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Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean

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ABSTRACT

During a two-week intensive field campaign conducted at a background location of the Eastern Mediterranean, consecutive 10-h air samples were collected under intense photochemical conditions and analyzed for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). The average gas-phase concentration of total PCBs and PBDEs was 73 ± 29 and 3.9 ± 2.1 pg m^{-3}, respectively. The study of Clausius–Clapeyron plots and air mass back-trajectories assigned the origin of air masses as the factor largely controlling the variation of PCB and PBDE air concentrations in the study area. Using principal component analysis, discrete differences in PCBs homologue profiles were revealed between day and night samples and attributed to the daytime reaction with hydroxyl radicals. In contrast, PBDE homologue profiles did not show any characteristic day-to-night shifts that could be attributed to hydroxyl radical reaction or photolysis.

1. Introduction

There is continuing concern about the presence of persistent semi-volatile organic compounds (SVOCs) in the environment, especially for those which undergo bioaccumulation, are subject to long-range transport and induce toxic effects in humans and wildlife. Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) encompass all of these distinguishing characteristics and their environmental fate is a topic of intensive research. Although the production and use of polychlorinated biphenyls was banned by the mid-1970s, these compounds are still present in the environment (Barra et al., 2005). In addition, polybrominated diphenyl ethers have become widespread global pollutants due to their heavy use as flame retardants and their concentration in the environment has risen exponentially since the 1980s (Hites, 2004).

Due to their moderate volatility, PCBs and PBDEs can evaporate from contaminated surfaces of urban areas or can be emitted into the atmosphere via the open burning of products containing these chemicals (Breivik et al., 2002a). Subsequently, PCBs and PBDEs partition between the gas phase and suspended particles, and they are carried away from sources by the movement of air masses. During transportation, the organic pollutants are subjected to various processes, such as wet and dry deposition, air–surface exchange, reactions with oxidants and photolysis, which can cause their gradual removal from the atmosphere (Wania, 2000).

Previous systematic measurements in urban areas have shown that temperature-driven air–surface exchange controls the atmospheric levels of PCBs and PBDEs (Lee et al., 1998; Gouin et al., 2002). However, in remote areas, where emissions are negligible, the effect from atmospheric transport and/or removal processes can be more pronounced (Mandalakis et al., 2003). Therefore, measurements of persistent pollutants in background areas in conjunction with the analysis of air mass back-trajectories can potentially provide clues about transportation pathways and the location of possible sources (Gouin et al., 2005). In addition, the investigation of changes in the composition profiles of PCBs and PBDEs can provide important evidence about the dominating removal processes (Mandalakis et al., 2003).

The importance of the various removal mechanisms will depend not only on the physicochemical properties of the different PCB and PBDE congeners but also on the meteorological conditions at the time of sampling. For example, photolysis and reactions with OH radicals occur only during the day. Consequently, measurements with high temporal frequency are required to ascertain if these processes have a significant effect on PCB and PBDE levels (Mandalakis et al., 2003).

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To date, a number of studies have investigated the short-term variation of atmospheric PCBs (Wallace and Hites, 1996; Lee et al., 1998; Gouin et al., 2002; Totten et al., 2002; Mandalakis et al., 2003; Mandalakis and Stephanou, 2007), while those for PBDEs are scarce (Gouin et al., 2002; Moeckel et al., 2008; Chen et al., 2009). Moreover, data about the levels of PBDEs in background aerosols of Europe are limited (Jaward et al., 2004; Ter Schure et al., 2004; Moeckel et al., 2008), and have not been reported for southeastern Europe up to now. In the present study, short-term air samples were collected during a two-week long intensive campaign at a background area of the Eastern Mediterranean (Finokalia), which has been previously shown to receive man-made air pollutants transported from three different continents: Europe, Asia and Africa (Lelieveld et al., 2002). The effect of temperature and air mass origin on ambient concentrations was investigated in order to assess whether local emission sources or atmospheric transport regulates the levels of atmospheric PCBs and PBDEs in this area. In addition, the day-to-night variations in PCB and PBDE homologue profiles were investigated to elucidate if reaction with OH radicals and/or photolysis, affect the atmospheric behavior of these pollutants.

2. Materials and methods

2.1. Air sampling

All measurements were performed at the marine background station of Finokalia (35°19′N, 25°40′E), a coastal site 70 km eastward of Heraklion (Crete, Greece). Twenty-six ($N = 26$) samples were consecutively collected from July 29 to August 12, 2006, using a high-volume air sampler. Air was first drawn through a 20 cm × 25 cm glass fiber filter (GFF) to collect total suspended particles and then through a polyurethane foam (PUF) plug (6.5 cm diameter and 10 cm length) to collect the vapor phase. The sampling frequency was two samples per day and the sampling duration was 10 h (one sample during daytime; 08:00–18:00 Eastern European Summer Time (EEST)) and one sample during nighttime (20:00–06:00 EEST). The high-volume air sampler was operating at a constant flow rate of 24 m^3 per hour, while the volume of sampled air was 240 m^3. Due to power failure, air sampling was not possible on August 4, 2006 (nighttime sample).

Preceding sampling, GFFs were heated at 450 °C for 5 h, whereas PUF plugs were rinsed with acetone and then extracted with dichloromethane:hexane (1:1) using an accelerated solvent extraction system (ASE 300, Dionex, Sunnyvale, CA, USA) with 5 min heat-up time, 5 min static time and 1 min purge time (11 min in total). Extracted PUF plugs were dried in vacuum desiccators and finally sealed in clean, solvent-rinsed amber glass jars. After each deployment, PUF and GFF samples were collected, resealed in the glass jars and stored at −18 °C until analysis.

2.2. Analytical procedure

All samples were loaded into stainless steel cartridges and extracted with dichloromethane:hexane (1:1) using the accelerated solvent extraction system. Prior to extraction, the samples were spiked with a range of recovery standards for PBDEs ($^{13}C_{12}$-labeled BDE 15, 28, 47, 99, 154, 153, 183, 197, 207 and 209) and PCBs (PCB 54 and 155), to monitor analytical recovery. The system's operating conditions were as follows: oven temperature: 90 °C, pressure: 1500 psi, heat-up: 5 min, static time: 5 min, number of cycles: 1, flash volume: 60% and purge time: 1 min (11 min in total). The extract was rotary evaporated to 1 mL and repeatedly treated with concentrated H_2SO_4 (until no color was visible in the acidic phase). Then the organic layer was separated from H_2SO_4, evaporated to 0.5 mL and transferred to a Pasteur pipette column packed with silica gel (SiO_2) in the bottom (1 cm) and 40% sulfuric acid silica gel (40% H_2SO_4–SiO_2) at the top (3 cm). The sample was eluted with 8 mL of dichloromethane and the volume was reduced to 0.5 mL. The solvent was then exchanged to hexane and the sample was applied to a Pasteur pipette column packed with 1 g of silica gel activated at 300 °C for 3 h. The column was eluted with 7 mL of hexane (first fraction), 5 mL of 20% dichloromethane in hexane (second fraction), 8 mL of 50% dichloromethane in hexane (third fraction) and 15 mL of 50% ethyl acetate in hexane (fourth fraction). The first fraction contained the largest portion of PCBs, while the second fraction contained PBDEs and a small amount of PCBs. Subsequently, the second fraction was rotary evaporated to 200 μL, transferred into a glass vial and further evaporated to approximately 5 μL under a gentle stream of N_2. Finally, 20 μL of $^{13}C_{12}$-labeled BDE 139 standard solution was added as an internal standard, to achieve a final volume of 25 μL. After the analysis of PBDEs, the first and second fractions were pooled together, evaporated to 5 μL, spiked with 20 μL PCB-204 (internal standard) and subsequently analyzed for PCBs.

The analysis of PCBs and PBDEs was conducted using a gas chromatograph (Agilent 6890 Series, Agilent Technologies, Palo Alto, CA, USA) equipped with a cool on-column injector and interfaced with a mass spectrometer (Agilent 6890 Series, Agilent Technologies, Palo Alto, CA, USA) operating in electron impact ionization (70 eV electron energy) and selected ion monitoring mode. Analytes were separated on a 15 m DB5-MS capillary column (5% phenyl-methylpolysiloxane, 0.25 mm internal diameter, 0.1 μm film thickness; Agilent Technologies, Palo Alto, CA, USA) operating with helium carrier gas (constant velocity 46 cm s^{-1}) under the following temperature program: from 90 °C to 140 °C at 50 °C min^{-1}, to 220 °C at 15 °C min^{-1} and finally to 295 °C at 10 °C min^{-1}. The temperature of the injector was initially set at 93 °C and then followed the temperature program of the oven. The temperature of the transfer line, ion source and quadrupole filter were kept constant at 300 °C, 230 °C and 150 °C, respectively. A total of 15 PBDE congeners (PBDE 15, 17, 25, 39, 28, 35 + 20, 62, 49, 47, 66, 100, 99, 154, 153, 209) and a total of 39 PCB congeners (PCB 18 + 17, 16 + 32, 25 + 26, 31 + 28, 20 + 33, 22, 53, 45, 52, 49, 47 + 48 + 75, 44, 41 + 64, 74, 70, 95, 91, 101, 99, 110, 118, 105, 149, 132, 153, 138 + 158 + 160, 174, 180, 170) corresponding to 14 and 29 chromatographic peaks, respectively, were regularly analyzed and quantified using the internal standard method. The identification of the different congeners in the samples was based on comparison of their MS data and retention times with those of authentic reference standards.

2.3. Quality control and assurance

Previous breakthrough tests indicated that the PUF plugs were large enough to enable efficient trapping of gaseous PBDEs (>90%) even after 240 m^3 of air sampling at 30 °C (Mandalakis et al., 2008), while similar results were obtained for PCBs (>85%). The trapping efficiency of the PUF plugs (332 cm^3 in volume) applied in the present study was also evaluated for the least retained analyte (PCB 16) based on the semi-empirical equations of Pankow (1989). By using the vapor pressure of PCB 16 (Falconer and Bidleman, 1994) adjusted at the average air temperature of the sampling events (26.5 °C), a gas phase retention volume of 420 m^3 was calculated. Considering that the air sampling volume (240 m^3) was about two times lower than the estimated retention volume, PCB 15 should be efficiently trapped onto PUF adsorbent material.

To prevent any possible photolysis of PBDEs, special care was taken to avoid the exposure of samples to light during their storage and analysis. All the sample preparations and treatments were