

From the City to the Lake: Loadings of PCBs, PBDEs, PAHs and PCMs from Toronto to Lake Ontario

Lisa Melymuk,^{†,§} Matthew Robson,^{‡,¶} Susan A. Csiszar,^{†,○} Paul A. Helm,^{≤,||} Georgina Kaltenecker,[≤] Sean Backus,[⊥] Lisa Bradley,[⊥] Beth Gilbert,[≤] Pierrette Blanchard,[⊞] Liisa Jantunen,[⊞] and Miriam L. Diamond^{*,†,‡,⊞}

[†]Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada

[§]Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Brno, 625 00, Czech Republic

[‡]Department of Geography, University of Toronto, Toronto, Ontario M5S 3G3, Canada

[≤]Ontario Ministry of the Environment, Toronto, Ontario M9P 3V6, Canada

^{||}School of the Environment, University of Toronto, Toronto, Ontario M5S 3E8, Canada

[⊥]Great Lakes Water Quality Monitoring, Environment Canada, Burlington, Ontario L7R 4A6, Canada

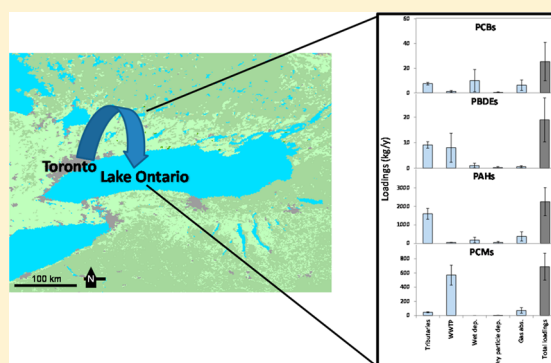
[⊞]Science and Technology Branch, Environment Canada, Toronto, Ontario M3H 5T4, Canada

Supporting Information

ABSTRACT: Loadings from Toronto, Canada to Lake Ontario were quantified and major sources and pathways were identified, with the goal of informing opportunities for loading reductions. The contaminants were polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs) and polycyclic musks (PCMs). Loadings were calculated from measured concentrations for three major pathways: atmospheric processes, tributary runoff, and wastewater treatment plant (WWTP) effluents.

Although atmospheric deposition to the Great Lakes has received the greatest attention, this was the dominant loading pathway for PCBs only (17 ± 5.3 kg/y or 66% of total loadings). PCB loadings reflected elevated urban PCB air concentrations due to, predominantly, primary emissions. These loadings contribute to consumption advisories for nearshore fish. PBDE loadings to the lake, again from mainly primary emissions, were 48% (9.1 ± 1.3 kg/y) and 42% (8.0 ± 5.7 kg/y) via tributaries and WWTPs, respectively, consistent with emissions deposited and subsequently washed-off of urban surfaces and emissions to the sewage system. PAHs loadings of 1600 ± 280 kg/y (71%) from tributaries were strongly associated with vehicle transportation and impervious surfaces. PCM loadings were 83% (± 140 kg/y) from WWTP final effluent, reflecting their use in personal care products.

Opportunities for source reduction lie in reducing the current inventories of in-use PCBs and PBDE-containing products, reducing vehicle emissions of PAHs and use of PAHs in the transportation network (e.g., pavement sealants), and improving wastewater treatment technology.



INTRODUCTION

Cities, which are centers of economic activity and home to >50% of the world's population, significantly impact their surrounding environments through contaminant emissions. This situation persists for wealthy cities that have shifted their economic base from primary industry and manufacturing to commerce and the service sector.¹ The impacts experienced as a result of largely nonpoint source emissions include adverse human health effects arising from both direct (e.g., air)^{2,3} and indirect (fish consumption)^{4,5} routes of exposure. Efforts to curb emissions in cities in developed countries have focused on point source controls which are easier to address than nonpoint source emissions. However, this should not dissuade us from

working toward identifying the major sources of nonpoint emissions and opportunities to reduce these emissions.

This paper presents contaminant loading estimates from Toronto, Canada, to adjacent nearshore Lake Ontario, drawn from a multiagency research program aimed at linking chemical inventories to loadings and ambient concentrations. Toronto, with city and regional populations of 2.6 and 6.3 million, respectively, is typical of many wealthy cities, with an economic base in commerce and the service sector. Like many cities, it is

Received: July 19, 2013

Revised: December 13, 2013

Accepted: January 8, 2014

Published: January 8, 2014

located on a waterbody that provides a source of drinking water, transportation (especially in the past), and recreation, and acts as a receptacle of treated wastewater. As such, the mechanistic understanding and insights gained from this study are relevant to other major cities.

Loadings were determined for three major pathways: atmospheric processes, and tributary and wastewater treatment plant (WWTP) discharges, for four compound classes: polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and polycyclic musks (PCMs). This paper builds on several associated publications from the project, including examinations of the dynamics of contaminants in air and precipitation,^{6,7} urban PCB and PBDE inventories,^{8,9} and multimedia modeling to improve our mechanistic understanding of contaminant pathways.^{10–12} These publications present details of measurement and analytical methods used, and concentrations and spatial analyses.

PCBs, PBDEs, PAHs, and PCMs were chosen as they represent different usage patterns and sources, they all have elevated urban concentrations, and all have the potential to enter waterbodies through multiple pathways. Despite 1970s PCB regulations, 437 tonnes of PCBs were estimated to be in use and storage in the Toronto area in 2006/2007.^{8,9} In North America the production and new use of penta- and octa-PBDEs ceased in 2004, and deca-BDE will be hopefully be phased out by the end of 2013.^{13–17} However, cities contain large inventories of PBDEs in-use, “hibernating” and in waste streams of consumer products.^{18,19} In Toronto, this amounted to an estimated 150–200 tonnes of penta-, 20–100 tonnes of octa-, and 1500–2000 tonnes of deca-BDEs in 2012.²⁰ Urban areas are sources of significant loadings of PAHs, particularly from vehicle use, industries, and coal tar sealants.^{21,22} The occurrence of PCMs is strongly correlated with population density, due to their use as synthetic fragrances in personal care products such as cosmetics, deodorants, and detergents.¹⁹

Results from a spatially resolved, coupled atmospheric transport model (the spatially-oriented multimedia urban model, SO-MUM) showed that PCB and PBDE emissions from Toronto are dominated by primary sources emanating from in-use inventories of these compounds.^{11,12} Air measurements showed that the intraurban spatial pattern of compound concentrations follows that of their respective inventories.¹⁹ Bulk water measurements of the compounds in Toronto’s tributaries indicated that concentrations are strongly influenced by water discharge and are dominated by particle-sorbed chemical transport for PCBs and PAHs during wet weather events, while PBDE and PCM concentrations are less associated with particle transport.²³ These observations suggest that current-use inventories are important contributors to tributary concentrations, and that environmental reservoirs (soils and sediments) could also be important for PCBs and PAHs in the tributaries, but to a lesser extent than primary emissions.

In this paper, we present loading estimates of PCBs, PBDEs, PAHs, and PCMs via major pathways from the city to adjacent Lake Ontario: atmospheric processes, tributary runoff, and final effluent discharge from wastewater treatment plants (WWTPs), and discuss the implications of these loadings to human and ecosystem health and environmental policy.

MATERIALS AND METHODS

Sampling and Analysis. Loadings representing one calendar year were based on measured concentrations of PCBs, PBDEs, PAHs, and PCMs obtained during sampling campaigns of air and precipitation across Toronto, tributaries passing through urban Toronto, and final effluents of Toronto WWTPs discharging to Lake Ontario.^{6,23,24} The sample collection and analysis methods are summarized briefly here and are given in full in the Supporting Information (SI).

Air sampling was conducted from 2007 to 2008 using PUF-based passive air samplers (PUF-PAS)²⁴ at 19 sites in the Toronto area (see SI Figure S1). The loadings estimates relied on the average of seasonal measurements from the urban sites nearest to Lake Ontario, a rural site located ~80 km north of downtown Toronto, and a site on an island located in Lake Ontario approximately 4 km south of Toronto’s central business district. PUF-PAS were extracted using pressurized fluid extraction (PFE) with dichloromethane (DCM), purified with alumina-silver nitrate (for PCBs and PBDEs) or silica (for PAHs and PCMs), and analyzed via gas chromatography–mass spectrometry (GC/MS). Since BDE-209 could not be quantified from the PUF-PAS, BDE-209 concentrations were obtained using a high volume air sampler colocated with a PUF-PAS on the campus of the University of Toronto in downtown Toronto. Air sampling, analysis and concentrations are discussed in detail by Melymuk et al.²⁴ and results are summarized in SI Table S3.

Wet deposition samples were collected at the University of Toronto site and at the integrated atmospheric deposition network (IADN) master station at Point Petre, a rural site on the north shore of Lake Ontario ~200 km east of Toronto (SI Figure S2). Wet deposition samples were collected from 2007 to 2009, and consisted of monthly integrated precipitation samples collected with an automated MIC-B precipitation sampler.⁶ Samples were extracted via liquid–liquid extraction with DCM, fractionated on a sodium sulfate-silica column, and analyzed via GC/MS. Precipitation concentrations are discussed by Melymuk et al.⁶

Tributary water samples were collected at six downstream watershed sites (SI Figure S3), as part of the Toronto Tributary Assessment Project throughout the year from late 2006 to 2009. This project was designed to measure contaminant concentrations over a variety of flow and land-use conditions in the Toronto area. Samples from the most intensely sampled years (2008–2009) were used for loading estimates ($n = 19–30$ per site). Sites were colocated with Water Survey of Canada stream gauging sites to provide stream discharge data. Bulk water grab samples (~20 L) were collected using ISCO 6712 samplers (Avensys Solutions, Toronto, Canada) at selected points on the discharge curve or at preselected water levels. Samples were spiked with mass-labeled surrogate standards and processed through glass fiber filters to capture solids and XAD-4 sorbent resin for dissolved analytes. XAD and filters were extracted via PFE with acetone:hexane (50:50 v/v), extracts were combined and dried over sodium sulfate, and then cleaned using silica column chromatography. Extracts were analyzed by GC/MS for PAHs and PCMs, cleaned further with a concentrated sulfuric acid wash, then analyzed by GC-high resolution mass spectrometry (HRMS) for PCBs and PBDEs. Further sampling and analysis are provided in the SI, and concentration ranges are listed in SI Table S4.

Final effluent samples from the three major Toronto WWTPs discharging directly to Lake Ontario, which together treat 98% of Toronto's wastewater and ~40% of stormwater,²⁵ were collected on 8–10 occasions per plant. The 9 L samples were 24-h composites collected by ISCO 3700 peristaltic pumps. Additionally, at one plant, operators collected four bypass discharge grab samples during storm events. Samples were processed and analyzed as per the tributary samples for each of the compound classes. Results are summarized in SI Table S5.

Loading Calculations. Loadings from Toronto to Lake Ontario were estimated using methods specific to each loading pathway. The objective was to obtain comparable order of magnitude loadings to identify the relative magnitude of input pathways for a range of compound classes; uncertainties in these loading estimates are discussed in a subsequent section. Loadings were calculated for \sum PCBs, \sum PBDEs, \sum PAHs, and \sum PCMs (defined in the SI), as well as a subset of individual congeners/compounds. The list of congeners/compounds is as follows: 8 PCBs (28/31, 52, 101, 118, 138, 153, and 180), 8 PBDEs (28, 47, 99, 100, 153, 154, 183, and 209), 15 PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[123-cd]pyrene, benzo[ghi]perylene, dibenz[ah]-anthracene), and 2 PCMs (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyran, HHCB, and 6-acetyl-1,1,2,4,4,7-hexamethyltetraline, AHTN). Atmospheric loadings of \sum_{86} PCBs and \sum_{27} PBDEs were calculated from the individual congeners by scaling up their fractional contributions to the total mass in either air or water, based on congener profiles from congener-specific measurements.^{24,26,27} For example, active sampler air data indicated that PCB-28 was on average 7.8% of \sum_{86} PCBs in Toronto gas-phase air. Thus, one iteration of \sum_{86} PCB gas absorption loadings was estimated by assuming the calculated PCB-28 gas absorption loadings were 7.8% of total loadings. This procedure was repeated for each of the 8 PCBs and 8 PBDEs congeners, and the final estimates of \sum_{86} PCBs and \sum_{27} PBDEs were based on the average of each individual scaling-up. Loadings of \sum PCBs and \sum PBDEs from tributaries, wet deposition, and WWTPs were calculated using total measured concentrations of the congeners listed above. The sum of the loadings of HHCB and AHTN were assumed to represent \sum PCMs, as these two PCMs typically account for >93% of the total PCMs in air and water.^{28,29}

Each pathway to the lake (dry particle deposition, wet deposition, gas absorption, tributaries and WWTPs) was estimated separately. For the purposes of this paper we assumed that Toronto influences an area 40 km offshore of the city (the "Toronto nearshore"), which captures the average extent of atmospheric plume.^{12,30} Tributary plumes are also contained well within this area.

Modeling Overlake Air Concentrations. Gas absorption, dry particle deposition, and wet deposition loadings were calculated using IADN methods,^{31,32} modified using a geographic information system (GIS) to develop a spatial model that incorporated the urban influence on overlake air concentrations. The modified method assumed that the distribution of contaminants over the lake offshore of Toronto could be modeled using a first-order exponential decay curve, where concentrations were highest at the Toronto shoreline

and decreased with increasing distance from the city. This decay curve is expressed as

$$C_a = R + (U - R)e^{-kd} \quad (1)$$

where the concentration in air at a given distance (C_a ; ng/m³) was estimated from the distance from the urban shoreline (d ; m), the background air concentration (R ; ng/m³), taken as the concentration measured at the 80 km north site, the urban air concentration (U ; ng/m³), and the exponential decay constant (k) expressing the decrease in concentration with distance. The urban concentration at $d = 0$ km was the average of the passive air sampler concentrations at sites within 3.5 km of the waterfront and that spanned a 10 km west-east transect (sites 5 km west, 1 km west, 0 km, 1 km east and 5 km east), as these best represented the concentration along the urban waterfront (SI Figure S1). The value of k was determined by fitting eq 1 to the concentrations at a site on the Toronto Island, 4.4 km south of the central business district (CBD). Toronto Island is a large parkland with few vehicles and buildings, and therefore we assumed that air concentrations at this site reflected diluted emissions from Toronto.

Air concentrations were calculated using eq 1 at distances of 0 km, 5 km, 10 km, 20 km, 30 km, and 40 km southward over the lake for each congener/compound and season, and were then inputted into a GIS (ArcGIS v.9.1) to estimate a concentration surface for the whole lake (Figure 1). The

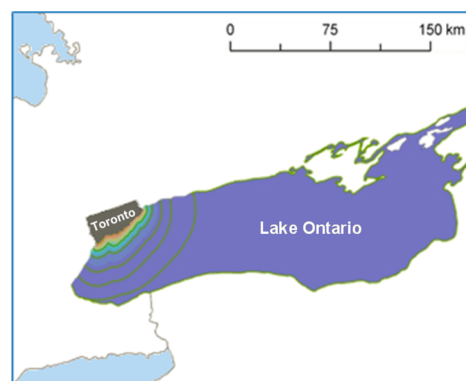


Figure 1. Estimated over lake distribution of phenanthrene in autumn 2007, based on Toronto and rural air concentrations. Red area indicates highest concentrations, blue area indicates lowest concentrations. Detailed site maps are given in SI Figures S1–S3.

concentrations were converted to a triangulated irregular network surface (TIN surface) and the 3-D Spatial Analyst function was used to determine the volume under the surface, representing the distribution of concentrations by unit area across the lake. The influence of Toronto on the Lake was then isolated by repeating the surface interpolation based only on rural background concentrations and subtracting that from the entire lake loadings.

Dry Particle Deposition. Dry particle deposition was calculated from the following equation,

$$L = C_a A v \theta \quad (2)$$

where loadings (L ; kg/y) are estimated from the concentration of a given compound in air (C_a ; ng/m³), the particle-associated fraction of a given compound (θ), the deposition velocity (v ; m/s), and the lake area (A ; km²).³² The TIN surface volume value replaced C_a , θ was determined for each compound from

seasonally averaged concentrations measured by a high-volume air sampler,²⁴ and ν was assigned a value of 0.2 cm/s to allow comparison with IADN measurements,³² although measured particle deposition velocities typically range from 0.05 to 5.0 cm/s.^{33,34}

Gas Absorption. Gas absorption was calculated from the overall air–water mass transfer coefficient (k_{OL} ; m/s), the ideal gas constant (R ; m³ Pa/K mol), temperature at the lake surface (T ; K), and the Henry's Law constant (H ; Pa m³/mol), using the following equation,^{31,32}

$$L = C_a A (1 - \theta) k_{OL} \frac{RT}{H} \quad (\text{Eq. 3})$$

As with dry particle deposition, the TIN surface volume replaced the $C_a A$ term. k_{OL} was calculated for each season from air-side and water-side mass transfer coefficients. Details of the calculation of k_{OL} are given in the SI.

Volatilization. Although not a loading pathway, we estimated volatilization to provide context to loadings entering the nearshore. Details of the volatilization calculation are in the SI.

Wet Deposition. Wet deposition loadings of SVOCs were estimated using 2007–2008 average volume weighted mean concentrations (C_p ; g/L)⁶ and estimated overlake precipitation volumes (P ; mm/y).³⁵ Loadings were calculated on a monthly basis as follows:

$$L = C_p AP \quad (5)$$

The volume under the TIN surface was substituted for $C_p A$. The method for calculating wet deposition loadings from Toronto to Lake Ontario is described in detail by Melymuk et al.⁶

Tributaries. The tributary loading estimates included six streams that flow from north to south through Toronto and discharge into Lake Ontario: Etobicoke Creek, Mimico Creek, Humber River, Don River, and Rouge River (SI Figure S3). Average annual discharges from these tributaries range from 1.26 (Mimico Creek) to 9.59 m³/s (Humber River),³⁶ and represent ~2% of the lake-wide tributary inputs.³⁷

Mean annual contaminant loadings were calculated from measured tributary water concentrations and the discharge data from Water Survey of Canada sites, using the LoadRunner interface³⁸ for LOADEST.³⁹ LOADEST is regression fitting software that extrapolates measured concentrations and stream discharge data to a wider discharge data set using three statistical estimation methods: adjusted maximum likelihood (AML) estimation, maximum likelihood estimation (MLE), and least absolute deviation (LAD). AML and MLE are appropriate to use when model residuals are normally distributed, which was the case. LOADEST computes the Akaike Information Criterion (AIC) to determine which model is optimal. The model with the lowest AIC was selected, and varied by compound class and tributary.⁴⁰

Wastewater Effluent. Loadings for each of the three WWTPs were calculated as the product of measured 24 h composite effluent sample concentrations (C_{WW} ; ng/L, 6–10 samples per plant) and the plant daily flow rate for the corresponding composite period (F_d ; L/day)

$$L = C_{WW} F_d \quad (6)$$

Mean annual loadings were then estimated by averaging the daily load calculations for each sample and multiplying by 365 days.⁴¹

Uncertainties. Significant uncertainty was associated with the loading estimates presented here. Strict QA/QC protocols were followed by all the laboratories involved (details in refs 6,23,42 and SI Table S2) to ensure analytical validity and to minimize uncertainties associated with the measured concentrations. However, measurement methods have inherent uncertainties, such as PUF-passive air samplers for the higher molecular weight compounds.⁴² Sampling/analytical uncertainty was estimated based on uncertainties in sampler calibration, laboratory methods, instrumental quantification, and laboratory performance analysis replicates. This component of the uncertainty ranged from 10 to 60%, depending on compound and analytical method, and generally was higher for the higher molecular weight compounds.

For atmospheric pathways, additional uncertainty arose from applying spatially averaged concentrations in air and precipitation to the whole shoreline. Finally, significant uncertainty was associated with a number of input parameters in the loadings calculations, particularly the particle deposition rate, ν , to which 100% uncertainty has been attributed,^{43,44} the Henry's Law constants, which are expected to have an uncertainty of 29%;^{31,43,45} and the air–water mass transfer coefficients, with an uncertainty of 32%.⁴⁶ Wet deposition was the least uncertain of the atmospheric pathways, with a total uncertainty of ~30%,⁶ as the calculation was based on measured properties (e.g., area, precipitation volume) with smaller associated errors. The largest uncertainty source in precipitation loadings was expected to be from the reliance on only one precipitation measurement site to represent the whole urban shoreline.

Uncertainties in tributary and wastewater treatment loadings were largely due to variations in flow and concentration that were not captured by the sampling regime. For tributary loadings, LOADEST calculates the standard error of the mean load estimate as a measure of uncertainty for each AML model using a linear approximation. Here, uncertainties ranged from 13 to 86%, depending upon the tributary and compound class. However, regression-based load estimation techniques are challenged by flashy urban streams^{47,48} which are typical of Toronto tributaries, and LOADEST is best suited to parameters with many measurements (e.g., total suspended particles, nutrients), rather than the compounds measured here. As a result, we expected greater uncertainty with tributary loading estimates than that expressed by the relative standard error, however the extent to which the uncertainties were underestimated varied temporally and by stream. Finally, relative standard errors in the wastewater mean loading estimate ranged from 6 to 73%, depending on the plant and the compound class.

To quantify the total uncertainty associated with each loading pathway, the uncertainties described above were propagated through the loading calculations, thereby providing a best estimate and a range for each loading pathway (Figure 2, SI Table S6). The relative uncertainty was largest for dry deposition (~130%), reflecting the high uncertainty in the particle dry deposition rate. However, this pathway consistently contributed the least to total loadings. Estimates of overall error for wet deposition, gas absorption, tributaries and WWTP pathways ranged from ~30–80%, and were similar to the uncertainty reported Hoff et al.³¹

RESULTS AND DISCUSSION

Loadings by Compound Class and Pathway. Total annual mass loadings for each major pathway from Toronto to

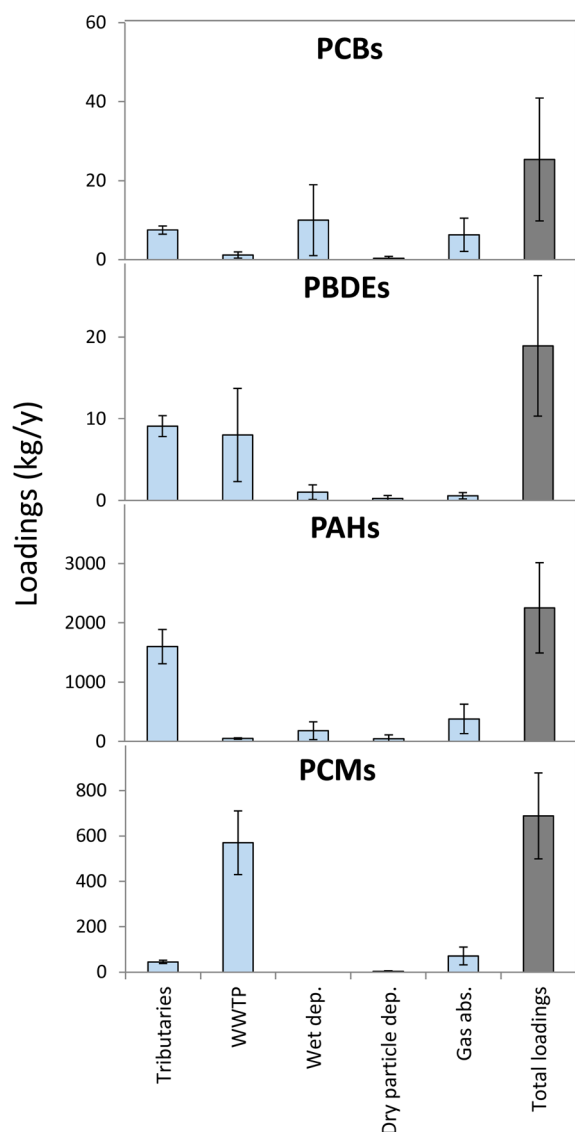


Figure 2. Loadings of PCBs, PBDEs, PCMs, and PAHs from Toronto to nearshore Lake Ontario via five loadings pathways.

Lake Ontario for 2008 are presented for each of the four compound classes in Figure 2. Selected individual compound/congener mass loadings are illustrated in Figure 3 and are listed in SI Table S6. Total loadings ranged over 2 orders of magnitude among the compound classes, with \sum PCB and \sum PBDE loadings of 25 ± 5.5 and 19 ± 6.0 kg/y, respectively, and \sum PCM and \sum PAH loadings of 690 ± 150 and 2300 ± 390 kg/y, respectively. Differences among compound classes reflects the order of magnitude differences in concentrations of the compounds in the urban environment.²⁴ However, within each compound class the distribution among pathways reflects the manner in which the compounds are used/emitted and their physical-chemical properties.

PCBs. PCBs were the only compound class for which atmospheric deposition dominated total loadings. Wet deposition and gas absorption contributed 10 ± 3.3 kg/y (39%) and 6.3 ± 4.2 kg/y (25%), respectively, tributaries contributed 7.5 ± 1.1 kg/y (30%), and dry deposition and WWTPs contributed <5%. Estimated total loadings of 25 ± 5.5 kg/y of \sum PCBs from Toronto to the lake were virtually equivalent to the estimated loss of 23 ± 15 kg/y by volatilization.

Although total inputs of PCBs appeared to be balanced by losses via volatilization from the nearshore of the lake, the congeners contributing to loadings differed from those contributing to volatilization. Total loadings to the lake were dominated by the hexa- and hepta-CBs entering the lake from tributaries and wet deposition, while volatilization was dominated by the tri- and tetra-CBs. For example, volatilization losses of CB-52 were 3.5 \times higher than total loadings, while loadings of CB-153 were 13 \times higher than volatilization losses. These results are consistent with those of Csiszar et al.¹² who found, through mass balance modeling, volatilization of lower molecular weight PCBs from the nearshore and transport of higher molecular weight PCBs via soil wash-off to surface waters. Thus, although the total net loadings suggest that the nearshore lake is close to equilibrium, in fact the lake received significant net loadings of higher molecular weight PCBs that will eventually be buried in sediment,⁴⁹ and experienced significant net losses of lower molecular weight PCBs via volatilization from the lake. The importance of soil reservoirs for high molecular weight PCBs stands in contrast to the

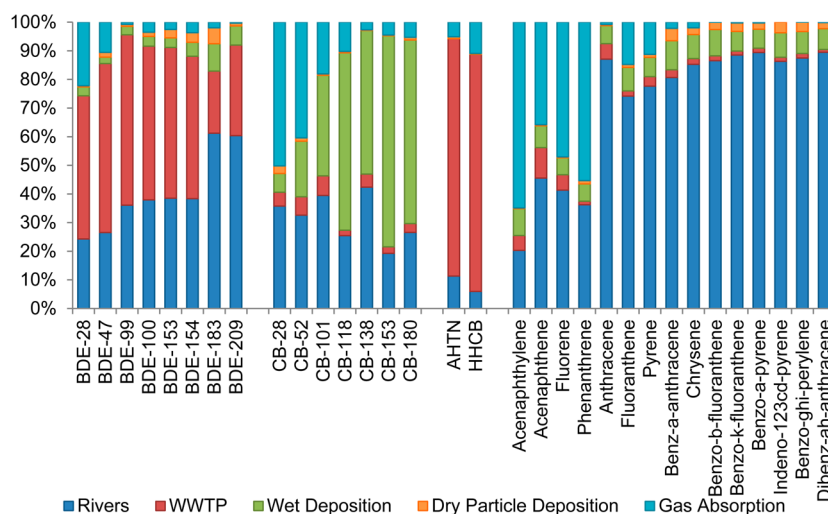


Figure 3. Relative distribution of individual compounds/congener loadings among the five loading pathways.

dominance of primary sources for lower molecular weight PCBs.¹²

PBDEs. Tributaries and WWTP effluents contributed equally to total PBDE loadings (9.1 ± 1.3 and 8.0 ± 5.7 kg/y, respectively). Atmospheric loading pathways each contributed <5%. Losses via volatilization were 1.9 ± 1.1 kg/y or 10% of total inputs. Multimedia model (SO-MUM) results support the dominant pathways of tributaries and WWTP. As with PCBs, PBDE air concentrations were found to be the result of primary emissions from the inventory of PBDEs in PBDE-containing products.¹² The combination of these results suggests the typical pathway of urban PBDE release: PBDEs move from consumer products into the indoor environment, then are transported outdoors, deposit onto urban surfaces, and wash-off to stormwater.¹²

An unexpected result of the loading estimates was the importance of the final treated WWTP effluent as a pathway for PBDEs to the nearshore lake. The relatively high concentration in final treated effluent suggests that levels of PBDEs entering the WWTP were very high,^{50,51} as most PBDEs are believed to be removed through sorption to sewage sludges. Thus, the mass of PBDEs in the final effluent represents only ~5–10% of the total mass of PBDEs entering the WWTP.^{52–54} There is a clear link between compounds from personal care products and WWTPs, but the explanation for WWTPs as an important pathway for PBDEs is less clear. The principle source of PBDEs to wastewater is believed to be PBDE-containing dust from textiles, furniture and electronics entering the WWTP system from cleaning and laundering.^{11,55–57} Another possible PBDE source is human excretion.⁵⁸ Finally, studies conducted in Spain and Australia suggested that although PBDEs in sewage originated from a combination of domestic and industrial sources,⁵⁰ particularly high concentrations of PBDEs were linked to industrial inputs to the waste stream.⁵⁹ Toronto did not have large documented industrial sources of PBDEs at the time of sampling,^{19,60} however numerous smaller industrial sources may have fallen below the regulatory reporting limits (e.g., small companies that apply flame retardants to fabrics). The WWTP with the least industrial contribution (<30% of influent; M. Shigishi, personal communication) had per capita annual loadings of \sum PBDEs that were 10 \times lower than from the other WWTPs, suggesting that small industries may have contributed PBDEs to the other Toronto WWTPs (SI Table S5). Differing residence times within the treatment plants and small contributions from combined sewers may have also contributed to variability in PBDE concentrations among WWTP.²⁵ Finally, stormwater was expected to contribute a fraction of PBDEs to WWTPs, as discussed above.

As with PCBs, the primary transport pathways differed by PBDE congener. For BDE-28, 22 and 24% of loadings were from gas absorption and tributaries, respectively, whereas for PBDE-183, the contribution from tributaries dominated, accounting for 61% of the loadings, while gas absorption was only 2%. Similarly, the tributaries were the source of 60% of BDE-209 loadings to the lake. These differences reflect three factors. First, at urban sites adjacent to the lakeshore, air concentrations of BDE-28 were 5 \times higher than BDE-183.²⁴ Second, the concentrations of higher molecular weight compounds dropped off more quickly over the lake with increasing distance from the city than did lower molecular weight compounds (SI Figure S4). Thus, while PBDE-183 concentrations reached rural background concentrations at 5–10 km offshore of Toronto, BDE-28 concentrations were

elevated up to 15–20 km offshore, leading to elevated gas absorption over a larger lake area. Similar decreases in the contribution of gas absorption with increasing molecular weight were observed for PCBs and PAHs. Third, as shown by Csiszar et al.,¹¹ higher molecular weight congeners emitted in the urban area deposit or condense onto urban surface films from where they are washed off by precipitation into stormwater and tributaries.

PAHs. PAH loadings were largely from tributaries (71% or 1600 ± 280 kg/y) followed by gas absorption (16% or 380 ± 250 kg/y). Wet and dry deposition and WWTP effluent each contributed <10%. PAH emissions to urban air were primarily from industrial sources⁶⁰ and transportation,^{61,62} of which a significant proportion likely deposits onto impervious surfaces.⁶³ Coatings on impervious surfaces, such as coal tar sealants, could also be a source of PAHs to waterbodies.^{21,64} The large mass loadings from tributaries suggest that the main pathway of PAH releases from the urban area was from washoff of impervious surfaces.^{21,63} Losses from the nearshore lake due to volatilization were 720 ± 590 kg/y or 30% of total inputs. The PAH loadings were dominated by phenanthrene, fluoranthene and pyrene, whereas volatilization fluxes were dominated by slightly more volatile compounds: acenaphthene, fluorene, and phenanthrene.

PCMs. PCM loadings to the lake were largely via WWTP effluent, which contributed 570 ± 140 kg/y or 83% of total loadings. Additional loadings were from gas absorption (10% or 71 ± 39 kg/y) and tributaries (7% or 45 ± 7.2 kg/y), with more than half of that associated with the Don River, which has an upstream WWTP.⁴⁰ Contributions from dry particle deposition were minimal. Wet deposition loadings were not calculated as PCMs were not measured in precipitation. However, based on PCM concentrations reported by Peters et al.,⁶⁵ we estimated that PCM loadings from wet deposition were likely in the same range as gas absorption.

PCM use is largely in “down-the-drain” personal care products, and hence their release via WWTP effluent. Although 70–92% of PCMs are removed during the wastewater treatment process,^{66,67} the concentrations in sewage are quite high, thus treated effluent is still the largest source of PCMs to the urban nearshore environment. Losses from the lake via volatilization were 210 ± 120 kg/y, or 31% of total inputs. While the volatilization of PCMs may elevate air concentrations on a local scale, PCMs are rapidly degraded in the atmosphere, which reduces their long-range transport potential.⁶⁸

Variability in Loading Pathways. Individual loading pathways have spatial and temporal variability that shape the overall pattern of urban loadings to nearshore Lake Ontario. The atmospheric pathways act as nonpoint sources to the lake, with the mass of loadings decreasing exponentially with increasing distance from the urban area (Figure 1). As discussed above, the distance over which loadings are elevated varies according to the compound in question, following the differential removal hypothesis: more volatile compounds are transported greater distances outward over the lake, while less volatile, particle-bound chemicals are more rapidly removed via deposition and thus influence a smaller lake area.

The largest source of all spatial and temporal variability is meteorological influences (e.g., precipitation, wind). For example, gas absorption varies according to wind speed and direction.

On average, concentrations of \sum PCBs and \sum PBDEs decreased to 10% of their initial concentration by 40–50 km

offshore,^{11,12,69–72} but this area of influence was found to vary rapidly, and ranged from zero to hundreds of kilometers depending on the strength and direction of off-shore winds.^{11,12,73} In contrast, tributary and WWTP discharges, and thus loadings, act as point sources to the nearshore. For example, 84% of the total loadings of Σ PCMs to the Toronto nearshore are released to water covering only 8% of this area.

In terms of temporal variability, tributary loadings, which were most important for PAH and PBDEs, are well-known to be highly episodic, although our data did not allow us to quantify this effect. Temporal variability was not as significant for WWTP loadings. The greatest temporal variability in WWTP discharge occurs during WWTP stormwater bypass events, however we found that bypasses only had a small contribution to annual WWTP loadings. In 2008, Toronto's WWTPs had 46 WWTP stormwater bypass events occurring during high volumes of precipitation, releasing to the lake 10^6 m³ of combined stormwater and sanitary sewer effluent which received only primary treatment.^{74–76} Without secondary treatment, concentrations were 2, 4, 4, and 6 \times higher for PCM, PCBs, PBDEs, and PAHs, respectively (SI Table S6). However, estimates using average bypass effluent concentrations (SI Table S6) suggested that WWTP bypass events contributed only 1–5% of total annual WWTP loadings per compound class, emphasizing that most WWTP loadings were from the 2.6×10^8 m³/y of final treated effluent, rather than from bypass effluent.

Policy Implications. Our research has estimated emissions from the city and resultant loadings to Lake Ontario, illustrating the role of various urban pathways in contributing PCBs, PBDEs, PAH, and PCMs according to their emission sources, types of uses, urban inventories, and physical-chemical properties. These estimates originated from a coordinated measurement and modeling effort that provided a more holistic perspective than that available from relying on one method only. The loadings are significant for the nearshore lake as this area is both environmentally and economically important, yet typically suffers the most from pollution.^{77,78} Three main policy outcomes emerged from this work.

1. Opportunities for Loading Reduction. A key outcome of this study and the companion measurement and modeling work^{11,12,19} is the application of this information to guide loading reductions. Loading reductions are challenging to achieve because the emission sources are diffuse (e.g., PAHs, PCMs) and legislative and/or policy controls have been put in place (for at least PCBs and PBDEs) but do not necessarily address the management of existing inventories. Unlike pollution sources of the past decades, minimal loadings originate from industrial point sources for which legislative and policy controls are most effective.

A recommendation that arises from this work is that once a chemical has been designated for control (e.g., PCBs and penta- and octa-BDE, listed in the Stockholm Convention), in-use inventories need to be aggressively reduced in order to stem ongoing emissions. In Canada, legislation was passed in 2008 to remove PCBs from use, however this legislation has seen an extension to 2025 as an end-date.⁷⁹ Federal regulations mandating the removal of PCBs from use in the U.S. have not been passed. Canadian and U.S. legislative controls of penta- and octa-BDEs do not extend to reducing the inventory of PBDEs already contained in products. Further reductions in PAH emissions could come with improved fossil fuel combustion efficiencies and the movement toward alternative

energy sources and away from fossil fuel combustion. We note, however, that energy-related emission reductions, at least for greenhouse gases, in part have been achieved in North America at the expense of higher emissions in countries that have emission-intensive exporting industries such as China.⁸⁰ Similar patterns of global emission shifting could or already has occurred for PAHs. Legislative restrictions in the use of coal tar sealants, as passed by some U.S. jurisdictions, could also be expected to reduce PAH loadings.

Another opportunity to reduce loadings lies in controlling emissions to WWTPs. Identifying the unknown sources of PBDEs to WWTP influent merits investigation. Efforts continue toward improving removal efficiencies (e.g., Melcer and Klečka⁸¹) which will reduce loadings to receiving water bodies but this is, at best, an end-of-pipe solution with very high capital costs.

2. The Importance of Tributary and WWTP Loadings. An unexpected result of our study was the importance of tributaries to total loadings; direct atmospheric deposition only dominated PCB loadings. However, atmospheric deposition to the Great Lakes has garnered the greatest attention,^{31,72,82} in contrast to tributary loadings that have received relatively little attention, aside from the connecting channels between lakes. Tributaries capture, focus and convey loadings to the lake from atmospheric deposition to urban surfaces, as well as from soil wash-off and illegal sewer connections. Although considerable uncertainty surrounds sources of PBDEs and PAH to the tributaries, we do know that major point source emissions are not the culprit and thus loading reductions ultimately must come from nonpoint source reductions.

3. Significance of Loadings to Human and Ecological Health. Of the four compound classes investigated, the direct significance of PCBs and PBDEs loadings to Lake Ontario lies in human exposure via fish consumption. People fish off the shores of Toronto^{83,84} and PCBs still drive fish advisories in nearshore Lake Ontario⁸⁵ some 40 years after Canada first introduced legislative controls for PCBs. Concentrations of PBDEs in some Great Lakes fish (including Lake Ontario but dependent on location, species and age of the fish) are approaching concentrations that would trigger a consumption advisory in the absence of PCBs (S. Bhavsar, personal communication). Nearshore loadings of PAHs were greatest among the compound classes investigated. PAH loadings are significant because of their toxicity to aquatic biota.⁸⁶

Recent changes in the nearshore food web structure have heightened the significance of contaminant loadings to the nearshore. Invasive zebra mussels (dreissenids) have increased nearshore water-to-sediment fluxes of nutrients, materials, and likely contaminants, resulting in reduced chemical transfer between nearshore and offshore areas.⁸⁷ Thus, loadings to the nearshore are now more likely to remain in the nearshore rather than undergo dilution in the lake, that is, the “nearshore shunt”.⁸⁷ While this is “good news” for offshore Lake Ontario, it implies that dilution can no longer be relied upon to reduce nearshore pollution.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: miriam.diamond@utoronto.ca.

Present Addresses

[¶]Dept. of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada and Ontario Ministry of the Environment, Toronto, Ontario M9P 3V6, Canada.

[○]Department of Environmental Health Sciences, University of Michigan, Ann Arbor, Michigan U.S.A. 48109-2029.

[@]Department of Earth Science, University of Toronto, Toronto, Ontario M5S 3B1, Canada, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada, and School of the Environment, University of Toronto, Toronto, Ontario M5S 3E8.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Funding was provided by a Great Lakes Atmospheric Deposition fund grant to Diamond, Helm, Blanchard and Backus, Environment Canada, the Ontario Ministry of the Environment and Toronto and Region Conservation Authority, NSERC to Melymuk and OGS to Csiszar. Thanks to Bruce Harrison, Orrin Carson, Mary Lou Archer and Brenda Treen for precipitation sampling and analysis; Dave Supper for water and wastewater sample collection; Rob Brennan and Sheng Yang for water sample processing; and Corina Brimacombe, Tony Chen, Terry Kolic, and Eric Reiner for water sample analyses. Martin Shigeishi and plant operators provided access to City of Toronto wastewater treatment plants for sampling, and Matthew Caschera provide WWTP flow information.

REFERENCES

- (1) Diamond, M. L.; Hodge, E. Urban contaminant dynamics: From source to effect. *Environ. Sci. Technol.* **2007**, *41*, 3796–3805.
- (2) Chen, S.-C.; Liao, C.-M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* **2006**, *366*, 112–23.
- (3) DeMarini, D. M. Genotoxicity biomarkers associated with exposure to traffic and near-road atmospheres: A review. *Mutagenesis* **2013**, *28*, 485–505.
- (4) Mendola, P.; Buck, G. M.; Sever, L. E.; Zielezny, M.; Vena, J. E. Consumption of PCB-contaminated freshwater fish and shortened menstrual cycle length. *Am. J. Epidemiol.* **1997**, *146*, 955–960.
- (5) Buck, G. M.; Vena, J. E.; Schisterman, E. F.; Dmochowski, J.; Mendola, P.; Sever, L. E.; Fitzgerald, E.; Kostyniak, P.; Greizerstein, H.; Olson, J. Parental consumption of contaminated sport fish from Lake Ontario and predicted fecundability. *Epidemiology* **2000**, *11*, 388–393.
- (6) Melymuk, L.; Robson, M.; Diamond, M. L.; Bradley, L. E.; Backus, S. M. Wet deposition loadings of organic contaminants to Lake Ontario: Assessing the influence of precipitation from urban and rural sites. *Atmos. Environ.* **2011**, *45*, 5042–5049.
- (7) Melymuk, L. Semi-Volatile Organic Contaminants in the Urban Atmosphere: Spatial and Seasonal Distributions and Implications for Contaminant Transport, PhD Thesis. University of Toronto, 2012, p. 265.
- (8) Robson, M.; Melymuk, L.; Csiszar, S. A.; Giang, A.; Diamond, M. L.; Helm, P. A. Continuing sources of PCBs: The significance of building sealants. *Environ. Int.* **2010**, *36*, 506–13.
- (9) Diamond, M. L.; Melymuk, L.; Csiszar, S. A.; Robson, M. Estimation of PCB stocks, emissions, and urban fate: Will our policies reduce concentrations and exposure? *Environ. Sci. Technol.* **2010**, *44*, 2777–83.
- (10) Csiszar, S. A.; Diamond, M. L.; Thibodeaux, L. J. Modeling urban films using a dynamic multimedia fugacity model. *Chemosphere* **2012**, *87*, 1024–31.
- (11) Csiszar, S. A.; Daggupaty, S. M.; Verkoeyen, S.; Giang, A.; Diamond, M. L. SO-MUM: A coupled atmospheric transport and multimedia model used to predict intraurban-scale PCB and PBDE emissions and fate. *Environ. Sci. Technol.* **2013**, *47*, 436–45.
- (12) Csiszar, S. A.; Diamond, M. L.; Daggupaty, S. M. The magnitude and spatial range of current-use PCB and PBDE emissions estimated using a coupled multimedia and air transport model. *Environ. Sci. Technol.* **2014**, *48*, 1075–1083.
- (13) Council of the European Union. Regulation (EC) No 1907/2006 of the European Parliament and of the Council Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH); Brussels, 2006.
- (14) U.S. Environmental Protection Agency. Polybrominated Diphenyl Ethers (PBDEs) Action Plan http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pbdes_ap_2009_1230_final.pdf.
- (15) U.S. Environmental Protection Agency. DecaBDE Phase-out Initiative <http://www.epa.gov/opptintr/existingchemicals/pubs/actionplans/deccadbe.html>.
- (16) UNEP. Stockholm Convention on Persistent Organic Pollutants; United Nations Environment Programme: Geneva, 2009; pp. 1–13.
- (17) Environment Canada. Polybrominated Diphenyl Ethers <https://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-18xml=5046470B-2D3C-48B4-9E46-735B7820A444> (accessed January 2013).
- (18) Batterman, S. A.; Chernyak, S. M.; Jia, C.; Godwin, C.; Charles, S. Concentrations and emissions of polybrominated diphenyl ethers from U.S. houses and garages. *Environ. Sci. Technol.* **2009**, *43*, 2693–2700.
- (19) Melymuk, L.; Robson, M.; Helm, P. A.; Diamond, M. L. Application of land use regression to identify sources and assess spatial variation in urban SVOC concentrations. *Environ. Sci. Technol.* **2013**, *47*, 1887–95.
- (20) Diamond, M. L.; Abbasi, G.; De Leon, F.; Saini, A.; Goosey, E.; Buser, A.; Soehl, A.; Murray, M. How can we manage the mountain of PBDEs plus “new” flame retardants? PBDE inventory, fate and policy analysis. *Organohalogen Compd.* **2013**, *75*.
- (21) Van Metre, P. C.; Mahler, B. J. Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes. *Sci. Total Environ.* **2010**, *409*, 334–44.
- (22) Van Metre, P. C.; Mahler, B. J.; Furlong, E. T. Urban sprawl leaves its PAH signature. *Environ. Sci. Technol.* **2000**, *34*, 4064–4070.
- (23) Diamond, M. L.; Helm, P. A.; Robson, M.; Csiszar, S. A.; Melymuk, L. Urban Sources and Loadings of Toxics to Lake Ontario from Integrated Measurements and Modeling; Toronto Report to the Great Lakes Commission, 2010; pp. 1–163.
- (24) Melymuk, L.; Robson, M.; Helm, P. A.; Diamond, M. L. PCBs, PBDEs, and PAHs in Toronto air: Spatial and seasonal trends and implications for contaminant transport. *Sci. Total Environ.* **2012**, *429*, 272–280.
- (25) City of Toronto. Wet Weather Flow Master Plan: The Plan in Action—5-Year Summary Report; Toronto, 2009; pp. 1–73.
- (26) Dove, A. PCB Concentrations in Lake Ontario; Burlington, Ontario, Canada, 2012; Personal Communication.
- (27) Andresen, J. A.; Muir, D. C. G.; Ueno, D.; Darling, C.; Theobald, N.; Bester, K. Emerging pollutants in the North Sea in comparison to Lake Ontario, Canada, Data. *Environ. Toxicol. Chem.* **2007**, *26*, 1081–9.
- (28) Peck, A. M.; Hornbuckle, K. C. Synthetic musk fragrances in Lake Michigan. *Environ. Sci. Technol.* **2004**, *38*, 367–372.
- (29) Peck, A. M.; Hornbuckle, K. C. Synthetic musk fragrances in urban and rural air of Iowa and the Great Lakes. *Atmos. Environ.* **2006**, *40*, 6101–6111.
- (30) Green, M. L.; DePinto, J. V.; Sweet, C. W.; Hornbuckle, K. C. Regional spatial and temporal interpolation of atmospheric PCBs: Interpretation of Lake Michigan mass balance data. *Environ. Sci. Technol.* **2000**, *34*, 1833–1841.

- (31) Hoff, R. M.; Strachan, W. M. J.; Sweet, W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmos. Environ.* **1996**, *30*, 3505–3527.
- (32) Blanchard, P.; Hulting, M. L.; Brice, K. A.; Backus, S. M.; Dryfhout-Clark, H.; Hites, R. A. *Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN Results Through 2005*; IADN: Toronto, Ontario, Canada and Chicago, 2008; pp. 1–224.
- (33) Holsen, T. M.; Noll, K. E.; Liu, S. P.; Lee, W.-J. Dry deposition of polychlorinated biphenyls in urban areas. *Environ. Sci. Technol.* **1991**, *25*, 1075–1081.
- (34) Cindoruk, S. S.; Tasdemir, Y. Deposition of atmospheric particulate PCBs in suburban site of Turkey. *Atmos. Res.* **2007**, *85*, 300–309.
- (35) Hunter, T. S.; Croley, T. E. I. Great Lakes monthly hydrologic data. In *NOAA Data Report ERL GLERL*; National Technical Information Service: Springfield, VA, 2009.
- (36) Environment Canada. Water Survey of Canada—Water Level and Streamflow Statistics. http://www.wsc.ec.gc.ca/staflo/index_e.cfm?cname=main_e.cfm.
- (37) Neff, B. P.; Nicholas, J. R. *Uncertainty in the Great Lakes Water Balance*, Scientific Investigations Report ; Reston, VA, 2005; p 2004–5100.
- (38) Booth, G.; Raymond, P.; Oh, N.-H. LoadRunner. <http://environment.yale.edu/raymond/loadrunner/>.
- (39) Runkel, R. L.; Crawford, C. G.; Cohn, T. A. *Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers*; U.S. Geological Survey: Lakewood, CO, 2004.
- (40) Helm, P. A.; Gilbert, B.; Robson, M.; Melymuk, L.; Diamond, M. L.; Brimacombe, C.; Chen, T.; Kolic, T.; Kaltenecker, G.; Reiner, E. J. Urban tributary contaminants: concentrations and mass flows of PCBs, PBDEs, PAHs, and polycyclic musks. Poster presentation, *Dioxin 2010: International Symposium on Halogenated Persistent Organic Pollutants*. Sept. 12–17, 2010; San Antonio, Texas.
- (41) Balogh, S. J.; Nolle, Y. H. Methylmercury input to the Mississippi River from a large metropolitan wastewater treatment plant. *Sci. Total Environ.* **2008**, *406*, 145–53.
- (42) Melymuk, L.; Robson, M.; Helm, P. A.; Diamond, M. L. Evaluation of passive air sampler calibrations: Selection of sampling rates and implications for the measurement of persistent organic pollutants in air. *Atmos. Environ.* **2011**, *45*, 1867–1875.
- (43) Venier, M.; Hites, R. A. Atmospheric deposition of PBDEs to the Great Lakes featuring a Monte Carlo analysis of errors. *Environ. Sci. Technol.* **2008**, *42*, 9058–9064.
- (44) Hoff, R. M. An error budget for the determination of the atmospheric mass loading of toxic chemicals in the Great Lakes. *J. Great Lakes Res.* **1994**, *20*, 229–239.
- (45) Cetin, B.; Odabasi, M. Measurement of Henry's Law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature. *Atmos. Environ.* **2005**, *39*, 5273–5280.
- (46) Cetin, B.; Odabasi, M. Air-water exchange and dry deposition of polybrominated diphenyl ethers at a coastal site in Izmir Bay, Turkey. *Environ. Sci. Technol.* **2007**, *41*, 785–91.
- (47) Runkel, R. L. LOADEST: Frequently Asked Questions. <http://water.usgs.gov/software/loadest/faq/>.
- (48) Medalie, L. *Effects of Urban Best Management Practices on Streamflow and Phosphorus and Suspended-Sediment Transport on Englesby Brook in Burlington, Vermont, 2000–2010*; U.S. Geological Survey, 2012; pp. 1–26.
- (49) Li, A.; Rockne, K. J.; Sturchio, N. C.; Song, W.; Ford, J. C.; Wei, H. PCBs in sediments of the Great Lakes—Distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environ. Pollut.* **2009**, *157*, 141–7.
- (50) Clarke, B.; Porter, N. A.; Symons, R.; Marriott, P.; Ades, P.; Stevenson, G. J.; Blackbeard, J. R. Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. *Chemosphere* **2008**, *73*, 980–9.
- (51) Kim, M.; Guerra, P.; Theocharides, M.; Barclay, K.; Smyth, S. A.; Alae, M. Parameters affecting the occurrence and removal of polybrominated diphenyl ethers in twenty Canadian wastewater treatment plants. *Water Res.* **2013**, *47*, 2213–21.
- (52) Vogelsang, C.; Grung, M.; Jantsch, T. G.; Tollefsen, K. E.; Liltved, H. Occurrence and removal of selected organic micro-pollutants at mechanical, chemical and advanced wastewater treatment plants in Norway. *Water Res.* **2006**, *40*, 3559–70.
- (53) North, K. D. Tracking polybrominated diphenyl ether releases in a wastewater treatment plant effluent, Palo Alto, California. *Environ. Sci. Technol.* **2004**, *38*, 4484–8.
- (54) Rayne, S.; Ikononou, M. G. Polybrominated diphenyl ethers in an advanced wastewater treatment plant. Part 1: Concentrations, patterns, and influence of treatment processes. *J. Environ. Eng. Sci.* **2005**, *4*, 353–367.
- (55) Stapleton, H. M.; Dodder, N. G.; Offenberg, J. H.; Schantz, M. M.; Wise, S. A. Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.* **2005**, *39*, 925–31.
- (56) Takigami, H.; Suzuki, G.; Hirai, Y.; Sakai, S.-I. Occurrence and control of brominated flame retardants in a laundry factory for home and office cleaning utensils. In *Fifth International Symposium on Brominated Flame Retardants*; Kyoto, Japan, 2010.
- (57) Davis, E. F.; Klosterhaus, S. L.; Stapleton, H. M. Measurement of flame retardants and triclosan in municipal sewage sludge and biosolids. *Environ. Int.* **2012**, *40*, 1–7.
- (58) Huwe, J.; Hakk, H.; Lorentzen, M. Bioavailability and mass balance studies of a commercial pentabromodiphenyl ether mixture in male Sprague-Dawley rats. *Chemosphere* **2007**, *66*, 259–66.
- (59) De la Torre, A.; Alonso, E.; Concejero, M. A.; Sanz, P.; Martínez, M. A. Sources and behaviour of polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in Spanish sewage sludge. *Waste Manag.* **2011**, *31*, 1277–84.
- (60) Environment Canada. National Pollutant Release Inventory. <http://www.ec.gc.ca/inrp-npri/> (accessed February 1, 2013).
- (61) Aceves, M.; Grimalt, J. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environ. Sci. Technol.* **1993**, *27*, 2896–2908.
- (62) Harrad, S. J.; Laurie, L. Concentrations, sources and temporal trends in atmospheric polycyclic aromatic hydrocarbons in a major conurbation. *J. Environ. Monit.* **2005**, *7*, 722–7.
- (63) Yang, H.-H.; Chiang, C.-F.; Lee, W.-J.; Hwang, K.-P.; Wu, E. M.-Y. Size distribution and dry deposition of road dust PAHs. *Environ. Int.* **1999**, *25*, 585–597.
- (64) Mahler, B. J.; Van Metre, P. C.; Bashara, T. J.; Wilson, J. T.; Johns, D. A. Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2005**, *39*, 5560–6.
- (65) Peters, R. J. B.; Beeltje, H.; van Delft, R. J. Xeno-estrogenic compounds in precipitation. *J. Environ. Monit.* **2008**, *10*, 760–9.
- (66) Simonich, S. L.; Begley, W. M.; Debaere, G.; Eckhoff, W. S. Trace analysis of fragrance materials in wastewater and treated wastewater. *Environ. Sci. Technol.* **2000**, *34*, 959–965.
- (67) Smyth, S. A.; Lishman, L. A.; McBean, E. A.; Kleywegt, S.; Yang, J.-J.; Svoboda, M. L.; Ormonde, S.; Pileggi, V.; Lee, H.-B.; Seto, P. Polycyclic and nitro musks in Canadian municipal wastewater: Occurrence and removal in wastewater treatment. *Water Qual. Res. J. Canada* **2007**, *42*, 138–152.
- (68) Aschmann, S. M.; Arey, J.; Atkinson, R.; Simonich, S. L. Atmospheric lifetimes and fates of selected fragrance materials and volatile model compounds. *Environ. Sci. Technol.* **2001**, *35*, 3595–600.
- (69) Offenberg, J. H.; Baker, J. E. Polychlorinated biphenyls in Chicago precipitation: Enhanced wet deposition to near-shore Lake Michigan. *Environ. Sci. Technol.* **1997**, *31*, 1534–1538.
- (70) Simcik, M. F.; Zhang, H.; Eisenreich, S. J.; Franz, T. P. Urban contamination of the Chicago/coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLUS. *Environ. Sci. Technol.* **1997**, *31*, 2141–2147.

- (71) Offenberg, J. H.; Baker, J. E. PCBs and PAHs in southern Lake Michigan in 1994 and 1995: Urban atmospheric influences and long-term declines. *J. Great Lakes Res.* **2000**, *26*, 196–208.
- (72) Offenberg, J. H.; Simcik, M. F.; Baker, J. E.; Eisenreich, S. J. The impact of urban areas on the deposition of air toxics to adjacent surface waters: A mass budget of PCBs in Lake Michigan in 1994. *Aquat. Sci.* **2005**, *67*, 79–85.
- (73) Hornbuckle, K. C.; Green, M. L. The impact of an urban-industrial region on the magnitude and variability of persistent organic pollutant deposition to Lake Michigan. *Ambio* **2003**, *32*, 406–11.
- (74) City of Toronto. *Ashbridges Bay Wastewater Treatment Plant 2008 Annual Report*; Toronto, 2009; pp. 1–66.
- (75) City of Toronto. *Highland Creek Wastewater Treatment Plant 2008 Annual Report*; Toronto, 2009; pp. 1–49.
- (76) City of Toronto. *Humber Wastewater Treatment Plant 2008 Annual Report*; Toronto, 2009; pp. 1–40.
- (77) Makarewicz, J. C. Nonpoint source reduction to the nearshore zone via watershed management practices: Nutrient fluxes, fate, transport and biotic responses—Background and objectives. *J. Great Lakes Res.* **2009**, *35*, 3–9.
- (78) Mackey, S. D.; Goforth, R. R. Great Lakes nearshore habitat science. *J. Great Lakes Res.* **2005**, *31* (Supple), 1–5.
- (79) Environment Canada. PCB Regulations: An Overview <http://www.ec.gc.ca/bpc-pcb/default.asp?lang=en&n=E794BDF1-1> (accessed June 28, 2013).
- (80) Kanemoto, K.; Lenzen, M.; Peters, G. P.; Moran, D. D.; Geschke, A. Frameworks for comparing emissions associated with production, consumption, and international trade. *Environ. Sci. Technol.* **2012**, *46*, 172–179.
- (81) Melcer, H.; Klečka, G. Treatment of wastewaters containing bisphenol A: State of the science review. *Water Environ. Res.* **2011**, *83*, 650–666.
- (82) Sun, P.; Basu, I.; Hites, R. A. Temporal trends of polychlorinated biphenyls in precipitation and air at Chicago. *Environ. Sci. Technol.* **2006**, *40*, 1178–1183.
- (83) Dawson, J.; Sheeshka, J.; Cole, D. C.; Kraft, D.; Waugh, A. Fishers weigh in: Benefits and risks of eating Great Lakes fish from the consumer's perspective. *Agric. Human Values* **2008**, *25*, 349–364.
- (84) Murkin, E.; Cole, D. C.; Kearney, J. P.; Sheeshka, J.; Dawson, J.; Project, F. W. N. Fish consumption practices among frequent consuming fishers of five Ontario Great Lakes Areas of Concern (AOCs). *J. Great Lakes Res.* **2003**, *29*, 436–447.
- (85) Bhavsar, S. P.; Awad, E.; Mahon, C. G.; Petro, S. Great Lakes fish consumption advisories: Is mercury a concern? *Ecotoxicology* **2011**, *20*, 1588–98.
- (86) Canadian Council of Ministers of the Environment. Canadian Water Quality Guidelines for the Protection of Aquatic Life - Polycyclic Aromatic Hydrocarbons. In *Canadian Environmental Quality Guidelines*; Environment Canada, Canadian Council of Ministers of the Environment: Winnipeg, Manitoba, Canada, 1999; pp 1–13.
- (87) Hecky, R. E.; Smith, R. E. H.; Barton, D. R.; Guildford, S. J.; Taylor, W. D.; Charlton, M. N.; Howell, T. The nearshore phosphorus shunt: A consequence of ecosystem engineering by dreissenids in the Laurentian Great Lakes. *Can. J. Fish. Aquat. Sci.* **2004**, *61*, 1285–1293.