Effect of Aging on the Volatility and Degradation of Brominated Flame Retardants and Organochlorine Pesticides in Urban Soil

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Introduction

Polybrominated diphenyl ether (PBDEs) have been widely used in consumer products as brominated flame retardants (BFRs) and are ubiquitously found in the environment. As the uses of PBDEs are being phased out in many countries, it is expected that soils could become an important secondary emission source to the atmosphere for the lower molecular weight PBDEs. It is also anticipated that the production and demand for alternative BFRs will grow. Initial study on alternative BFRs suggested that they are persistent, bioaccumulative and endocrine disruptors (Harju et al., 2008; Khalaf et al., 2009). These alternative BFRs have been found in seal blubber (Von der Recke and Vetter, 2007), beluga whales (Tomy et al., 2008) and bird eggs (Gauthier et al., 2009). Their environmental fate and behaviour in soils is unknown. The objectives of this study are to: 1) determine changes in volatility over time of BFRs and organochlorine pesticides (OCPs) spiked into an urban soil; 2) determine the degradation rates of BFRs and OCPs in soils; including the enantioselective degradation of chiral BFRs.

Materials and Methods

A low organic carbon (3.6%) urban soil from Toronto, Ontario, Canada was used in this study. Approximately 2 kg of the soil was sieved with 2 mm mesh. A portion of the soil (200 g) was spiked with known amounts of BFRs and OCPs in acetone, dried for two hours, and mixed with the remaining soil for 30 minutes. The chemicals spiked into soils were: OCPs α-hexachlorocyclohexane, α-HCH (25 ng g^{-1}) and *trans*-chlordane, TC (20 ng g^{-1}); PBDEs 17, 28, 99, 100 (200−400 ng g^{-1}); and non-BDE BFRs β-1,2,5,6-tetrabromocyclooctane, TBCO (160 ng g^{-1}); α- and β- 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane, TBECH (165 ng g^{-1}) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether, DPTE (390 ng g^{-1}).

The spiked Experimental soil was divided into portions of 200 g, sealed in glass jars and aged in the laboratory under room temperature and darkness. A set of Controls was similarly prepared by sterilizing 200-g portions of soil in glass jars using γ-irradiation (50 kGy), then spiking with the same suite of chemicals as the Experimental soils. The Controls were aged in the laboratory, as for the Experimental soil.

The volatility (fugacity) of the chemicals in soils is being monitored periodically for one year. Volatility was measured by a placing the soils into a fugacity meter as described by Meijer et al., (2003). In the fugacity meter, air was first passed through a water reservoir to achieve 100% relative humidity before it entered the soil column, where soil-air exchange occurs. The effluent air was passed through an adsorbent trap to capture the volatilized chemicals. Measurements were performed under equilibrium conditions. C_{AIR} was determined by eluting the adsorbent trap with 40 mL of dichloromethane: hexane (1:1). C_{SOIL} was determined by Soxhlet extraction with 200 mL of dichloromethane (DCM), followed by cleanup on a column of 3 g neutral alumina (6% water, deactivated), eluted with 35 mL of 20% DCM in hexane. The air and soil extracts were concentrated to 1 mL and solvent exchanged to isooctane. BFRs and OCPs were determined by GC-electron capture negative ion mass spectrometry. Quantitative analysis were performed on a DB-5 column (15 m × 0.25 mm i.d., 0.10 µm film thickness). Chiral analysis of α-TBECH and β-TBCO was carried out on a BGB-176 column (15 m × 0.25 mm i.d., 0.18 µm film thickness).

The volatility of a chemical is described by the soil-air partition coefficient, $K_{SA} = C_{SOIL}/C_{AIR}$, where C_{SOIL} (ng g^{-1}) and C_{AIR} (ng m^{-3}) are concentrations in soils and air respectively. K_{SA} is made dimensionless by multiplying by the dry solid soil density, g m^{-3}.

Results and Discussion

Volatility. K_{SA} of the spiked OCPs (α-HCH, TC) and BFRs (α/β-TBECH, β-TBCO, PBDE 17, 28) increased from D10 to 60 and leveled off from D60 to 90. K_{SA} of PBDE 47, 99 and DPTE increased to D90 (Figure 1) and perhaps afterwards. Results suggest that the volatility of BFRs and OCPs decreases over time as the chemicals become more strongly bound to the soil (higher K_{SA}). This is similar to our previous findings for the OCPs in muck soil.

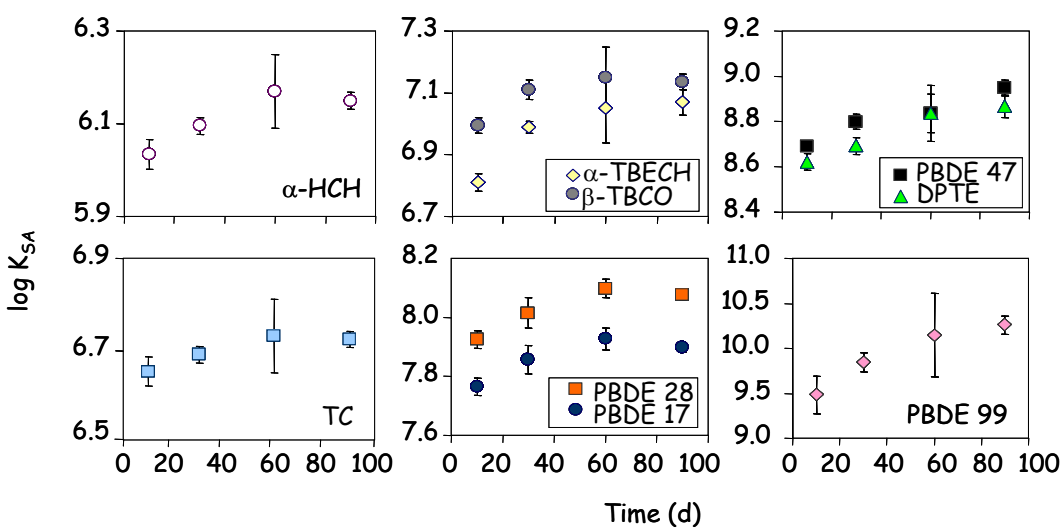

Figure 2. Soil-air partition coefficients (log K_{SA}) of BFRs and OCPs over 90 d of aging.

Degradation. Degradation of non-BDE BFRs and α-HCH was evident over 90 d, but did not follow a first-order relationship (Figure 2). Degradation was faster over the first 30-60 and then slowed down. No significant degradation of PBDEs and TC was observed over the 90 d.. These results suggested that the alternative BFRs are more vulnerable to degradation than the PBDEs.

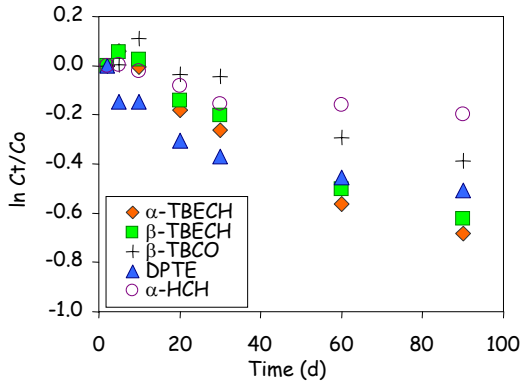

Figure 2. Degradation of selected BFRs and α-HCH over 90 d of indoor aging. C_0 and C_t are soil concentrations initially and at time = t.

Degradation of Chiral BFRs. Enantioselective degradation of α-TBECH and β-TBCO was expressed as enantiomer fraction, EF = area of the $1^{st}/(1^{st}+2^{nd})$ eluting peaks. Standards were racemic (EF = 0.504 and 0.500 for α-TBECH and β-TBCO) when first spiked into the soil. The 2nd eluting enantiomer of each compound was preferentially degraded during aging, resulting in increasing EFs of α-TBECH from 0.509 to 0.607 and of β-TBCO from 0.500 to 0.540 (Figure 3). The same enantioselective degradation pattern was observed in the corresponding air.

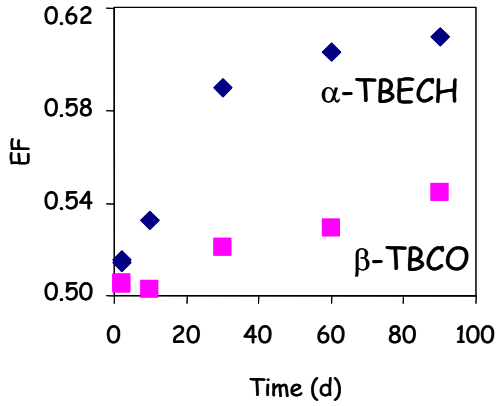

Figure 3. Enantioselective degradation of α-TBECH and β-TBCO in Experimental soils aged over 90 d.

Conclusions

Results up to 90 d of aging show a gradual increase in K_{SA} over time for the spiked BFRs and OCPs, indicating formation of bound residues and reduced volatility. The non-BDE BFRs were degraded more rapidly than the PBDEs, which showed no declines over the 90-d period. Microbial processes were implicated by the enantioselective degradation of α-TBECH and β-TBCO. Analysis of the sterilized Control soils is underway in order to verify this and to study the role of microbial activities in the formation of bound residues. Results of this study will improve our knowledge of the environmental fate of PBDEs and non-BDE BFRs in soil as well as enhance soil-air exchange models by allowing the aging effect on secondary emissions to be taken into account.

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