Passive sampler derived air concentrations of PBDEs along an urban rural transect: spatial and temporal trends

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Introduction

Passive air samplers are cost-effective and simple tools that have been successfully employed for assessing air concentrations of persistent organic pollutants (POPs) over large spatial regions.[1,2] Information obtained from such campaigns helps to address questions regarding sources of POPs, their spatial pattern and chemical signature. As a result of their widespread use as flame retardants in commercial products, indoor environments and hence urban centers are believed to represent an important emission source of PBDEs. In this study, passive samplers comprised of polyurethane foam (PUF) disks were deployed at seven sites along an urban-rural transect in Toronto to assess spatial and temporal trends of polybrominated diphenyl ethers. Ultimately, the levels and patterns of PBDEs along the transect will be compared to other classes of POPs to gain insight into their fate and transport. Results will also be compared to levels of PBDEs in indoor air which is believed to be the key source to the outside.

Materials and Methods

Previous papers describe the theory of PUF disk samplers.[3,4] Briefly, the uptake of POPs by PUF disk samplers is air-side controlled with an outdoor sampling rate of approximately 3.5 m^3 day^{-1}. Samplers were deployed for three, 3-month integration periods at seven sites along an urban-rural transect extending ~75km north of downtown Toronto (Fig. 1). Three field blanks were also taken. During one sampling period, PUF disks were deployed at 30m and 300m along the side of the CN Tower to investigate the altitudinal profile of PBDEs. During all deployments, PUF disks were housed in stainless steel chambers that reduced the influence of wind speed on uptake rate and also protected the PUF disks from precipitation, direct particle deposition and UV sunlight.

Prior to deployment, PUF disks comprised of virgin, untreated foam were precleaned by soxhlet extraction using acetone and then petroleum ether. PUF disks were stored in glass jars prior to deployment and after harvesting. PUF disk samples were extracted by soxhlet using

petroleum ether, concentrated to 1mL using UHP nitrogen and then cleaned-up and separated into 3 fractions using florisil (1.2 % deactivated) column chromatography.[5] These three fractions were analyzed for several POPs classes including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs) and results are presented elsewhere.[4] For PBDE analysis, these fractions were recombined, fortified with $_{13}C_{12}$ bromodiphenyl ether surrogate and further cleaned with columns consisting of silica gel/Na_2SO_4 and then neutral alumina / Na_2SO_4. Extracts were concentrated and PBDEs were determined by GC/HRMS. Analytical and instrument details are identical to those given in Shoeib et al.[6,7] Method and PUF recoveries were performed by spiking with a calibration solution of the target analytes and treating as samples.

Results and Discussion

Passive-sampler derived air concentrations and quality assurance/quality control (QA/QC) information is shown in Table 1. Briefly, PUF and method recoveries were good and no correction to the data was required. Although PBDEs were detected in field blanks, samples values were mostly greater than the LOD value (~85% of samples). The data presented in Table 2 are blank corrected using the mean value. Figure 2 summarizes ΣPBDE values along the urban-rural transect for three seasons. Concentrations were in the range 3 to 30 pg m^{-3}. This is similar to a mean value of 5 pg m^{-3} derived from an analysis of outdoor window films[8] and to high volume air sampling data in the range 38-48 pg m^{-3} collected over the same transect.[6] Concentrations were generally lower at the suburban sites in Richmond Hill and Aurora but only by a factor of approximately 2. The rural site at Egbert shows lower concentrations during the summer/fall period in 2000 but not for the spring/summer in 2001. The relatively uniform PBDE spatial pattern differs from the 5 to 10 times urban-rural gradient observed for PCBs over the same transect.[4] This may reflect a more regionally diffuse indoor air source for PBDEs. Indoor air concentrations of PBDEs in Toronto were shown to be ~15 times greater than outdoor values.[6] Lowest concentrations of PBDEs occurred during the winter period, possibly reflecting reduced inputs from indoor air during this season. Surprisingly, there is little change in the PBDE congener composition between sites and between seasons (Table 1, figure not shown). A comparison with high volume air samples (where gas-phase and particle–phase PBDEs were distinguished)[6] indicates that PUF-disk samplers collect mainly the gas-phase (figure not shown). Lastly, results from the CN Tower for the winter period indicate an altitudinal gradient. The concentration at 30m elevation (12 pg m^{-3}) was consistent with other downtown samples that were collected at similar heights (Table 2); whereas at 300m, the concentration was almost half (5.5 pg m^{-3}). In summary, passive air samplers deployed for 3 month periods were able to detect the horizontal and vertical spread of the PBDE plume that emanates from the city of Toronto with lower concentrations in the winter.

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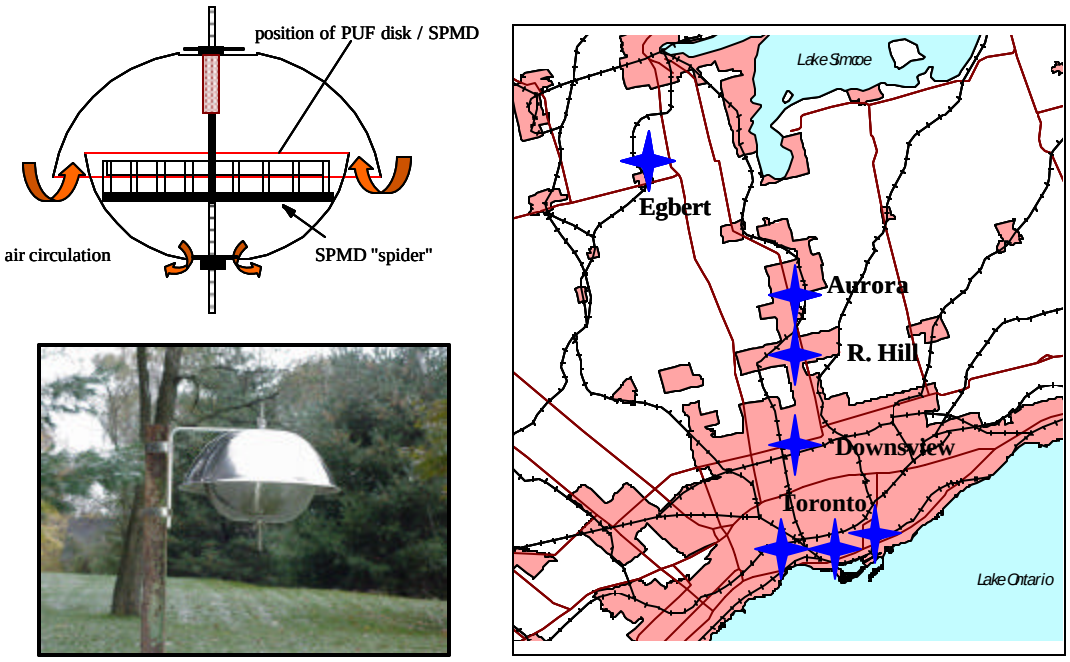

Figure 1. Description of PUF disk passive air sampler and sampling locations along an urban-rural transect in Toronto. Samplers were deployed for 3, 3-month integration periods – summer/fall, 2000; winter, 2001 and spring/summer 2001.

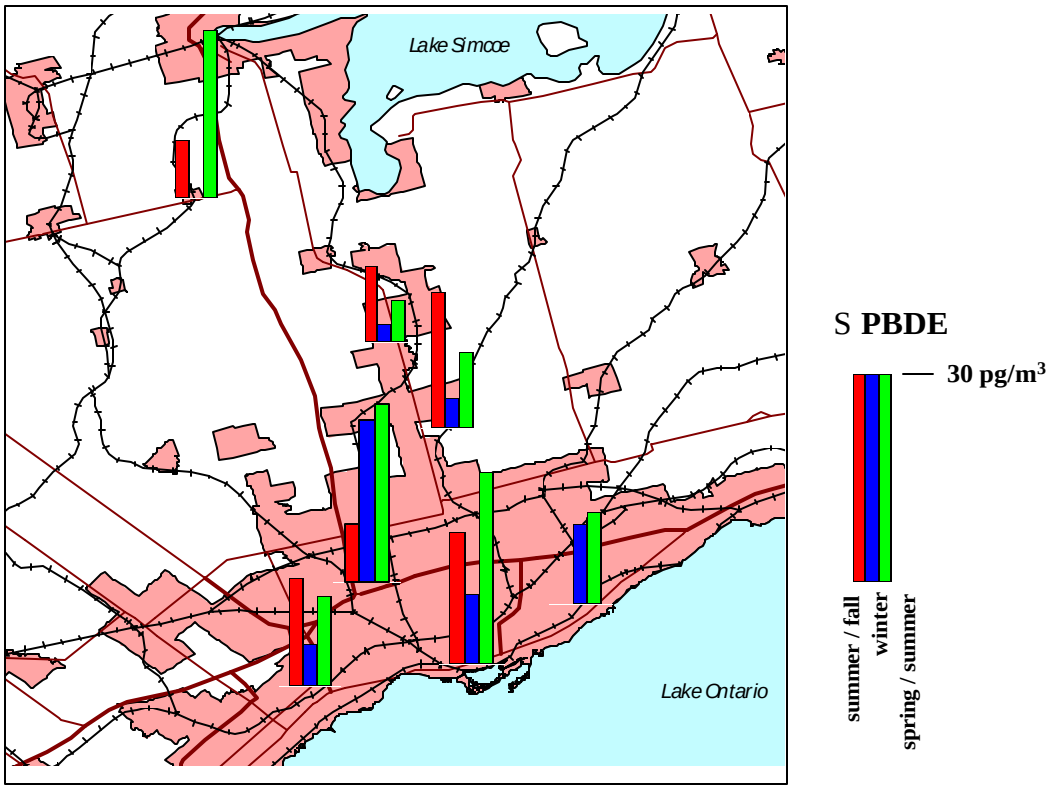

Figure 2. Passive-sampler air concentrations for ΣPBDE for 3 seasons along an urban-rural transect.

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Table 1. Passive sampler derived air concentrations (pg m^{-3}) and QA/QC for PBDEs.

	BDE-17	BDE-28	BDE-47	BDE-49	BDE-66	BDE-99	BDE-100	BDE-153	BDE-183	ΣPBDE
Summer/Fall, 2000										
Gage	0.43	1.11	11.21	0.59	0.31	3.88	0.93	0.18	0.25	19.2
Junction	0.22	0.59	7.74	0.40	0.24	4.62	1.02	0.25	0.16	15.7
S. Riverdale										
Downsview - A	0.06	0.11	3.91	0.13	0.11	2.96	0.55	0.37	0.25	8.8
Downsview - B										
R. Hill	0.25	0.69	12.07	0.49	0.27	4.80	1.17	0.19	0.09	20.4
Aurora	0.11	0.28	5.26	0.25	0.15	3.59	0.80	0.18	0.11	11.1
Egbert	0.12	0.26	4.11	0.23	0.13	2.39	0.60	0.06	0.06	8.2
Winter, 2000-2001										
Gage	0.25	0.65	5.30	0.27	0.13	2.26	0.61	0.20	0.13	10.0
Junction	0.13	0.30	3.14	0.18	0.08	1.54	0.39	0.00	0.14	6.1
S. Riverdale	0.22	0.56	6.47	0.37	0.17	2.54	0.78	0.25	0.15	11.8
Downsview - A	0.85	2.19	15.84	0.83	0.38	6.04	1.73	0.47	0.14	29.2
Downsview - B	0.51	1.38	10.44	0.40	0.16	4.46	1.19	0.38	0.09	19.5
R. Hill	0.13	0.32	2.63	0.13	0.05	0.69	0.22	0.11	0.19	4.5
Aurora	0.07	0.16	1.50	0.06	0.03	0.53	0.17	0.04	0.08	2.7
Egbert										
CN Tower - 30m	0.27	0.68	5.44	0.31	0.24	2.32	0.70	0.37	0.58	11.7
CN Tower - 300m	0.12	0.28	2.92	0.21	0.12	1.11	0.36	0.12	0.15	5.5
Spring/Summer, 2001										
Gage	0.55	1.93	15.29	1.12	0.47	5.78	1.79	0.39	0.29	27.9
Junction	0.21	0.60	6.50	0.36	0.18	3.21	0.92	0.37	0.20	12.9
S. Riverdale	0.22	0.57	7.21	0.39	0.22	3.25	1.00	0.26	0.19	13.6
Downsview - A	0.43	1.29	15.70	0.80	0.42	7.34	2.36	0.61	0.23	30.0
Downsview - B	0.30	0.88	11.10	0.51	0.28	7.04	1.77	0.57	0.11	23.3
R. Hill	0.15	0.43	5.72	0.27	0.14	2.87	0.86	0.33	0.38	11.5
Aurora	0.09	0.29	2.89	0.15	0.06	1.75	0.52	0.19	0.07	6.2
Egbert	0.53	1.58	15.19	0.82	0.36	3.54	1.29	0.31	0.27	24.3
QA/QC										
Mean Blank (pg m^{-3}, n=3)		0.02	0.48	0.02	0.01	0.47	0.12	0.06	0.03	
LOD (pg m^{-3})		0.09	3.30	0.10	0.08	3.54	0.84	0.38	0.10	
IDL (pg m^{-3})	0.04	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	
Recovery (%) - PUF media	126	125	126	107	102	119	102	132	126	
Recovery (%) - method	121	120	107	99	98	103	99	136	140	