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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 ($\delta^{13}C$) of the processed and the unprocessed standard materials. The differences in the $\delta^{13}C$ 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 $\delta^{13}C$ 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 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_2SO_4) 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. 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 μL by evaporating the HEX solvent.

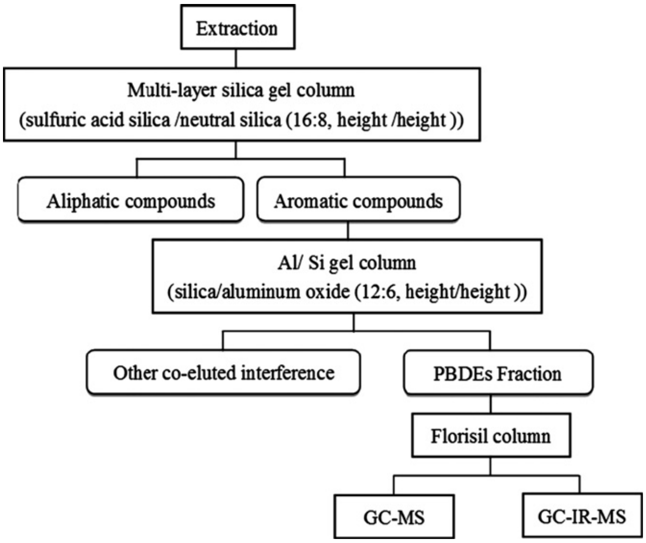

Fig. 1. Extraction and purification procedures for compound-specific isotope analysis of PBDEs in sediment.

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 × 0.25 mm i.d. × 0.25 μm 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

290 °C in the splitless mode (split opened after 1 min). The carrier gas was helium at a constant flow of 1.5 mL/min. Analytes were separated on a DB-5 MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The oven temperature program was set to start at 110 °C (held for 1 min), increase to 200 °C at 8 °C/min (held for 1 min), then increase to 240 °C at 3 °C/min (held for 2 min), followed by an increase to 280 °C at 5 °C/min (held for 10 min), and finally increased to 310 °C at 10 °C/min (held for 10 min). The combustion interface temperature was 940 °C throughout the course of the experiment. For calculation purposes, CO_2 reference gas was automatically introduced into the isotopic ratio mass spectrometer in a series of pulses at the beginning and end of each run. The carbon isotopic compositions are reported in the delta (δ) notation

$$\delta^{13}\mathrm{C}\ (‰) = ((R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1) \times 1000$$

where R_{sample} and R_{standard} are the $^{13}C/^{12}C$ ratios of the sample and reference standard Vienna Pee Dee Belemnite (V-PDB), respectively. The reliability of IRMS was verified by injecting a standard mixture at the beginning of the samples analysis containing 10 *n*-alkanes with known isotopic composition (provided by University of Indiana, Bloomington, USA). The stability of the system was tested daily, and the performance of the GC-C-IRMS system was tested regularly by analyzing the penta-BDE standard. The $\delta^{13}C$ values of each of the individual BDE congeners differed by less than 0.5‰ throughout the entire instrument analysis period. Each extract was analyzed in triplicate, and the data were only considered if the $\delta^{13}C$ values of the three injections varied by less than 0.5‰.

3. Results and discussion

3.1. Selection of proper purification procedures and developing system

The extract can be an extraordinarily complex matrix for sediment samples. With the goal of producing less complex extracts, activated alumina and Florisil were added in the paper tube during the Soxhlet extraction reference from the matrix solid-phase dispersion [23]. A fraction of the interfering compounds was thought to be partially retained on the alumina and Florisil sorbent particles. The partial retention of these compounds served to reduce the complexity of the extract and aid in the clean-up of the sediment. The weight of the total extracted organic matter was reduced by 9 ± 2% when sorbents were added in the paper tube. The color of the extract from the modified extraction (with sorbents) was lighter than the color of the traditional extraction. When the extracts were treated with the same volume of concentrated sulfuric acid, a complete emulsification was observed for the traditional extract method, but little sign of emulsion was found for the modified extraction method. These results do indicate that the interfering compounds were preferentially retained by the alumina and Florisil adsorbents.

The extracts were too dirty to allow direct analysis of the PBDEs. According to the clean-up method in our previous study [24], the extracts were initially treated using a silica gel column packed with sulfuric acid silica and neutral silica (16 cm:8 cm) to eliminate polar compounds. A mixture of HEX/DCM (25 mL, 1/1, v/v) was used as the eluting solvent to recover the PBDEs. The recovery of the PBDEs was nearly 100% when the elution test was conducted using penta-BDE mixtures (Table 1). After clean-up by the silica column, the extracts were clean enough for direct injection into the GC–MS for quantitative analysis. A test by GC–MS in full-scan mode indicated that the extracts suffered from interference of co-extracts. A large hump due to an UCM was observed (Fig. 2A).

The sample extracts were further purified using Al/Si columns. Aromatic compounds can be separated from aliphatic hydrocarbons and other polar components using an Al/Si column [20]. An elution test was conducted using penta-BDE mixture as standard and HEX as eluting solvent to determine the necessary volume of eluting solvent. The result showed that PBDEs were recovered in the second (10–20 mL) and the third (20–30 mL) 10 mL HEX fractions, with a majority of the eluting taking place in the third

Table 1
Elution test of silica (multi-layer silica gel column), Al/Si (Al/Si gel column), and Florisil (Florisil column) to recover PBDEs.

Sorbent	Compound	Fraction volume				
Silica		0–5 mL[a]	5–10 mL[a]	10–15 mL[a]	15–25 mL[a]	25–30 mL[a]
	BDE28			83.4	16.6	
	BDE47			83.9	16	0.1
	BDE99			85.5	14.4	0.1
	BDE85			83.5	16.5	
	BDE100			85.4	14.6	
	BDE154			87.1	12.9	
	BDE153			87.8	12.2	
Al/Si		0–10 mL[b]	10–20 mL[b]	20–25 mL[b]	25–30 mL[b]	0–15 mL[a]
	BDE28			64.1	35.9	
	BDE47		1.3	64.4	33.4	1.1
	BDE100		15.6	84.4	0	
	BDE99		6.8	75.5	17.6	
	BDE85			49.5	50.5	
	BDE154		21.7	74.2	4.1	
	BDE153		14.6	85.4	0	
Florisil		0–5 mL[b]	5–10 mL[b]	10–30 mL[b]	30–35 mL[b]	35–50 mL[b]
	BDE28			91.6	8.4	
	BDE47			89.1	8.4	2.5
	BDE100			97.8	2.1	0.1
	BDE99			97.3	2.5	0.3
	BDE85			85.8	8.5	5.7
	BDE154			100		
	BDE153			100		

[a] HEX/DCM (1/1, v/v).

[b] HEX; experiments were carried out in duplicate ($n=3$).

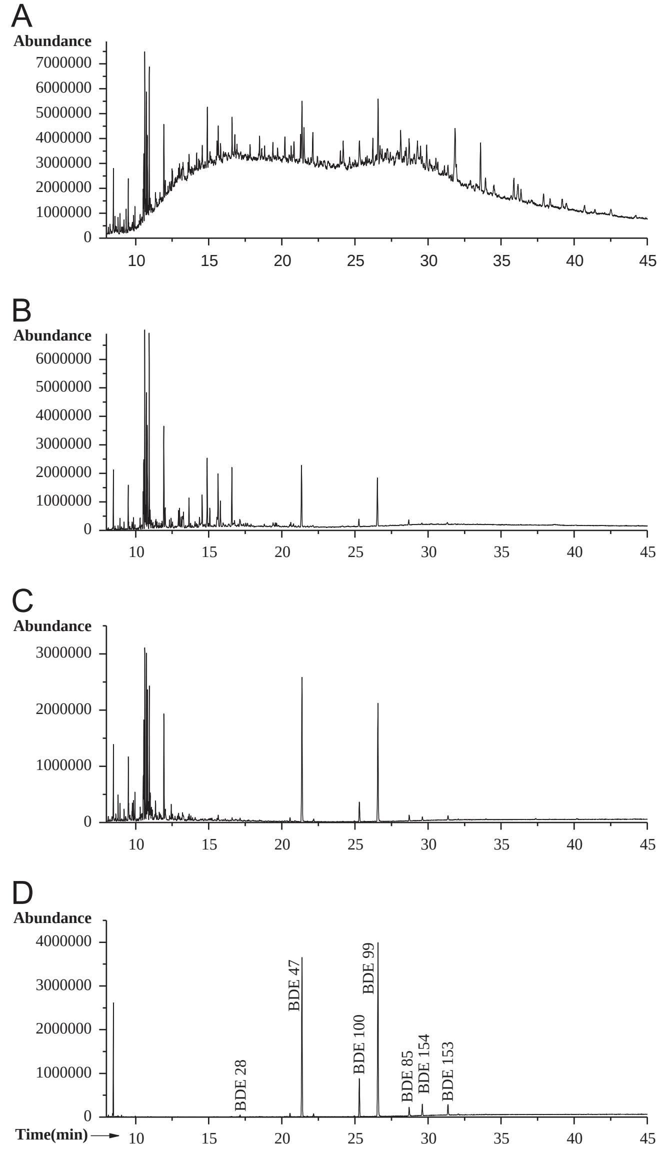

Fig. 2. Full scan GC–MS chromatograms of spiked samples after each clean-up step. A: Multi-layer silica gel column; B: Al/Si gel column; C: Florisil column, and D: the penta-BDE mixture standard.

10 mL fraction (Table 1). To eliminate the most possible interference compounds, only the third 10 mL was collected when performing purification using the Al/Si column. The purity of the extracts after being treated by Al/Si column chromatography was analyzed by GC–MS in full scan mode and the chromatogram is shown in Fig. 2B. The hump due to interference compounds disappeared and most aliphatic hydrocarbons such as normal alkanes, linear alkylbenzene, and others that could be detected in the first purified extract were undetectable. However, there was still some co-elution interference with PBDEs and the retention times of some compounds were very close to those of PBDE congeners (Fig. 2B). Additionally, the baseline was still too high to perform CSIA.

A further purification step using Florisil was carried out. HEX was selected as the eluting solvent. No PBDE congeners were detected when the column was eluted with 10 mL HEX, but all of the PBDEs were eluted between 10 and 30 mL Hex, and the recoveries of the PBDEs were greater than 85% (Table 1). The purity of the isolated compounds was confirmed by the full scan GC–MS analysis. As shown in Fig. 2C, the peak resolution was improved and the baseline sharply decreased after the Florisil step. The GC–MS chromatogram of the major PBDE congeners in the spiked samples (Fig. 2C) was very similar to those of the penta-BDE mixture (Fig. 2D). There were also similarities between the mass spectra of the major PBDE congeners in spiked samples and the penta-BDE mixture (in Supporting information, Fig. S2), indicating that there was minimal interference from co-eluting compounds.

3.2. *Recoveries of the method and the accuracy and precision of CSIA*

The absolute recoveries for the entire clean-up method were evaluated using the spiked matrix (1 mg/mL added for the penta-BDE mixture) and the spiked blanks. The recoveries of all the PBDE congeners of interest in the spiked blanks and the spiked matrices were calculated by comparing the peak areas of the spiked samples to those of the penta-BDE standards (Table S1). The average recoveries of seven PBDE congeners were in the range between 76.2 ± 0.2% (BDE85) and 82.4 ± 0.2% (BDE100) for the spiked matrices and in the range between 72.0 ± 3.8% (BDE85) and 84.8 ± 2.1% (BDE28) for the spiked blanks.

Ensuring that no modification in the isotopic composition occurred during the purification was very important for the accurate and precise analysis of isotopic compositions. The $\delta^{13}C$ values of the penta-BDE mixture after (processed standard materials) and before (unprocessed standard materials) the purification procedures are presented in Table 2. The $\delta^{13}C$ values of seven congeners in the penta-BDE mixture were between −31.10‰ and −24.19‰ and the standard deviation (S.D.) range was from 0.05‰ to 0.78‰ (Table 2). As anticipated, the higher the degree of bromination, the more negative the $\delta^{13}C$ values became. This change in $\delta^{13}C$ is consistent with the previous report [25]. The differences in $\delta^{13}C$ values for individual congeners between the processed and unprocessed standards were in the range of 0.04‰ to 0.54‰. All of the deviations, except for BDE100, were less than 0.5‰, demonstrating a stable isotopic conservation throughout the purification procedure.

3.3. *Application to environmental samples*

The purification and isotope analysis method was used to analyze sediment samples collected from an e-waste contaminated pond to verify the utility of this method. The sediments in this pond have extremely high PBDE levels, as reported in our previous studies [26]. PBDEs were extracted from six sediment samples and then combined to form two composite samples to obtain enough PBDEs for CSIA.

The PBDE concentrations ranged from 3000 to 3700 ng/g of sediment dry weight. BDE209, BDE183, BDE99, BDE47 were the main congeners in the sediment, accounting for 64.9%, 6.8%, 3.5%,

Table 2
Average $\delta^{13}C$ values of the PBDEs congeners in the unprocessed standard material and the processed standard material (‰).

Congener	Unprocessed standard material		Processed standard material		
	$\delta^{13}C$(‰)	S.D. (n=3)	$\delta^{13}C$(‰)	S.D. (n=3)	$\Delta\ \delta^{13}C$
BDE28	−24.19	0.78	−24.58	0.38	−0.39
BDE47	−26.19	0.16	−25.95	0.14	0.24
BDE100	−27.27	0.02	−26.73	0.46	0.54
BDE99	−28.58	0.04	−28.46	0.22	0.12
BDE85	−31.10	0.48	−30.63	0.41	0.47
BDE154	−31.05	0.45	−30.95	0.35	0.10
BDE153	−31.26	0.05	−31.30	0.38	−0.04

$\Delta\delta^{13}C$ (‰)=$\delta^{13}C$ (‰)$_{\text{processed standard material}}$−$\delta^{13}C$ (‰)$_{\text{unprocessed standard material}}$, S.D.: standard deviation.

and 3.1% of the total PBDEs. In our preliminary experiment, BDE183 and BDE209 were difficult to combust in the oxidation tube. BDE209 can also thermally degrade when performing GC–MS analysis, especially when using a long capillary column [27]. Therefore, only lower brominated congeners were analyzed for stable carbon isotopic compositions. Stable carbon isotopic composition can be accurately determined for three congeners (BDE47, BDE99, and BDE100). Nevertheless, it was still valuable to conduct CSIA for sediment samples because these three BDE congeners are the most frequently detected PBDE congeners in environmental samples [1]. The δ^{13}C values in the samples were -23.91 ± 0.21‰ for BDE47, -27.54 ± 0.76‰ for BDE100 and -29.96 ± 1.8‰ for BDE99. The δ^{13}C values of BDE100 and BDE99 were more negative than the values of BDE47 in the sediments, which was in good agreement with the pattern detected for technical PBDE mixtures [25].

Sediments can be a PBDE source for the nearby biota. The δ^{13}C values of PBDEs in sediment, to some extent, are the basic information for the source determination of the nearby biota samples (e.g., fish). If the δ^{13}C values of PBDE congeners in biota samples are similar to those of sediment, it would indicate that the PBDEs in biota samples most likely originated from the sediment. If they exhibit clearly different isotope ratios, it indicates the involvement of a remote source or significant biotransformation. Thus, the detected δ^{13}C values of PBDEs in sediment were proposed to be useful for determining the source and degradation behavior of PBDEs in abiotic or biota samples.

4. Conclusions

Summarily, an optimized method was developed for the measurement of δ^{13}C of individual PBDEs that contain three to six substituted bromine atoms in sediment samples. The addition of activated alumina and Florisil in the paper tube during the Soxhlet extraction provided for less complex extracts. Aliphatic hydrocarbons and other interfering compounds were removed by silica gel columns, Al/Si gel columns, and Florisil column. The improved purification method allowed the CSIA of PBDEs in sediment while retaining the original isotopic composition. The successful application of the purification and isotope analysis method to address environmental sediment samples confirmed the usability of the proposed method. Future application of CSIA for PBDE in the environment is feasible.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.02.036.

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