POLYBROMINATED DIPHENYL ETHERS AND ALTERNATIVE FLAME RETARDANTS IN AIR AT A WASTE WATER TREATMENT PLANT

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Introduction

Flame retardants (FRs) are used in a wide variety of products and applications. They can either be incorporated into various materials, such as in plastics, foams and textiles, or they can be added to protective coatings. Polybrominated diphenyl ethers (BDEs) have been the most studied FRs over the past two decades. The phase out of PentaBDE and OctaBDE formulations in North America and Europe has led to the increased use of alternate FRs (non-BDEs) to meet flammability standards for different products. Organophosphate esters (OPs), in particular triesters, are high-production-volume chemicals used also as FRs and plasticizers to protect or to enhance the properties of plastics, textiles, furniture and many other materials.[1] Presumably FRs can enter waste streams and subsequently wastewater treatment plants (WWTPs) through releases from treated products and inputs from industrial waste. Some of the highest concentrations of BDEs in North America have been measured in sewage sludge [2], biosolids and in municipal wastewater influent [3]. The presence of high levels of BDEs in municipal wastewater influent is likely due to contaminated residential wastewater from homes that contain BDE-treated products.

Occurrences of BDEs and non-BDE FRs in the biota and environmental media in remote regions suggests that FRs are subject to long-range transport via the atmosphere or ocean currents. Emissions of other contaminants from WWTPs and landfills to air have been reported [4-6]. The objectives of this study include, (i) to evaluate the emission of FRs from WWTPs to the atmosphere, (ii) determine the atmospheric gas-particle partitioning of several classes of alternative FRs, and (iii) evaluate the sorbent-impregnated polyurethane foam (SIP) disk passive air sample (PAS) for collecting alternative FRs To our knowledge no studies have investigated emission of FRs from WWTPs to air.

Materials and methods

Chemicals Target analytes included a mixture of BDE 17, 28, 49, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190 and 209 (Cambridge Isotope Laboratories) and individual standards of the following analytes: g-hexabromocyclododecane (HBCD), allyl-2,4,6- tribromophenyl ether (ATE), syn-Dechlorane Plus (syn-DP), anti-Dechlorane Plus (anti-DP) bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), tri-phenyl phosphate (TPP) and tris (1,3-dichloro-2-propyl) phosphate (TDCPP) (Wellington Laboratories and Sigma-Aldrich).

Sampling collection Air samples were collected at a municipal waste water treatment plant (WWTP) in Ontario, Canada, during two separate campaigns [4,5]. In the first campaign, air samples were collected using SIP disks situated on and around the WWTP (i.e. at the primary clarifier, aeration tank, secondary clarifier, and at four nearby background sites) [4]. SIP disks (*n*=12) were deployed for 63 days between July and September 2009. Four field blanks were collected by placing the SIP disks in the sampler housing and then removing them after 1 min. In the second campaign, high-volume (hi-vol) air samples were collected at the same WWTP during spring 2010[5]. Hi-vol air samples were collected over 24 h, twice a week over a period of six weeks at aeration tanks (*n*=15) and a secondary clarifier (*n*=15). Glass fibre filters (GFFs) followed by PUF/XAD/PUF were used to collect the particle-phase and gas-phase respectively. In addition, SIP disks were deployed (in duplicate) for 37 days in parallel with hi-vol at both sampling sites to provide time-integrated samples (*n*=4). Two field blanks were collected for the hi-vol media and the SIP disks.

Analysis The extraction method is described elsewhere [4,5]. Extracts were analysed for OPs, then the SIP disk and PUF/XAD/PUF cartridges were further cleaned using 1 g of 6% deactivated alumina, for BDEs and non-BDEs analysis. Analyses of BDEs, non-BDE and OPs were performed using an Agilent 5980 gas chromatograph, fitted with a 15 m DB-5MS capillary column (0.1 μm film thickness 0.25 mm i.d; J &W Scientific) coupled to an Agilent 5973 mass selective detector. Quantifications were performed in NCI mode for BDEs and non-BDEs. OP were monitored in EI with ions: TCEPP (249/251), TCPP (99/125), TPP (326/325) and NCI for TDCPP (319/317)

Results and discussion

QA/QC Extraction recoveries were satisfactory for BDEs, non-BDEs and OPs ranged from 89% to 137%. Alumina clean up was also good for BDEs and non-BDEs ranging from 79% to 123%. However OPs were almost completely retained in the alumina column yielding very low recoveries, therefore OPs analysis was performed before the alumina cleanup. Average blanks were at least 5 times lower than any of the sample analyzed, however results were blank corrected.

Spatial mapping of FRs using SIP PAS Figure 1 shows the spatial pattern of target analytes determined from SIP disks deployed at various locations at the WWTP and at 4 reference sites that were nearby (100m-500m) the WWTP. There was no obvious spatial pattern showing elevated FRs at any of the WWTP sampling sites, when compared to the reference sites. Mean levels of BDEs in air were slightly elevated at the WWTP compared to the four reference sites. This is in contrast to 3 to 15 times higher concentrations of perfluorinated chemicals and siloxanes that were observed at the WWTP compared to the reference sites [4,6].

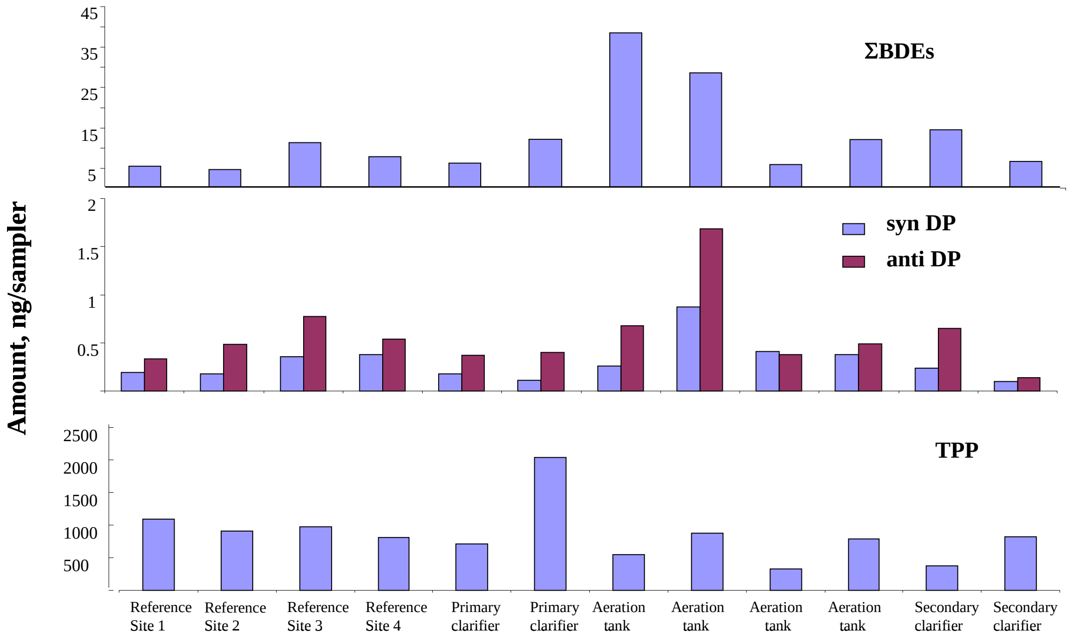

Figure 1. Spatial distributions of of ΣBDEs, DPs and TPP flame retardants around the waste water treatment plant and at reference sites, derived from SIP disk samplers deployed for 63 days during summer 2009.

Gas- and particle-phase air concentrations Figure 2 shows the gas- and particle-phase air concentrations of FRs at the secondary clarifier and the aeration tank from high-vol samples collected in spring 2010. The gas /particle percent distribution of various FRs is shown in Figure 3. Fewer compounds were detected in the gas-phase compared to the particle-phase due to the low-volatility of many of the target analytes. The dominant BDEs in the gas-phase were BDEs 28, 47, 99 and 100, at concentrations ranging from 0.8 to 13 pg m^{-3}. Among non-BDEs only ATE was detected in the gas-phase at 17 pg m^{-3} and 11 pg m^{-3} at the aeration and secondary clarifier respectively. While for OPs in the gas-phase, TPP was detected at the aeration tank with concentrations of 3000 ± 1800 pg m^{-3} but surprisingly not at the secondary clarifier. OPs FRs generally were more than 2 orders of magnitude higher than BDEs and non-BDEs, which is consistent with the results obtained from the SIP disks PAS during 2009 campaign. The higher level of OPs could reflect their high production volume and the mode in which they are employed (i.e. mixed into but not chemically bonded to the product they are intended to protect). This would facilitate their release from products to the surrounding environment[1].

BDE 209 was the dominant BDE measured in the particle-phase with average concentrations of 67 ± 47 pg m^{-3} and 61 ± 66 pg m^{-3} at the aeration and secondary clarifier, respectively. BDE 209 level observed at the WWTP was similar to the level reported at Cleveland urban sites at 56 ± 15 pg m^{-3} which was attributed to a local source[7]. HBCD, BEHTBP, syn-DP and anti-DP were detected in the few tenths of pg m^{-3} which are comparable to the levels reported in Great Lakes air [7-9]. The OPs, TCEP, TCPP, TPP and TDCPP were observed at the ng m^{-3} level at both sites (ranging from 100 to 5800 ng m^{-3}). Other studies reported levels in the hundreds of ng m^{-3}; for example, OPs exceeded 150 ng m^{-3} in indoor air[1] while ambient levels in the North Sea and the arctic were in the 10s of ng m^{-3} [10,11]. There were no apparent differences in levels and/or partitioning of target analytes between the secondary clarifier and the aeration tank, indicating that the aeration process did not contribute to air emissions of these FRs. Aeration was previously shown to be a driving force behind emissions of perfluorinated chemicals and siloxanes to air [4-6].

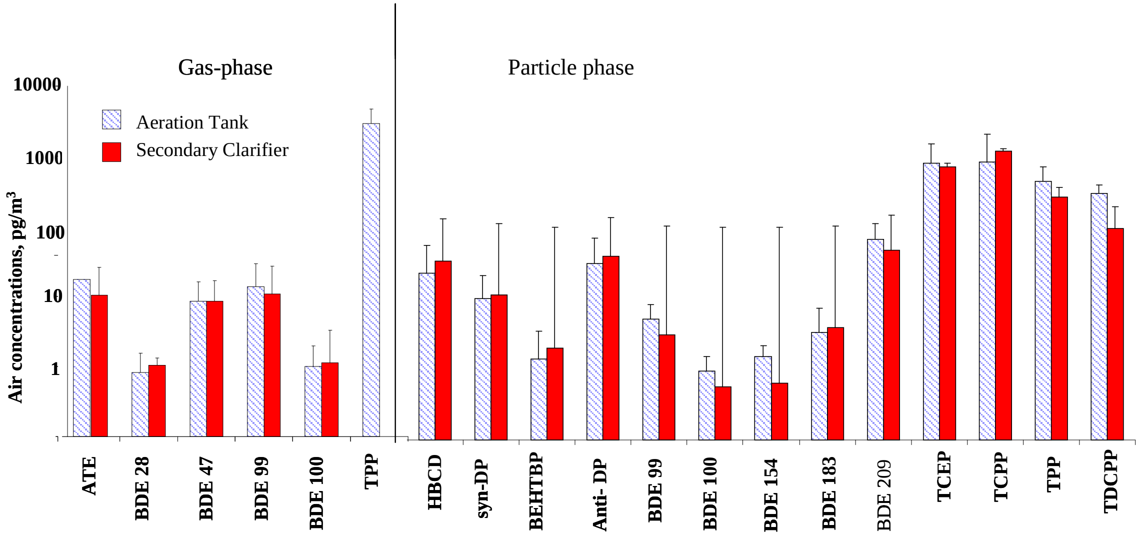

Figure 2. Hi-vol results from spring 2010 showing the gas- and particle-phase air concentrations (pg m^{-3}) of selected flame retardants at the aeration tank and secondary clarifier. Bars represent mean values (n=15) and whiskers represent one standard deviation.

Comparison of active and passive sampling techniques Air samples were collected in parallel at the aeration tank and secondary clarifiers using hi-vol and SIP disks during the spring 2010 campaign. The SIP disks were deployed 100% of the time while the hi-vols account for ~30% of the study period. A previous long-term calibration revealed that this design of PAS collects mainly gas-phase compounds and that approximately 10% of the particle-phase is sampled[12]. The gas-phase sampling rate for SIP disk is on the order of 4 m^3 day^{-1} while the particle-phase sampling rate is about 0.4 m^3 day^{-1}. Air concentrations for SIP disk samplers (calculated as the amount accumulated on the SIP disk divided by the sample air volume) were based on sample volumes that took into consideration the gas- and particle-phase fractions of the target analytes and their respective sampling rates, to generate a weighted sample air volume[13]. This results in a lower sample air volume for particle-associated chemicals.

Agreement between the air concentrations derived from hi-vol and SIP disks was within a factor of 2 for DP, which is mainly on particles. This is a good agreement considering the differences between the two techniques and the additional variability associated with differences in sampling times, with the hi-vol representing only 30% of the time sampled by the SIP disk, which may have resulted in missed high or low concentration episodes. In the case of the OP FRs (TCEP, TCPP, TPP and TDPP), there was disagreement between the hi-vol and SIP disk results, with about 30 times higher air concentrations obtained from the SIP disks. Further calibration of SIP disks samplers is currently underway to improve the calibration of SIP disks for this emerging class of air contaminants and to better understand the extent to which particle-phase compounds are collected.

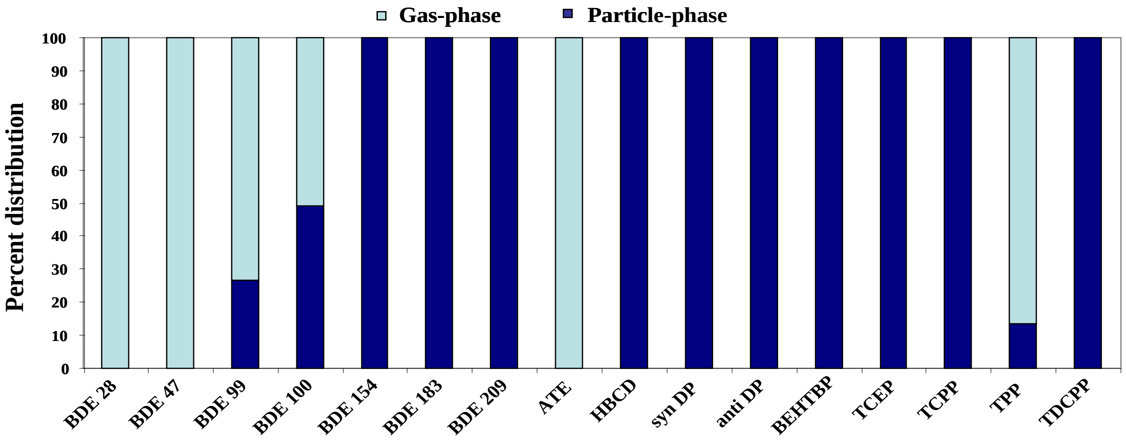

Figure 3. Gas- and particle-phase distribution of flame retardants at the aeration tank

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