PBDD/Fs CONCENTRATIONS AND DISTRIBUTIONS IN FARMLAND SOIL OF GUIYU, CHINA

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Abstract

A continuous study on PBDD/Fs in farmland soil of Guiyu was performed after previous PCDD/Fs survey. Twelve 2,3,7,8-PBDD/Fs congeners were quantified, and I-TEQ in electronic wastes (EWs) disposal area soil were 3.1-25.9 pg TEQ/g, which was higher than that of background sites, SL district was heavily contaminated in Guiyu, since SL district was a typical EWs combustion area. The dominant congeners were 1234678-HpBDF and OBDF in most of soil, congener profiles of PBDD/Fs were similar as wastes combustion mode, and impurities of PBDEs also contributed a part of PBDD/Fs.

Introduction

Guiyu, a small town located in the southeastern of Guangdong province, China, is the largest and most famous electronic wastes (EWs) dismantling area all over the world. EWs are disposed to recycle particular material in Guiyu[1], more than 80% of the local families have been engaged in this vocation since 1995 and more than 1 million tons of EWs are disposed each year. Thermal disposal manner of EWs were popular in Guiyu, such as open burning of EWs scrap, roasting of circuit board and cable. Since the existence of abundant brominated flame retardants (BFRs) in EWs, it is inclined to generate Polybrominated Dibenzo-p-dioxins and Dibenzofurans (PBDD/Fs) in these disposal processes, BFRs can act as the precursors of PBDD/Fs[2]. Li *et al.*[3] report severe PCDD/Fs and PBDD/Fs pollution in air around Guiyu, a comprehensive soil survey on PCDD/Fs covering all of Guiyu town has been done in our previous study[4], a continuous study on PBDD/Fs in farmland soil of Guiyu is presented here.

Materials and Methods

Standard solutions

PBDD/Fs Calibration Solution (EDF-5381), Cleanup Spike (EDF-5382), Syringe Spike Stock (EDF-5383-4X) were all purchased from Cambridge Isotope Laboratories, Inc. (USA).

Sampling

Guiyu was divided into three districts geographically, Nanyang (NY), Shanglian (SL) and Huamei (HM) located in the north, southeast and southwest of Guiyu, respectively. Five sites in every district were designed. Yaocuowei (YCW) village and Longmen (LM) village，which bordered on the northwestern of Guiyu, were also EWs disposal area, so 2 sites in YCW and 1 site in LM were designed. A total of 18 soil sites in EWs disposal area were monitored. Two background sites called Fushan village (FS) and Yaocuowei village (YCW) located in the northern of Guiyu, they were on the windward direction of Guiyu and away from EWs disposal area. The map of Guiyu and sampling sites were shown in Figure1. Each sampling site consisted of five sub-sites in an area of 10×10 m^2, the top soil at a depth of 0-20 cm was collected with a stainless steel shovel. Soil was air dried at room temperature, sub-sites samples were mixed thoroughly and sifted through a 60-mesh sieve, the homogeneous samples were stored in brown glass jar at -20℃ until analyses.

Analysis processes

20 g soil was spiked with ^{13}C-labelled standards (EDF 5382) and extracted by ASE with toluene, the extract was filtered through anhydrous sodium sulfate and exchanged solvent to hexane. A multi-layer silica gel column was packed from bottom to top with 2 cm height anhydrous sodium sulfate, 0.5 g silica gel, 2 g 2% potassium hydroxide-impregnated silica gel, 3 g 44% sulfuric acid-impregnated silica gel, 4 g 22% sulfuric acid-impregnated silica gel, 0.5 g silica gel and 2 cm height anhydrous sodium sulfate. The packed column was preconditioned with 100 mL n-hexane, the concentrated extract was applied to the column, the n-hexane eluate

200 mL was collected and concentrated. Then 1 g active carbon-impregnated silica gel column was used to separate interfering material, DCM/hexane (1/3, v/v) 200 mL and toluene 200mL were used to elute the column sequentially. Toluene fraction containing PBDD/Fs was collected and concentrated to dryness under a gentle nitrogen stream, the injection standard (EDF 5383-4X) was spiked, and the sample redissolved volume was 50 µL decane for analysis.

A HRGC/HRMS (Agilent 6890N/Waters Autospec Ultima NT) with a DB-5HT column (15 m×0.25 mm×0.1 µm) was used to determine twelve 2,3,7,8-PBDD/Fs, i.e. 2378-TBDF, 12378-PeBDF, 23478-PeBDF, 123478-HxBDF, 1234678-HpBDF, OBDF, 2378-TBDD, 12378-PeBDD, 123478-HxBDD, 123678-HxBDD, 123789-HxBDD, OBDD. GC injection mode was pulse splitless, injection volume was 1 µL. The initial flow was set at 4.2 ml/min within 0.8 min, and the final flow was 0.8 ml/min after 0.8 min. The temperature program of oven were as follow: 130℃ (held for 2 min), increased at 30℃/min to 230℃, then increased at 10℃/min to325℃ (held for 3 min). HRMS was equipped with an EI+ source, electron energy and trap current were 35eV and 650µA, ion accelerating voltage was 8000V. HRMS resolution was above 10000 (10% peak valley definition). The temperatures of inlet, source and interface were 270℃, 250℃ and 270℃, respectively.

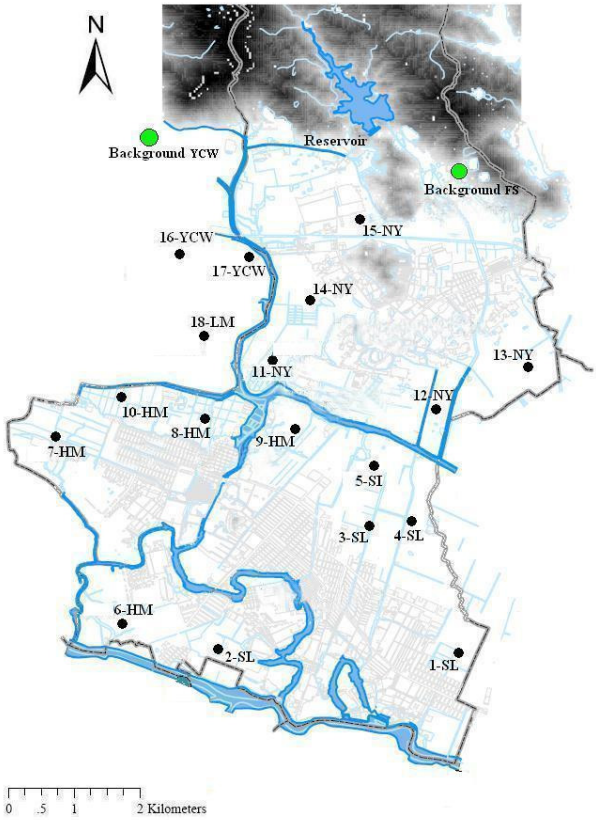

Figure1 Map of Guiyu and sampling sites

Results and discussion

I-TEQ of PBDD/Fs in farmland soil of Guiyu

Only twelve 2,3,7,8-PBDD/Fs congeners were quantified because of limitation of standard compounds, it was suggested by WHO that the I-TEFs of PCDD/Fs could be applied to calculate I-TEQ of the corresponding brominated congeners, based on their similar toxicity[5]. I-TEQ of PBDD/Fs in 18 EWs disposal area soil were 3.1-25.9 pg TEQ/g, and the levels in background FS and YCW were 0.7 and 1.1 pg TEQ/g, respectively. Figure2 showed I-TEQ of PBDD/Fs and PCDD/Fs in Guiyu soil, PBDD/Fs levels in SL district were commonly higher than that of the other areas, which were similar as the trend of PCDD/Fs[4]. This might be attributed to regional division of EWs disposal manner in Guiyu, some specific disposal manner only prevailed in particular district in

Guiyu, SL district majored in melting of plastic, open burning and acid leaching of EWs scrap; HM district prevailed roasting of circuit board; The north of Guiyu (NY district, YCW and LM villages) pursued manual disassembly and shredding of EWs. SL district was a typical EWs combustion area, so PBDD/Fs and PCDD/Fs were higher than other areas. The guidelines of PCDD/Fs in agricultural soil stipulated by the Netherlands and Germany were 1 and 5 pg I-TEQ/g, considering the similar toxicity, PBDD/Fs in farmland soil of Guiyu had exceed guidelines.

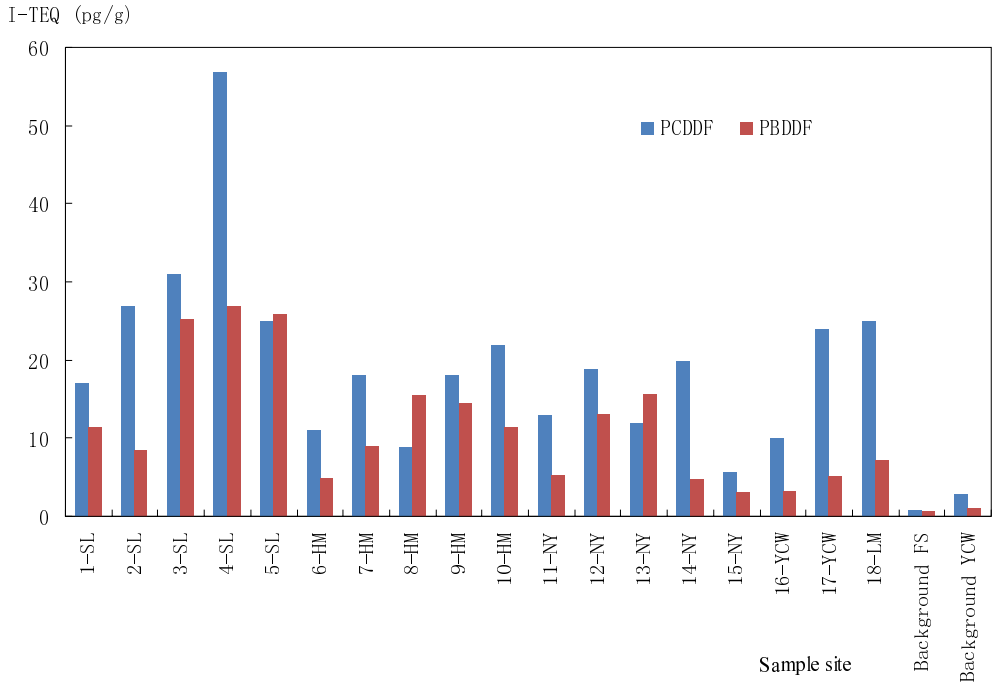

Figure2 I-TEQ of PCDD/Fs and PBDD/Fs in farmland soil of Guiyu

Congeners profiles of PBDD/Fs in farmland soil of Guiyu

The mass concentration of twelve 2,3,7,8-PBDD/Fs were normalized to summation, as shown in Figure3, the congeners profiles in most of samples were characterized by: (1) PBDFs were much more abundant than PBDDs; (2) 1234678-HpBDF and OBDF were the dominant congeners, accounting for 23-79% and N.D.-70% of the total concentrations, respectively; (3) Tetra- to hexa-BDFs were all detected, 2378-TBDF and 123478-HxBDF were relatively abundant; (4) PBDDs were only detected 2378-TBDD and OBDD, the other BDDs were lower than the detection limit. The sample 13-NY showed a different profile from the others, 12378-PeBDF was the dominant congener. Two background sites didn't be discussed since their low PBDD/Fs levels and N.D. for most of congeners. For PBDD/Fs source identification, most of the studies proved that PBDD/Fs were relevant to bromic wastes combustion or impurity of BFRs, Wang *et al.*[6] investigated PBDD/Fs in stack flue gases, bottom ashes and fly ashes of municipal solid waste incinerators (MSWIs), the major congeners were 1234678-HpBDF and OBDF. Ren *et al.*[7] presented PBDD/Fs concentrations and distributions in commercial decabromodiphenyl ether (DBDE) mixtures as impurities, OBDF was the dominant congener, followed by 1234678-HpBDF; OBDD and 123478-HxBDF were also detectable. In present study, most of the samples in Guiyu had similar congeners profile as above studies, a preliminary conclusion that PBDD/Fs in Guiyu were derived from EWs thermal disposal could be drawn. Open burning of EWs resulted in combustion of BFRs, and roasting of circuit board released PBDEs directly, PBDD/Fs sources could be traced to these disposal processes. The sample 13-NY might be influenced by other potential source, since its different congener profile from other samples. The relationship between PBDD/Fs and EWs disposal manner should be studied further, and the other potential sources of PBDD/Fs deserved to trace.

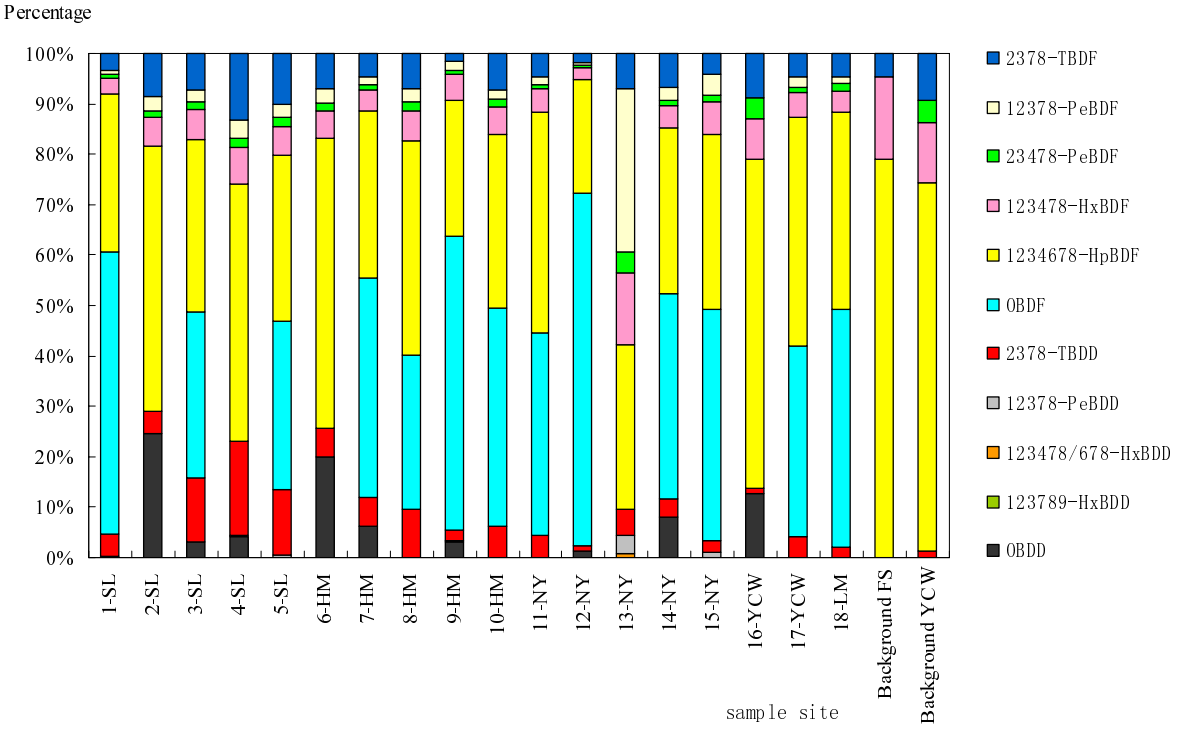

Figure3 Mass concentration profiles of PBDD/Fs congers in farmland soil of Guiyu

Acknowledgements

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