

# A Purification Method for 10 Polybrominated Diphenyl Ethers in Soil Using Accelerated Solvent Extraction-Solid Phase Extraction



XIANG Lei-Lei<sup>1,2</sup>, SONG Yang<sup>2</sup>, BIAN Yong-Rong<sup>2</sup>, SHENG Hong-Jie<sup>2</sup>, LIU Guang-Xia<sup>2</sup>, JIANG Xin<sup>2</sup>, LI Guo-Hua<sup>1,\*</sup>, WANG Fang<sup>2,\*</sup>

<sup>1</sup> Jiangsu Key Laboratory of Pesticide Science, College of Science, Nanjing Agricultural University, Nanjing 210095, China

<sup>2</sup> State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

**Abstract:** An optimized method was established for the determination of 10 polybrominated diphenyl ethers (PBDEs) in soil using gas chromatography coupled with electron capture detector (GC-ECD). Accelerated solvent extraction (ASE) was used to extract 10 PBDEs from soil and a comparative study on 4 kinds of extraction systems (*i*-hexane, *i*-hexane-acetone (4:1, *V/V*) *n*-hexane-acetone (1:1, *V/V*), *n*-hexane-dichloromethane (1:1, *V/V*)) was conducted to obtain an optimal extraction effect of PBDEs. The purification of 10 PBDEs in soil solution was completed by solid phase extraction (SPE). Ten kinds of SPE columns with different filters were applied to the purification process. The optimized conditions were acquired using the extraction system of *n*-hexane-acetone (4:1, *V/V*) and purification with acid silica gel column. Under the optimized conditions, the average recoveries of 10 PBDEs in soil ranged from 85.4% to 103.1% with the RSDs of 1.7%–4.6%. Method detection limits (MDLs) were 0.04–0.22 ng mL<sup>-1</sup>. The method was simple, rapid and efficient, and quite feasible for the determination of the 10 PBDEs in contaminated soil.

**Key Words:** Soil; Polybrominated diphenyl ethers; Accelerated solvent extraction; Solid phase extraction

## 1 Introduction

Polybrominated diphenyl ethers (PBDEs), as a class of brominated flame retardants (BFRs), are widely used in electronics, textiles, building materials, furniture and other industrial products. PBDEs are known as persistent organic pollutants (POPs) due to their high lipophilicity, persistence and bioaccumulative properties. PBDEs are resistant to degradation, easy to be adsorbed in the particulate matters and sediments, and can conduct long-term migration<sup>[1]</sup>. Trace PBDEs in air, water and soil are harmful to human health through food chain, and can cause worldwide pollution by "grasshopper effect"<sup>[2]</sup>. Furthermore, toxicological studies indicate that PBDEs may cause liver and thyroid toxicity<sup>[3–7]</sup>

in humans and in wildlife since they are proved to have endocrine disrupting properties<sup>[7–9]</sup>. Meanwhile, they may have a potential carcinogenicity<sup>[10]</sup>.

At present, the known methods for the extraction of PBDEs in soil include Soxhlet extraction<sup>[11–13]</sup>, ultrasonic-assisted extraction<sup>[14]</sup>, microwave-assisted extraction, accelerated solvent extraction<sup>[13–19]</sup>, *etc.* Soxhlet extraction is a time-consuming method with a high organic solvent consumption. Ultrasonic-assisted extraction and microwave-assisted extraction can shorten extraction time and reduce solvent, but the extractions are uncomplete<sup>[11]</sup>. Accelerated solvent extraction (ASE) has the advantages such as simple operation, high extraction efficiency, high speed, and low organic solvent consumption. As a time-saving, safe and

Received 17 October 2015; accepted 6 January 2016

\*Corresponding author. Email: liguohua@njau.edu.cn; wangfang@issas.ac.cn

This work was supported by the National Natural Science Foundation of China (Nos.21277148, 41271464), the Natural Science Foundation of Jiangsu Province for Distinguished Young Scholars, China (No. BK20150050), the Major State Basic Research Development Program of China (No. 2014CB441105), and the Natural Science Foundation of Jiangsu Province, China (No. BK20131463).

Copyright © 2016, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. Published by Elsevier Limited. All rights reserved.

DOI: 10.1016/S1872-2040(16)60929-5

automating method, ASE was widely applied in the analysis of pesticide residues, polychlorinated biphenyl (PCBs), polycyclic aromatic hydrocarbons (PAHs) and PBDEs, etc.<sup>[12,14,16,19,20]</sup>.

As the well-known environmental contaminants, different environmental monitoring programs were established to detect traces of PBDEs. SPE sample pretreatment technique has the advantages such as high efficiency, high selectivity, fast convenience, and has been widely applied in the pretreatment of environmental sample analysis<sup>[21–27]</sup>. At present, the purification process of PBDEs in soil is relatively complicated. The amount of organic solvent is relatively large, the sensitivity is relatively low, and the reproducibility is relatively poor<sup>[14,28,29]</sup>. The key of efficiency, good recovery and reproducibility is how to choose an appropriate packing of SPE. In this experiment, the solid phase extraction (SPE) technique was applied to the purification of soil samples. Hence, this work focused on the optimized ASE extraction and SPE purification, and combined with gas chromatography with electron capture detector (GC-ECD) to build an efficient, fast PBDEs analysis method in soil with high sensitivity and low detection limit.

## 2 Experimental

### 2.1 Standards and chemicals

*n*-Hexane, acetone and dichloromethane (DCM) purchased from Merck (Germany) were of HPLC grade. Kieselguhr was purchased from Fluka (100–200 mesh, USA). Florisil was purchased from TEDIA (60–100 mesh, USA). Anhydrous sodium sulfate, alumina (100–200 mesh), silica gel (100–200 mesh), quartz sand, and concentrated sulfuric acid (pure analysis) were purchased from Sinopharm chemical reagent company (China). 4,4'-Dibrominated diphenyl ether (BDE-15), 2,4,4'-Tribrominated diphenyl ether (BDE-28), 2,2',4,4'-tetrabrominated diphenyl ether (BDE-47), 2,2',3,4,4'-pentabrominated diphenyl ether (BDE-85), 2,2',4,4',5-pentabrominated diphenyl ether (BDE-99), 2,2',4,4',6-pentabrominated diphenyl ether (BDE-100), 2,2',4,4',5,5'-hexabrominated diphenyl ether (BDE-153), 2,2',4,4',5,6'-hexabrominated diphenyl ether (BDE-154), and 2,2',3,4,4',5,6'-heptabrominated diphenyl ether (BDE-183) were all purchased from Accustandard (New Haven, CT, USA). Deionized water was used in this experiment.

### 2.2 Samples collection

The blank soil was Hainan red soil, the contaminated soil was brown soil. All samples were collected from 0–20 cm surface soil, followed by drying, removal of debris, fine roots and stones, and through 20 mesh sieve. The treated samples were stored in –20 °C refrigerator till to be used.

### 2.3 Instrumental analysis

PBDEs analysis was carried out on an Agilent 6890 gas chromatograph (Agilent Technologies, USA) with ECD. The chromatographic conditions were as follows. The column was a DP-5 capillary column (30 m × 0.25 mm × 0.25 μm, Agilent). Nitrogen (purity 99.999%) was employed as carrier gas at constant column flow of 2.0 mL min<sup>-1</sup>. The detector temperature was set at 298 °C. The injector temperature was held at 265 °C, the injection volume was 1 μL, and the injection was performed in the splitless mode. The GC oven temperature was programmed from 140 °C (2 min) to 180 °C at 5 °C min<sup>-1</sup>, from 180 °C (5 min) to 265 °C (5 min) at the rate of 5 °C min<sup>-1</sup>, from 265 °C (5 min) to 315 °C (10 min) at the rate of 15 °C min<sup>-1</sup>.

Standard mixtures of PBDEs at concentration of 10, 25, 50, 100, 250, 500 ng mL<sup>-1</sup> were prepared and identified by GC. A standard curve was drawn with the injection concentration as an abscissa and the peak area as an area ordinate. The limits of detection (LOD) for the ten PBDEs congeners were defined as the signal-to-noise ratio of 3 (*S/N* = 3).

### 2.4 Sample extraction

Four commonly used fillers in laboratory (silica, kieselguhr, florisil and alumina (Al<sub>2</sub>O<sub>3</sub>)) and three modified fillers (acid silica, acid kieselguhr and acid florisil, obtained by modifying method with concentrated sulfuric acid) were used for the SPE columns. All SPE columns were packed with spacer, 0.5 g of anhydrous sodium sulfate, filler, 1 g of anhydrous sodium sulfate and spacer (bottom-up). Based on single and complex combinations of different fillers, we prepared a total of 10 kinds of SPE columns (Table 2).

The column that was activated with 5 mL of *n*-hexane, and 40 μL of standard mixture of PBDEs (1000 ng mL<sup>-1</sup>) was added into the column, then eluted with 1 mL of *n*-hexane. The steps above were repeated until the total volume of eluate up to 18 mL. The eluate was then dried under a gentle stream of nitrogen, dissolved in 500 μL of *n*-hexane, and analyzed by GC. An eluate curve was drawn with the eluate volume as an abscissa and the total recovery as an area ordinate.

### 2.5 Accelerated solvent extraction

All soil samples were extracted using an ASE200 accelerated solvent extraction (ASE) system with stainless extraction cells (22 mL) from Thermo Scientific (Waltham, MA, USA). Approximately 1.0 g of soil sample and 40 μL of standard mixtures of PBDEs (1000 ng mL<sup>-1</sup>) were added to 2 g of kieselguhr and homogenized, then transferred to a 22-mL cell. The oven temperature was set at 100 °C and the pressure was set to 1500 psi. The extraction process was as follows. The extract was firstly heated for 5 min, then static extracted

Download English Version:

<https://daneshyari.com/en/article/1182533>

Download Persian Version:

<https://daneshyari.com/article/1182533>

[Daneshyari.com](https://daneshyari.com)