Chemosphere 126 (2015) 25–31

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polybrominated diphenyl ethers in resident Eurasian Tree Sparrow from Shanghai: Geographical distribution and implication for potential sources

Wei-biao Tang, Kai Huang, Jian-hua Zhao, Zheng Zhang, Si Liang, Lili Liu, Wei Zhang, Kuang-fei Lin *

School of Resources and Environmental Engineering, East China University of Science and Technology/State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, Shanghai 200237, China

HIGHLIGHTS

- BDE 209 was the predominant individual congener, followed by BDE 47, 99 and 100.
- The study reports the geographical distribution of PBDEs in ETS muscles.
- Shanghai Laogang Municipal Landfill was an important emission source of PBDE.
- ETS could be used as a useful biomonitoring tool for PBDEs in Shanghai.

ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 8 December 2014
Accepted 10 December 2014
Available online 6 February 2015

Handling Editor: Myrto Petreas

Keywords:
Polybrominated diphenyl ethers
Eurasian Tree Sparrow
Geographical distribution
Potential sources

ABSTRACT

An investigation of polybrominated diphenyl ethers (PBDEs) in Eurasian Tree Sparrow (*Passer montanus*) samples ($n = 37$) collected from different land use areas in Shanghai provided information about the levels, compositional patterns, geographical distribution, potential sources of PBDEs and the evaluation of contamination status in Shanghai. The concentrations of BDE 209 and Sum-PBDEs were within the range of 8.20–292.0 ng g^{-1} lw (median: 47.0 ng g^{-1} lw) and 33.16–375.63 ng g^{-1} lw (median: 78.7 ng g^{-1} lw), respectively. As the predominant individual congener, BDE 209 was detected in all samples with a mean percentage of 62.8%, followed by BDE 47, 99 and 100 sequentially. The geographical distribution of PBDEs in ETS muscles followed the order below: landfill > urban > industrial parks > suburban > rural > remote, indicating that Shanghai Laogang Municipal Landfill was an important emission source of PBDEs in Shanghai, and also the PBDE levels were in association with urbanization and industrialization. Compared with other regions, contamination status in Shanghai was relatively good with the exception of these high concentration areas. There was significant correlation ($r^2 = 0.89$, $P < 0.01$) between PBDEs concentrations in soil and ETS, indicating ETS could be used as a useful biomonitoring tool for PBDEs in Shanghai.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used industrial flame retardants that are commonly added in a variety of manufactured products, e.g., plastics, rubbers, textiles, and electronic and electrical devices, to improve their fire resistance (de Wit, 2002; Alaee et al., 2003). PBDEs were available in three commercial mixtures named as the penta-, octa- and deca-mixtures corresponding to their average bromine content. PBDEs have a great tendency to leach out of goods and products during manufacture, volatilization, recycling and disposal of wastes containing PBDEs. Due to their persistence, bioaccumulation and potential adverse effects on wildlife and humans, penta- and octa- mixtures have now been banned as additional global persistent organic pollutants (POPs) under the Stockholm Convention (UNEP, 2010). The deca-mixture has also been restricted in Europe in 2008, and is now being phased out in the U.S. by the end of 2013 (USEPA, 2010a).

Both terrestrial and aquatic birds have long been used as sentinel species for monitoring POPs contamination because they are

* Corresponding author at: State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, School of Resource and Environmental Engineering, East China University of Science and Technology, No. 130, Mei Long Road, Shanghai 200237, China. Tel.: +86 (0)21 64253188; fax: +86 21 64252737.
E-mail address: kflin@ecust.edu.cn (K.-f. Lin).

http://dx.doi.org/10.1016/j.chemosphere.2014.12.044
0045-6535/

widespread and sensitive to environmental changes and occupy the top position in the food chain (Herzke et al., 2003). Resident birds are good indicators of local contamination status. Growing interest in PBDEs has been focused in resident birds from e-waste recycling region in China. Meanwhile, available data suggested that high-speed industrialization and urbanization caused elevated PBDEs burden in birds from Hong Kong, Xiamen, Quanzhou and Beijing. However, there is still very little information on PBDEs contamination in birds from Shanghai, one metropolitan city served as industrial and economic development center in China. At present, Shanghai are facing serious environmental pollution problems due to the rapid growth of industrialization and urbanization. PBDEs were widely detected in air, soil and sediments in Shanghai.

Eurasian Tree Sparrow (ETS) predominantly feeding on seed and grain is one of terrestrial passerine birds, which is wide-spread and numerous in Shanghai. They are easily sampled and bred in small territories and foraging areas located in urban center, parks, farms and rural woods from Shanghai. To our best knowledge, this was the first report on PBDEs in resident passerine avian specie from Shanghai. Resident passerine birds have been found to be particularly suited to monitor local contamination for BFRs (Dauwe et al., 2006; Van den Steen et al., 2009; Sun et al., 2012). In this study, resident ETS samples were collected to investigate the geographical distribution of PBDEs levels and to explore the potential sources of PBDEs in Shanghai. Meanwhile, concentration and composition of PBDEs were compared to Passeriformes from all over the world.

2. Materials and methods

2.1. Study area and sampling

Located in the eastern China, Shanghai has a total area of 6341 km^2. The sampling locations covered urban districts, Pudong, Jiading, Qingpu, Songjiang, Jinshan, Minghang, Fengxian and Nanhui districts (Fig. 1). 37 ETS samples were collected between September 2012 and March 2013 from urban (U), suburban (S), rural (R) and remote (Re) areas in Shanghai. The detailed information in each sampling site and location is given in Table 1. ETS samples were shot under license and the necessary permit was obtained from Forestry Bureau of Shanghai for this research. Soil samples were collected from the same site meanwhile. The refuse in the upper layers were removed, and around 80–100 g of soil samples were sampled at a depth of 1–10 cm. Immediately after collection, samples were transported to the laboratory. Various tissues were excised and stored at −20 °C until further treatment. Pectoral muscle was used in the present study. Before extraction, samples were freeze-dried and homogenized.

2.2. Standard materials

Standards of BDE 28, 47, 99, 100, 153, 154, 183, and 209 were purchased as targets from AccuStandard (New Haven, CT, USA), and stock solutions were prepared with pesticide grade (re-distilled) iso-octane and stored at −20 °C. Surrogates (^{13}C-PCB141 and ^{13}C-BDE 209), internal standards (^{13}C-PCB 208) were also purchased from AccuStandards (New Haven, CT, USA). All chemicals used were of reagent grade with purity >99.8% and were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). Sodium sulfate was dried in a 650 °C muffle furnace for 4 h prior to use.

2.3. Analytical procedure

The method used for analysis was same to our previous work in Chongming Island, Yangtze estuary, China (Huang et al., 2013a). 1.0–5.0 g pectoral muscle and 10 g soil samples spiked with ^{13}C-PCB 141 (24 ng per sample) and ^{13}C-BDE 209 (10 ng per sample) were extracted with 40 ml acetone/hexane (1:1/v:v) for 8 h in soxhlet apparatus (Buchi, Switzerland). Baked sodium sulfate was added during extraction to remove water in the samples. The lipid content was determined by gravimetric measurement from an aliquot of extract. The extract was concentrated with a rotary evaporator (Buchi, Switzerland) and then transferred into a glass bottle with 6 mL hexane. They were treated with concentrated sulfuric acid to remove the lipid compound, followed by an additional cleanup step to remove other interferences. Further cleanup was done on a 30 cm × 10 mm i.d. glass column (Buchi, Switzerland) containing, from the bottom to top, with 3% deactivated aluminum oxide (6 cm), 3% deactivated neutral silica gel (2 cm), 25% sodium hydroxide silica (5 cm), 3% deactivated neutral silica gel (2 cm), 50% sulfuric acid silica (8 cm), and anhydrous sodium sulfate (1 cm). The column was eluted with 70 ml of hexane: methylene chloride (1:1), and the final extract was concentrated to approximately 1 mL with rotary evaporator and evaporated under a gentle stream of nitrogen gas and re-dissolved in 1.0 mL hexane. A known amount of ^{13}C-PCB 208 as internal standard was added to the final extract prior to instrumental analysis.

The analysis of PBDEs was conducted on an Agilent 7890A series gas chromatograph equipped with Agilent 5875C mass spectrometer (Agilent Technologies, Wilmington, DW, USA) using negative chemical ionization (GC–NCI-MS) in the selected ion monitoring (SIM) mode. The gas chromatograph column was a 15 m × 0.25 mm i.d. DB-5HT capillary column with a film thickness of 0.10 μm (J&W Scientific, Folsom, CA, USA). A 1 μL aliquot of sample solution was injected in a splitless mode with 3 min solvent delay time. Helium was used as carrier gas at constant flow (1.5 mL min^{-1}) and methane was used as reagent gas. The column temperature started from 110 °C (1 min for initial time) to 320 °C at a rate of 8 °C min^{-1}, and held for 3 min. The ionization temperature and interface temperature were 150 °C and 280 °C, respectively. The m/zs for triBDE to heptaBDE congeners (79, 81), BDE 209 (486, 488), ^{13}C-PCB 208 (476, 478) and ^{13}C-BDE 209 (494, 496) were selected.

2.4. Quality control and quality assurance (QA/QC)

Before extracting the authentic samples, spiked test were performed to evaluate the recoveries of PBDEs during extraction and cleanup procedures. EST pectoral muscles (n = 36) were spiked with a standard solution of PBDEs containing eight native congeners. Recoveries of these congeners were in the range of 80–110%. The surrogate standard ^{13}C-PCB141 and ^{13}C-BDE 209 exhibited 95.2% ± 13.8% and 82.6% ± 12.6%, respectively, among 9 blanks and 36 authentic samples. The analyzed concentrations were not corrected for the recoveries. Quantification was performed using an internal calibration method (more than five concentration levels). A procedure blank was included for each set of 8 field samples, and no target substances were detected. The limit of detection (LOD), defined as a signal/noise ratio (S/N) of 5 (S/N = 3 for BDE 209), ranged from 0.48 to 33.1 ng g^{-1} lw for triBDE to heptaBDE, and from 1.38 to 35.6 ng g^{-1} lw for BDE 209, depending on the sample size. PBDEs concentrations were expressed as ng g^{-1} lipid weight (lw). For soil samples (n = 37), The recoveries of ^{13}C-PCB141 and ^{13}C-BDE 209 were in the range of 82–105% and 75–96%, respectively. The procedure blank were included for each batch of samples, and no target substances were detected. The limit of detection (LOD), defined as a signal/noise ratio (S/N) of 5 (S/N = 3 for BDE 209), ranged from 2 to 25 pg g^{-1} dw for triBDE to heptaBDE, and from 490 to 506 ng g^{-1} dw for BDE 209, depending on the sample size.