 2008).

In addition to applying the emission estimation method to other SVOCs, it can also be applied to other cities and to compare emission rates per inventory. This would provide further assessment of the method as well as provide information about the relationship between sources and emissions for that particular city. Intra-urban PCB and PBDE air concentrations have also been measured in various other cities such as Brisbane, Philadelphia, and Chicago (Du et al., 2009; Hearn et al., 2012; Hu et al., 2010). Applying SO-MUM to other cities with different
geographic characteristics, for example, a city without a large urban water body such as a lake or a ocean may also give insight into different chemical recycling pathways (Choi and Wania, 2011).

SO-MUM is an initial extension of the one-box MUM into a multi-box and coupled air transport model, and as such, it can be further extended and improved. Most notably, SVOC air concentrations have been measured to vary on scales less than 5 km (Du et al., 2009; Hearn et al., 2012; Hu et al., 2010) and thus reducing the grid spacing may result in a more accurate reproduction of measured concentrations and chemical behavior. Stein et al. (2007) modeled benzene air transport on a 1 km scale using the Community Multi-scale Air Quality model (CMAQ) and coupling MUM to a more spatially resolved air transport model may present a future research possibility. A finer scale model could also be used to simulate the effects of urban wind canyons where vertical mixing may be more pronounced than horizontal mixing and thus have implications for air pollutant transport within the city (Chu et al., 2005). This may be especially interesting to study for chemicals such as PCBs where downtown (in the case of Toronto) has a very high geographic concentration of the mass inventory and thus acts as a point source to the rest of the urban area. Another improvement would be using temperature dependent emissions rather than a constant emission rate over the entire simulation period. This may improve the model sensitivity to changes in temperature as urban PCB and PBDE air concentrations have been found to be related to temperature (Hu et al., 2010; Melymuk et al., 2012).

The watershed chemical transport has a rather simple representation in the model and likely did not capture all the significant surface water processes as SO-MUM underestimated tributary concentrations of both PCBs and PBDEs compared to measured values. Several gridded and more complex watershed chemical transport models have been developed (e.g. Hollander et al., 2006; Suzuki et al., 2004; Velleux et al., 2008) and concepts and techniques from these models could be incorporated into SO-MUM. These models provide additional details such as multiple soil compartments with run-off to rivers and a networked river database (Hollander et al., 2006; Suzuki et al., 2004). This additional model detail may provide further insight into the mechanisms of surface water loadings from Toronto into Lake Ontario. More information about storm water pathways (e.g. proportion that flows directly into rivers or into waste water treatment plants, WWTPs) would also give further insight into the contribution of surface film
wash-off to rivers and WWTPs. Since SO-MUM estimated that surface films are a more significant source of PBDEs than soil and the converse for PCBs, it would be interesting for this prediction to be evaluated by sampling run-off from soils and impervious surfaces and comparing chemical concentrations between these two sources. Eckley and Branfireun (2008), for example, measured mercury concentrations in run-off from impervious surfaces in Toronto; these techniques could be applied to obtain PCB and PBDE measurements for comparison with model results.

SO-MUM, as with all environmental models, depends on various data inputs including media concentrations, physical-chemical properties, and geographic characteristics. The current application of SO-MUM did not include various inputs, such as emission rates from nearby cities (e.g. Hamilton and Mississauga, Ontario) or longer range sources (e.g. from the United States), which could be used assess the effects of elevated air concentrations in cities and the region neighboring Toronto. Few data are available on lake water concentrations on both a spatial and temporal scale which could be used for studies on air-water exchange to assess the magnitude of the source/sink nature of Lake Ontario. Several studies have identified the need for chemical air-water exchange calculations (e.g. Blanchard et al., 2008; Martinez et al., 2010; Meng et al., 2008; Sandy et al., 2012) and more water concentration data would improve the accuracy of current estimates for Lake Ontario. Finally, SO-MUM predicted that modeled air deposition processes are sensitive to dry particle deposition velocities for more particle associated chemicals, such as PBDEs and values in the literature range over orders of magnitude (e.g. Cetin and Odabasi, 2007; Venier and Hites, 2008a). More studies measuring deposition velocities such as those of Tasdemir and Holsen (2005) and Bozlaker et al. (2008) may help in the parameterization of multimedia or air transport models as well as aid in depositional calculations. Another approach may be to add a more complex deposition velocity module where velocities are calculated based particle sizes and densities (e.g. Zhang et al., 2001). This would also allow for size-based partitioning of chemicals where chemical could be distributed amongst particle size fractions. Moeckel et al. (2010), for example, modeled PBDE partitioning to a coarse and fine fraction and their particle size distribution could be added to SO-MUM.

SO-MUM and other fugacity models depend on a large array of input parameters. A more complex sensitivity analysis and adding an uncertainty analysis would give insight into a range of possible model outcomes (MacLeod et al., 2002). Sensitivity analyses were performed using
the one-box steady- and unsteady-state version of the model by varying one parameter at a time, yielding results for one 'slice' of the multi-dimensional parameter space. However, varying multiple parameters simultaneously using the multi-box model would give information about ranges of model outputs based on various input parameters as a whole, in addition to providing information about spatial results, for example urban travel distances. Some methods used to quantify uncertainty in environmental models include Monte Carlo techniques (e.g. Matthies et al., 2004; Schenker et al., 2009) and Taylor series error propagation (e.g. Hong et al., 2010; MacLeod et al., 2002).

As SO-MUM was formed by coupling MUM to BLFMAPS, which includes a boundary layer forecast model, it also has the capabilities of modeling the effects of vertical wind velocities and boundary layer heights on chemical air concentrations. Gasic et al. (2009) and Moeckel et al. (2010) included boundary layer height in their multimedia fugacity model of PCBs and PBDEs and observed that it can explain diurnal variations in air concentrations. SO-MUM could be used to give further insights into the effects of boundary layer height and travel potential; for example, at lower boundary layer heights when chemicals are trapped in the boundary layer less chemicals may be advected out of the city.

In conclusion, this thesis improved our understanding of SVOC emissions and fate relative to an urban area through the development of a coupled multimedia fugacity model and air transport model, and presented a novel method for estimating urban POP emissions based on mass inventories. The model was able to reproduce environmental concentrations within an order of magnitude of measured results and give insight into spatially resolved urban emissions and urban effects on neighboring regions. The model can be extended in various ways and applied to other chemicals and cities and give further insight into chemical removal strategies and inform policy decisions and highlights the need for removing chemical stock in order to reduce emissions.

5.4 References


Daggupaty, S.M., Banic, C.M., Cheung, P., Ma, J.M., 2006. Numerical simulation of air concentration and deposition of particulate metals around a copper smelter in northern Quebec, Canada. Geochemistry-Exploration Environment Analysis 6, 139-146.


urban source strength in Zurich, Switzerland. Environmental Science & Technology 43, 769-776.


Appendix 1: Supporting Information for Chapter 2

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Air</td>
<td>[ V_1 Z_{B1} \frac{df_1}{dt} = -(D_{12} + D_{13} + D_{14} + D_{16} + D_{17} + D_{i_w} + D_{R1}) f_1 + D_{21} f_2 \ + D_{12} f_2 + D_{15} f_3 + D_{41} f_4 + D_{6} f_6 + D_{71} f_7 + I_1 + E_1 ]</td>
</tr>
<tr>
<td>Upper Air</td>
<td>[ V_2 Z_{B2} \frac{df_2}{dt} = -(D_{21} + D_{42} + D_{R2}) f_2 + D_{12} f_1 + I_2 + E_2 ]</td>
</tr>
<tr>
<td>Water</td>
<td>[ V_3 Z_{B3} \frac{df_3}{dt} = -(D_{31} + D_{35} + D_{36} + D_{R3}) f_3 + D_{13} f_1 + D_{43} f_4 + D_{53} f_5 + I_3 ]</td>
</tr>
</tbody>
</table>
| Soil        | Dry conditions: \[ V_4 Z_{B4} \frac{df_4}{dt} = -(D_{41} + D_{43} + D_{46} + D_{47} + D_{R4}) f_4 + D_{14} f_1 + D_{64} f_6 \]  
*Rain event: \[ V_4 Z_{B4} \frac{f_4^{n+1} - f_4^n}{\Delta t} = -(D_{41} + D_{43} + D_{46} + D_{47} + D_{R4}) f_4^{n+1} \]  
\[ + D_{14} f_1^{n+1} + D_{64} f_6^{n+1} + (1 - R) W_m^n \] |
| Sediment    | \[ V_5 Z_{B5} \frac{df_5}{dt} = -(D_{51} + D_{56} + D_{R5}) f_5 + D_{15} f_3 \] |
| Vegetation  | \[ V_6 Z_{B6} \frac{df_6}{dt} = -(D_{61} + D_{64} + D_{R6}) f_4 + D_{16} f_4 + D_{56} f_4 \] |
| Film        | Growth: \[ Z_{B7} \frac{d(V_7 f_7)}{dt} = -(D_{71} + D_{R7}) f_7 + D_{17} f_1 \]  
*Wash-off: \[ Z_{B7} \frac{V_7^{n+1} f_7^{n+1} - V_7^n f_7^n}{\Delta t} = -(D_{17} + D_{R7}) f_7^{n+1} + D_{17} f_7^{n+1} - W_m^n \]  
where \[ W_m^n = \frac{Z_{B7} V_7^n f_7^n}{\Delta t} \] and \[ V_7^n = W_E V_7^n . \] |

Table A1.1 Mass balance equations used in dynamic model.

Notes: Subscripts are defined as follows 1: lower air, 2: upper air, 3: water, 4: soil, 5: sediment, 6: vegetation, 7: film, and sw: storm water. \( V, Z_B, f, \) and \( D \) refer to volume, bulk Z-value, fugacity, and D-value, respectively. \( D_{AI}, D_{RI}, D_{ij} \) refer to advection, reaction, and inter-compartmental D-values, respectively. \( I \) and \( E \) refer to input and emission, respectively. We assumed that the Z- and D-values remained constant during the simulation (as temperature was kept constant) and that volumes stayed constant for all compartments except film. Film wash-off is an instantaneous process modeled to occur at the beginning of the time step, hence this process is represented in discretized form. \( W_E \) is the wash-off efficiency as defined in the manuscript text. \( t_n = n \Delta t, \) where \( n \) and \( \Delta t \) represent the time step number and length of a time step and we use the convention where \( t_n \) represents the current time and \( t_{n+1} \) represents one time step into the future.
<table>
<thead>
<tr>
<th>Location</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lower Air</strong></td>
<td><strong>Upper air:</strong> (D_{12} = U_a A_1 Z_{g1})</td>
</tr>
<tr>
<td><strong>Water:</strong></td>
<td>gas diffusion: (D_{vw} = \left( \frac{1}{k_{wa} A_3 Z_a} + \frac{1}{k_{pw} A_3 Z_w} \right)^{-1})</td>
</tr>
<tr>
<td></td>
<td>dry particle deposition: (D_{dw} = A_3 U_p F_{pa} Z_p)</td>
</tr>
<tr>
<td></td>
<td>wet gas deposition: (D_{rw} = A_3 Z_{w})</td>
</tr>
<tr>
<td></td>
<td>wet particle deposition: (D_{qw} = A_3 RQF_{pa} Z_p)</td>
</tr>
<tr>
<td></td>
<td>total: (D_{13} = D_{vw} + D_{dw} + D_{rw} + D_{qw})</td>
</tr>
<tr>
<td><strong>Soil:</strong></td>
<td>gas diffusion: (D_{sv} = \left( \frac{1}{k_{sa} A_4 Z_a} + \frac{Y_4}{(A_4 B_{ca} Z_a + A_4 B_{cw} Z_w)} \right)^{-1})</td>
</tr>
<tr>
<td></td>
<td>dry particle deposition: (D_{sv} = A_4 U_p F_{pa} Z_p)</td>
</tr>
<tr>
<td></td>
<td>wet gas deposition: (D_{sv} = A_4 Z_{w})</td>
</tr>
<tr>
<td></td>
<td>wet particle deposition: (D_{sv} = A_4 RZF_{pa} Z_p)</td>
</tr>
<tr>
<td></td>
<td>total: (D_{14,1} = D_{sv} + D_{rs} + D_{qw} + D_{dv})</td>
</tr>
<tr>
<td><strong>Vegetation:</strong></td>
<td>gas diffusion: (D_{sv} = \left( \frac{1}{k_{sv} A_5 Z_a} + \frac{1}{k_{iv} A_5 Z_{lv}} \right)^{-1})</td>
</tr>
<tr>
<td></td>
<td>dry particle deposition: (D_{sv} = A_5 U_p F_{pa} Z_{p} I_{f\delta})</td>
</tr>
<tr>
<td></td>
<td>wet gas deposition: (D_{sv} = A_5 Z_{w})</td>
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<tr>
<td></td>
<td>wet particle deposition: (D_{sv} = A_5 RQF_{pa} Z_p)</td>
</tr>
<tr>
<td></td>
<td>total: (D_{15} = D_{sv} + D_{dv} + I_{f\delta} (D_{sv} + D_{qv}))</td>
</tr>
<tr>
<td><strong>Film:</strong></td>
<td>gas diffusion: (D_{sf} = \left( \frac{1}{k_{sf} A_7 Z_a} + \frac{1}{k_{ff} A_7 Z_f} \right)^{-1})</td>
</tr>
<tr>
<td>Component</td>
<td>Equation</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>dry part deposition</td>
<td>( D_{df} = A_f U_p F_{pa} Z_p )</td>
</tr>
<tr>
<td>wet gas deposition</td>
<td>( D_{gf} = A_f RZ_w )</td>
</tr>
<tr>
<td>wet part dep.</td>
<td>( D_{gf} = A_f RQF_{pa} Z_p )</td>
</tr>
<tr>
<td>total dry</td>
<td>( D_{17} = D_{gf} + D_{df} )</td>
</tr>
<tr>
<td>Air to soil via vegetation</td>
<td>( D_{14,6} = (1 - I_{fu})(D_{rv} + D_{sw}) ) (canopy drip) ( ^b )</td>
</tr>
<tr>
<td>Air to soil via film</td>
<td>( D_{14,7} = (1 - RR)(D_{rf} + D_{qf}) ) ( ^c )</td>
</tr>
<tr>
<td>Air to soil total</td>
<td>( D_{14} = D_{14,1} + D_{14,6} + D_{14,7} ) ( ^c )</td>
</tr>
<tr>
<td>Air to storm water via film</td>
<td>( D_{1,sw} = RR(D_{rf} + D_{qf}) ) ( ^c )</td>
</tr>
</tbody>
</table>

| Upper Air                     | Lower air: \( D_{21} = U_f A_f Z_{B2} \)                                 |

| Water                         | Lower air: \( D_{31} = D_{sw} \)                                         |

**Sediment**

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion</td>
<td>( D_{rx} = \left( \frac{1}{k_{sw} A_S Z_w} + \frac{Y_5}{B_{sw} A_S Z_w} \right)^{-1} )</td>
</tr>
<tr>
<td>deposition</td>
<td>( D_{dx} = A_f U_d Z_{ss} )</td>
</tr>
<tr>
<td>total</td>
<td>( D_{35} = D_{rx} + D_{dx} )</td>
</tr>
</tbody>
</table>

| Soil                          | Lower air: \( D_{41} = D_{sv} \)                                         |

**Water**

<table>
<thead>
<tr>
<th>Water</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>soil run-off</td>
<td>( D_{sw} = A_f U_{sw} Z_s )</td>
</tr>
<tr>
<td>water run-off</td>
<td>( D_{ww} = A_f U_{ww} Z_w )</td>
</tr>
<tr>
<td>total</td>
<td>( D_{43} = D_{sw} + D_{ww} ) (rain) or ( D_{43} = 0 ) (no rain)</td>
</tr>
</tbody>
</table>

**Ground water**

| Ground water                 | \( D_{4g} = A_f Z_w U_g \)                                               |

**Vegetation**

| Vegetation                   | \( D_{4s} = V_4 R_s Z_{Bs} \) (rain splash) \( ^a \)                    |

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Water:</th>
</tr>
</thead>
<tbody>
<tr>
<td>re-suspension</td>
<td>( D_{rx} = A_f U_{rx} Z_{sc} )</td>
</tr>
<tr>
<td>total</td>
<td>( D_{s3} = D_{rx} + D_{rx} )</td>
</tr>
</tbody>
</table>

**Vegetation**

| Vegetation                   | Lower air: \( D_{61} = D_{vv} \)                                         |
Soil:

wax erosion: \( D_{we} = A_6 k_{we} Z_{lc} \)

litterfall: \( D_{lf} = V_6 R_{lf} Z_{lv} \)

total: \( D_{64} = D_{we} + D_{lf} \)

**Film**

**Lower air:** \( D_{21} = D_{vf} \)

**Advection**

(air and water only)

\( D_{Ai} = G_i Z_{Bi} \)

**Reaction**

\( D_{Ri} = V_i Z_{Bi} k_{Ri} \)

---

**Table A1.2 D-values used in dynamic model**

Notes: \( A_i, Z_{Bi}, G_i, V_i \) and \( k_{Ri} \) refer to area, bulk Z-value, advective flow rate, volume, and reaction rate of compartment \( i \), respectively; and \( R, RR, \) and \( V_{fw} \), refer to rain rate, run-off ratio, and volume of washed-off film, respectively. Other parameters are defined in Table A1.2b. \(^a\)

Equations are from or adapted from Diamond et al. (2001) and Priemer and Diamond (2002) \(^b\)

Adapted from Prevedourous et al. (2008) \(^c\)

This paper

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_a )</td>
<td>transport rate between lower and upper air</td>
</tr>
<tr>
<td>( U_p )</td>
<td>dry particle deposition velocity</td>
</tr>
<tr>
<td>( F_{pa} )</td>
<td>volume fraction of particles in air</td>
</tr>
<tr>
<td>( Q )</td>
<td>scavenging coefficient</td>
</tr>
<tr>
<td>( Y_d )</td>
<td>diffusion path length in soil</td>
</tr>
<tr>
<td>( B_{ea} )</td>
<td>air diffusion rate in soil</td>
</tr>
<tr>
<td>( B_{ew} )</td>
<td>water diffusion rate in soil</td>
</tr>
<tr>
<td>( B_{wx} )</td>
<td>water diffusion rate in sediment</td>
</tr>
<tr>
<td>( I_{fd} )</td>
<td>canopy dry interception fraction</td>
</tr>
<tr>
<td>( I_{fw} )</td>
<td>canopy wet interception fraction</td>
</tr>
<tr>
<td>( Y_s )</td>
<td>diffusion path length in sediment</td>
</tr>
<tr>
<td>( U_{dx} )</td>
<td>sediment deposition rate</td>
</tr>
<tr>
<td>( U_{sw} )</td>
<td>solid run-off rate from soil</td>
</tr>
<tr>
<td>( U_{ww} )</td>
<td>water run-off rate from soil</td>
</tr>
<tr>
<td>( U_g )</td>
<td>soil transfer rate to ground water</td>
</tr>
<tr>
<td>Parameter</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$R_s$</td>
<td>rain splash rate constant</td>
</tr>
<tr>
<td>$U_{rx}$</td>
<td>sediment re-suspension rate</td>
</tr>
<tr>
<td>$U_{bx}$</td>
<td>sediment burial rate</td>
</tr>
<tr>
<td>$R_{lf}$</td>
<td>litter fall rate constant</td>
</tr>
<tr>
<td>$k_{ma}$</td>
<td>air-side MTC over water</td>
</tr>
<tr>
<td>$k_{mw}$</td>
<td>water-side MTC air over water</td>
</tr>
<tr>
<td>$k_{sa}$</td>
<td>air side MTC over soil</td>
</tr>
<tr>
<td>$k_{av}$</td>
<td>air side MTC over vegetation</td>
</tr>
<tr>
<td>$k_{vv}$</td>
<td>vegetation side MTC over vegetation</td>
</tr>
<tr>
<td>$k_{af}$</td>
<td>air side MTC over film</td>
</tr>
<tr>
<td>$k_{ff}$</td>
<td>film side MTC over film</td>
</tr>
<tr>
<td>$k_{sw}$</td>
<td>water side MTC over sediment</td>
</tr>
<tr>
<td>$k_{we}$</td>
<td>MTC for wax erosion</td>
</tr>
</tbody>
</table>

Table A1.2b Additional definitions of parameters used in Table A1.2
Notes: MTC = mass transfer coefficient

<table>
<thead>
<tr>
<th>Medium</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$Z_a = \frac{1}{RT}$</td>
</tr>
<tr>
<td>Water</td>
<td>$Z_w = \frac{1}{RT}$</td>
</tr>
<tr>
<td>Soil solids</td>
<td>$Z_s = 0.41K_{ow}Z_w f_{OC_s} \rho_s / 1000$</td>
</tr>
<tr>
<td>Sediment solids</td>
<td>$Z_{ss} = 0.41K_{ow}Z_w f_{OC_{ss}} \rho_{ss} / 1000$</td>
</tr>
<tr>
<td>Vegetation leaf cuticle</td>
<td>$Z_{lc} = Z_w K_{ow} f_{OC_v}$</td>
</tr>
<tr>
<td>Film</td>
<td>dissolved film: $Z_f = Z_a K_{fa} / f_{OM,f}$</td>
</tr>
<tr>
<td>Particulates</td>
<td>$Z_p = Z_a K_p \rho_p 10^9$</td>
</tr>
<tr>
<td>Suspended sediment</td>
<td>where $K_p = 10^{\left(\log K_{oa} + Log_{f_{OM,p}} - 11.91\right)}$</td>
</tr>
<tr>
<td>Suspended sediment</td>
<td>$Z_{ss} = 0.41K_{ow}Z_w f_{OC_{ss}} \rho_{ss} / 1000$</td>
</tr>
</tbody>
</table>

Bulk

| Air          | $Z_{ba} = Z_a + Z_p F_{pa}$                                            |
Table A1.3 Z-values

Notes: Parameters are defined as follows. \( R, T, \) and \( H \) refer to gas constant, temperature, and Henry’s Law constant, \( f_{OC,i}, f_{OM,i}, \) and \( \rho_i \) refer to fraction organic carbon content, organic matter content, and density of compartment \( i. \) \( K_{ow}, K_{oa}, \) and \( K_{fa} \) refer to the octanol-water, octanol-air, and film-air partition coefficients, respectively. \( F_{ij} \) refers to volume fraction of compartment \( i \) in \( j \) where \( a, w, s, se, v, ss, p, \) and \( r \) refer to air, water, soil, sediment, vegetation, suspended sediment, particulates, and storm water. Equations for air, water, soil, sediment, and vegetation are from or adapted from Diamond et al. (2001) and equations for film and storm water are from this paper.

<table>
<thead>
<tr>
<th>PCB Congener</th>
<th>( \log K_{ow} )</th>
<th>( \log K_{aw} )</th>
<th>( \log K_{oa} )</th>
<th>( dU_{ow} ) (kJ mol(^{-1}))</th>
<th>( dU_{aw} ) (kJ mol(^{-1}))</th>
<th>( dU_{oa} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>5.92</td>
<td>-1.93</td>
<td>7.86</td>
<td>-26.6</td>
<td>51.8</td>
<td>-78.4</td>
</tr>
<tr>
<td>52</td>
<td>6.26</td>
<td>-1.96</td>
<td>8.22</td>
<td>-27.5</td>
<td>53.8</td>
<td>-81.3</td>
</tr>
<tr>
<td>101</td>
<td>6.76</td>
<td>-2.08</td>
<td>8.83</td>
<td>-19.3</td>
<td>65.2</td>
<td>-84.4</td>
</tr>
<tr>
<td>153</td>
<td>7.31</td>
<td>-2.13</td>
<td>9.45</td>
<td>-26.6</td>
<td>68.2</td>
<td>-94.8</td>
</tr>
<tr>
<td>180</td>
<td>7.66</td>
<td>-2.51</td>
<td>10.17</td>
<td>-26.1</td>
<td>69.0</td>
<td>-95.2</td>
</tr>
</tbody>
</table>

Table A1.4 Physical-chemical properties of modeled PCB congeners

Notes: The partition coefficients \( K_x \) are given at 25 °C and were temperature corrected using their corresponding energies of phase transition \( (dU_x). \) All values are from Schenker et al. (2005).

<table>
<thead>
<tr>
<th>PCB Congener</th>
<th>( B_w ) (m(^2) h(^{-1}))</th>
<th>( B_a ) (m(^2) h(^{-1}))</th>
<th>( M ) (m(^2) h(^{-1}) °C(^{-1}))</th>
<th>( b ) (m(^2) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>1.9E-06</td>
<td>0.016</td>
<td>1.0 \times 10^{-8}</td>
<td>0.014</td>
</tr>
<tr>
<td>52</td>
<td>1.9E-06</td>
<td>0.016</td>
<td>9.6 \times 10^{-5}</td>
<td>0.013</td>
</tr>
<tr>
<td>101</td>
<td>1.8E-06</td>
<td>0.015</td>
<td>9.1 \times 10^{-5}</td>
<td>0.013</td>
</tr>
<tr>
<td>153</td>
<td>1.7E-06</td>
<td>0.014</td>
<td>8.7 \times 10^{-5}</td>
<td>0.012</td>
</tr>
</tbody>
</table>
### Table A1.5 Air and water chemical diffusivities of modeled PCB congener

Notes: $B_w$ and $B_a$ represent chemical diffusivity in water and air at 18 °C and 25 °C, respectively, where $B_a$ was temperature corrected based on a linear regression using values from SPARC On-line Calculator (University of Georgia, 2008) where $M$ represents the slope and $b$ the y-intercept.

<table>
<thead>
<tr>
<th></th>
<th>Upper air</th>
<th>Lower air</th>
<th>Water</th>
<th>Soil</th>
<th>Sediment</th>
<th>Vegetation</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m²)</td>
<td>$2.0 \times 10^7$</td>
<td>$2.0 \times 10^7$</td>
<td>$6.0 \times 10^5$</td>
<td>$7.5 \times 10^6$</td>
<td>$6.0 \times 10^5$</td>
<td>$9.0 \times 10^6$</td>
<td>$2.7 \times 10^7$</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>450</td>
<td>50</td>
<td>12</td>
<td>0.02</td>
<td>0.02</td>
<td>0.002</td>
<td>variable</td>
</tr>
<tr>
<td>Advective Flow (m³ h⁻¹)</td>
<td>$4.3 \times 10^{10}$ b</td>
<td>$2.9 \times 10^9$ b</td>
<td>$8.2 \times 10^4$ c</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction Half-lives at 25 °C (h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB-28</td>
<td>62 d</td>
<td>62</td>
<td>5500 e</td>
<td>10000 e</td>
<td>17000 e</td>
<td>620 f</td>
<td>620 f</td>
</tr>
<tr>
<td>PCB-52</td>
<td>109</td>
<td>109</td>
<td>10000</td>
<td>17000</td>
<td>55000</td>
<td>1090</td>
<td>1090</td>
</tr>
<tr>
<td>PCB-101</td>
<td>214</td>
<td>214</td>
<td>31000</td>
<td>100000</td>
<td>55000</td>
<td>2140</td>
<td>2140</td>
</tr>
<tr>
<td>PCB-153</td>
<td>401</td>
<td>401</td>
<td>55000</td>
<td>550000</td>
<td>170000</td>
<td>4010</td>
<td>4010</td>
</tr>
<tr>
<td>PCB-180</td>
<td>642</td>
<td>642</td>
<td>55000</td>
<td>1000000</td>
<td>170000</td>
<td>6420</td>
<td>6420</td>
</tr>
</tbody>
</table>

### Table A1.6 Model area properties

Notes: a Diamond et al. (2010) b Wind speeds from Environment Canada (2002) c River flows from Environment Canada (2003) d Air reaction rates were calculated based on first order reaction rates with the OH radical; rates are from Episuite 4.0, and OH radical concentration is from Totten et al. (2002). e Water, soil, and sediment half-lives from Wania and Daly (2002) f Film and vegetation half-lives are described in the text of this paper. Half-lives were temperature corrected using activation energies from Wania and Daly (2002).

<table>
<thead>
<tr>
<th>PCB</th>
<th>L. Air Conc. (pg/m³)</th>
<th>U. Air Conc. (pg/m³)</th>
<th>L. Air Emission (g/d)</th>
<th>Water Conc. (µg/m³)</th>
<th>Soil Conc. (mg/m³)</th>
<th>Sediment Conc. (mg/m³)</th>
<th>Vegetation Conc. (µg/m³)</th>
<th>Film Conc. (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>14</td>
<td>7.8</td>
<td>1.1</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>52</td>
<td>16</td>
<td>8.8</td>
<td>2.9</td>
<td>0.2</td>
<td>0.03</td>
<td>0.3</td>
<td>5.3</td>
<td>5.1</td>
</tr>
<tr>
<td>101</td>
<td>18</td>
<td>9.8</td>
<td>2.4</td>
<td>0.2</td>
<td>0.3</td>
<td>3.3</td>
<td>22</td>
<td>25</td>
</tr>
</tbody>
</table>
Table A1.7  Bulk concentrations and bulk air emissions used to initialize unsteady-state model and the case study in Toronto. Note this figure has been revised from the original manuscript as per the addendum in Chapter 2.

Notes: Concentrations were obtained by setting initial values to steady-state results and running for a 10 day spin up period. Original lower air concentrations are from Motelay-Mossei et al. (2005) and were used in the steady-state model to back-calculate bulk air emissions. Gas-phase air concentrations and emissions are corrected to bulk-phase values as in Diamond et al. (2010).

Figure A1.1 Sum of modeled net air-to-film transfer (mmol h\(^{-1}\)) over a five day simulation period for (a) CB-28 and (b) CB-180 over various temperatures and rain events lasting for 2 hours and beginning 12 hours after the start of the simulation.
Figure A1.2 Modeled initial mass (mg) of PCB washed off during a rain event following an initial dry period of 0, 5, or 20 days for varying impervious surface area fractions for (a) CB-28 and (b) CB-180.

Figure A1.3 Modeled mass (mmol) of CB-28 (♦) and CB-180 (□) accumulated in film over a 30 dry day simulation at an air temperature of 18 °C at varying film growth rates (nm d⁻¹).
Figure A1.4 Precipitation data used for September 2000 Toronto simulation. Data is from Environment Canada (2010).

Figure A1.5 Modeled film concentrations of $\sum PCB$ over the September simulation period. Rain rates were derived from Figure A1.1 where it was assumed that it rains for 2 hours at the beginning of the day. Note this figure has been revised from the original manuscript as per the addendum in Chapter 2.

References


University of Georgia, 2008. SPARC on-line calculator.

Appendix 2: Supporting Information for Chapter 3

A2.1 Model Details

MUM Equations

Mass balance equations, D-values, and Z-values used in MUM are presented in Csiszar et al. (2012). Updates to model equations are listed below.

Air-water mass transfer coefficient (mtc)

Air-side mtc, $k_{a,PCB}$

The air side mass transfer coefficient was calculated using

$$k_{a,PCB} = \frac{D_{PCB,a}}{D_{wa}}$$

where $D_{PCB,a}$ and $D_{wa}$ are the diffusion coefficients of the PCB and water in air, respectively, (Schwarzenbach et al., 1993) and $k_{aw}$ is given by

$$k_{aw} = 0.2u_{10} + 0.3$$

where $u_{10}$ is the wind speed (m s$^{-1}$) at a height of 10 m (Schwarzenbach et al., 1993; Hornbuckle et al., 1994).

Water-side mtc, $k_{w,PCB}$

The water side mass transfer coefficient was calculated using

$$k_{w,PCB} = k_{w,CO2} \left( \frac{D_{PCB,w}}{D_{CO2,w}} \right)^{-a}$$

where $a=0.67$ if $u_{10} \leq 4.2$ m s$^{-1}$ and $a=0.5$ if $u_{10} > 4.2$ m s$^{-1}$, $D_{PCB,w}$ and $D_{CO2,w}$ are the diffusion coefficients of PCB and CO$_2$ in water, respectively, (Schwarzenbach et al., 1993) and $k_{w,CO2}$ (cm h$^{-1}$) is given by
Temperature dependent diffusion coefficients for PCBs and water in air were calculated using SPARC (University of Georgia, 2008) and fit to a linear regression in order to calculate temperature dependent values of $D_{\text{PCB,a}}$, and $D_{\text{wa}}$ in MUM as in Csiszar et al. (2012).

Temperature dependent diffusion coefficients for PCBs and CO$_2$ in water were calculated as

$$D_{s,w} = \frac{7.4 \times 10^{-8} \Phi M_w \frac{1}{2} T}{\mu_w V_A^{0.6}}$$

(A2.5)

where $M_w$, $T$, $\mu_w$, and $V_A$ are the molar mass of water (g mol$^{-1}$), temperature (K), water viscosity (cP), molar volume of chemical A (cm$^3$ mol$^{-1}$), respectively, and $\Phi=2.6$ for water (Basmadjian, 2004). PBDE diffusivities in air were calculated using

$$D_{C,a} = \frac{0.001 T^{1.75} (1/M_C + 1/M_a)}{P (V_C^{1/3} + V_a^{1/3})^2}$$

(A2.6)

where $M_C$, $M_a$, $P$, $V_a$ are the molar masses of chemical, C, and air (g mol$^{-1}$), total pressure (atm), and molar volume of air (cm$^3$ mol$^{-1}$), respectively (Basmadjian, 2004).

The water viscosity (cP) was calculated as

$$\log \mu_w = \frac{A + B}{C - T}$$

(A2.7)

where $A=-4.5318$, $B=-220.57$, and $C=149.39$ (Viswanath, 2007).

**Air-soil mass transfer coefficient**

The air-side air-soil mass transfer coefficient, $k_{sa}$ was calculated as

$$k_{sa} = \frac{D_{\text{PCB,a}}}{d_{\text{bound}}}$$

(A2.8)
where $d_{\text{bound}}$ is the air boundary layer thickness over soil (m) with a value of 0.00475 (Ghirardello et al., 2010).

**Model Parameterization**

Land use data used by MUM were obtained from land-use base maps (DMTI Spatial Inc., 2008) that were extracted using Geographic Information Systems (GIS). Toronto has two larger tributaries (Humber and Don with average spring flow rates of 13 and 7 m$^3$ s$^{-1}$, respectively) and three secondary tributaries (Etobicoke Creek, Rouge River, and Highland Creek with average spring flow rates of 4, 3, and 2 m$^3$ s$^{-1}$, respectively). All tributaries flow from north to south and ultimately feed into Lake Ontario (Figure 3.1b) or a waste water treatment plant (WWTP). The cells containing these tributaries were linked by setting a cell's river input term to that of the output term of the upstream cell, with final tributary outputs in cells (2,1), (3,2), DT, (8,5), and (9,6) (the cell labeling system is defined in Figure 3.1b). Flow rates and depths were updated daily for the 5 modeled tributaries using archived data from Environment Canada (2010). The minor tributaries were given constant flow rates and depths set to the average values of minor tributaries with available data in Toronto. Inflow water concentrations into the Toronto tributaries were set to average measured values at two sites upstream of the city (Robson et al., 2008; Melymuk et al., In Prep.) and are listed in Table A2.1.

Physical-chemical properties used in the model are listed in Csiszar et al. (2012) for PCBs and in Tables A2.2-4 for PBDEs; in particular, we used internally consistent partition coefficients of Schenker et al. (2005; 2008). Meteorological data were provided by BLFMAPS as well as surface water and soil temperatures over the model simulation period. Additional atmospheric parameters needed by MUM included OH radical ($\text{OH}^+$) concentrations and solar irradiance (both used to determine chemical degradation rates in air), dry particle deposition velocities, and total suspended particulate (TSP) concentrations. We used constant daytime and nighttime OH$^+$ concentrations rather than spatially and temporally variable concentrations because of a lack of data and the low sensitivity of model results for PCBs to reaction with OH$^+$ on an urban scale (Gasic et al., 2010). Daytime and nighttime solar irradiances were used to calculate photodegradation rates of PBDEs (Table A2.5).
Total suspended particle (TSP) concentrations are required to partition total chemical in air between gas and particle phases via the octanol-air partition coefficient ($K_{oa}$) relationship of Harner and Bidleman (1998). TSP concentrations were updated every hour, however, in the absence of geographically resolved measurements, we used the same TSP concentrations in each model cell. These values were the averages of hourly PM$_{2.5}$ measured at four sites in Toronto by the Ontario Ministry of Environment (MOE) (Ontario Ministry of Environment). We then extrapolated PM$_{2.5}$ to TSP using PM$_{2.5}$ to TSP ratios calculated from the National Air Pollution Surveillance Network (NAPS) (Environment Canada).

Dry particle deposition velocities, $v_d$, used in PCB and PBDE calculations vary over an order of magnitude generally ranging from 0.2 cm s$^{-1}$ to average empirical urban values of 4.2 and 5.8 cm s$^{-1}$ for PCBs and PBDEs, respectively (Cetin and Odabasi, 2007; Raff and Hites, 2007; Tasdemir et al., 2007; Venier and Hites, 2008; Moeckel et al., 2010). We performed a sensitivity analysis using a one-box USS version of MUM in a downtown (5,3) cell in order to assess the effects of $v_d$ on various model outcomes (air concentrations and air advection and deposition) with further details below in Section 2.0 of Appendix 2. For PCBs, we present SO-MUM simulation results using congener-specific values of $v_d$ measured in Chicago (Tasdemir and Holsen, 2005) (Table A2.6) which were similar to those reported by Bozlaker et al. (2008) in Turkey. For PBDEs, we present SO-MUM simulation results using $v_d$ values (Table A2.7) within the ranges listed above and similar to those used by Moeckel et al. (2010).

**Initial SO-MUM Concentrations**

We used the steady-state (SS) version of MUM in each Toronto cell to set initial concentrations in tributaries, soil, sediment, vegetation, and film. For this, SS-MUM was parameterized with data (e.g. wind speed, temperature) averaged over the entire simulation period of SO-MUM. Each cell's emission rate and an air inflow concentration were used as input to the SS version of MUM. We used measured air concentrations as inflow concentrations in cells with sample sites. For the cells without measured data, we scaled the air concentrations to those of the measured cells using the inventory in the same manner as we used to scale emissions. For PBDEs the initial "guess" soil concentrations calculated using SS-MUM overestimated measured concentrations ~2 times. In order to more realistically model air-soil and soil-water transfer...
processes, we adjusted the modeled SS soil concentrations to use as initial soil concentrations (see below in Section 2.0 of Appendix 2 and Table A2.8).

**PBDE Mass Inventory**

The amount of products in commercial buildings were estimated based on building floor areas (DMTI Spatial, 2005; Municipal Property Assessment Corporation, 2006; Diamond et al., 2010b). This was done by assigning the number products per floor area to each product type listed above (GSA Office of Governmentwide Policy, 2002; Harler, 2006), and then multiplying this number by the total floor area. For post-secondary and non post-secondary educational buildings the number of computers per room type and the number of computers per school was estimated, respectively (Toronto District School Board, 2007). For residential buildings, census data were used to estimate the amount of each product type in a household based on income. Census data were then used to estimate the total number of each product type according to census dissemination district and in turn, these estimates were aggregated to the SO-MUM cell size. The number of cars was estimated based on the average number of cars per household on a city ward basis (Data Management Group, 2009). Further details can be found in Tables A2.9-10.

**Tables**

<table>
<thead>
<tr>
<th>Congener</th>
<th>Inflow bulk river concentration (pg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>2.6</td>
</tr>
<tr>
<td>PCB 52</td>
<td>1.3</td>
</tr>
<tr>
<td>PCB 101</td>
<td>2.2</td>
</tr>
<tr>
<td>PCB 153</td>
<td>7.5</td>
</tr>
<tr>
<td>PCB 180</td>
<td>2.7</td>
</tr>
<tr>
<td>BDE 28</td>
<td>0.0</td>
</tr>
<tr>
<td>BDE 47</td>
<td>0.0</td>
</tr>
<tr>
<td>BDE 100</td>
<td>0.06</td>
</tr>
<tr>
<td>BDE154</td>
<td>0.0</td>
</tr>
<tr>
<td>BDE 183</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table A2.1 Bulk inflow river water concentrations used in model. Data is average of two sites upstream from Toronto urban rivers from (Diamond et al., 2010a; Melymuk et al., In Prep.).
### Table A2.2 PBDE half-lives in modeled media.

Notes:  

- **Air** reaction rates were calculated based on reaction rates with the OH radical and photolysis, both in the gas phase; rates are from Schenker et al. (2008)
- **Water** and **soil** half-lives from Schenker et al. (2008)
- **Sediment** half-lives from Episuite 4.0
- **Film** and vegetation half-lives were set to be 10 times slower longer than air half-lives (Csiszar et al., 2012). Half-lives were temperature corrected using activation energies of Wania and Dugani (2003).

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>Air (^a) ((\text{day/night average}))</th>
<th>Water (^b)</th>
<th>Soil (^b)</th>
<th>Sediment (^c)</th>
<th>Veg’n (^d)</th>
<th>Film (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-28</td>
<td>91</td>
<td>2496</td>
<td>5016</td>
<td>13000</td>
<td>910</td>
<td>910</td>
</tr>
<tr>
<td>BDE-47</td>
<td>128</td>
<td>4608</td>
<td>9240</td>
<td>38900</td>
<td>1280</td>
<td>1280</td>
</tr>
<tr>
<td>BDE-100</td>
<td>233</td>
<td>8496</td>
<td>16968</td>
<td>38900</td>
<td>2330</td>
<td>2330</td>
</tr>
<tr>
<td>BDE-154</td>
<td>550</td>
<td>15696</td>
<td>31392</td>
<td>38900</td>
<td>5500</td>
<td>5500</td>
</tr>
<tr>
<td>BDE-183</td>
<td>770</td>
<td>21120</td>
<td>42216</td>
<td>38900</td>
<td>7700</td>
<td>7700</td>
</tr>
</tbody>
</table>

### Table A2.3 Physical-chemical properties of modeled PBDE congeners. The partition coefficients \((K_x)\) are given at 25 °C and were temperature corrected using their corresponding energies of phase transition \((dU_x)\). All values are from Schenker et al. (2008).

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>log (K_{ow})</th>
<th>log (K_{aw})</th>
<th>log (K_{oa})</th>
<th>(dU_{ow}) ((kJ/mol))</th>
<th>(dU_{aw}) ((kJ/mol))</th>
<th>(dU_{oa}) ((kJ/mol))</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>5.92</td>
<td>-2.70</td>
<td>9.16</td>
<td>-11.1</td>
<td>62</td>
<td>-73</td>
</tr>
<tr>
<td>47</td>
<td>6.53</td>
<td>-3.12</td>
<td>10.4</td>
<td>-30.6</td>
<td>66</td>
<td>-97</td>
</tr>
<tr>
<td>100</td>
<td>6.68</td>
<td>-3.78</td>
<td>11.3</td>
<td>-28.5</td>
<td>57</td>
<td>-105</td>
</tr>
<tr>
<td>154</td>
<td>7.36</td>
<td>-3.68</td>
<td>12.1</td>
<td>-21.5</td>
<td>76.7</td>
<td>-98</td>
</tr>
<tr>
<td>183</td>
<td>7.26</td>
<td>-4.28</td>
<td>12.6</td>
<td>-23.9</td>
<td>65.6</td>
<td>-90</td>
</tr>
</tbody>
</table>

### Table A2.4 Air and water PBDE diffusivities at 25 °C. Values were calculated at each time step using Equation A2.5 and A2.6.

<table>
<thead>
<tr>
<th>PBDE Congener</th>
<th>(B_w) ((\text{m}^2\text{h}^{-1}))</th>
<th>(B_a) ((\text{m}^2\text{h}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>2.5×10^{-6}</td>
<td>0.0039</td>
</tr>
<tr>
<td>47</td>
<td>2.4×10^{-6}</td>
<td>0.0037</td>
</tr>
<tr>
<td>100</td>
<td>2.3×10^{-6}</td>
<td>0.0036</td>
</tr>
<tr>
<td>154</td>
<td>2.2×10^{-6}</td>
<td>0.0034</td>
</tr>
<tr>
<td>183</td>
<td>2.2×10^{-6}</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

### Table A2.5 OH• Concentration \(^a\) \((\text{molecules cm}^{-3})\)

<table>
<thead>
<tr>
<th>Day</th>
<th>(3 \times 10^6)</th>
</tr>
</thead>
</table>

\(^a\) Air concentration.
### Table A2.5 OH radical concentrations, average total suspended particulate (TSP) values, and solar irradiance used in the model.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Night</td>
<td>$3 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>Average TSP $^b$</td>
<td>(µg m$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Solar Irradiance $^c$</td>
<td>(kW m$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

Notes: $^a$ Daytime value is from Totten et al. (2002) and nighttime value was set to be 2 orders of magnitude lower based on Lu and Khalil (1992). $^b$ TSP was updated hourly in the model based on hourly archived PM$_{2.5}$ values from (Ontario Ministry of Environment) and extrapolated to TSP using data from (Environment Canada). $^c$ Solar irradiance was set to zero during the night time. Daytime value is the seasonal average midday irradiance from (NASA, 2012).

### Table A2.6 Dry particle deposition velocities used for PCBs from Tasdemir and Holsen (2005).

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>PCB 52</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>PCB 101</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>PCB 153</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>PCB 180</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

### Table A2.7 Dry particle deposition velocities used for PBDEs in SO-MUM which were calculated using the average logs of the ranges reported by Raff and Hites (2007) and Cetin and Odabasi (2007).

<table>
<thead>
<tr>
<th>Site/Cell</th>
<th>Measured (ng g$^{-1}$)</th>
<th>Initial values used in SO-MUM (ng g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W20</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>W10</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>W5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Product</td>
<td>Building Type</td>
<td>Details</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Computer</strong></td>
<td>Office/Commercial</td>
<td>- Estimated number of employees in an office based on recommended space usage (floor area) per person (GSA Office of Governmentwide Policy, 2002)</td>
</tr>
<tr>
<td></td>
<td>Educational: Post-secondary</td>
<td>- Surveyed University of Toronto rooms to estimate number of computers per area based on room classifications</td>
</tr>
<tr>
<td></td>
<td>Educational: Non post-secondary</td>
<td>- Determined approximate number of computers per school based on data from the Toronto District School Board (2007)</td>
</tr>
<tr>
<td></td>
<td>Residential</td>
<td>- Determined household income from Canadian Census (Statistics Canada, 2010)</td>
</tr>
<tr>
<td><strong>Printers</strong></td>
<td>Office/commercial</td>
<td>- Used number of printers per employee (Harler, 2006)</td>
</tr>
<tr>
<td></td>
<td>Educational: Post-secondary</td>
<td>- Surveyed University of Toronto rooms to estimate number of printers per student</td>
</tr>
<tr>
<td></td>
<td>Residential</td>
<td>- Used percentage of households with numbers of printers (0 to 3) to calculate number of printers per residential area (Natural Resources Canada, 2010a)</td>
</tr>
<tr>
<td><strong>Television</strong></td>
<td>Commercial (hotels)</td>
<td>- The number of hotel rooms per area was estimated based on data from the Arlington Economic Development (Holzheimer, 2010)</td>
</tr>
<tr>
<td></td>
<td>Residential</td>
<td>- Same method as computers</td>
</tr>
<tr>
<td><strong>Furniture</strong></td>
<td>Commercial (offices)</td>
<td>- Assumed one office chair per person</td>
</tr>
<tr>
<td></td>
<td>Commercial (hotels)</td>
<td>- Assumed one double bed per room and 2 pillows per bed</td>
</tr>
</tbody>
</table>
| Residential Bedrooms: | - Estimated number of bedrooms per household based on income and spending profiles (Statistics Canada, 2009)  
- Assumed one double bed per room and 2 pillows per bed  
Sofas: | - Estimated number of rooms per household based on income and spending profiles (Statistics Canada, 2009)  
- Subtracted number of bedrooms, one kitchen, and one bathroom from the total number of rooms  
- Assumed one sofa in each resulting room  
Office chairs: | - Assumed one office chair per computer  

| Vehicles | - Calculated number of vehicles in each city ward based on number of households and average number of vehicles per household (Data Management Group, 2009)  
- Summed vehicles for entire city  
- Divided into older than 2005 and newer than 2005 (Natural Resources Canada, 2010b) |

Table A2.9 Methods used to estimate the amount of computers, printers, televisions, furniture, and vehicles in the City of Toronto.

Notes: a Split into inkjet (70%) and laser (30%) types (Printcountry.com, 2010).

<table>
<thead>
<tr>
<th>Product</th>
<th>BDE Concentration</th>
<th>Reference and notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computers</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Penta: 0.15 (0.14-0.16) g/computer  
Octa: 22 (20-24) g/computer  
Deca: 14 (13-15) g/computer | (Morf et al., 2002)  
(Morf et al., 2005)  
Based on plastic casing |
| Inkjet Printers | Octa: 1.0 g/printer  
Deca: 11 g/printer | (Morf et al., 2002) |
| Laser Printers | Octa: 2.3 g/printer  
Deca: 33 g/printer | (Morf et al., 2002) |
| Televisions   | Penta: 0.34 (0.29-0.40) g/television  
Octa: 52 (42-62) g/television | (Morf et al., 2002)  
(Morf et al., 2005) |
| Office chairs | Penta: 4.4 (0.01-44) g/chair | (Allen et al., 2008)  
(Zhang et al., 2009) |
| Mattresses    | Penta: 3.8 (0.1-70) g/mattress | (Allen et al., 2008)  
(Furniture Re-use Network, 2009) |
| Pillows       | Penta: 0.04 (0.004-2) g/pillow | (Allen et al., 2008)  
(Furniture Re-use Network, 2009) |
| Sofas         | Penta: 16 (0.2-285) g/sofa | (Allen et al., 2008)  
(Furniture Re-use Network, 2009) |
### A2.2 Results

#### Comparison between measured and modeled concentrations

**Soils**

Modeled $\Sigma_5$PCBs soil solids concentrations (ng g$^{-1}$ dry weight) were compared to those measured by Wong et al. (2009). Measured values were for surface soil concentrations at four locations in Toronto which fall into the (3,5), (5,5), (3,2), and (5,3) cells. Modeled soil concentrations which reflect a soil depth of 2 cm, did not change substantially during the 3 month simulation period. The average (over the simulation period) $\Sigma_5$PCBs soil concentrations were within an order of magnitude of measured values in 3 cells (underestimated ~1.3 times on average) and were ~7 times lower in the (5,5) cell (Table A2.14). The underestimation of the modeled soil concentration at that cell compared to the measured value may reflect a history of higher concentrations at nearby locations of PCB use (Wong et al., 2009).

Diamond et al. (2010a) measured surface soil concentrations for PBDEs in Toronto which were similar to concentrations reported by Harrad and Hunter (2006) in Birmingham, England. The initial "guess" used to initialize soil concentrations in SO-MUM were calculated using SS-MUM. The SS-MUM soil concentrations overestimated measured concentrations ~2 times. In order to more realistically model air-soil and soil-water transfer processes, we adjusted the modeled SS soil concentrations to use as initial soil concentrations (Table A2.8). Over the model simulation, the soil concentrations did not change substantially.

**Surface Films**
Gingrich et al. (2001) measured PCB concentrations in window films at urban and suburban sites in Toronto from spring to autumn. We compared the geometric mean and ranges of measured concentrations at their urban and suburban sites to the modeled range of concentrations for the DT and (3,5) cells, respectively. For ease of comparison, modeled $\Sigma_6$PCBs film concentrations were scaled to $\Sigma_{68}$PCBs based on the film congener composition reported by Gingrich et al. (2001). Modeled film $\Sigma_{68}$PCBs concentrations for the DT and (3,5) cells of 88 (2-380) and 15 (0.2-62) ng m$^{-2}$ were in agreement with measured values of 95 (4-5800) and 14 (4-160) ng m$^{-2}$, respectively (Table A2.11).

Butt et al. (2004) measured PBDE concentrations in window films at urban and suburban sites in Toronto in summer 2001. However, it is difficult to compare SO-MUM modeled to the measured values of Butt et al. (2004) as their back-calculated air concentrations were ~7 times lower than those measured by Melymuk et al. (2012) that were used in this study. We compared measured concentrations at the same sites as we did for PCBs (DT and (3,5) cells) (Table A2.11). Modeled $\Sigma_{4}$PBDEs (47, 100, 154, 183) concentration ranges overlapped with measured values with the mean modeled value in closer agreement with the measurement if the ~7 times difference in air concentrations was taken into consideration (assuming a linear relationship between air and film concentrations).

Precipitation

Melymuk et al. (2011) measured monthly PCB concentrations in precipitation at the 0KM site. Modeled precipitation concentrations were calculated by summing the mass of chemical washout via wet deposition and dividing by the total rain volume over a simulation period. The modeled $\Sigma_3$PCB and $\Sigma_3$PBDE concentrations were within an order of magnitude of measured values, however PCBs were underestimated on average ~3 times and PBDEs were overestimated on average ~3 times (Table A2.13).

Tributaries

Modeled average $\Sigma_3$PCBs concentrations in the Humber and Don Rivers in cells (3,2) and (5,3), respectively, were within the range of measured values, although on the lower end (Robson et al., 2008; Melymuk et al., In Prep.) (Table A2.12). Modeled average $\Sigma_3$PBDEs concentrations were within the range of measured values in the Humber River and underestimated values in the
Don River (Melymuk et al., In Prep.) (Table A2.12). The concentrations in river water were underestimated, indicating that soil to water wash-off may not be the only source of chemical to the rivers. This was recently found to be the case in Houston, TX and New York/New Jersey where urban storm water was found to contribute to river water concentrations (Howell et al., 2011; Rodenburg et al., 2011). Daily averaged modeled tributary water concentrations follow similar patterns for PCBs and PBDEs (Figure A2.5).

<table>
<thead>
<tr>
<th>ng m⁻²</th>
<th>Measured</th>
<th>Modeled</th>
<th>Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ₆₈PCB in film (urban)</td>
<td>a 95 (4-5800)</td>
<td>b 88 (2-380)</td>
<td>DT</td>
</tr>
<tr>
<td>Σ₆₈PCB in film (suburban)</td>
<td>a 14 (4-160)</td>
<td>b 15 (0.2-62)</td>
<td>(3,5)</td>
</tr>
<tr>
<td>Σ₄PBDE in film (urban)</td>
<td>d 2.1</td>
<td>26 (1-83)</td>
<td>DT</td>
</tr>
<tr>
<td>Σ₄PBDE in film (suburban)</td>
<td>d 2.1</td>
<td>19 (0.8-55)</td>
<td>(3,5)</td>
</tr>
</tbody>
</table>

Table A2.11 Comparison between measured and modeled PCB and PBDE concentrations in surface films.

Notes: a Gingrich et al (2001) b Modeled Σ₆₈PCB concentrations (average of simulation) were extrapolated to 68 congeners based on PCB profiles in film (Gingrich et al., 2001), c PBDE congeners 47, 100, 154, 183, d Butt et al. (2004).

<table>
<thead>
<tr>
<th>Bulk tributary water concentrations (pg L⁻¹)</th>
<th>Don River</th>
<th>Humber River</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Modeled</td>
</tr>
<tr>
<td>Σ₃PCB</td>
<td>1040 (200-2280)</td>
<td>470 (240-940)</td>
</tr>
<tr>
<td>Σ₃PBDE</td>
<td>1310 (770-2400)</td>
<td>180 (90-340)</td>
</tr>
</tbody>
</table>

Table A2.12 Comparison between measured and modeled PCB and PBDE concentrations in bulk tributary water (Melymuk et al., In Prep.).

<table>
<thead>
<tr>
<th>Concentration in precipitation (ng L⁻¹)</th>
<th>April</th>
<th>Modeled</th>
<th>May</th>
<th>Modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ₃PCB</td>
<td>2.4</td>
<td>1.9</td>
<td>2.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Σ₃PBDE</td>
<td>0.4</td>
<td>1.6</td>
<td>0.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Concentration in June Season Average
<table>
<thead>
<tr>
<th>precipitation (ng L⁻¹)</th>
<th>Measured</th>
<th>Modeled</th>
<th>Measured</th>
<th>Modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ₂PCB</td>
<td>7.1</td>
<td>1.1</td>
<td>4.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Σ₂PBDE</td>
<td>0.8</td>
<td>1.1</td>
<td>0.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table A2.13 Comparison between measured and modeled concentrations in precipitation in the DT cell. Measured precipitation values from Melymuk et al. (2011) also in the DT cell.

<table>
<thead>
<tr>
<th>Site/Grid</th>
<th>Measured (ng g⁻¹)</th>
<th>Modeled (ng g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wong et al. 2009</td>
<td>This study</td>
</tr>
<tr>
<td>Downsview/(3,5)</td>
<td>0.46</td>
<td>0.7</td>
</tr>
<tr>
<td>North York/(5,5)</td>
<td>3.61</td>
<td>0.5</td>
</tr>
<tr>
<td>High Park/(3,2)</td>
<td>1.41</td>
<td>0.9</td>
</tr>
<tr>
<td>Riverdale/(5,3)</td>
<td>6.39</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table A2.14 Σ₂PCB soil concentrations (ng g⁻¹ dry weight) measured by Wong et al. (2009) and modeled average (over simulation time period) soil solids concentrations at four sites in Toronto corresponding to the four model cells indicated.

Dry Deposition Velocity Sensitivity Analysis

Dry particle deposition velocity, \( v_{dp} \), is of key importance to capturing spatial patterns of deposition of more particle-sorbed chemicals such as PBDEs. As mentioned in Section 2.5 of the main text, we performed a sensitivity analysis on dry particle deposition velocity, as there is a large range in values reported in the literature. We investigated the effects of changing \( v_{dp} \) on various model outputs including air advective and depositional loss, and air concentrations. We used these outputs because they inform chemical fate as air concentration, advective, and depositional losses affect air transport to neighboring regions.

\( v_{dp} \) depends on various factors such as particle size and density, depositional surface properties, as well as meteorological conditions (e.g. wind speeds) (Zhang et al., 2001). We opted to use a single, constant \( v_{dp} \) in our SO-MUM calculations as we based air-particle partitioning on TSP which is particle size-independent (Harner and Bidleman, 1998). Additionally, reported values of \( v_{dp} \) in the literature vary widely for PCBs and PBDEs and including additional particle property details in the calculations would not necessarily aid in reducing uncertainties in \( v_{dp} \).
We ran the USS-MUM model in cell (5,3) and varied $v_d$ from 0.1 to 10 cm s$^{-1}$ using a constant chemical emission rate of 10 g d$^{-1}$ (for $\Sigma_5$PCBs and $\Sigma_5$PBDEs) and no inflow concentration. The same time dependent wind speeds, temperature, and rain rates corresponding to the same values used in the SO-MUM simulation were used in each model run. Results are discussed in Section 3.4 in the main text.

**Emission Estimates Sensitivity Analysis**

As air concentrations predicted by SO-MUM were most sensitive to wind speeds, we performed a sensitivity analysis in order to compare the effects of changing horizontal and vertical wind speeds on back-calculated emission estimates using the DT cell as an example. We also included $v_d$ in this analysis due to its uncertainty. For this analysis, we used a steady-state version of the single-box MUM model parameterized for the urban cell (5,3), varying one at a time, the horizontal wind speed, $v_h$, from 0.1-10 m s$^{-1}$, the vertical wind speed between the upper and lower air compartments, $v_v$ from 0.01-0.1 m s$^{-1}$, and $v_d$ from 0.1 to 10 cm s$^{-1}$. Results are discussed in Section 3.4 in the main text.

**Air Transport and Meteorological Factors**

Air concentrations were very weakly positively correlated with temperature on a daily basis ($r^2=0.1$) for $\Sigma_5$PCBs and $\Sigma_5$PBDEs. On a yearly basis, several studies have established that air concentrations of SVOCs are positively correlated with temperature, including those of urban air (Hu et al., 2010; Melymuk et al., 2012), however, this relationship may not be as apparent within one season as at similar air temperatures wind speed can also have a substantial effect on air concentrations (Hsu et al., 2003). Seasonal variations in SVOC air concentrations have been attributed to increased primary emissions from sources such as building sealants and consumer products (Alcock et al., 2003; Robson et al., 2010) which is supported by our finding of $EI_i$ varying inversely with vapor pressure. Although increased volatilization from secondary sources such as soil (Currado and Harrad, 2000; Ter Schure et al., 2004) has been suggested to account for this increase, our analysis suggests that the secondary sources would be inadequate to account for such an increase. Additionally, increased building ventilation rates during warmer seasons (Wallace et al., 2002) may increase indoor to outdoor chemical transfer (Currado and Harrad, 2000; Batterman et al., 2009). SO-MUM likely underestimates the
relationship between temperature and emissions from primary sources and building ventilation. Modeled air concentrations were not sensitive to rain intensity which is consistent with the findings of Melymuk et al. (2012) who did not find a statistically significant relationship between PCB and PBDE air concentrations and the duration of rain events one week prior to sampling.

On a daily basis, air concentrations in the cells with the highest emissions (DT and (5,3) for PCBs and PBDEs, respectively), were inversely related to wind speed ($r^2=0.3$) since winds dilute air emissions (Figure A2.4). Conversely, for downwind cells with a relatively low emission rate (e.g. (7,4)) (Figure 3.3), wind speed and air concentrations were not correlated for either PCBs or PBDEs. These results support the observation that atmospheric transport of PCBs from locations with higher PCB sources and hence high air concentrations were significantly positively correlated with air concentrations at downwind locations lacking such sources (Simcik et al., 1997; Green et al., 2000; Brunciak et al., 2001; Offenberg et al., 2005).

**Additional Tables**

<table>
<thead>
<tr>
<th>EI ($g$ y$^{-1}$ kg$^{-1}$)</th>
<th>Mean</th>
<th>High</th>
<th>Low</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ₃PCB</td>
<td>0.04</td>
<td>0.09</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Σ₃PBDE</td>
<td>0.2</td>
<td>0.4</td>
<td>0.03</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table A2.15 PCB and PBDE emission rates per mass inventory, $EI$, ranges and standard deviations of calculated emission rates per inventory in the 9 model cells.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Percent Aroclor</th>
<th>Mean Inventory (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>4.2</td>
<td>19</td>
</tr>
<tr>
<td>PCB 52</td>
<td>3.0</td>
<td>13</td>
</tr>
<tr>
<td>PCB 101</td>
<td>2.6</td>
<td>12</td>
</tr>
<tr>
<td>PCB 153</td>
<td>2.3</td>
<td>10</td>
</tr>
<tr>
<td>PCB 180</td>
<td>1.8</td>
<td>8</td>
</tr>
<tr>
<td>Percent penta</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 28</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>BDE 47</td>
<td>38.2</td>
<td>50</td>
</tr>
<tr>
<td>BDE 100</td>
<td>13.1</td>
<td>17</td>
</tr>
<tr>
<td>BDE 154</td>
<td>4.54</td>
<td>6</td>
</tr>
<tr>
<td>Percent octa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 183</td>
<td>42</td>
<td>38</td>
</tr>
</tbody>
</table>
Table A2.16 Percent PCB composition of Aroclor (calculated based on a weighted average of 1242, 1254, and 1260 sales in the United States (Christensen and Lo, 1986) and Aroclor composition (Frame et al., 1996)) and percent BDE composition of the penta (DE-71) and octa (DE-79) mixtures (La Guardia et al., 2006). The mean inventories were derived by multiplying the total inventory by the percentage congener contribution.

<table>
<thead>
<tr>
<th>Emission (kg y⁻¹)</th>
<th>One-box Toronto Average of city sites</th>
<th>One-box Toronto Average of 0KM &amp; N10</th>
<th>Multi-box Toronto</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ₂PCBs</td>
<td>14-29</td>
<td>35-64</td>
<td>19 (2-41)</td>
</tr>
<tr>
<td>Σ₂PBDEs</td>
<td>16-22</td>
<td>30-42</td>
<td>18 (3-42)</td>
</tr>
</tbody>
</table>

Table A2.17 Comparison between emission estimates using the one-box and multi-box representation of the City of Toronto. Two concentration combinations were used in the one-box calculations: average of all sampled city cells and average of the 0KM and N10 sites (Figure 3.1b).

<table>
<thead>
<tr>
<th>Emission rate (kg y⁻¹)</th>
<th>Horizontal wind</th>
<th>Vertical wind</th>
<th>Dry particle deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Σ₂PCB</td>
<td>0.9</td>
<td>12.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Σ₂PBDE</td>
<td>3.2</td>
<td>16.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table A2.18 Maximum and minimum emission rates back-calculated using ranges of horizontal, vertical, and dry deposition speeds of 0.1-10 m s⁻¹, 0.01-0.1 m s⁻¹, and 0.1 to 10 cm s⁻¹, respectively in the DT cell.

<table>
<thead>
<tr>
<th>ν_d (cm s⁻¹)</th>
<th>Air advective loss (g d⁻¹)</th>
<th>Net air deposition (g d⁻¹)</th>
<th>Average air concentration (pg m⁻³)</th>
<th>Average film concentration (ng m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (min)</td>
<td>10.0</td>
<td>0.1</td>
<td>67</td>
<td>0.7</td>
</tr>
<tr>
<td>10.0 (max)</td>
<td>9.7</td>
<td>0.3</td>
<td>65</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table A2.19 Results of uncertainty analysis of dry deposition velocity, ν_d, for Σ₂PCBs using the USS-MUM in cell (5,3). The relationship between ν_d and all these outputs were linear (r²=0.99-1.0). Σ₂PCBs emissions were set to 10 g d⁻¹.

<table>
<thead>
<tr>
<th>ν_d (cm s⁻¹)</th>
<th>Air advective loss (g d⁻¹)</th>
<th>Net air deposition (g d⁻¹)</th>
<th>Average air concentration (pg m⁻³)</th>
<th>Average film concentration (ng m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (min)</td>
<td>9.3</td>
<td>0.6</td>
<td>61</td>
<td>10</td>
</tr>
<tr>
<td>10.0 (max)</td>
<td>4.9</td>
<td>5.0</td>
<td>29</td>
<td>289</td>
</tr>
</tbody>
</table>
Table A2.20 Results of uncertainty analysis of dry deposition velocity, $v_d$, for $\Sigma_5$PBDEs using the USS-MUM in cell (5,3). The relationship between $v_d$ and all these outputs were near-linear ($r^2=0.93-0.95$). $\Sigma_5$PBDEs emissions were set to 10 g d$^{-1}$.

Figures

Figure A2.1 Measured (passive PUF sampler) and modeled bulk air concentrations for a) $\Sigma_5$PCB (28, 52, 101, 153, 180) and b) $\Sigma_5$PBDE (28, 47, 100, 154, 183). Modeled vs. measured bulk air concentrations overlaid with the best fit line for c) $\Sigma_5$PCB (excluding the W20 site) and d) $\Sigma_5$PBDE (excluding the DT site). Error bars represent the ranges in estimated emissions.
Figure A2.2 Daily averaged modeled and measured bulk air concentrations at the 0KM site and the DT cell for a) $\Sigma_5$PCBs and b) $\Sigma_5$PBDEs.
Figure A2.3 Estimated spatial mass inventories of (a) penta- and (b) octa-BDE in Toronto (not including cars).
Figure A2.4 Averaged daily modeled $\Sigma_5$PCB concentrations overlaid with averaged daily modeled wind speeds for a) $\Sigma_5$PCBs in the DT cell and b) $\Sigma_5$PBDEs in the (5,3) cell.
Figure A2.5 Dynamic modeled bulk water concentrations in the a) Humber and b) Don Rivers (at cells (3,2) and (5,3), respectively).

References


Environment Canada, National Air Pollution Surveillance Network.


Melymuk, L., Robson, M., Diamond, M.L., Helm, P., Keltenecker, G., Backus, S., Bradley, L., Csiszar, S.A., Blanchard, P., In Prep. From the City to the Lake: Loadings of PCBs, PBDEs, PAHs and PCMs from Toronto to Lake Ontario.


Ontario Ministry of Environment, Historical Air Quality Pollutant Data.


Robson, M., Melymuk, L., Gilbert, B., Helm, P., Diamond, M., Blanchard, P., Backus, S., 2008. Comparison of concentrations and loadings of PCBs and PAHs in urban and rural streams during base flow and storm events. Organohalogen Compounds. 70, 685-688.


University of Georgia, 2008. SPARC on-line calculator.


Appendix 3: Supporting Information for Chapter 4

Figure A3.1 Map of City of Toronto with air sampling sites (black dots), modeled rivers (blue lines), and grid naming system. The grids are 5×5 km².

A3.1 Model Parameterization

<table>
<thead>
<tr>
<th>Congener</th>
<th>$v_d$ (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>1.0</td>
</tr>
<tr>
<td>PCB 52</td>
<td>1.2</td>
</tr>
<tr>
<td>PCB 101</td>
<td>0.9</td>
</tr>
<tr>
<td>PCB 153</td>
<td>1.0</td>
</tr>
<tr>
<td>PCB 180</td>
<td>1.0</td>
</tr>
<tr>
<td>BDE 28</td>
<td>1.4</td>
</tr>
<tr>
<td>BDE 47</td>
<td>1.1</td>
</tr>
<tr>
<td>BDE 100</td>
<td>1.2</td>
</tr>
<tr>
<td>BDE 154</td>
<td>1.0</td>
</tr>
<tr>
<td>BDE 183</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table A3.1 Dry particle deposition velocities, $v_d$, used for PCBs and PBDEs.

Notes: Values were determined by averaging 0.2 cm s⁻¹ with empirical values (logs of values) of Tasdemir and Holsen (2005) and Cetin and Odabasi (2007) for PCBs and PBDEs, respectively, as described in (Csiszar et al., Submitted).

Lake Ontario water concentrations
Due to lack of spatially detailed lake water concentrations, values were interpolated over the modeled area using data from a few sampling locations (Figures A3.1 and A3.2). Data for PCBs and PBDEs were obtained using the PoPCart sampler as described in (Blanchard et al., 2008) and represent dissolved phase concentrations. PCB and PBDE data are from Dove (2011) and Ueno et al. (2008), respectively. Lake water concentrations were kept constant during the simulation. The exponential equation used was

$$C(x) = C_0 e^{-ax}$$

(A3.1)

where $C(x)$ is the concentration at distance $x$ from the DT cell (centre to centre), $C_0$ is the concentration in the DT cell, and $a$ is the exponential derived from the measured data. The values for $C_0$ and $a$ can be found in Table A3.2.

<table>
<thead>
<tr>
<th>Congener</th>
<th>$C_0$ (pg L$^{-1}$)</th>
<th>$a$ (km$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>45</td>
<td>0.05</td>
</tr>
<tr>
<td>PCB 52</td>
<td>47</td>
<td>0.06</td>
</tr>
<tr>
<td>PCB 101</td>
<td>23</td>
<td>0.06</td>
</tr>
<tr>
<td>PCB 153</td>
<td>8.1</td>
<td>0.05</td>
</tr>
<tr>
<td>PCB 180</td>
<td>5.2</td>
<td>0.05</td>
</tr>
<tr>
<td>BDE 28</td>
<td>2.8</td>
<td>0</td>
</tr>
<tr>
<td>BDE 47</td>
<td>65</td>
<td>0.04</td>
</tr>
<tr>
<td>BDE 100</td>
<td>0.0</td>
<td>N/A</td>
</tr>
<tr>
<td>BDE 154</td>
<td>0.0</td>
<td>N/A</td>
</tr>
<tr>
<td>BDE 183</td>
<td>0.0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table A3.2 Values used in exponential Equation A3.1 to interpolate Lake Ontario water concentrations. PCB and PBDE data are from Dove (2011) and Ueno et al. (2008), respectively.
Figure A3.2 Interpolated Lake Ontario water concentrations for $\Sigma_3$PCBs used in model. Black dots indicate sampling locations that the exponential was based on.

Figure A3.3 Interpolated Lake Ontario water concentrations for $\Sigma_4$PCBs used in model. Black dots indicate the locations that the exponential was based on and represent approximate sampling locations.
A3.2 Results

Background soil volatilization

To put the magnitude of the urban emission into the context of secondary emissions from soils on a regional scale we calculated the soil volatilization rate at background sites. Σ5PCB and Σ3PBDE volatilization from background soils were 0.02 and 0.002 g y⁻¹ km⁻² such that soil areas of 9×10⁵ and 8×10⁶ km² are needed to reach the levels of the urban emission rate, respectively which are ~3 orders of magnitude larger than the urban area (820 km²).

We used the average of measured surface soil solids concentrations at rural/suburban (in relation to Toronto) sites of Wong et al.(2009) (PCBs) and Diamond et al.(2010) (PBDEs) for the following calculations (Table A3.3). The volatilization D-value for soil to air transport, $D_{vs}$ (mol m⁻³ Pa⁻¹) from Csiszar et al. (2012) is

$$D_{vs} = \left( \frac{1}{k_{sa} A_s Z_a} + \frac{Y_s}{(A_s B_{ca} Z_a + A_s B_{ew} Z_w)} \right)^{-1} \tag{A3.2}$$

where $k_{sa}$ (m h⁻¹), $A_s$ (m²), $Z_a$ (mol m⁻³ Pa⁻¹), $B_{ca}$ (m² h⁻¹), and $B_{ew}$ (m² h⁻¹) are the air side mass transfer coefficient over soil, soil area, air Z-value, air diffusion rate in soil, and water diffusion rate in soil, respectively. The volatilization rate from soil (mol h⁻¹) was calculated by multiplying $D_{vs}$ by the soil fugacity (Pa). Soil fugacities were calculated using the soil solids Z-value as described in Csiszar et al. (2012) and measured soil solids concentrations (Table A3.3). We assumed that the air concentration was zero to estimate the maximum volatilization potential from soil.

<table>
<thead>
<tr>
<th>Congener</th>
<th>Soil solids concentration (ng g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>0</td>
</tr>
<tr>
<td>PCB 52</td>
<td>0.02</td>
</tr>
<tr>
<td>PCB 101</td>
<td>0.1</td>
</tr>
<tr>
<td>PCB 153</td>
<td>1.1</td>
</tr>
<tr>
<td>PCB 180</td>
<td>0.5</td>
</tr>
<tr>
<td>BDE 28</td>
<td>0</td>
</tr>
<tr>
<td>BDE 47</td>
<td>0.06</td>
</tr>
<tr>
<td>BDE 100</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Table A3.3 Soil solids concentrations at rural/suburban sites used in background soil volatilization calculations. Data is from Wong et al. (2009) (average of sites Borden and Richmond Hill) and Diamond et al. (2010) (average of sites N80 and N40).

<table>
<thead>
<tr>
<th></th>
<th>BDE 154</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE 183</td>
<td></td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table A3.4 Distances (km) above which the specified value is less than 1/e or 1/10 of the highest modeled value in the DT cell (PCBs) or (5,3) cell (PBDEs) rounded to the nearest 5 km.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma_5$PCB</th>
<th>$\Sigma_3$PBDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/e$</td>
<td>(km)</td>
<td>(km)</td>
</tr>
<tr>
<td>Particulate deposition flux</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Rain deposition flux</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Film concentration</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>$1/10$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulate deposition flux</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>Rain deposition flux</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Film concentration</td>
<td>45</td>
<td>45</td>
</tr>
</tbody>
</table>
Figure A3.4 Net air-to-soil and air-to-film exchange rates in an urban cell (5,3) for a) \( \sum_i \text{PCBs} \) and b) \( \sum_i \text{PBDEs} \).
Figure A3.5 Daily averaged film and bulk air concentrations in an urban cell (5,3) for a) $\sum_s$PCBs and b) $\sum_s$PBDEs.
Figure A3.6 Magnitude of net air-lake exchange (wet and dry deposition plus gas absorption minus volatilization), and soil wash-off and film wash-off loadings to near-shore Lake Ontario. Negative values refer to loss from near-shore Lake Ontario.

Figure A3.7 Net air-lake exchange rates for a) $\Sigma_5$PCBs b) $\Sigma_5$PBDEs. Negative values indicate net lake-to-air exchange.

References


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