STUDY ON DISTRIBUTION AND SOURCE APPORTIONMENT OF PBDD/FS IN URBAN ENVIRONMENT

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Introduction

Shanghai is a provincial-level administrative region, municipality directly under the central government of the People's Republic of China. While the large population in cities is driving the continuous economic growth, the environmental pollution of dioxin-like compounds caused by the incineration of domestic waste, automobile exhaust, and the production, use and disposal of industrial chemicals cannot be ignored. Throughout the country, there are relatively few studies on dioxin-like compounds in Shanghai, and even fewer studies on brominated dioxins. In order to estimate the health risks of Shanghai urban residents due to environmental exposure of PBDD/Fs, One municipal solid waste incinerator in downtown Shanghai was selected as urban contaminated research area and 44 municipal environmental atmospheric monitoring points in the 16 administrative regions of Shanghai were selected as the urban background research area. The concentrations of PBDD/Fs in ambient atmosphere and soil samples from contaminated and background areas in Shanghai, as well as the distribution characteristics of congeners, and qualitative pollution sources identification, were studied in this research.

Materials and methods

The MSWI is located in the northwest of Shanghai. As this plant is in close proximity to residential areas, the potential exposure of people to hazardous pollutants is a serious concern in this city. Southeasterly or northwesterly winds prevailed throughout the year in the study area, and they changed seasonally. 4 sampling sites were set in vicinity this MSWI. Control point 2 and sensitive point 2 were located in northwest of the MSWI, with the distance of approximately 750m and 3500m respectively; Control point 1 and sensitive point 1 were located in southeast of the MSWI, with the distance of approximately 1000m and 3000m respectively (Fig. 1). The atmospheric samples were collected 4days in summer and winter using active sampling technique in 2017.

The soil samples were collected during spring in 2017, with a total of 61 soil samples collected within a 4km radius of the MSWI (Fig. 1). In each direction, one sampling site was set every 300m in the first 1000m from the incinerator, every 500m from 1000–3000m, with one sampling site located outside the 3000m radius. Every site was located using the global positioning system (GPS). The sampling locations were on open fields, not excessively covered by crops. Three samples of top soil were taken within a 5-10 m radius of each sampling site at a depth of 0-20 cm using a pre-cleaned steel spoon. The three samples were then mixed in a glass bottle and transported to the laboratory.

For the background area in Shanghai, the atmospheric samples were collected from July to August in 2019 and from Dec in 2019 to Jan in 2020 using passive sampling technique at 44 municipal environmental atmospheric monitoring points in the 16 administrative regions of Shanghai (Fig. 2).

Each sample was spiked with $^{13}C_{12}$-labeled internal standard EDF- 5408 (Cambridge Isotope Laboratories, USA) before being extracted to allow the extraction efficiency and losses during the extraction and cleanup procedures to be measured. Each sample was then extracted with a 1:1 (v/v) mixture of hexane and dichloromethane in an accelerated solvent extraction system (ASE 200; Thermo, USA) for soil samples, and an automatic Soxhlet extractor (B-811; Büchi Switzerland) for atmospheric samples. And then the extract was concentrated using a Multy-samples Quantitative Concentrator (Syncore Analyst; Büchi Switzerland). Purification was conducted using an acid silica gel column, silica gel column containing silver nitrate silica gel and florisil column. The PBDD/Fs were then eluted from the florisil column using 80 mL of 4:6 (v/v) mixture of hexane and dichloromethane, condensed to about 20 μL using a pressure blowing concentrator under a gentle stream of nitrogen.

The PBDD/Fs were analyzed using DFS (DFS, Thermo) with a high resolution gas chromatograph and a high resolution mass spectrometer, using a DB-5MS column (30m×0.25mm×0.1μm). The mass spectrometer had a resolution of at least 10,000 and was operated in selected-ion-monitoring mode.

A blank sample was analyzed for every batch of ten samples, and a duplicate sample was analyzed for every two batches for soil samples. The blank samples did not contain any PBDD/Fs concentrations above the method detection limits, which were ranged from 0.005 to 0.113pg·g^{-1} (calculated with 10g sample) for soil samples, and were ranged from 0.001 to 0.009pg·m^{-3} (calculated with 100m^3 sample) for ambient atmospheric samples. The average recoveries of soil samples ranged from 36.2% to 123%. The average recovery of the atmosphere samples obtained by active sampling techniques was between 52.0% and 127%. The average recovery of the atmosphere samples obtained by passive sampling techniques was between 48.9% and 119%.

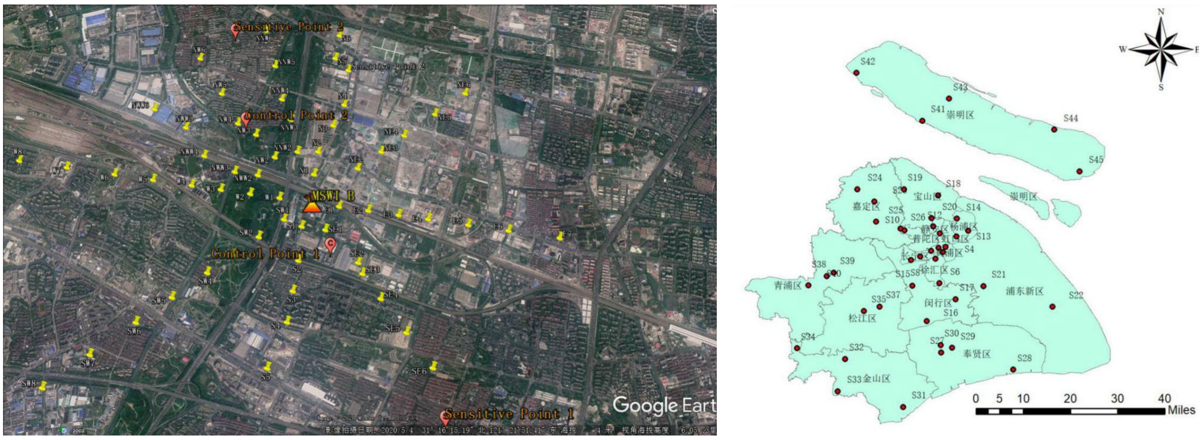

Figure 1 Sampling sites around the MSWI in Shanghai and distribution of ambient atmospheric sampling points in Shanghai

Results and discussion

PBDD/Fs concentrations in soil and ambient atmosphere samples in Shanghai

For soils in vicinity of the MSWI in Shanghai, the concentrations of PBDD/Fs ranged from 17.7 ng·kg^{-1} to 838 ng·kg^{-1} (average of 54.9 ng·kg^{-1}), and the corresponding toxic equivalent (TEQ) concentration ranged from 0.561 to 15.9 ng·TEQ·kg^{-1} (average of 3.66 ng·TEQ·kg^{-1}). In this study, the concentrations of PBDD/Fs in soil samples in vicinity of the MSWI in Shanghai were much lower than the concentrations of PBDD/Fs (ranging from 716 to 800,000 ng·kg^{-1} (46.30 to 3680 ng·TEQ·kg^{-1}))in the soil near e-waste disposal sites in eastern China detected by Ma et al in 2009 (Ma et al., 2009); and was similar to the concentrations of PBDD/Fs in the soil samples from Guiyu, Guangdong (2.5 to 17 ng· TEQ ·kg^{-1}) (Xu et al., 2017); and were slightly higher than the concentration of PBDD/FS in the soil samples from chemical industrial parks in Shanghai (0- 427 ng·kg^{-1} (2.5-17 ng·TEQ·kg^{-1})) (Ma et al., 2009); were significantly higher than the concentration level of PBDD/Fs in the soil samples from industrial parks in southern Taiwan (average: 0.25 ng·TEQ·kg^{-1}) (Kuo et al., 2014). Limited research data indicate that the concentrations of PBDD/Fs in urban soils are all increasing, and the pollution risk requires further attention.

Figure 2 shows TEQ concentrations of PBDD/Fs in soil samples from different wind directions around MSWI. Statistical analysis results showed that there was no significant difference in PBDD/Fs concentration between different wind directions (P value: 0.061). Due to the barrier of buildings and traffic arteries, the dominant wind direction has little influence on the concentrations of PBDD/Fs in soil samples in vicinity of MSWI.

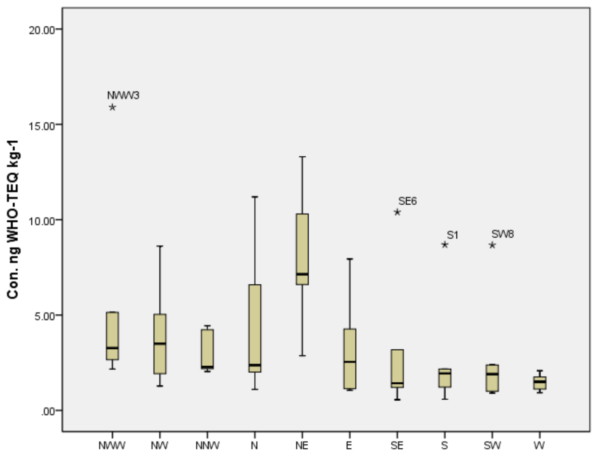

Figure 2 The TEQ concentrations of PBDD/Fs in soil samples from different wind directions in vicinity of MSWIs in Shanghai

For the ambient atmosphere samples, collected by active sampling techniques in vicinity of the MSWI in Shanghai, the concentrations of PBDD/Fs ranged from 0.488 to 2.42 pg·m^{-3} (average of 1.12 pg·m^{-3}), and the corresponding TEQ concentration ranged from 0.0138 to 0.115 pg·TEQ·m^{-3} (average of 0.0443 pg·TEQ·m^{-3}). The concentrations of PBDD/Fs in the ambient atmosphere in summer ranged from 0.488 to 2.42 pg·m^{-3}, (average of 1.07 pg·m^{-3}), and the corresponding TEQ concentration ranged from 0.0138 to 0.0801 pg·TEQ·m^{-3}(average of 0.0347 pg·TEQ·m^{-3}). The concentrations of PBDD/Fs in winter ambient atmosphere ranged from 0.489 to 2.01pg·m^{-3} (average of 1.16 pg·m^{-3}), and the corresponding TEQ concentration ranged from 0.0214 to 0.115 pg·TEQ·m^{-3}(average of 0.0540 pg·TEQ·m^{-3}). The TEQ concentrations of PBDD/Fs in the ambient atmosphere in vicinity of the MSWI in Shanghai were much lower than that form electronic waste recycling plant (70.1-108 (91.3) pg·TEQ·m^{-3}) (Ren et al., 2014); and were slightly lower than that of Li et al. (2008) (0.147-0.304 pg· TEQ ·m^{-3}) in Shanghai urban area in 2008; and were slightly higher than that in the atmosphere surrounding the waste incineration plant in Taiwan (0.0122 pg· TEQ·m^{-3}) (Wang et al., 2010).

For the ambient atmosphere samples, collected by passive sampling techniques from background area in Shanghai, only 1234678-HpBDF can be detected. The monitoring and research of PBDD/Fs by passive sampling techniques needs further confirmation.

It is worth noticing that the concentrations of PBDD/Fs in the ambient atmosphere in vicinity of the MSWI in Shanghai is far less than that of PCDD/Fs, but the concentrations of PBDD/Fs in the soil samples were equal to or even higher than that of PCDD/Fs. The results indicated that there were obvious sources of PBDD/Fs in urban soil except dry and wet atmospheric deposition. As brominated flame retardants are still being produced and used on a large scale in China, and long-term light and microbial degradation in the soil may lead to the conversion of PBDEs into PBDD/Fs in part of the soil, while such conversion reaction is relatively weak in the ambient atmosphere. Further attention should be paid to the effects of brominated organic pollution in urban polluted areas.

Characteristics of PBDD/Fs congeners in soil and ambient atmosphere samples in Shanghai

The average profiles of 11 kinds 2,3,7,8-PBDD/Fs congeners in soil and ambient atmosphere samples in vicinity of the MSWI in Shanghai were presented in Figure 3. For soil samples in vicinity of the MSWI in Shanghai, the dominant congeners were 1234678-HpBDF, 123478-HxBDF and 1234678-HpBDD, accounting for 86.1%, 7.68% and 2.38% of the total concentration on average, respectively. The percentage of other congeners were less than 2%. For the ambient atmosphere samples, the dominant congeners were also 1234678-HpBDF, 123478-HxBDF and 1234678-HpBDD, accounting for 75.0%, 11.5% and 9.00% of the total concentration on average, respectively. The concentrations of bromodibenzofurans (PBDFs) in all samples in this study were significantly higher than that of the corresponding bromodibenzodiee-in (PBDDs), which was similar to the PBDD/Fs composition pattern from other regions (Ma et al., 2009; Xu et al., 2017).

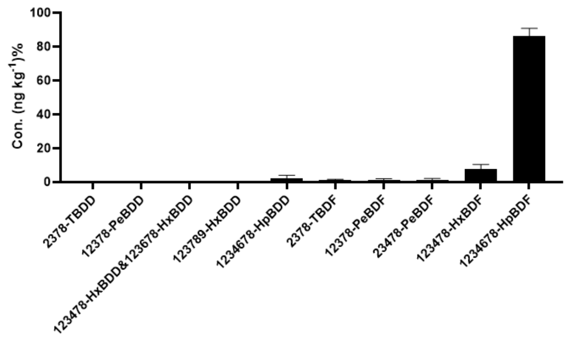

Figure 3a Congeners distribution of PBDD/Fs in soil samples in vicinity of MSWI

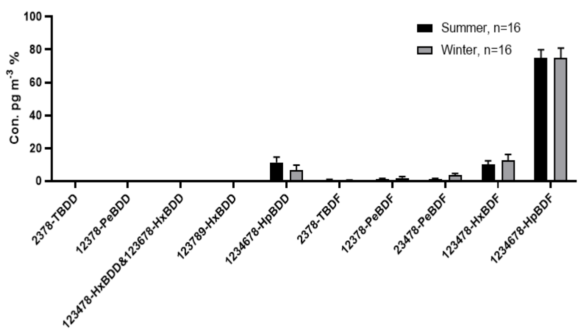

Figure 3b Congeners distribution of PBDD/Fs in ambient atmosphere samples in vicinity of MSWI

Source apportionment of PBDD/Fs in soil and ambient atmosphere samples in Shanghai

Due to the relatively later start of PBDD/Fs research and unstable analysis methods, there were relatively fewer sources information of PBDD/Fs available at present, as well as the information of congeners in some available source information was incomplete. For example, some studies only obtain the data of 4-6 brominated PBDD/Fs (Wang et al., 2010; Ren et al., 2017; Sindiku et al., 2015).

Principal component analysis (PCA) was used to analyze the composition of PBDD/Fs congeners in these pollution sources and the soil and ambient atmosphere samples in Shanghai. As shown in Figure 4, PBDD/Fs in the soil and ambient atmosphere samples in Shanghai may be mainly affected by commercial Deca-BDE products and brominated flame retardants (EW plastic) in electronic waste, while little influenced by other pollutant sources, such as metallurgical boilers and domestic waste incinerators. It should be noted that the traceability analysis is not comprehensive and perfect due to the absence of some congeners data in the pollutant source. The traceability analysis conducted after obtaining sufficient source data would be more referential.

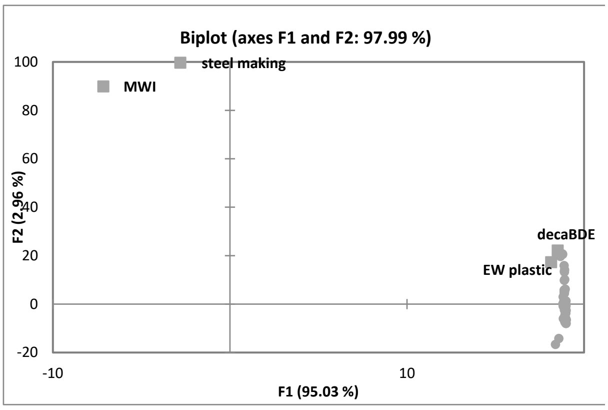

Figure 4a The principal component plot of PBDD/Fs in soil samples

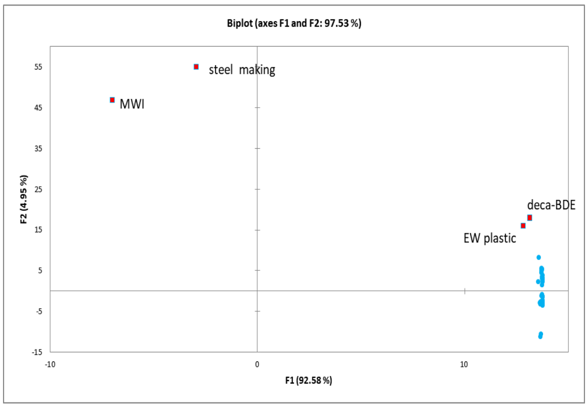

Figure 4b The principal component plot of PBDD/Fs in ambient atmosphere samples

Acknowledgements

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