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Polychlorinated biphenyls and polybrominated diphenyl ethers in the North American atmosphere

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A continental passive air sampling network reveals atmospheric distribution patterns of two classes of industrial chemicals.

Abstract

To assess the spatial concentration variability of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the atmosphere on a large continental scale, their annually integrated air concentrations were determined in 2000/2001 using XAD-based passive air samplers (PAS). The network included 40 stations in Canada, the United States, Mexico, Belize and Costa Rica, and covered 72 degrees of latitude and longitude. Total concentrations of PCB and PBDE congeners ranged from below the detection limit to 130 ng PAS^{-1} and 24 ng PAS^{-1}, respectively. PCBs displayed a large variation between urban, rural and remote sites, whereas PBDEs did not follow such a pattern. Open burning of "Penta"-containing waste may have contributed to the PBDEs detected in the air samples from rural and remote areas. Air from the Canadian Arctic had a relatively higher percentage of lighter PCB congeners than air sampled in the tropical region, which is interpreted as evidence for global fractionation.

Keywords: Passive air sampling; Polychlorinated biphenyls; Polybrominated diphenyl ethers; Global fractionation

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1. Introduction

Polychlorinated biphenyls (PCBs) are well known persistent organic pollutants (POPs) due to their toxicity, bioaccumulation, and resistance to environmental degradation. Following their introduction in 1929, PCBs were used in industrial and consumer applications worldwide, especially in electrical equipment. They were identified in environmental samples almost four decades after their introduction (Jensen, 1972). Since then, their occurrence has been reported in samples from different animal species, environmental compartments, and geographical regions (UNEP, 2002), confirming large scale dispersion and deposition to areas far from the original sites of industrial application. Due to their persistence, PCBs have remained major global pollutants, with numerous investigations reporting their continued and ubiquitous presence in the global atmosphere (Jaward et al., 2004; Davidson et al., 2004; Harrad and Mao, 2004). Extensive measurements of PCBs in the atmosphere involving multiple sampling sites and multi-year time periods have been performed in the Great Lakes region and the Canadian Arctic (Buehler and Hites, 2002; Hung et al., 2001). These studies demonstrate that atmospheric transport and deposition is the major input pathway for PCBs into the lakes and the Arctic ecosystem, but

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sampling in these monitoring programs is limited to a regional scale. For a continental perspective, the sampling stations are too far apart and too small in number. In addition, comparing air concentrations from different studies to examine spatial patterns of PCBs in the atmosphere is difficult because of differences in sampling methods, sampling times, analytical techniques, data processing and reporting. The large scale distribution of PCBs across North America therefore remains largely elusive.

Polybrominated diphenyl ethers (PBDEs) are a group of flame retardant additives that are used in a variety of commercial and household products to reduce their flammability. Their use in a wide range of materials and their detection in numerous environmental samples, have made PBDEs important emerging contaminants (Alaee and Wenning, 2002). Their concentrations in the environment are increasing over time, even in remote regions (Luross et al., 2002; Norén and Meironyté, 2000; Ikonomou et al., 2002). Many studies on PBDEs focus on their occurrence in sediments, fish, marine mammals, and human samples (Hites, 2004). There are only a few investigations reporting concentrations in the atmosphere (e.g. Strandberg et al., 2001; Gouin et al., 2002, 2005; ter Schure et al., 2004; Jaward et al., 2004).

When mixtures of semivolatile chemicals, such as the PCBs and PBDEs, undergo long range transport (LRT) to remote areas, they might be subject to global fractionation (Wania and Mackay, 1993, 1996), resulting in a shift toward more volatile chemicals with increasing latitude. To find field evidence for such shifts, it is essential that sampling locations are far from potential source regions, and samples are collected simultaneously and represent long term average conditions. It is extremely difficult to achieve such a goal using traditional HiVol air samplers because they sample only a small fraction of the time, and there is often no electricity supply in remote regions. The emergence of inexpensive, simple and shippable passive air sampling devices (Harner et al., 2003; Wania et al., 2003) has opened the possibility for cost-effective mapping of POP air concentrations on a continental, and even global scale (Shen et al., 2004, 2005; Jaward et al., 2004). Therefore, passive air sampling should be suited for identifying global fractionation pattern. In this study, a large-scale network of 40 passive air sampling stations was used to better characterize the atmospheric distributions of PCBs and PBDEs across North America and find evidence for global fractionation. These passive air samplers (PAS) were deployed for an entire year to yield one annually averaged concentration at each station. The 40 stations from Central America (10°N) to the Canadian Arctic (82°N) represent the largest latitudinal transect of simultaneous airborne PCB measurements.

2. Materials and methods

2.1. Passive air sampling

2.1.1. Sampler design

The PAS consists of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a galvanized steel can with an open bottom (Wania et al., 2003). The PAS is deployed at 1.5 m above ground except in locations with a deep snow pack, where deployment height is increased to ensure that the PAS is not covered by snow. Contaminants are taken up in the resin from the atmosphere by diffusion, whereby previous experiments established independence of the sampling rate over a wide range of wind speeds (Wania et al., 2003). Measurements of the sorption coefficients for the XAD-2 resin (Shen et al., 2002) as well as year long calibration experiments in Arctic and southern Canada (Wania et al., 2003) confirmed that most semi-volatile organic compounds do not reach equilibrium between the atmospheric gas phase and the resin. This makes it feasible to compare the amounts of PCBs and PBDEs quantified in PAS deployed at different locations.

2.1.2. Sampler preparation

XAD-2 was cleaned by Soxhlet extraction, and the PAS were filled and assembled in a clean room (HEPA® and carbon filtered air) at the National Water Research Institute (NWRI) in Burlington, ON. The XAD-2 resin (20/60 mesh, 350 m^2/g surface area, 9 nm pore diameter, Supelco) was rinsed with Milli-Q water and Soxhlet extracted three times for four days each, using in turn methanol, acetonitrile and dichloromethane. After washing with sodium hydroxide to remove potential acidic interferents, dichloromethane and methanol, the XAD-2 was stored in methanol. Approximately 60 mL of wet resin (XAD-2 in methanol) was added to a pre-cleaned stainless steel mesh container plugged with a small amount of clean glass wool at the bottom, and covered with glass wool on the top. The column was then transferred to a big amber glass jar, dried in a flow of purified nitrogen and then sealed in the shipping containers until use (Wania et al., 2003).

2.1.3. Sampling sites

Passive air samplers were deployed at 40 stations across North America with 31 located in Canada, 5 in the United States, and 4 in Central America (Southern Mexico, Belize, Costa Rica) (Table 1). A north-south transect in the eastern part of the continent covered 72 degrees of latitude (10° to 82°N) from the Arctic to Central America. An east-west transect in southern Canada ranged from eastern Newfoundland to Vancouver Island covering 72 degrees of longitude (53° to 125°W). Four of these stations constituted an altitudinal transect in the Southern Canadian Rocky Mountains, covering a range of elevation of more than 1500 m. The criteria used in the selection of the sampling sites are given in Shen et al. (2004).

2.1.4. Sampling procedures

PAS, installation instructions, and laboratory gloves were mailed in May to July 2000 to local contact people, who installed duplicates at the sampling sites. In some cases, we installed the PAS ourselves. After 1 year, the contacts received retrieval instructions and were asked to return the XAD-filled mesh cylinder to NWRI using the same air-tight Teflon shipping tubes in which they had received the samplers. At NWRI, they were stored frozen until analysis. Eight of the stations received additional XAD-mesh cylinders, which remained in the shipping containers throughout the 1-year deployment period, during which they were taped to the posts holding the sampling shelters. These samples served as field blanks (Shen et al., 2004).

2.2. PCB and PBDE determinations

Extraction and clean-up of passive air samples, chemical analysis, and quality assurance are described in a previous publication (Wania et al., 2003). In short, the XAD-2 was extracted with methanol and dichloromethane. Methanol in the combined eluent was then removed by 3% sodium chloride. After the extracts were concentrated on a rotary evaporator and solvent exchanged to iso-octane, they were fractionated on a silica gel (70/230 mesh, high purity, Supelco) column, eluting sequentially with hexane as Fraction A and a 1:1 mixture of hexane: dichloromethane as Fraction B. To each fraction, iso-octane was added, and the sample was concentrated to 1.0 mL with nitrogen. PCBs in fraction A were analyzed on a Hewlett Packard (HP) 5890 gas chromatograph (GC) equipped with dual electron capture detectors (ECDs). HP-5 and HP-1 (both 30 m × 0.25 m × 0.25 μm) capillary columns were employed. Helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The GC-ECD was operated under the following conditions: injector temperature 220 °C, detector temperature 350 °C, temperature program 80 °C for