Bull Environ Contam Toxicol (2009) 83:926–930
DOI 10.1007/s00128-009-9818-1

Polybrominated Diphenyl Ethers in the Soil of Typical Industrial City

K. Li · S. Fu · Z. Z. Yang · X. B. Xu

Received: 15 January 2009 / Accepted: 25 June 2009 / Published online: 8 July 2009

Abstract Linfen is generally recognized as one of the most polluted industrial cities in China. Indeed, Linfen is affected by heavy polluting industries and faces pollution by polybrominated diphenyl ethers (PBDEs). For this study, ten surface soil samples covering all of Linfen were collected and analyzed for 42 BDE congeners. The total PBDEs concentration ranged from 0.064 to 136.1 ng g^{-1}. Moreover, source analysis indicated that PBDEs may be associated with the prevalent use of Deca-BDE in the industrial area of the city. Furthermore, higher levels of PBDE contamination were observed in south Linfen due to the distribution of industrial plants.

Keywords China · Contamination · Polybrominated diphenyl ethers · Soil

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals that are used extensively as flame retardants in a wide variety of plastics, textiles and electronic components (Pirard and Pauw 2007). Technical PBDEs are synthesized by electrophilic substitution of diphenyl ethers. There are three commercial formulations of PBDEs: penta-, octa- and deca-brominated diphenyl ethers, which are named after their mean bromine contents (de Wit 2002). PBDEs have the potential for endocrine disruption, bioaccumulation, and long-range transport (Moon et al. 2007), therefore, an increasing number of studies have been conducted to evaluate their carcinogenic and mutagenic properties (Knoth et al. 2007; Naert et al. 2007). Recently, certain commercial mixtures of PBDEs (penta and octa formulations) were banned in Europe because of their persistence and their potential environmental and human health risks (Kemmlein et al. 2003). However, the demand for PBDEs has been increasing rapidly, and all commercial BDE mixtures are used without regulation in Asia (Tan et al. 2007).

Linfen is located in southwest Shanxi Province, China. The city occupies an area of 20,275 km^2 and has a population of 339,800. The city's climate is dominated by a temperate semi-wet monsoon pattern and there is a mean annual temperature of 12.2°C. China clay is the primary representative soil type in Linfen. According to China's State of the Environment Report for 1999, Linfen is one of the most polluted cities in China. The reasons for pollution problems in Linfen include the fact that more than 75% of its industrial GDP is from polluting heavy industries (Mestl et al. 2005). Linfen, one of the key bases of industries in China, has such pillars as heavy chemical industry, energy and metallurgy. With the development of industry that has occurred in recent years, Linfen has provided increasing amounts of chemical products and secondary energy, such as coke and electric power. Because most of the heavy polluting facilities are situated in the south urban area of Linfen, there is the potential for the residents to be exposed to PBDEs. Furthermore, environmental contamination in Linfen has increased, but the levels of PBDE residues in the soil of Linfen have not been investigated in detail to date. Therefore, we conducted this study to investigate the composition, distribution and characteristics of PBDEs in soil samples obtained from both urban areas and industrial

K. Li · S. Fu (✉) · Z. Z. Yang · X. B. Xu (✉)
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, 100085 Beijing, People's Republic of China
e-mail: fu_shan@sina.com

X. B. Xu
e-mail: xuxb1006@sina.com

areas in Linfen. The primary objectives of this study were to investigate the pollution status of the typical industrial city, identify possible sources of pollution, and explore possible factors affecting contamination.

Materials and Methods

Surface soil samples (0–10 cm depth) were obtained from 5 urban sites and 5 industrial plants in Linfen, Shanxi Province (Fig. 1), China, in January 2006. The industrial plants (sites 6–10) belonged to the Chemical Industry, Refractory Materials Industry, Textile Industry, Paper-making Industry and Iron-Steel Industry. For sample collection, any overlying vegetation was removed, after which surface soil samples were collected in triplicate using a hand-held coring device. Each composite urban soil sample consisted of 9 sub-samples in the same grid pattern at each sampling site. Each composite industrial plant soil sample consisted of 3 sub-samples. The gathered samples were freeze-dried, mixed thoroughly, passed through a 60 mesh sieve (International standard size, 250 μm), transferred to amber glass and stored at 4°C until analysis. The remaining water content in the soil was determined gravimetrically after air-drying individual composite soil samples at 105°C for 12 h. All results were reported on a dry weight basis.

A standard solution of 39 PBDE congeners (EPA method 1614 standard solution; Accustandard, New Haven, CT, USA) was used to quantify the following mono- through hepta-brominated BDEs: mono-BDEs (BDE-1, 2, and 3); di-BDEs (BDE-7, 8, 10, 11, 12, 13, and 15); tri-BDEs (BDE-17, 25, 28, 30, 32, 33, 35, and 37); tetra-BDEs (BDE-47, 49, 66, 71, 75, and 77); penta-BDEs (BDE-85, 99, 100, 116, 118, 119, and 126); hexa-BDEs (BDE-138, 153, 154, 155, and 166); and hepta-BDEs (BDE-181, 183, and 190). BDE-205 and 206 were purchased from Cambridge Isotope Laboratories (Andover, MA). BDE-209 was purchased from the Laboratory of Dr. Ehrenstorfer (Augsburg, Germany). All solvents used in this study were of pesticide grade (J. T. Baker, USA).

Five grams of each urban surface soil sample or three grams of each industrial plant soil sample were weighed and then ground with anhydrous sodium sulfate until they formed a free-flowing powder. The samples were then extracted with 40 mL of hexane/dichloromethane (1:1, v/v) by ultrasonication for 4 min, after which they were separated by centrifugation. This process was repeated three times. Next, the extracts were collected and evaporated using a rotary evaporator, followed by reduction to 2 mL. The concentrated extracts were then cleaned on a 15-mm i.d. column packed from the bottom to top with 1 g activated silica gel, 3 g basic silica gel, 1 g activated silica gel, 4 g acid silica gel (44% concentrated sulfuric acid, w/w), 4 g acid silica gel (22% concentrated sulfuric acid, w/w), 1 g activated silica gel and 1 cm anhydrous sodium sulfate. The first fraction was eluted with 100 mL hexane. The eluate was then evaporated using a rotary evaporator and subsequently reduced to 2 mL. Next, the concentrated extracts were cleaned on a 10-mm i.d. column packed from the bottom to top with 2 g silver nitrate silica gel (10%, w/w), 2 g activated silica gel and 1 cm anhydrous sodium sulfate. The first fraction was eluted with 40 mL hexane, after which the PBDEs were eluted with 40 mL of hexane/dichloromethane (1:1, v/v). The eluate was then evaporated using a rotary evaporator and reduced to 20 μL under a gentle N_2 stream for analysis. Throughout the extraction, cleanup and analysis procedure, the analytes were

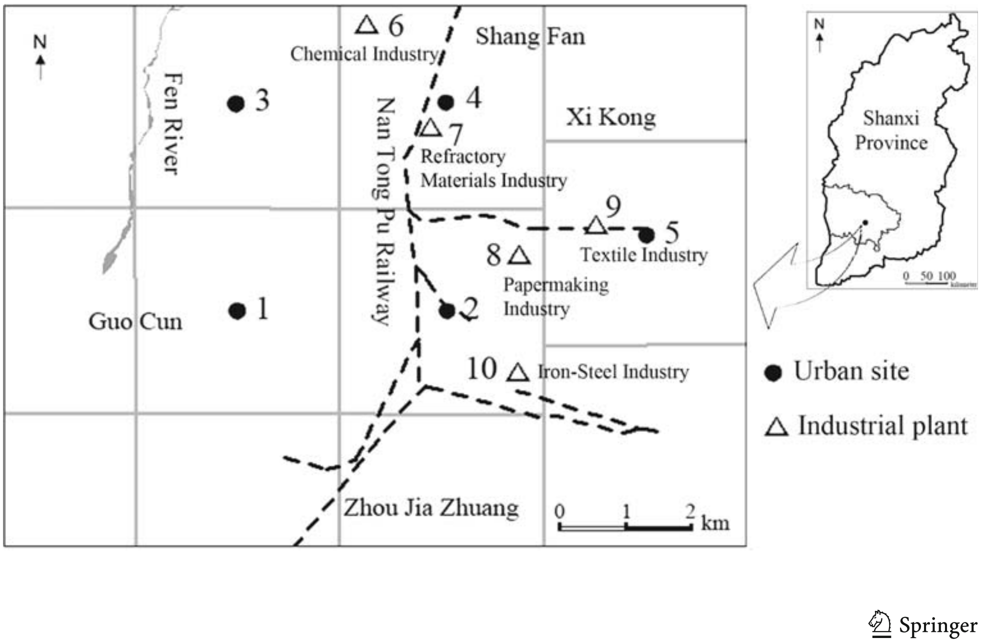


Fig. 1 Surface soil sampling sites in urban areas and industrial plants of Linfen

protected from light by wrapping the containers with aluminum foil or using amber glassware.

We analyzed the PBDEs using an Agilent 6890 series gas chromatograph (GC) coupled with an Agilent 5973 mass spectrometer (MS) using a negative chemical ionization source in SIM mode. The MS source temperature was 150°C, and the electron energy was 70 eV. The GC was equipped with a split-splitless injector that was held at a constant temperature of 270°C. Gas chromatographic separation was performed on a 15-m DB-5MS capillary column (30 m × 0.25 mm, internal diameter; 0.25-μm film thickness). We maintained the GC column at 80°C for 1 min and then increased the temperature at 10°C min^{-1} to 200°C, after which it was ramped at 20°C min^{-1} to 300°C, where it was held for 5 min. The compounds were monitored at m/z 79 and 81 (for PBDE congeners except BDE-209) and m/z 486.7 and 488.7 (for BDE-209 only).

A laboratory method control group was also analyzed to demonstrate the lack of interference and cross-contamination. In addition, a procedural blank was run in parallel for every set of 5 samples to further check for interference and cross-contamination. Duplicate samples were analyzed in the laboratory along with the regular samples as an additional quality control tool to ensure valid results. The instrument stability and relative response factor variance were determined by analyzing the calibration standard solutions in each sample batch.

Quantification of PBDE was performed using an external standard method. Three quality control criteria were used to ensure correct identification of the target compounds: (1) the GC retention times matched those of the standard compounds within ±0.05 min; (2) the signal-to-noise ratio was greater than 3:1; (3) each compound had two monitored ions. Isotopic ratios between the quantification and confirmation ions were within ±15% of the theoretical values. The SRM sample (NIST-2585) was analyzed to validate the analytical method employed. The results were satisfactory, with a z-score of ≤ 1 being observed for all congeners (range: 0.32–0.86 for the PBDEs, p F 0.05). The limits of detection (LOD) for PBDE were within the range of 0.001–0.05 ng g^{-1} (dry weight) for di- to nona-BDE, and 0.1 ng g^{-1} (dry weight) for BDE-209.

Results and Discussion

Polybrominated diphenyl ethers (42 BDE congeners, including some co-eluting BDE congeners) were identified in each of the urban area and industrial plant soil samples. The detection rates of the PBDEs in the soils were up to 100%, which indicated wide occurrence of these compounds in Linfen City. The concentrations of PBDEs in the urban surface soil samples ranged from 0.064 to 1.670 ng g^{-1} (median 0.474 ng g^{-1}, dry weight). The highest concentration was found at site 1, while the lowest concentration was observed at site 5. The concentrations of PBDEs in the industrial plant soils ranged from 2.661 to 136.1 ng g^{-1} (dry weight). The highest polluted area was found at site 8 (136.1 ng g^{-1}, dry weight), which was a Papermaking industry. However, the levels observed at the other sites were all less than 23.81 ng g^{-1} (dry weight). These results indicate that the industrial area was the most polluted region in Linfen (Table 1).

We compared the concentrations of PBDEs in soil in Linfen with those of other cities in Shanxi Province. The PBDE concentrations in Linfen were lower than those in Taiyuan (0.016–211.4 ng g^{-1} in the urban surface soil; 5.961–144.1 ng g^{-1} in the industrial plant soil) (Li et al. 2008). We also compared the results with values reported for other areas in China and found that the concentrations of PBDE were lower in Linfen than in the surface soil of an e-waste recycling site in Guiyu, Guangdong Province (0.26–824 ng g^{-1}) (Wang et al. 2005), and in the Pearl

Table 1 Total concentration of PBDEs in each sample

	1	2	3	4	5	6	7	8	9	10
di-BDEs	0.002	0.002	0.001	0.009	0.001	0.032	0.009	0.008	0.023	0.082
tri-BDEs	0.009	0.003	0.005	0.004	0.002	0.114	0.084	0.034	0.117	0.269
tetra-BDEs	0.038	0.013	0.019	0.010	0.004	0.125	0.155	0.040	0.220	0.392
penta-BDEs	0.036	0.010	0.017	0.006	0.004	0.146	0.148	0.060	0.262	0.329
hexa-BDEs	0.027	0.003	0.005	0.004	0.001	0.046	0.066	0.113	0.169	0.144
hepta-BDEs	0.085	0.003	0.010	0.005	0.001	0.065	0.124	0.273	0.470	0.226
octa-BDEs	ND	ND	ND	ND	ND	ND	ND	0.034	0.012	0.007
nona-BDEs	0.148	0.023	0.012	0.020	0.006	0.203	0.354	8.229	1.421	1.092
BDE-209	1.326	0.292	0.037	0.122	0.046	1.931	3.613	127.3	15.67	21.27
ΣPBDE	1.670	0.350	0.107	0.179	0.064	2.661	4.552	136.1	18.36	23.81

data units are in nanograms per gram

ND not detected

River Delta (0.028–70.5 ng g^{-1}) (Zou et al. 2007). When compared to the levels in other countries, with the exception of BDE-209, the levels observed in the present study were lower than those in background soils in the United Kingdom and Norway (65–12,000 ng g^{-1}) (Hassanin et al. 2004), and Izmir, Turkey (0.05–2,840 ng g^{-1}) (Cetin and Odabasi 2007).

Of the PBDE homologues, the dominant PBDE detected in this study was BDE-209, which accounted for more than 65% of the total PBDEs in most sampling locations at both urban areas and industrial plants (Fig. 2). BDE-209 was also the primary PBDE homologue in Taiyuan (Li et al. 2008), the e-waste pollution area in southeast China (Zou et al. 2007), Kyoto, Japan (Hayakawa et al. 2004) and

Fig. 2 Total concentration of the PBDE homologues in each sample

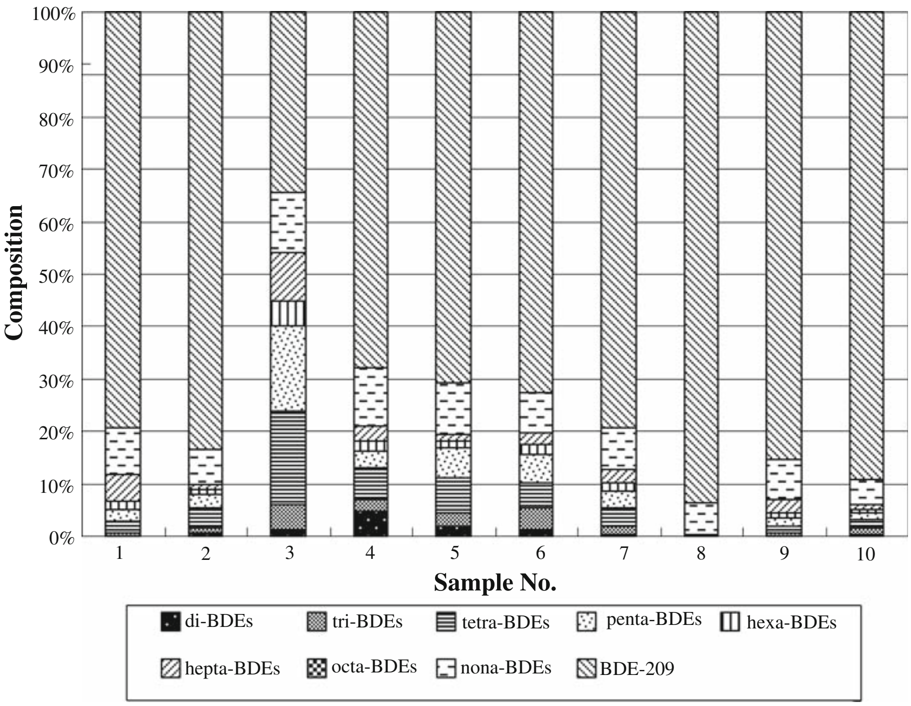
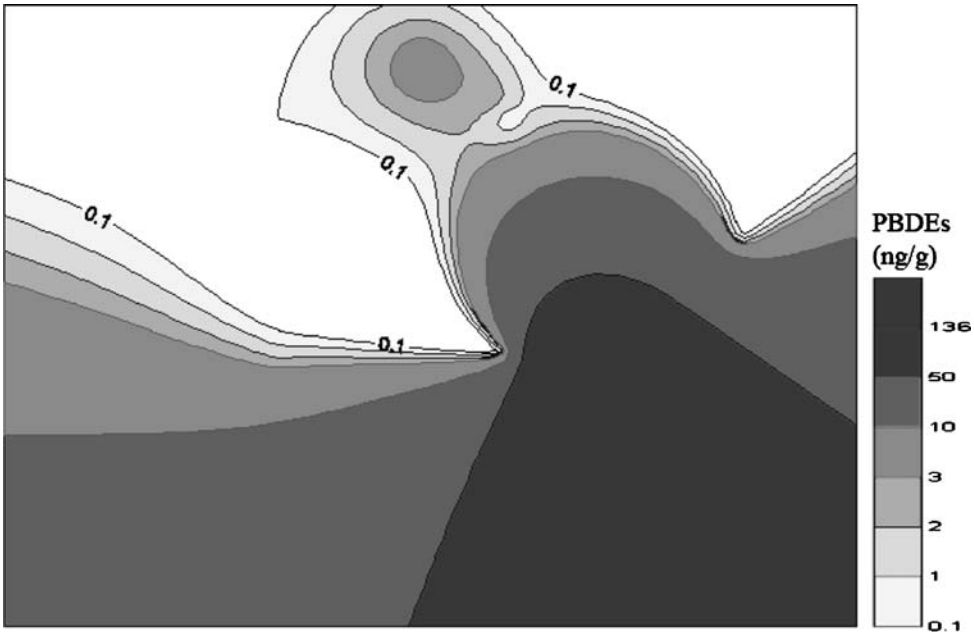


Fig. 3 The distributions of PBDEs in the soils in Linfen (data in the figure are in ng g^{-1})



Izmir, Turkey (Cetin and Odabasi 2007). These findings indicate that BDE-209 is the primary PBDE homologue present in soil worldwide. Lower brominated congeners were detected at relatively lower levels. The PBDE congener profile of the soil in Linfen was similar to that of technical deca-BDE products (Saytex 102E and Bromkal 82-0DE) (LaGuardia et al. 2006). These results may indicate that BDE-209 firmly bound to particles due to its low volatility.

Principal component analysis (PCA) was performed to evaluate the similarities or differences between the PBDE congener patterns of each sample. To accomplish this, all data were normalized to a percent of the sum of PBDEs and PCs were identified by eigenvalues of over 1. Two extracted PCs could explain 93.2% of the data variance. Furthermore, a loading plot and score plot rotation were obtained using the varimax method. The score plot indicated that the PBDEs found in soil in Linfen could be classified into two main groups. In addition, the PCA results indicated that the compositions of PBDEs in the surface soil of urban areas differed from those in industrial regions, and that PBDE pollution primarily originated from industrial areas.

The distribution of PBDEs in the soil samples is shown in Fig. 3, which revealed an increasing trend from north to south Linfen. The most contaminated area was the southeast urban area in Linfen. The increased contamination in this area may have been because the industrial plants belonging to the Iron-Steel industry and the Chemical industry are located in southeast Linfen. Conversely, the north and west urban areas are primarily composed of residential areas, downtown, recreational areas and schools. Overall, the results of this study indicate that the contamination of industrial plant soils may act as a sink and source of PBDEs, which would explain the contamination status of Linfen.

Acknowledgments This study was supported by the Ministry of Science and Technology of the People's Republic of China (No. 2007BAC27B01 and No. 2006BAK02A10) and the National Natural Scientific Foundation of China (No. 20707031). We also thank the research staff at the Inst. of Geochem. Geophys. Exploration, especially Prof. Cheng and Prof. Liu, for sample collection and technical assistance.

References

Cetin B, Odabasi M (2007) Particle-phase dry deposition and air-soil gas-exchange of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. Environ Sci Technol 41:4986–4992

de Wit CA (2002) An overview of brominated flame retardants in the environment. Chemosphere 46:583–624

Hassanin A, Breivik K, Meijer SN, Steinnes E, Thomas GO, Jones KC (2004) PBDEs in European background soils: levels and factors controlling their distribution. Environ Sci Technol 38:738–745

Hayakawa K, Takatsuki H, Watanabe I, Sakai S (2004) Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-*p*-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. Chemosphere 57:343–356

Kemmlein S, Herzke D, Law RJ (2003) BFR-governmental testing programme. Environ Int 29:781–792

Knoth W, Mann W, Meyer R, Nebhuth J (2007) Polybrominated diphenyl ether in sewage sludge in Germany. Chemosphere 67:1831–1837

LaGuardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 40:6247–6254

Li K, Fu S, Yang Z, Xu X (2008) Composition, distribution and characterization of polybrominated diphenyl ethers (PBDEs) in the soil in Taiyuan, China. Bull Environ Contam Toxicol 81:588–593

Mestl HES, Aunan K, Fang J, Seip HM, Skjelvik JM, Vennemo H (2005) Cleaner production as climate investment-integrated assessment in Taiyuan City, China. J Clean Prod 13:57–70

Moon HB, Kannan K, Lee SJ, Choi M (2007) Atmospheric deposition of polybrominated diphenyl ethers (PBDEs) in coastal areas in Korea. Chemosphere 66:585–593

Naert C, Van Peteghem C, Kupper J, Jenni L, Naegeli H (2007) Distribution of polychlorinated biphenyls and polybrominated diphenyl ethers in birds of prey from Switzerland. Chemosphere 68:977–987

Pirard C, Pauw ED (2007) Absorption, disposition and excretion of polybrominated diphenyl ethers (PBDEs) in chicken. Chemosphere 66:320–325

Tan J, Cheng SM, Loganath A, Chong YS, Obbard JP (2007) Polybrominated diphenyl ethers in house dust in Singapore. Chemosphere 66:985–992

Wang D, Cai Z, Jiang G, Leung A, Wong MH, Wong WK (2005) Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. Chemosphere 60:810–816

Zou MY, Ran Y, Gong J, Mai BX, Ey Zeng (2007) Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: occurrence, inventory, and fate. Environ Sci Technol 41:8262–8267