

ENVIRONMENTAL LEVELS AND TRENDS

PASSIVE AIR SAMPLING RESULTS FOR POLYBROMINATED DIPHENYL ETHERS ALONG AN URBAN-RURAL TRANSECT

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Introduction

Research into the fate and transport of persistent organic pollutants (POPs) has identified the need to map distributions of POPs to investigate temporal and spatial trends. Because of the complexities and logistic limitations associated with conventional high volume air samplers (e.g. high equipment cost and requirement of a source of electricity), passive air samplers are the most feasible tool for such investigations. Past researchers have used natural phases (vegetation, soil, butter)¹⁻³ that accumulate chemical to assess contaminant levels. More recently, synthetic passive air samplers have been investigated e.g. semipermeable membrane devices (SPMDs)^{4,5} and polyurethane foam (PUF) discs⁶. These devices have the advantage that they are uniform and consistent and therefore more easily calibrated than natural phases. With knowledge of the passive sampling uptake rate over the exposure period, average air concentrations over the exposure period can be calculated^{4,6}.

Polybrominated diphenyl ethers (PBDEs) are an emerging class of chemicals that have characteristics of POPs. PBDEs have been detected in biological samples from temperate regions and far away regions such as the arctic where an exponential increase has been observed in ringed seal over the past two decades⁷. Despite the recent activity in Europe to restrict use of selected PBDE technical formulations, no similar action has yet occurred in North America.

To date, few studies have reported PBDE concentrations in North American air. PBDEs have been reported in air from the Great Lakes region⁸ where Σ PBDE ranged from 0.5 pg m^{-3} at background sites near the Great Lakes to as high as 50 pg m^{-3} in urban Chicago. The Great Lakes study also highlighted partitioning to aerosols as a relevant process for PBDEs. Recently, Gouin et al.⁹ observed a "spring-pulse" of PBDEs at a rural site in Ontario where PBDE concentrations were as high as 1250 pg m^{-3} , exceeding PCB levels. There is a need to study the spatial and temporal distribution of PBDEs in order to assess the key partitioning mechanisms and fate of PBDEs in the environment. To help address some of these needs, passive air samplers (SPMDs and PUF discs) were deployed at several sites along a ~80 km urban-rural transect over four, four-month integration periods. In this paper results are presented for the first two deployment periods representing Spring and Summer of 2000, respectively.

Material and Methods

Passive samplers were deployed over four, four-month periods (Period 1, Feb. 20, 2000-June 20, 2000; Period 2, June 20, 2000 – Nov. 1, 2000; Period 3, Nov. 1, 2000 – March 20, 2001; Period 4, March 20, 2001-July 20, 2001). During period 1, SPMDs were deployed at five sites; in period 2, SPMDs and PUF discs were co-located at 7 sites. Samplers were housed in stainless steel chambers. The uptake rate of the passive sampling materials contained within the chambers was determined

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during a controlled laboratory study¹⁰. Based on results from a wind study, outdoor sampling rates are expected to be $\sim 7 \text{ m}^3 \text{ d}^{-1}$ for PUF discs and $\sim 9 \text{ m}^3 \text{ d}^{-1}$ for SPMDs¹⁰. Thus the 120 day exposure corresponds to approximately 700 and 1100 m^3 air respectively. One blank was collected during each sampling period and separate external recoveries were conducted by spiking a PUF disc and SPMD with a surrogate solution prior to extraction. Details of the extraction and clean-up method are presented elsewhere⁶. Extracts were analyzed by GC-HRMS using a VG-Autospec high-resolution mass spectrometer (Micromass, Manchester, U.K.). Analytical details and instrument parameters are presented elsewhere⁷. During a separate analytical process, extracts were analyzed for several other compound classes including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs)¹⁰.

Results and Discussion

At the time of writing this manuscript PBDE results were available for Period 1 (5 sites, SPMD) and Period 2 (7 sites SPMD, 6 sites PUF disc). Sample extracts were analyzed for a suite of 37 PBDE congeners. External recoveries were in the range 75-100%.

Figure 1 and Table 1 summarize the available results from the transect study. In Fig. 1, results are presented for the dominant PBDE congeners – 47, 99 and 100 – accumulated by the passive sampling media. The top panel (A) shows results for SPMDs deployed during Spring 2000. A strong rural-urban gradient exists with lowest concentrations at the two downtown locations. High concentrations were observed at a rural site and a semi-urban location. Previously determined passive air sampling rates were used to back-calculate air concentrations over the integration period (Table 1). Σ PBDE was on average $\sim 7\text{-}8 \text{ pg m}^{-3}$ at the urban sites and between $20\text{-}46 \text{ pg m}^{-3}$ at the three locations north of the city center. The higher values at the less-developed sites is consistent with the “spring-pulse” observed by Gouin et al. (2002) at a rural location. These authors believe that PBDEs are concentrated in surface soil and vegetation (e.g. forest litterfall) over the cold winter months when partitioning to environmental organic phases is favoured¹¹. These chemicals are then released as a pulse during the first thawing/warming period during the springtime. It should be noted that PCBs and PAHs analyzed in the same extracts exhibit a strong urban-rural gradient, with approximately 6-8 times higher concentrations at the urban sites. The urban-rural gradient was expected for PCBs and PAHs because these chemicals are associated with industrial and emission sources characteristic of cities. The reverse gradient for PBDEs during the spring period and very weak urban-rural gradient in the summer period indicates that PBDEs are possibly released differently to the environment and/or once released they undergo different partitioning because of their physical chemical properties.

One property that distinguishes PBDEs from PCBs and PAHs is their volatility or octanol-air partition coefficient (K_{OA}). PBDEs have much higher K_{OA} values than the PCBs and PAHs¹¹. This results in enhanced partitioning to aerosols, soil and other environmental organic phases. This may also result in preferential accumulation and deposition of PBDEs in rural areas that are “downwind” and impacted by advected urban source air.

Figure 1B shows the PBDE profile in SPMDs deployed during Summer 2000. Concentrations of PBDEs (Table 1) at the urban sites are slightly higher but similar to Spring 2000 levels. However, the apparent “pulse” observed in the outlying areas has diminished resulting in a weak urban-rural gradient of PBDE levels. This is confirmed by the profile observed in the co-located PUF discs shown in Fig. 1C. Back-calculated air concentrations for PBDEs for Summer 2000 (Table 1) are in the range $3\text{-}10 \text{ pg m}^{-3}$. It is encouraging that results for co-located PUF discs and SPMDs are in agreement.

In summary, passive air samplers were used to map PBDE air burdens along an urban-rural transect. Elevated air concentrations of PBDEs were observed at non-urban locations during the spring sampling period resulting in a strong rural-to-urban gradient. During the summer sampling period,

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concentrations at non-urban location declined, resulting in a weak urban-to-rural gradient. Back-calculated air concentrations of PBDEs were consistent with previous determinations in the Great Lakes region. Lastly, this study highlights the feasibility of passive air sampling technology to provide useful information regarding seasonal and spatial trends of POPs in the atmosphere.

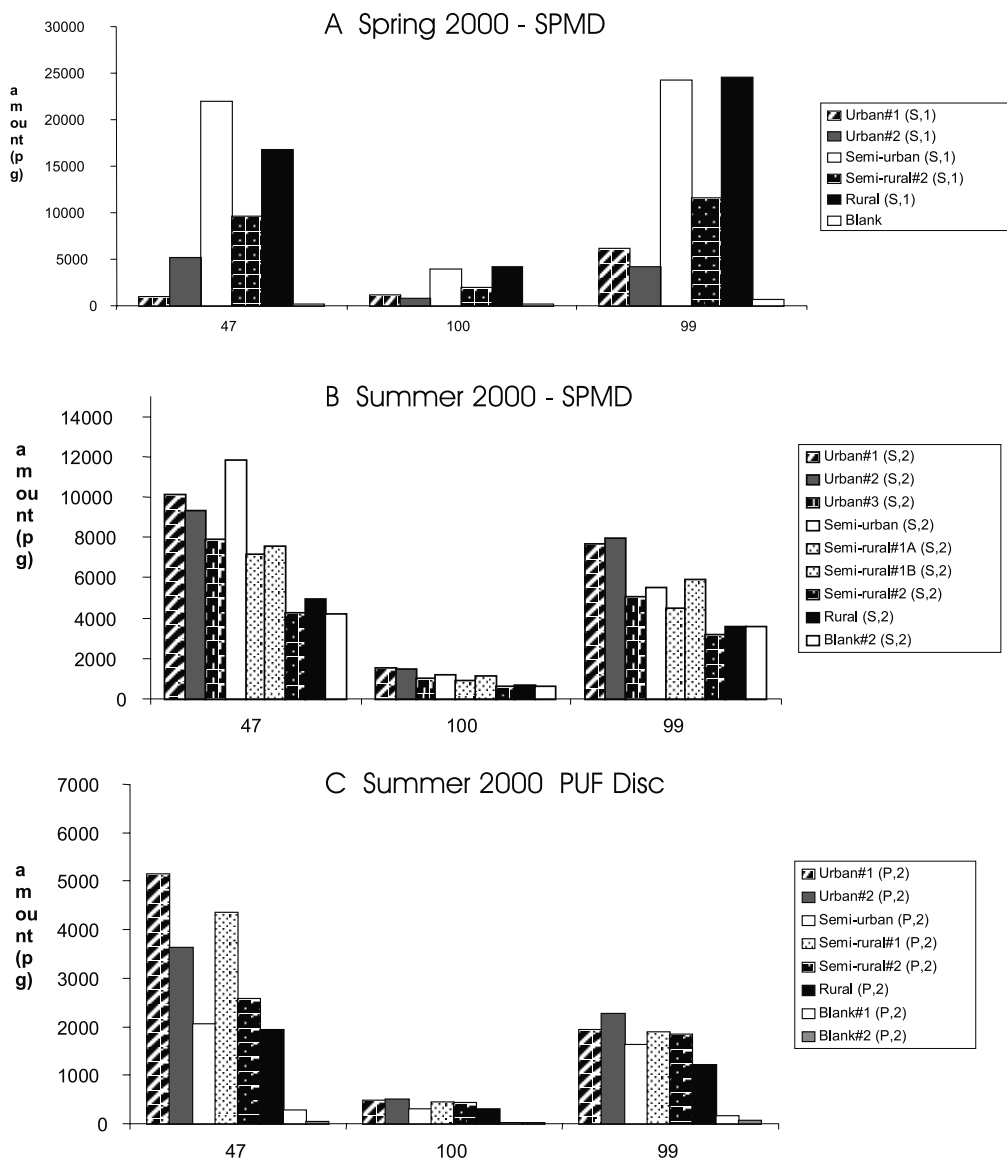


Figure 1. Dominant PBDE congeners (pg) sequestered by SPMDs in spring 2000 (A), Summer 2000 (B) and by PUF discs in Summer 2000 (C) along an urban-rural transect. Deployment time was 120-130 days.

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Table 1. Calculated air concentrations (pg m^{-3}) of SPBDE for SPMDs (Period 1 and 2) and PUF discs (Period 2) deployed along an urban-rural gradient

Location	Period 1 – SPMD	Period 2 – SPMD	Period 2 – PUF Disc
Urban#1	7.7	10	8
Urban#2	8.4	9.5	6.7
Urban#3		5.1	
Semi-urban	46	9.3	4.1
Semi-rural#1		4.7	7.0
Semi-rural#2	21		4.9
Rural	41		3.4

Period 1 duration = 120 days; Period 2 duration = 130 days

SPMD and PUF disc sampling rates were $\sim 9\text{m}^3\text{d}^{-1}$ and $7\text{m}^3\text{d}^{-1}$ respectively.

Results based on blank corrected amounts.

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