



# Method for the purification of polybrominated diphenyl ethers in sediment for compound-specific isotope analysis

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## ABSTRACT

A purification method for lower polybrominated diphenyl ethers (PBDEs, from tri- to hexa-BDE) in sediment for compound-specific isotope analysis (CSIA) was developed in this study. The compounds were extracted using a Soxhlet apparatus with addition of activated alumina and Florisil in the paper tube during the Soxhlet extraction provided for less complex extracts. Then, the extract was isolated from polar compounds using a multi-layer silica gel column, separated into different fractions using alumina/silica (Al/Si) gel columns and finally purified using a Florisil column. The mean recoveries of the major PBDE congeners in the spiked samples ranged from 76.2% to 82.4%. The purity of the samples was verified by GC–MS in full scan mode. The stable isotopic integrity of the spiked samples after the purification was tested by comparing the stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of the processed and the unprocessed standard materials. The differences in the  $\delta^{13}\text{C}$  values for each compound between the processed and unprocessed standards were less than 0.5‰, with the exception of BDE100 (0.54‰). Finally, the purification and isotope analysis method was successfully applied to measure the  $\delta^{13}\text{C}$  of PBDEs in sediments. This application of the method indicated that CSIA seems to be a promising method for providing intrinsic characteristics for further environmental fate studies of PBDEs.

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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been heavily used as flame retardants in consumer products since 1970s [1]. PBDEs are seeded, but are not covalently bound, into polymer matrices. Thus, they can easily escape into the environment. PBDEs have been detected ubiquitously in the environment (i.e., aerosol, water, sediment, biota, and humans) [2–6]. Increasing scientific evidence has shown that PBDEs tend to be persistent in nature, and toxic to both fauna and humans [7–9]. Due to increasing international concerns, PBDE production has been banned throughout Europe, Asia, and United States [10]. The regulation of PBDEs resulted in a decline in their environmental concentrations on a large-scale [11]. However, PBDEs are still serious pollutants due to the existing stocks remaining in service and in landfills. Sediments are the main reservoir for PBDEs because of their high hydrophobicity and relatively low volatility [12].

Studies have shown that PBDEs undergo long-range environmental transport and potential photochemical and biological degradation in water, soil, and sediments [13–15]. Therefore, a specific PBDE congener in the sediment can be (i) an accumulated

contaminant from nearby, (ii) from remote regions or (iii) the product of the debromination of higher-brominated congeners. Conventional methods for the determination of PBDEs, however, are generally based on the measurement of their composition and concentration in a matrix. These methods make it impossible to elucidate the source of the individual PBDE congeners. Consequently, it is imperative to explore a sensitive and reliable analytical method for environmental studies of PBDEs.

The analysis of the stable isotope composition of individual organic compounds is a useful tool for source definition and assessing the degradation of pollutants because of the unique stable isotopic compositions for different sources and the isotopic fractionation that occurs during degradation [16,17]. Compound-specific isotope analysis (CSIA) using gas chromatography in combination with isotope ratio mass spectrometry (GC–C-IRMS) relies on conventional gas chromatography to separate the target compounds prior to their conversion to  $\text{CO}_2$  as determined by isotope ratio mass spectrometry. CSIA analysis requires that there is no interference from co-elution and no unresolved complex mixtures (UCM). Environmental samples, such as sediments, are complex matrices that can contain a large number of compounds that may co-elute with the analytes and disturb the isotope ratio analysis. Therefore, exploring a refined purification method to produce high-purity extracts is crucial for the accurate and precise analysis of isotope composition.

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Typical purification procedures used for the separation of PBDEs in environmental samples include gel permeation chromatography, silica gel and alumina with varying degrees of activation [18,19]. These purification methods, however, are normally designed for quantification analysis. To the best of our knowledge, few purification methods used for CSIA of semi-volatile organic compounds have been developed [20,21].

The objective of this study was to develop an effective purification method of PBDEs in sediments for CSIA. The purity of the extracts was verified by GC–MS in full scan mode, the stable carbon conservation was confirmed by GC–C–IRMS using spiked samples, and the purification and isotope analysis method was used to analyze sediment samples that were collected from a natural pond in an electronic waste (e-waste) recycling site.

## 2. Methods

### 2.1. Chemicals and materials

Technical Penta-BDE mixture (DE-71) was acquired from Wellington Laboratories Inc. Dichloromethane (DCM) and *n*-hexane (HEX) were both HPLC grade. Acetone (AR, distilled before use) was purchased from Tianjing Chemical Reagent Factory, China. Guaranteed reagent grade concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and anhydrous sodium sulfate were purchased from Guangzhou Chemical Reagent Factory, China.

Silica gel (80–100 mesh, Qingdao Oceanic Chemical Factory, China) and neutral alumina (100–200 mesh, Jiangsu Wuxi Chemical Reagent Company, China) were Soxhlet extracted for 72 h in DCM. The neutral silica gel was heated to 180 °C for 12 h, cooled to room temperature, then deactivated with 3% (w/w) distilled water before being preserved in HEX. The sulfuric acid silica gel used in the study was the deactivated neutral silica impregnated with 44% concentrated sulfuric acid (w/w) preserved in HEX. Alumina was heated to 250 °C for 12 h, cooled to room temperature, deactivated with 3% distilled water (w/w) and preserved in HEX. The silica gel column (i.d.=1.0 cm) was packed with 8 cm of neutral silica and 16 cm of sulfuric acid silica and was topped with a 1-cm layer of anhydrous sodium sulfate. The Al/Si gel column (i.d.=1.0 cm) consisted of 12 cm of neutral silica and 6 cm of alumina and was topped with a 1-cm layer of anhydrous sodium sulfate. Both varieties of column were pre-eluted using HEX (30 mL) to remove the background contaminants in the columns.

Florisil (60–100 mesh) was obtained from Sigma-Aldrich Laborchemikalien GmbH (USA). Florisil was activated at 650 °C for 6 h, cooled to room temperature, deactivated with 3% (w/w) distilled water and preserved in HEX. The Florisil column (i.d.=1.0 cm) was packed with 18 cm Florisil and was pre-eluted using HEX (30 mL) before use.

Sediments ( $n=6$ ) were collected in 2011 from a natural pond located in an e-waste recycling region in Qingyuan county, Guangdong province, South China. This pond has been contaminated by e-waste discarded by surrounding e-waste recycling workshops. Three ( $n=3$ ) lake sediment samples were also prepared as spiked matrices.

### 2.2. Clean-up and fractionation

The procedure to separate and purify PBDEs from extracts for stable carbon isotope ratio analysis is shown in Fig. 1. Sediment samples were freeze-dried, ground, and homogenized. The samples (~90 g) were placed into an extraction cell in which 12 g of activated alumina and 6 g of Florisil were added. Extraction cells were Soxhlet extracted with HEX/acetone (1/1, v/v) for 24 h.

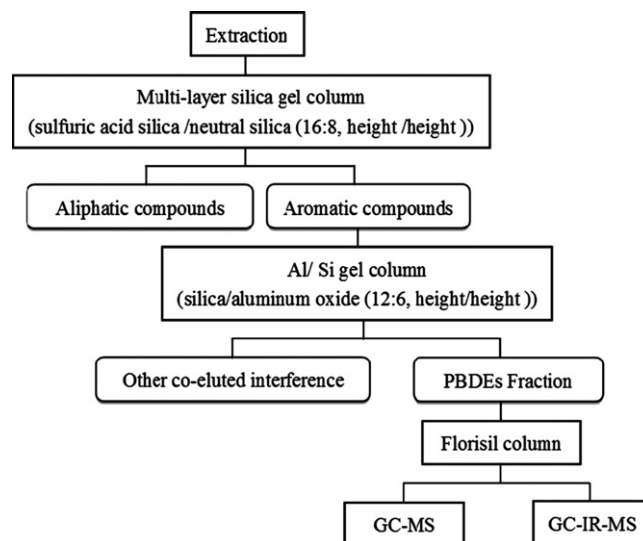


Fig. 1. Extraction and purification procedures for compound-specific isotope analysis of PBDEs in sediment.

Activated copper granules were added to the flasks for sulfur elimination. The extracts were concentrated and transferred to the top of the silica gel column. The first elution of the silica column with 10 mL HEX/DCM (1/1, v/v) was discarded, and the aromatic compounds were obtained by eluting with 15 mL HEX/DCM (1/1, v/v). The aromatic compound fraction was further purified by the Al/Si gel column. The interfering compounds were eluted with 20 mL of HEX, and PBDEs were collected in the second fraction eluted with 10 mL HEX. The fraction containing the PBDEs collected from the Al/Si gel column was subjected to further separation by a Florisil column. The column was first eluted with 10 mL of HEX. The PBDEs were obtained in the fraction eluted with the subsequent 20 mL HEX. This fraction was concentrated to a volume of 50  $\mu$ L by evaporating the HEX solvent.

### 2.3. PBDE quantification

One tenth of the extracts were used to measure PBDE concentrations. The analysis of PBDEs, including sample clean-up and instrumental analysis, was performed following the procedure described by Mai et al. [22]. The remaining extracts were used to perform CSIA.

Before the CSIA, the purity of the extracts was analyzed by GC–MS (Agilent 7890A/5975B MSD; Agilent Technologies, CA) with an electron impact ion source in full scan mode. GC separation was performed using a DB-5MS capillary column (60 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). The initial oven temperature was held at 70 °C for 1.5 min, increased to 230 °C at 30 °C/min, then increased to 270 °C at 4 °C/min (held for 1 min), followed by an increase to 280 °C at 5 °C/min (held for 0.5 min), and finally to 310 °C at 5 °C/min (held for 30 min). The individual PBDE congeners were identified on the basis of the comparison of both the mass spectra and the retention times of the target compounds with the penta-BDE standard. The GC–MS chromatogram of the extract is shown in Fig. S1 (Supporting information).

### 2.4. Compound specific isotope analysis (CSIA)

Stable carbon isotope analysis of individual PBDEs was performed using an Agilent 6890 gas chromatograph coupled to a GV Isoprime isotope ratio mass spectrometer (GV Instruments UK) via a modified GC combustion interface. Samples were injected at

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