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PCBs, PBDEs, and PAHs in Toronto air: Spatial and seasonal trends and implications for contaminant transport

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ABSTRACT

The distributions of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of Toronto, Canada and the surrounding suburban/rural area were examined. A series of temporally- and spatially-distributed air samples was collected over a 1-year period with a high-volume active air sampler at one downtown site and polyurethane foam passive air samplers at 19 sites. Passive sampler air concentrations of ΣPAHs ranged from 0.27 to 51 ng/m^3. Concentrations of ΣPCBs ranged from 6.0 to 1300 pg/m^3, and concentrations of ΣPBDEs ranged from 0.47 to 110 pg/m^3. All compounds exhibited the highest concentrations in the urban core, and lowest concentrations in the surrounding rural areas, however the exact ratio depended on location since concentrations varied considerably within the city. Results from the application of a radial dilution model highlighted the influence of the central business district (CBD) of the city as a source of contaminants to the surrounding environment, however the radial dilution comparison also demonstrated that sources outside the CBD have a significant influence on regional contaminant concentrations.

A strong relationship between temperature and partial pressure of the gas-phase PCBs, low molecular weight PBDEs and less-reactive PAHs suggested that their dominant emissions originated from temperature-controlled processes such as volatilization from local sources of PCBs, PAHs and PBDEs at warm temperatures, condensation and deposition of emissions at cold temperatures, and ventilation of indoor air with elevated concentrations. The relationship between temperature and atmospheric PAH concentrations varied along the urban–rural gradient, which suggested that in highly urbanized areas, such as downtown Toronto, temperature-related processes have a significant impact on air concentrations, whereas winter emissions from domestic heating have a greater influence in areas with less impervious surface coverage.

1. Introduction/background

The distribution of semi-volatile organic contaminants (SVOCs) in the urban environment has been the subject of extensive study (inter alia Du et al., 2009; Gasic et al., 2009; Gingrich et al., 2001; Harner et al., 2004; Motelay-Massei et al., 2005; Persoon et al., 2010). These studies have illustrated the complicated characteristics of urban distributions of SVOCs, stemming from a high density of varied emission sources combined with the inter-compartmental transport and meteorological effects that control SVOC movement. The literature is consistent in identifying elevated urban concentrations of a wide array of chemical compounds and that the resulting "urban plume" is a chemical source to surrounding regions (Hodge and Diamond, 2010; Hornbuckle and Green, 2003; Offenberg and Baker, 1999; Zhang et al., 1999). These observations provide an incentive for us to better understand urban contaminant dynamics. In particular, gaps in understanding remain with respect to the relative importance of source types, the nature of seasonal variations in both sources and concentrations that are specific to urban areas, and the spatial distribution of sources within cities.

The contaminants evaluated in this study were polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs). This suite of contaminants was chosen to give a broad picture of contaminant dynamics in the urban region, covering compounds with different chemical sources, physical–chemical properties and use/emission histories. The compounds have a range of volatilities, from those found almost entirely in the gas phase to those found entirely in the particle phase, with the compounds of intermediate volatility shifting between primarily gas and primarily particle phases with seasonal changes in temperature. PCB manufacturing has been banned and its use restricted since the 1970s (Diamond et al., 2010), while PBDEs, in use since 1965 (Vonderheide et al., 2008), have recently been subjected to regulations and reductions in manufacturing (Ward et al., 2008). PAHs have

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a long record of emissions from anthropogenic sources (Environment Canada, 2009; Gabrieli et al., 2010; U.S. EPA, 2011).

The goal of this paper is to provide a coherent picture of SVOC distributions and transport in the urban atmosphere through a comparison of source types and identification of the major environmental processes governing atmospheric fate. We used passive and active air samples to provide both spatial and seasonal resolution of concentration patterns, and characterized the spatial concentration gradients within the urban region using a radial dilution model.

2. Sample collection

2.1. Site selection

Nineteen sites were selected along two transects centered over Toronto, Canada, spanning the Greater Toronto Area (GTA) (Fig. 1). The sites ranged from high-density commercial/residential land-use, to low density suburban residential areas adjacent to multi-lane highways, to rural/agricultural land. Samples were mainly collected in parks or residential gardens. Meteorological data were obtained for each site from the nearest Environment Canada weather station (Environment Canada, 2010). Additional site characteristics are given in Table S1 of the Supplementary information (SI).

2.2. Passive air samples

Passive air samples were collected at each of the 19 sites from October 2007 to October 2008. All passive air samples were collected using "dome"-type polyurethane foam (PUF) samplers (Harner et al., 2004) as depicted in Fig. S1 and with details listed in Melymuk et al. (2011b). Passive samplers were deployed in four 3-month deployment periods: October to December 2007 (Autumn), January to March 2008 (Winter), April to June 2008 (Spring), and July to October 2008 (Summer). Samplers were located in trees at a height of 3–4 m above ground level. Sampling rates were obtained from a calibration study using 10 separate passive air samplers and a low-volume sampler conducted at the 0 km site, as described by Melymuk et al. (2011b). A key finding from this calibration study was that PUF-passive samplers collect both gas- and particle-phase compounds and thus passive sampler results are best treated as indicative of bulk air concentrations.

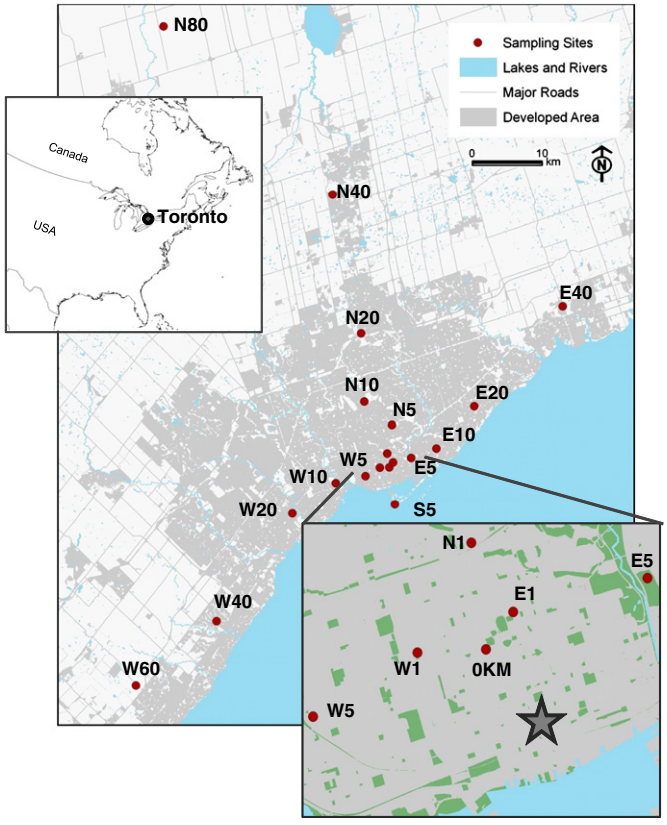

Fig. 1. Sampling locations. The star on the inset map indicates the middle of Toronto's central business district. Site names refer to the direction (north, south, east or west) and approximate distance (in km) of each site from the central (0 km) sampling point.

2.3. High-volume air samples

A high-volume air sampler (Tisch Environmental) was used to collect samples at the 0 km site, with a sampling train consisting of a glass fiber filter (GFF) and two PUF plugs. The site was located on the roof of a small 3-storey building on the University of Toronto campus in downtown Toronto. Approximately 475 m^3 of air was collected over a 24 hour period, every 12 days from October 2007 to October 2008. A meteorological station collecting temperature, wind speed and direction, relative humidity and precipitation was co-located with the high-volume air sampler.

3. Analysis

Details of the extraction, clean-up, analysis and QA/QC have been published by Melymuk et al. (2011b), and are given in full in the SI. Briefly, samples were extracted via pressurized fluid extraction using dichloromethane. Samples were split into two fractions: one for PCB and PBDE analysis and one for PAH analysis. The PCB/PBDE fraction was washed with concentrated H_2SO_4, and then purified on an Al_2O_3–$AgNO_3$ column. The PAH fraction was purified on a silica column. 86 PCBs, 27 PBDEs and 15 PAHs were quantified via gas chromatography–mass spectrometry (GC-MS). Non-detects were treated as zero, as per Harrad and Hunter (2006). Although this may result in low values for the sums of compounds at rural sites, we chose to treat non-detects as zero because the relatively higher detection limits of the hepta- to decaBDEs would excessively bias the results towards high molecular weight PBDEs. The compounds, instrument conditions, QA/QC and detection limits for each class are summarized in the SI.

4. Results and discussion

4.1. ΣPAH concentrations

Passive sampler-measured ΣPAH concentrations ranged from 0.27 ng/m^3 (N80 site in summer) up to 51 ng/m^3 (E10 — spring) (Table 1). Active air sampler measurements of ΣPAH in bulk air, taken at the 0 km site, ranged from 3.0 ng/m^3 (Oct. 9th) to 50 ng/m^3 (July 5th) (Fig. 2). There was a good agreement between the concentrations measured by the passive and active samplers at the 0 km site, with average passive and active sampler concentrations of 15 ± 5.2 and 14 ± 11 ng/m^3, respectively. These concentrations were within the range reported for other sites in the Great Lakes region of North America (Motelay-Massei et al., 2004; Sun et al., 2006b) and urban areas in Western Europe (Harrad and Laurie, 2005; Ras et al., 2009) and China (Wang et al., 2010).

4.2. ΣPCB concentrations

Passive sampler-measured concentrations of ΣPCBs ranged from 6.0 pg/m^3 (N80 — spring and summer) to 1300 pg/m^3 (0 km — summer) (Table 1). At the 0 km site active air sampler measurements of ΣPCBs in bulk air ranged from 72 pg/m^3 (Oct. 9th) to 3800 pg/m^3 (July 17th) (Fig. 2). The average ΣPCB concentration measured by high-volume air sampler at the 0 km site was 1100 ± 890 pg/m^3, which compared well with the passive air sampler concentration of