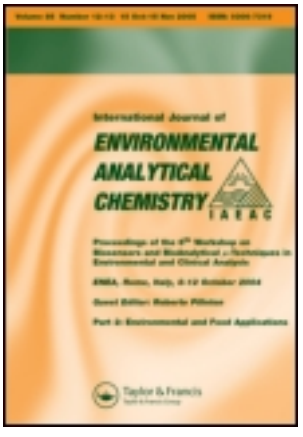


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

# Determination of 41 polybrominated diphenyl ethers in soil using a pressurised solvent extraction and GC-NCI-MS method

Xue Li [a b], Jun Huang [a b], Wang Zhang [a b], Gang Yu [a b], Shubo Deng [a b] & Siwen Wang [a b]

[a] POPs Research Center, Tsinghua University, Beijing 100084, China

[b] Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Available online: 11 Oct 2011

To cite this article: Xue Li, Jun Huang, Wang Zhang, Gang Yu, Shubo Deng & Siwen Wang (2011): Determination of 41 polybrominated diphenyl ethers in soil using a pressurised solvent extraction and GC-NCI-MS method, International Journal of Environmental Analytical Chemistry, 91:12, 1135-1150

To link to this article: http://dx.doi.org/10.1080/03067310903428750

*Intern. J. Environ. Anal. Chem.*
Vol. 91, No. 12, October 2011, 1135–1150

Taylor & Francis
Taylor & Francis Group

# Determination of 41 polybrominated diphenyl ethers in soil using a pressurised solvent extraction and GC-NCI-MS method

Xue Li[ab], Jun Huang[ab], Wang Zhang[ab], Gang Yu[ab]*, Shubo Deng[ab] and Siwen Wang[ab]

[a]*POPs Research Center, Tsinghua University, Beijing 100084, China;* [b]*Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China*

(*Received 29 July 2009; final version received 20 October 2009*)



A rapid and reliable analytical method based on pressurised solvent extraction (PSE) and GC-NCI-MS was developed for the determination of 41 different PBDEs in soil. All PBDEs, including mono- to hepta-BDEs (sum of 39 congeners), one nona-BDE and deca-BDE, were efficiently extracted from soil samples using the extraction technology of PSE. The extract was then cleaned up on a florisil column. Satisfactory separation of 41 PBDE congeners was obtained on a 15-m DB-5MS capillary column, saving the use of another 30-m column specific for the separation of mono- to hepta-BDEs. PBDEs were identified and quantified by GC-MS in negative chemical ionisation (NCI) mode, and further confirmed in semi electron impact (SEI) mode when the ion source was also NCI. The method detection limits ranged from 0.01 to 0.03 ng $g^{-1}$ dw for mono- to hepta-BDEs, 1.43 ng $g^{-1}$ dw for the nona-BDE and 0.20 ng $g^{-1}$ dw for deca-BDE. The applicability of the method was tested in soil samples collected from an e-waste recycling site at Guiyu. Twenty-one PBDEs (mono- to deca-) were detected, and eighteen congeners were quantified. The concentration range of PBDEs was 0.78–436 ng $g^{-1}$ dw. BDE-47, BDE-99, BDE-153, BDE-183, BDE-206 and BDE-209 were the dominant congeners, and BDE-209 accounted for 62% of the total PBDEs. The congener profiles of PBDEs in soil samples were similar to those in three commercial PBDE products (Penta-, Octa- and Deca-BDE), and Deca-BDE product was the most important contributor.

**Keywords:** PBDEs; PSE extraction; GC-NCI-MS; soil; e-waste recycling site

## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of synthetic organic chemicals and widely used as brominated flame retardants (BFRs). To reduce the potential fire hazard, PBDEs have been added into various consumer products such as plastics, textiles, coatings and electrical components that are involved in the production of computers, televisions and electrical appliances [1]. Three commercial PBDE products have been manufactured as Penta-, Octa- and Deca-BDE, which contain PBDE congeners with mainly 4-6, 7-10 and 10 bromine atoms, respectively [2]. Since commercial PBDE mixtures are physically incorporated into the polymer and other substrates, they are more easily released into the environment during initial manufacture, incorporation into the products, and application,

*Corresponding author. Email: yg-den@.tsinghua.edu.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067310903428750
http://www.tandfonline.com

reuse and disposal of the products [3]. In recent years, PBDEs have been of great concern due to their global distribution and increasing levels in environmental and human samples [4]. PBDEs are highly lipophilic and readily bioaccumulate; they are resistant to various degradation processes and persistent in the environment [1]. Hitherto, the use of Penta-BDE and Octa-BDE have been banned in the EU market, and since 2005 they have no longer been produced in the United States. In May 2009, tetra-, penta-, hexa- and hepta-BDEs, the major components in legacy commercial Penta-BDE and Octa-BDE products, were decided as new persistent organic pollutants (POPs) at the 4th meeting of the Conference of the Parties (COP4) to the Stockholm Convention [5].

Recently, high levels of PBDEs have been reported in soils from e-waste recycling sites at Guiyu, southeast China [6–10]. In these studies, soil samples were Soxhlet extracted and cleaned up sequentially using a silica gel column and an alumina column. The analysis of the extracts was performed by GC-NCI-MS [6], GC/MS/MS [7–9] or HRGC-HRMS [10]. Two different capillary columns were generally recommended for the separation of mono- to deca-BDEs [6,12]. A 30-m column was used for the separation of mono- to hepta-BDEs, and another shorter one (e.g. 12.5 m or 15 m) with thinner film thickness was used for the separation of octa- to deca-BDEs in order to avoid the potential thermal degradation of higher brominated PBDEs during the chromatographic run. According to the reported analytical protocols, mono- to deca-BDEs were identified in soil samples from e-waste recycling sites, and the total PBDEs (sum of 21 congeners) were in the range of 2720–4250 ng $g^{-1}$ dw in soil from an acid leaching site and 893–2890 ng $g^{-1}$ dw in soil from a printer roller dump site [10].

On the other hand, pressurised solvent extraction (PSE) provides another promising extraction technology for the pretreatment of PBDE-contaminated soil. In previous studies, PSE has been successfully applied to extract mono- to deca-BDEs from sediment samples [11,12], and mono- to hepta-BDEs from milk samples [13]. Moreover, PSE has faster extraction time and less consumption of organic solvent compared with Soxhlet extraction. However, to the best of our knowledge, little information is available on the application of PSE to the extraction of mono- to deca-BDEs from soil samples. In this regard, the aim of our study has been to develop an efficient and reliable method using PSE for the congener-specific determination of 41 different PBDEs in soil. PBDEs selected in this study were from mono- to hepta-BDEs (sum of 39 congeners), one nona-BDE and deca-BDE. Deca-BDE was considered since it was the most dominant congener in soil samples from e-waste recycling sites [10]; the nona-BDE was included considering that nona-BDEs were the major degradation products of deca-BDE in soil [6,14]. The study was based on: (a) extraction of 41 PBDEs from soil by PSE; (b) a clean-up procedure using a florisil column; (c) separation of 41 PBDEs on a 15-m capillary column; and (d) identification and quantification of PBDEs by GC-MS in negative chemical ionisation (NCI) mode, and confirmation in semi electron impact (SEI) mode when the ion source was also NCI.

## 2. Experimental

### 2.1 *Chemicals and materials*

Standard mixture solution of 39 native PBDE congeners (BDE-AAP-A-15X) was purchased from AccuStandard (New Haven, CT, USA). The BDE-AAP-A-15X contained three mono-BDEs (BDE-1, 2 and 3), seven di-BDEs (BDE-7, 8, 10, 11, 12, 13 and 15),

eight tri-BDEs (BDE-17, 25, 28, 30, 32, 33, 35 and 37), six tetra-BDEs (BDE-47, 49, 66, 71, 75 and 77), seven penta-BDEs (BDE-85, 99, 100, 116, 118, 119 and 126), five hexa-BDEs (BDE-138, 153, 154, 155 and 166) and three hepta-BDEs (BDE-181, 183 and 190). The concentrations of PBDE congeners ranged from 1.5 to 3.75 mg $L^{-1}$. Seven individual PBDE congeners (BDE-47, 99, 100, 153, 154, 183 and 206) were also purchased from AccuStandard, and dissolved in isooctane at a concentration of 50 mg $L^{-1}$. Their synthesis, purity and spectroscopic and chromatographic properties were described in the documents delivered with the standards. Solid decabrominated diphenyl ether (BDE-209, >98% purity) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan). $^{13}$C-labelled 2,2′,3,4,5,5′-hexaCB ($^{13}$C-PCB-141) and 2,2′,3,3′,4,5,5′,6,6′-nonaCB ($^{13}$C-PCB-208) were obtained from Cambridge Isotope Laboratories (Andover, MA), and applied as surrogate and internal standards, respectively. A series of standard solutions were prepared in hexane for a five-point internal calibration curve, in which the concentrations of 41 PBDEs ranging from 0.7 μg $L^{-1}$–12.4 mg $L^{-1}$ while the concentrations of $^{13}$C-PCB-141 and $^{13}$C-PCB-208 were always at 87.0 μg $L^{-1}$.

Organic solvents were of HPLC grade. Methylene chloride, hexane and acetone were supplied by J.T. Baker (USA), and methanol was from Fisher Scientific (USA). Florisil was of pesticide reagent grade (60–100 mesh) and provided by Riedel-de Haen (Seelze, Germany). Florisil was placed on a flat stainless steel tray and heated at 430°C for 4 h in a muffle furnace to remove the potential interferences and obtain consistent separation performance [15]; in addition, the treated florisil was left in a drying oven at 130°C for 12 h before use. Soil (GBW07415) purchased from National Research Center for Geoanalysis (Beijing, China) was used as soil matrix for method development. The soil matrix was rinsed sequentially with methanol, acetone and hexane to remove potential interferences, and air-dried before use. Concentrated sulphate acid, granular anhydrous sodium sulphate and copper powder were of analytical grade. The copper powder was activated in diluted hydrochloric acid, and rinsed with Milli-Q water (with the resistivity greater than 18.2 MΩ cm) until the rinsing water has a neutral pH. Then, the activated copper powder was further rinsed sequentially with organic solvents in a similar way to the soil matrix.

### 2.2 *Sample preparation and analysis*

The environmental samples were collected from an e-waste recycling site at Guiyu, Guangdong Province, southeast China. The samples were wrapped in aluminum foil and stored at −20°C in the laboratory prior to preparation. Before extraction, samples were freeze-dried, sieved (<0.25 mm) and homogenised. Ten grams of a soil sample was spiked with 20 μL of 1 mg $L^{-1}$ surrogate standard ($^{13}$C-PCB-141), and mixed with one gram of activated copper powder. The mixture was then extracted using a PSE system (One PSE, Applied Separations, USA). The extraction was performed as follows: a 33-mL extraction cell was loaded by inserting two pre-baked (400°C, >4 h) Millipore glass fibre prefilter (pore size: 1.2 μm) into the cell bottom, followed by the mixture of soil and copper powder, and topped with pre-cleaned silicon sand. The extraction cell was filled with the mixture of hexane and methylene chloride (1 : 1, v/v) until the pressure reached 104 bar (1 bar = 105 Pa), and heated to 100°C. Then 10 min static extraction was carried out at constant pressure and temperature; the cell and lines were flushed sequentially with fresh solvent for 25 sec and high-purity nitrogen (purity ≥ 99.999%) for 2 min. The extraction

was cycled twice. The total extraction time was about 30 min and the total volume of the extract was about 30 mL.

The clean-up procedure was performed as described by Rieck [15] with slight modification. Thus, a brief description will be given here. First, the extract was treated with 60 mL of concentrated sulfuric acid in a 250-mL separatory funnel to remove fat and colouring matters. The organic layer was separated and concentrated to the volume of 1 mL under a gentle stream of high-purity nitrogen. The florisil column (300 mm length, 10 mm i.d.) with a fritted glass disc at the bottom was packed from the bottom to the top with granular anhydrous sodium sulphate (0.6 cm), pre-treated florisil (10 g), activated copper powder (1 cm), and granular anhydrous sodium sulphate (1.3 cm). The column was firstly activated with 40 mL of hexane, and the effluents were discarded. Then, the concentrated extract was applied to the column and eluted with the mixture of hexane and methylene chloride (1 : 2, v/v). The volume of eluting solvent was pre-optimised with eight environmentally abundant congeners (BDE-47, 99, 100, 153, 154, 183, 206 and 209), and determined as 240 mL. The elute was concentrated to the volume of 5–10 mL by rotary evaporation and further quantitatively concentrated to the volume of 200 μL under a gentle nitrogen stream. Finally, 10 μL of 2 mg $L^{-1}$ internal standard ($^{13}$C-PCB-208) was added to the concentrated elute before GC-NCI -MS analysis.

GC-NCI-MS analysis was performed on a gas chromatography/mass spectrometer (Shimadzu GCMS-QP 2010 Plus, Kyoto, Japan). A DB-5MS capillary column (15 m × 0.25 mm i.d., 0.10 μm film thickness) was used for the separation of mono- to deca-BDEs. Helium was used as the carrier gas at a constant linear velocity of 72.9 cm $sec^{-1}$. GC oven temperature was programmed from 60°C (held for 2 min) to 140°C (held for 1 min) at 15°C $min^{-1}$, and to a final temperature of 300°C (held for 5 min) at 8°C $min^{-1}$. 1 μL of the sample was auto-injected in the high-pressure splitless mode (high pressure of 289 kPa for 2 min) when the injector temperature was set at 280°C.

The mass spectrometer was operated in NCI mode using methane as chemical ionisation moderating gas and the pressure in the ion source was $2.8 \times 10^{-4}$ Torr (1 Torr = 133.33 Pa). The ion source and interface temperatures were set at 250 and 280°C, respectively. Acquisition was performed in selective ion monitoring (SIM) and full scan modes ($m/z$ = 70–970). As shown in Table 1, characteristic fragment ions at $m/z$ 79 and 81 were monitored for 39 mono- to hepta-BDEs and the nona-BDE (BDE-206) while $m/z$

Table 1. Characteristic fragment ions for GC-NCI-MS analysis.

| Congeners | Window (min) | Ions monitored (m/z) |
|---|---|---|
| Mono-BDEs | 6:00–14:80 | 79/81 $[Br]^-$ |
| Di-BDEs | | |
| Tri-BDEs | | |
| $^{13}$C-PCB-141 | 14:80–15:10 | 372/374 $[M]^-$ |
| Tetra-BDEs | 15:10–18:00 | 79/81 $[Br]^-$ |
| $^{13}$C-PCB-208 | 18:00–18:25 | 476/478 $[M]^-$ |
| Penta-BDEs | 18:25–29:00 | 79/81 $[Br]^-$ |
| Hexa-BDEs | | |
| Hepta-BDEs | | |
| Nona-BDEs | | |
| Deca-BDE | 29:00–33:33 | 79/81 $[Br]^-$, 486.7/488.7 $[C_6Br_5O]^-$ |

486.7 and 488.7 were used for deca-BDE (BDE-209). For surrogate and internal standards, $m/z$ 372 and 374 were monitored for $^{13}$C-PCB-141, and 476 and 478 for $^{13}$C-PCB-208, respectively. Thus, six chromatographic windows were established, four for mono- to deca-BDEs and two for labelled PCBs.

The elution order of 41 PBDE congeners was determined by referring to the GC-RRT database reported previously [16,17]. Confirmation criteria for PBDE detection and quantification should include the following [18]: (a) all monitored ions for a given analyte should maximise simultaneously ±1 s; and (b) the ratio between $[Br]^-$ cluster at $m/z$ 79 and 81 should be within 15% of the theoretical value (1.03). In addition, GC-MS analysis was also performed in semi electron impact (SEI) mode when the NCI ion source was used. Thus, the full-scan mass spectrum ($m/z = 70-970$) was obtained with no need of changing the ion source. The full scan mass spectrum can provide better structural information and improve the accuracy of PBDE identification. All PBDE congeners were quantified using an internal calibration procedure and each peak was quantified only if the signal-to-noise ratio (S/N) ≥ 10.

### 2.3 *QA/QC*

Quality assurance and quality control (QA/QC) samples included solvent blank, blank matrix and spiked matrix. The spiked matrix samples were used for the evaluation of method performance and prepared as follows: ten grams of pre-cleaned soil was spiked with 50 μL of hexane solution containing 41 PBDEs and 20 μL of 1 mg $L^{-1}$ surrogate standard, and kept over night for equilibration. Linearity range and calibration curves for each PBDE congener were obtained by analyzing the standard solutions. Instrumental detection/quantification limits (IDLs/IQLs) were calculated using S/N of 3 and 10, respectively. Analysis of triplicate spiked samples was carried out and the recoveries were calculated using PSE and florisil column clean-up, as described in section 2.2. Method detection/quantification limits (MDLs/MQLs) were calculated based on IDLs/IQLs, together with recovery and concentration factor. Standard deviations (*SD*) and coefficient of variation (*CV*) were used to evaluate method accuracy and precision.

## 3. Results and discussion

### 3.1 *Identification of individual PBDEs*

Satisfactory chromatographic separation was obtained for 41 PBDE congeners on a 15-m DB-5MS capillary column (Figure 1), and the retention times of PBDE congeners, $^{13}$C-PCB-141 and $^{13}$C-PCB-208 are listed in Table 2. Compared with previous studies, the degree of separation achieved in our work was similar to that on the 30-m capillary columns [17]. The total run time was 33.33 min and about forty minutes faster than that obtained on the 30-m capillary column [7,9]. In regard to the co-elution profiles, BDE-12 co-eluted with BDE-13, BDE-28 co-eluted with BDE-33, BDE-138 co-eluted with BDE-166, and BDE-85 partially co-eluted with BDE-126. However, the co-elution of these PBDE congeners was also unavoidable while using 30-m capillary columns [17].

GC-NCI-MS in SIM mode was applied for PBDE identification and quantification. The method can provide 1000 times more sensitivity than GC-EI-MS, and PBDEs were determined in a wider range at low levels [18]. The NCI-MS spectra of mono- to hepta-BDEs were dominant by the mass fragment $[Br]^-$ ($m/z$ 79/81) whereas the molecular

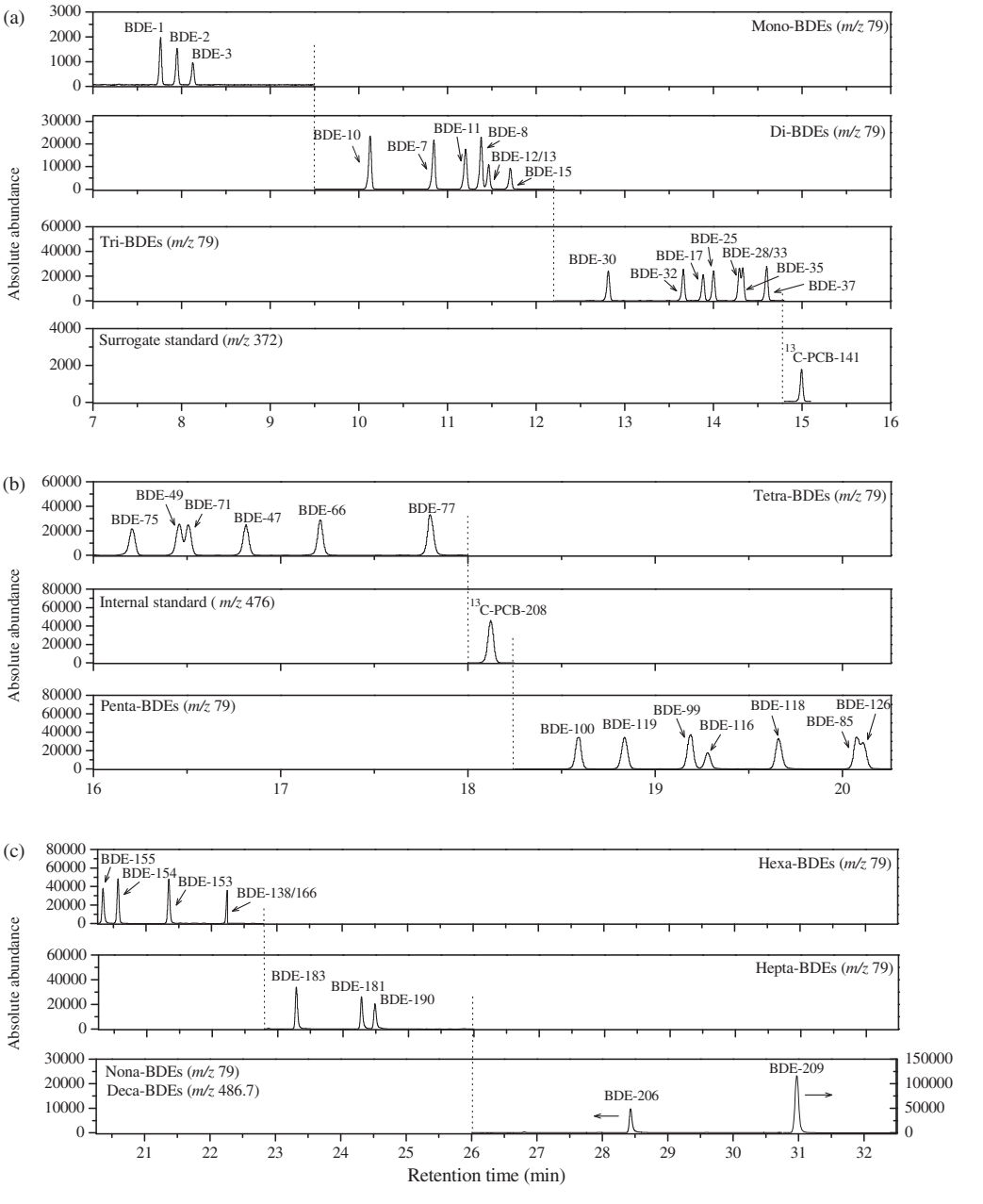


Figure 1. GC-NCI-MS (SIM) chromatogram of a standard solution containing 41 PBDEs, surrogate standard ($^{13}$C-PCB-141) and internal standard ($^{13}$C-PCB-208), obtained on a 15-m DB-5MS capillary column: (a) 7.00–16.00 min: mono- to tri-BDEs (35.7 μg L$^{-1}$) and $^{13}$C-PCB-141 (87.0 μg L$^{-1}$); (b) 16.00–20.26 min: tetra-BDEs (35.7 μg L$^{-1}$), penta-BDEs (53.6 μg L$^{-1}$) and $^{13}$C-PCB-208 (87.0 μg L$^{-1}$); (c) 20.26–32.49 min: hexa- (71.4 μg L$^{-1}$), hepta- (89.3 μg L$^{-1}$), nona- (238 μg L$^{-1}$) and deca-BDEs (619 μg L$^{-1}$).

Table 2. Retention times, calibration curves, $R^2$, IDLs, IQLs, the percentage recovery (%$R$, corrected by the surrogate standard), standard deviation ($SD$) ($n=3$), percentage coefficient of variation (%$CV$), MDLs and MQLs of 41 PBDEs.

| Congeners | RT (min) | Calibration curves | $R^2$ | IDLs ($\mu g\,L^{-1}$) | IQLs ($\mu g\,L^{-1}$) | %$R$ | %$CV$ | MDLs ($ng\,g^{-1}$ dw) | MQLs ($ng\,g^{-1}$ dw) |
|---|---|---|---|---|---|---|---|---|---|
| *Mono-BDEs* | | | | | | | | | |
| BDE-1 | 7.753 | $Y=0.1056\ X$ | 0.9998 | 0.7 | 2.2 | 118 ± 22 | 18.3 | 0.02 | 0.04 |
| BDE-2 | 7.940 | $Y=0.0993\ X$ | 0.9998 | 0.7 | 2.1 | 113 ± 16 | 14.2 | 0.02 | 0.04 |
| BDE-3 | 8.120 | $Y=0.0663\ X$ | 0.9990 | 1.3 | 4.2 | 118 ± 26 | 21.8 | 0.03 | 0.08 |
| *Di-BDEs* | | | | | | | | | |
| BDE-10 | 10.117 | $Y=0.8538\ X$ | 0.9992 | 0.2 | 0.4 | 133 ± 4 | 2.9 | 0.01 | 0.01 |
| BDE-7 | 10.833 | $Y=0.7170\ X$ | 1.0000 | 0.2 | 0.4 | 113 ± 17 | 15.1 | 0.01 | 0.01 |
| BDE-11 | 11.193 | $Y=0.7571\ X$ | 0.9997 | 0.2 | 0.4 | 102 ± 6 | 5.9 | 0.01 | 0.01 |
| BDE-8 | 11.370 | $Y=0.7483\ X$ | 0.9996 | 0.1 | 0.3 | 99 ± 5 | 5.3 | 0.01 | 0.01 |
| BDE-12/13 | 11.453 | $Y=0.3735\ X$ | 0.9997 | 0.3 | 0.8 | 101 ± 10 | 9.6 | 0.01 | 0.02 |
| BDE-15 | 11.700 | $Y=0.3732\ X$ | 0.9995 | 0.2 | 0.6 | 93 ± 4 | 4.1 | 0.01 | 0.02 |
| *Tri-BDEs* | | | | | | | | | |
| BDE-30 | 12.807 | $Y=0.5754\ X$ | 1.0000 | 0.2 | 0.5 | 118 ± 12 | 10.4 | 0.01 | 0.01 |
| BDE-32 | 13.650 | $Y=0.6097\ X$ | 1.0000 | 0.2 | 0.4 | 123 ± 7 | 5.4 | 0.01 | 0.01 |
| BDE-17 | 13.873 | $Y=0.5049\ X$ | 0.9988 | 0.2 | 0.4 | 125 ± 9 | 7.0 | 0.01 | 0.01 |
| BDE-25 | 13.991 | $Y=0.5302\ X$ | 0.9997 | 0.1 | 0.5 | 125 ± 9 | 7.0 | 0.01 | 0.01 |
| BDE-28/33 | 14.280 | $Y=1.2346\ X$ | 1.0000 | 0.1 | 0.3 | 129 ± 9 | 7.3 | 0.01 | 0.01 |
| BDE-35 | 14.320 | $Y=1.2303\ X$ | 0.9982 | 0.1 | 0.4 | 129 ± 9 | 7.3 | 0.01 | 0.01 |
| BDE-37 | 14.587 | $Y=0.6118\ X$ | 0.9995 | 0.2 | 0.4 | 127 ± 9 | 7.3 | 0.01 | 0.01 |
| $^{13}$C-PCB-141 | 14.983 | | | | | 95 ± 8 | 9.0 | | |
| *Tetra-BDEs* | | | | | | | | | |
| BDE-75 | 16.193 | $Y=0.6776\ X$ | 0.9980 | 0.2 | 0.5 | 124 ± 7 | 6.0 | 0.01 | 0.01 |
| BDE-49 | 16.450 | $Y=0.6777\ X$ | 0.9980 | 0.2 | 0.4 | 111 ± 11 | 9.8 | 0.01 | 0.01 |
| BDE-71 | 16.496 | $Y=0.6687\ X$ | 0.9990 | 0.2 | 0.4 | 111 ± 11 | 9.8 | 0.01 | 0.01 |
| BDE-47 | 16.807 | $Y=0.5752\ X$ | 0.9998 | 0.2 | 0.4 | 113 ± 9 | 8.3 | 0.01 | 0.01 |
| BDE-66 | 17.203 | $Y=0.5969\ X$ | 0.9999 | 0.2 | 0.4 | 113 ± 11 | 9.9 | 0.01 | 0.01 |
| BDE-77 | 17.793 | $Y=0.7033\ X$ | 0.9997 | 0.2 | 0.4 | 95 ± 11 | 12.0 | 0.01 | 0.01 |
| $^{13}$C-PCB-208 | 18.113 | | | | | | | | |

(*Continued*)

Table 2. Continued.

| Congeners | RT (min) | Calibration curves | $R^2$ | IDLs ($\mu g\,L^{-1}$) | IQLs ($\mu g\,L^{-1}$) | $\%R$ | $\%CV$ | MDLs ($ng\,g^{-1}$ dw) | MQLs ($ng\,g^{-1}$ dw) |
|---|---|---|---|---|---|---|---|---|---|
| *Penta-BDEs* | | | | | | | | | |
| BDE-100 | 18.577 | $Y = 0.7448\ X$ | 0.9999 | 0.1 | 0.4 | $89 \pm 10$ | 11.5 | 0.01 | 0.01 |
| BDE-119 | 18.827 | $Y = 0.6984\ X$ | 1.0000 | 0.2 | 0.4 | $87 \pm 13$ | 14.7 | 0.01 | 0.01 |
| BDE-99 | 19.180 | $Y = 0.7319\ X$ | 0.9995 | 0.1 | 0.3 | $88 \pm 12$ | 13.8 | 0.01 | 0.01 |
| BDE-116 | 19.270 | $Y = 0.7319\ X$ | 0.9995 | 0.3 | 0.8 | $88 \pm 12$ | 13.8 | 0.01 | 0.02 |
| BDE-118 | 19.650 | $Y = 1.2281\ X$ | 0.9996 | 0.2 | 0.5 | $60 \pm 5$ | 8.2 | 0.01 | 0.02 |
| BDE-85 | 20.067 | $Y = 1.2281\ X$ | 0.9996 | 0.2 | 0.5 | $62 \pm 6$ | 10.2 | 0.01 | 0.02 |
| BDE-126 | 20.100 | $Y = 1.2281\ X$ | 0.9996 | 0.2 | 0.5 | $62 \pm 6$ | 10.2 | 0.01 | 0.02 |
| *Hexa-BDEs* | | | | | | | | | |
| BDE-155 | 20.333 | $Y = 0.9846\ X$ | 0.9990 | 0.3 | 0.8 | $91 \pm 15$ | 16.5 | 0.01 | 0.02 |
| BDE-154 | 20.560 | $Y = 0.9829\ X$ | 0.9994 | 0.2 | 0.4 | $69 \pm 11$ | 16.5 | 0.01 | 0.01 |
| BDE-153 | 21.337 | $Y = 0.8091\ X$ | 0.9975 | 0.2 | 0.5 | $59 \pm 10$ | 16.8 | 0.01 | 0.02 |
| BDE-138/166 | 22.233 | $Y = 0.8286\ X$ | 0.9982 | 0.3 | 0.9 | $59 \pm 10$ | 16.8 | 0.02 | 0.04 |
| *Hepta-BDEs* | | | | | | | | | |
| BDE-183 | 23.277 | $Y = 0.5714\ X$ | 0.9956 | 0.3 | 0.9 | $47 \pm 4$ | 7.8 | 0.02 | 0.04 |
| BDE-181 | 24.270 | $Y = 0.4206\ X$ | 0.9987 | 0.4 | 1.3 | $54 \pm 6$ | 11.3 | 0.02 | 0.05 |
| BDE-190 | 24.473 | $Y = 0.3356\ X$ | 0.9977 | 0.5 | 1.6 | $48 \pm 8$ | 16.6 | 0.03 | 0.07 |
| *Nona-BDEs* | | | | | | | | | |
| BDE-206 | 28.423 | $Y = 0.0629\ X$ | 0.9948 | 21.3 | 71.2 | $31 \pm 3$ | 11.0 | 1.46 | 4.88 |
| *Deca-BDE* | | | | | | | | | |
| BDE-209 | 31.013 | $Y = 0.3434\ X$ | 0.9947 | 2.2 | 7.1 | $24 \pm 2$ | 9.7 | 0.20 | 0.63 |

cluster was not observed or contributed to a minority peak. As a result, less structural information was provided in the NCI mode, and interferences could be introduced due to the co-elution of PBDE congeners with different degree of bromination. In addition, brominated interferences such as polybrominated biphenyls (PBBs) and Tetrabromobisphenol-A (TBBPA), can also be introduced under NCI conditions. However, these problems can be resolved by the EI-MS approach. GC-EI-MS can provide better structural information by giving the molecular ions and the sequential losses of bromine atoms. In EI mass spectra, $[M]^+$ was the predominant peak for mono- to tetra-BDEs while $[M\text{-}Br_2]^+$ was the most intense peak for penta- to deca-BDEs. However, the EI ionisation source was different from that of NCI and had to be changed when both ionisation sources need to be used, causing inconvenience in the analysis. In this study, the dilemma was tackled by using a SEI approach available in the present GCMS-QP 2010 Plus system. In the SEI mode, EI spectra can be acquired for each PBDE with no need of changing the ionisation source. As a result, both satisfactory sensitivity and selectivity were achieved using the NCI and SEI modes in the present study.



### 3.2 *Calibration curves and quantification*

Quantification was achieved with $m/z$ 79 for all PBDEs except BDE-209, for which $m/z$ 486.7 was used. The linear calibration range were 0.7–150.0 $\mu g\,L^{-1}$ for mono- to tetra-BDEs, 1.0–225 $\mu g\,L^{-1}$ for penta-BDEs, 1.3–300 $\mu g\,L^{-1}$ for hexa-BDEs, 1.5–375 $\mu g\,L^{-1}$ for hepta-BDEs, 3.8 $\mu g\,L^{-1}$–2.5 $mg\,L^{-1}$ for BDE-206 and 4.0 $\mu g\,L^{-1}$–12.4 $mg\,L^{-1}$ BDE-209, respectively. Linear calibration curves for individual PBDE congener were shown in Table 2. Good determination coefficients ($R^2$) were obtained, which ranged from 0.9947 to 1.0000. The IDLs and IQLs were calculated as described in section 2.3 and listed in Table 2. The IDLs of mono- to hepta-BDEs were in the range of 0.1–1.3 $\mu g\,L^{-1}$, in which the IDLs were similar from di- to hepta-BDEs (0.1–0.5 $\mu g\,L^{-1}$) whereas a bit higher for mono-BDEs (0.7–1.3 $\mu g\,L^{-1}$). This result was comparable to that reported by de la Cal *et al*. [11]. However, the sensitivity for higher brominated PBDEs decreased considerably; the IDLs were 21.3 $\mu g\,L^{-1}$ for BDE-206 and 2.2 $\mu g\,L^{-1}$ for BDE-209, respectively. In regard to the IQLs, the values were 0.3–4.2 $\mu g\,L^{-1}$ for mono- to hepta-BDEs, 71.2 $\mu g\,L^{-1}$ for BDE-206 and 7.1 $\mu g\,L^{-1}$for BDE-209, respectively.

Moreover, in the present study, the lower IDL/IQL for BDE-206 than that for BDE-209 should be attributed to its lower response factor. As for the determination of IDLs, ion fragments m/z 79 and 81 $[BR]^-$ were monitored for BDE-206, while 486 and 488 were used for BDE-209. The ion fragments were selected according to the full spectra obtained in full scan mode by GC-NCI-MS. The ion fragments of m/z 486 and 488 were the most dominant fragments in the NCI spectrum of BDE-209. As for the NCI spectrum of BDE-206, the ion fragments of m/z 79 and 81 were the most dominant ones. However, even though the most abundant ion fragments were used, the response factor for BDE-206 was still unsatisfied compared with other PBDE congeners. In addition, Qu *et al*. have also chosen the ion fragments m/z 79 and 81 $[BR]^-$ to be monitored for BDE-206 [19].

### 3.3 *Performance of the analytical method*

Recoveries of 41 PBDEs and $^{13}$C-PCB-141 were obtained using PSE followed by florisil column clean-up (Table 2). The assays were carried out in triplicate. $^{13}$C-PCB-141 was

selected as surrogate standard instead of PBDEs because the labelled PBDEs have the same base peak ($m/z$ 79/81) with their native forms when GC-NCI-MS method was used. The recovery of $^{13}$C-PCB-141 was calculated for each sample to ensure that the pretreatment procedures and instrumental analysis were properly performed. We considered that PBDEs were not sufficiently extracted from soil samples if the recovery of $^{13}$C-PCB-141 was lower than 70%, and the pretreatment procedures should be further improved. In addition, since no PBDEs were detected in solvent or matrix blanks, the final results were obtained without performing the blank correction.

In the spiked matrix samples, the recoveries of $^{13}$C-PCB-141 varied from 89 to 104% with the *CV* of 9.0%. The recoveries of mono- to deca-BDEs were in the range of 24–133%. Good recoveries were obtained for mono- to tetra-BDEs, which ranged from 93 to 133%, and the *CV*s varied from 2.9 to 21.8%. As for penta-BDEs, BDE-99, BDE-100, BDE-116 and BDE-119 showed satisfactory recoveries of 90% and the *CV*s were in the range of 11.5–14.7%; on the other hand, lower recoveries of 60% were obtained for BDE-85, BDE-118 and BDE-126 with the *CV*s varied from 8.2 to 10.2%. The recoveries of hexa-BDEs varied from 60–90% and the *CV*s were about 16%. The recoveries for higher brominated PBDEs (hepta- to deca-) were relatively lower compared with those of mono- to hexa-BDEs, and the values were 47–54% for hepta-BDEs, 31% for the nona-BDE and 24% for deca-BDE, respectively. The *CV*s were in the range of 8–16%.

MDLs and MQLs for individual PBDE were calculated as described in section 2.3 and shown in Table 2. From mono- to hepta-BDEs, the MDLs varied from 0.01–0.03 ng g$^{-1}$ dw, which was comparable to the result of 0.01–0.25 ng g$^{-1}$ dw reported by Wang *et al.* [7]. The MDLs of BDE-206 and BDE-209 were 1.46 and 0.20 ng g$^{-1}$ dw, respectively. As for the MQLs, the values were 0.01–0.08 ng g$^{-1}$ dw for mono- to hepta-BDEs, 4.88 ng g$^{-1}$ dw for BDE-206 and 0.63 ng g$^{-1}$ dw for BDE-209, respectively. The lower MQL/MDL for BDE-206 compared with BDE-209 was due to its lower IQL/IDL, as discussed in section 3.2.

In addition, as shown above, the recoveries of higher brominated PBDEs (starting with hexa- through deca-BDE) showed a continuous decrease, and it may be due to a solubility problem. Since toluene is suggested to be a good keeper for higher brominated PBDEs when the extract is reconstituted or concentrated, tests were carried out to investigate the effect of toluene on keeping PBDEs in the extract when the extract was concentrated. First, 150 μL of toluene was added into 8 mL of hexane solution that contained eight PBDEs, including tetra- to deca-BDEs (BDE-47, 99, 100, 153, 154, 183, 206 and 209), and then the solution was concentrated under a gentle stream of nitrogen (purity ≥ 99.999%) to the volume of 200 μL. The experiments were performed in triplicate, and the same hexane solutions without adding toluene were used as control samples. Furthermore, the effect of PBDE concentrations on the concentration procedure was also considered. As for the high PBDE concentration, the concentration of BDE-47, 99, 100, 153, 154, 183 and 206 was 49.6 mg L$^{-1}$ and the concentration of BDE-209 was 254 mg L$^{-1}$. As for the low PBDE concentration, the concentration of BDE-47, 99, 100, 153, 154, 183 and 206 was 0.4 mg L$^{-1}$ and the concentration of BDE-209 was 2.1 mg L$^{-1}$.

However, the absolute response of eight PBDEs in all concentrated samples with toluene was lower than that in the samples without toluene at either high or low PBDE concentrations (Figure 2). As a result, the continuous decrease of higher brominated PBDE recoveries in the present study may be not a solubility problem.

On the other hand, Lacorte and Guillamon have also found the similar problem that the recoveries for the higher brominated congeners (starting from tetra- to hepta-) were

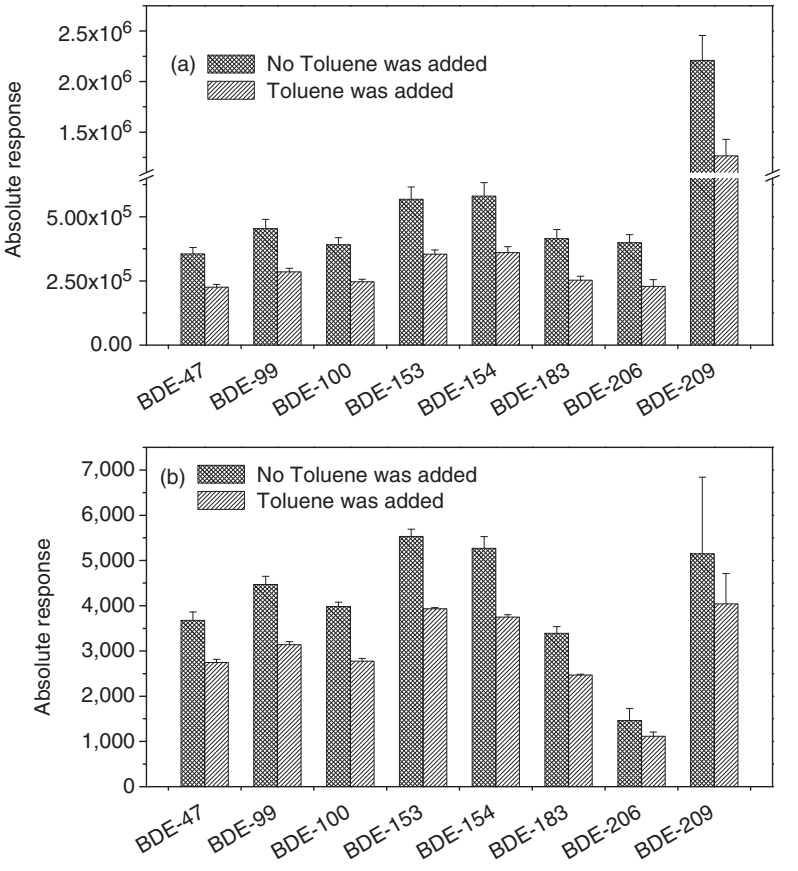


Figure 2. The absolute response of BDE-47, 99, 100, 153, 154, 183, 206 and 209 (tetra- to deca-) on GC-ECD in two concentrated samples containing high (a) and low (b) concentrations of PBDEs, respectively.



lower in their study [13]. The recoveries were obtained using PLE and alumina SPE clean-up. When 2 g alumina SPE was used, the recoveries were 85–117% for mono- to tri-BDEs, 61–72% for tetra-BDEs, 31–45% for penta-BDEs, 22–47% for hexa-BDEs, and 14–17% for hepta-BDEs. However, when the extract was purified with 5 g alumina SPE instead of 2 g one, the recoveries for tetra- to hepta-BDEs were increased to the values higher than 90%. As a result, further optimisation can be performed especially for the higher brominated PBDEs in terms of organic solvents used for the extraction, the operating parameters of the PSE system, and the amount of florisil for the clean-up procedure.

### 3.4 *Application of the method to environmental samples*

The developed method was applied to the determination of PBDEs in soil samples collected in the vicinity of an open e-waste recycling site located at Guiyu, southeast China. Twenty-one PBDEs (mono- to deca-) were identified in soil samples (Figure 3) and eighteen congeners were quantified using internal standard method (Table 3).

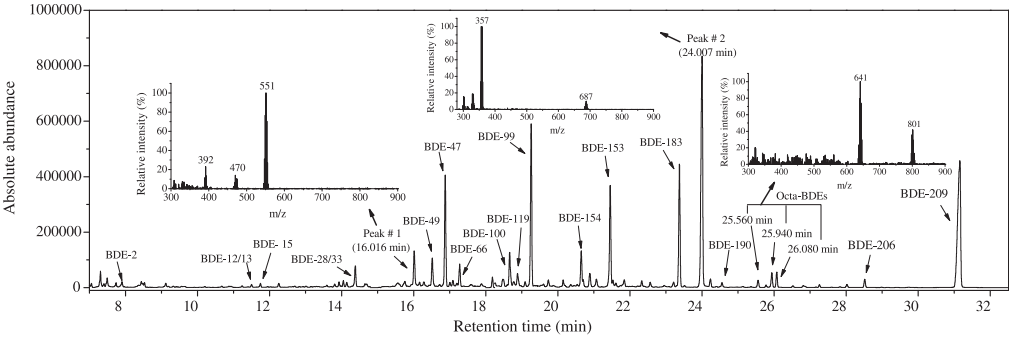


Figure 3. GC-NCI-MS (SIM) chromatogram of PBDE congeners and brominated interferences in soil samples, and the SEI-MS spectra of three identified octa-BDEs (25.560 min: BDE-197; 25.940 min: BDE-203; 26.080 min: BDE-196) and two brominated interferences (16.016 min: HBB; 24.007 min: BTBPE).

Table 3. Levels of PBDEs in soil samples collected from an e-waste recycling site at Guiyu (ng g$^{-1}$ dw, $n = 2$).

| congener | S-1 | S-2 | *Average* | SD |
|---|---|---|---|---|
| Mono-BDEs | 8.05 | 4.48 | 6.27 | 2.52 |
| BDE-2 | 8.05 | 4.48 | 6.27 | 2.52 |
| Di-BDEs | 2.01 | 1.85 | 1.93 | 0.12 |
| BDE-12/13 | 0.86 | 0.70 | 0.78 | 0.12 |
| BDE-15 | 1.15 | 1.15 | 1.15 | 0.00 |
| Tri-BDEs | 2.29 | 2.65 | 2.47 | 0.26 |
| BDE-28/33 | 2.29 | 2.65 | 2.47 | 0.26 |
| Tetra-BDEs | 21.1 | 26.7 | 23.9 | 3.96 |
| BDE-49 | 3.51 | 4.41 | 3.96 | 0.63 |
| BDE-47 | 15.0 | 18.8 | 16.9 | 2.71 |
| BDE-66 | 2.54 | 3.41 | 2.98 | 0.61 |
| Penta-BDEs | 34.3 | 49.7 | 42.0 | 10.9 |
| BDE-100 | 6.00 | 8.68 | 7.34 | 1.89 |
| BDE-119 | 2.29 | 3.41 | 2.85 | 0.79 |
| BDE-99 | 26.0 | 37.6 | 31.8 | 8.19 |
| Hexa-BDEs | 31.4 | 37.9 | 34.7 | 4.66 |
| BDE-154 | 6.52 | 9.50 | 8.01 | 2.12 |
| BDE-153 | 24.8 | 28.4 | 26.6 | 2.55 |
| Hepta-BDEs | 65.5 | 79.8 | 72.7 | 10.1 |
| BDE-183 | 60.3 | 73.5 | 66.9 | 9.39 |
| BDE-190 | 5.29 | 6.32 | 5.80 | 0.73 |
| Octa-BDEs | – | – | – | – |
| BDE-197 | – | – | – | – |
| BDE-203 | – | – | – | – |
| BDE-196 | – | – | – | – |

(*Continued*)

Table 3. Continued.

| congener | S-1 | S-2 | *Average* | SD |
|---|---|---|---|---|
| Nona-BDEs | 46.9 | 62.1 | 54.5 | 10.8 |
| BDE-206 | 46.9 | 62.1 | 54.5 | 10.8 |
| Deca-BDE | 336 | 535 | 436 | 141 |
| BDE-209 | 336 | 535 | 436 | 141 |
| Total PBDEs | 570 | 834 | 702 | 187 |



The concentration range of PBDEs was from 0.78 to 436 ng $g^{-1}$ dw, and BDE-47, BDE-99, BDE-153, BDE-183, BDE-206 and BDE-209 were the dominant congeners. This result was in agreement with those reported in previous studies [7,10]. The recoveries of $^{13}$C-PCB-141 were 98% and 73% for the duplicate soil samples, respectively.

Mono-BDE of BDE-2 was detected at the concentration of 6.27 ng $g^{-1}$ dw, and this congener was also found in road and farmland soils from an e-waste recycling region in south China in a recent study [6]. The concentrations of three di-BDEs (BDE-12/13 and BDE-15) were 0.78 and 1.15 ng $g^{-1}$ dw, respectively. Tri-BDEs of BDE-28/33 were detected at the concentration of 2.47 ng $g^{-1}$ dw, and comparable to that reported in soil and sediment samples at e-waste recycling sites [7]. Three tetra-BDEs of BDE-47, BDE-49 and BDE-66 were detected at the levels of 16.9, 3.96 and 2.98 ng $g^{-1}$ dw, respectively, and BDE-47 was the dominant congener. Three penta-BDEs of BDE-99, BDE-100 and BDE-119 were detected at the concentrations of 2.85–31.8 ng $g^{-1}$ dw, and BDE-99 was the dominant congener. Hexa-BDEs of BDE-153 and BDE-154 were detected at the concentrations of 26.6 and 8.01 ng $g^{-1}$ dw, respectively, and BDE-153 was the dominant congener. Hepta-BDEs of BDE-183 and BDE-190 were detected at the concentrations of 66.9 and 5.80 ng $g^{-1}$ dw, respectively, and the concentration of BDE-183 was more than ten times higher than that of BDE-190.

Three chromatographic peaks, which eluted after BDE-190, were tentatively identified as octa-BDEs based on the full-scan SEI-MS spectra (Figure 3). Furthermore, these three octa-BDEs were supposed to be BDE-197 (25.560 min), BDE-203 (25.940 min) and BDE-196 (26.080 min) based on the following reasons: (a) the relative retention times (RRT) of these three peaks versus the peak eluted at 26.080 min are in accordance with those of BDE-197, BDE-203 and BDE-196 versus that of BDE-196 [20,21]; (b) BDE-196, BDE-197 and BDE-203 are the only octa-BDE congeners previously reported in soil samples at Guiyu [6,10]; and (c) BDE-196, BDE-197 and BDE-203 are the most abundant octa-BDE congeners in commercial octa-BDE products [20].

One nona-BDE was identified as BDE-206 and detected at the concentration of 54.5 ng $g^{-1}$ dw. BDE-209 was the most abundant PBDE congener and detected at the concentration of 436 ng $g^{-1}$ dw. The level of BDE-209 was comparable to those reported in soils collected from printer roller dump site and duck pond within e-waste recycling regions at Guiyu [10].

In addition, two unknown brominated interferences were also detected in the soil samples, whose chromatographic peaks (Peaks 1 and 2) eluted at the retention times of 16.016 and 24.007 min, respectively. For Peaks 1 and 2, the ratios between m/z 79 and 81 were 1.05 and 1.02, respectively, both of which were within 15% of the theoretical value

(1.03). In this regard, these two unknown interferences should also contain bromine atoms. However, according to the full-scan SEI-MS spectra, they were obviously not PBDE congeners (Figure 3), and instead suggested to be another two BFRs: hexabromobenzene (HBB) [22] and 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) [23], respectively.

The levels of each PBDE homologue group were also calculated, and the levels varied from 1.93 to 436 ng $g^{-1}$ dw (Table 3). The groups were ranked in the order of increasing levels: di- <tri- <mono- <tetra- <hexa- <penta- <nona- <hepta- <deca-homologue group. The concentrations of mono- to tri-homologue groups were in the range of 1.93–6.27 ng $g^{-1}$ dw and contributed 0.3–0.4% to the total PBDEs. The levels of tetra-, penta-, hexa-, hepta- and nona-homologue groups were of the same magnitude, and ranged from 23.9 to 72.7 ng $g^{-1}$ dw. The contribution of these groups to the total PBDEs were in the range of 3.4–10.3%. Deca-homologue group was the most dominant group (436 ng $g^{-1}$ dw), and contributed 62% to the total PBDEs.

Contamination sources of PBDEs at the studied site were also investigated by comparing PBDE congener profiles to those of three commercial products (Penta-, Octa- and Deca-BDE). The congener pattern of tetra- and penta-BDEs in soils was similar to those of the Penta-BDE product formulation [24]. In addition, the concentration ratio between BDE-47 and BDE-99 was 0.6, and close to that in the Penta-BDE product of DE-71 (0.6–0.8) whereas lower than that in Bromkal 70-5DE (1.0–1.1) [6]. This result implied that it was DE-71 rather than Bromkal 70-5DE attributed to the occurrence of tetra- and penta-BDEs in the studied region. The hepta-BDE of BDE-183, one of the dominant congeners identified in our work (Table 3), has been reported as a marker for the Octa-BDE product [10,25]. As a result, the Octa-BDE commercial mixture was the potential source for hepta-BDEs contamination in the soil samples. Hexa-BDEs are the components of both Penta-BDE and Octa-BDE products, and thus the presence of hexa-BDEs in soil was attributed to both of the two products. As for the contamination source of BDE-209, BDE-209 is the major component in commercial Deca-BDE product (97%, w/w) [20], and the deca-BDE product should account for the significant level of BDE-209 in soil. In summary, the contamination sources of PBDEs to soil samples were all of three commercial PBDE products, in which Deca-BDE product was the major source.

## 4. Conclusions

A rapid and reliable analytical protocol for the determination of forty-one different PBDEs (from mono- to hepta-, one nona- and deca-) in soil has been developed using the extraction technology of PSE and GC-NCI-MS method. The pretreatment procedure of PSE followed by florisil column clean-up showed comparable performance to the methods using Soxhlet extraction followed by the clean-up using an acidic silica gel column and an activated neutral alumina column. Meanwhile, the extraction time and the volume of organic solvent were considerably reduced by PSE. In regard to the GC-NCI-MS analysis, forty-one PBDEs were successfully separated on a 15-m capillary column without using an extra 30-m column. Both satisfactory sensitivity and selectivity were achieved by using the NCI and SEI modes when the ion source was NCI.

The developed method was further tested by applying to the determination of PBDEs in soil samples from an e-waste recycling site at Guiyu. Twenty-one PBDEs were

identified, and eighteen congeners were quantified. The concentration range of PBDEs was 0.78–436 ng $g^{-1}$ dw, and BDE-47, BDE-99, BDE-153, BDE-183, BDE-206 and BDE-209 were the dominant congeners. BDE-209 contributed 62% to the total PBDEs. Contamination sources of PBDEs in soil samples were identified as all of three commercial PBDE products (Penta-, Octa- and Deca-BDE), and Deca-BDE was the most important contributor.

**Acknowledgements**

This research was supported by the National Natural Science Foundation of P.R. China (No. 20507010 and 50538090) and the Distinguished Young Scholars Project (50625823) and the program of 'Research on key Technology of Environment Pollution Control and Quality Improvement' (No. 2007DFC90170).



**References**

[1] F. Rahman, K.H. Langford, M.D. Scrimshaw, and J.N. Lester, Sci. Total Environ. **275**, 1 (2001).
[2] A. Sjödin, L. Hagmar, E. Klasson-Wehler, K. Kronholm-Diab, E. Jakobsson, and Å. Bergman, Environ. Health Perspect. **107**, 643 (1999).
[3] Y.W. Wang, G.B. Jiang, P.K.S. Lam, and A. Li, Environ. Int. **33**, 963 (2007).
[4] R.A. Hites, Environ. Sci. Technol. **38**, 945 (2004).
[5] The 4th meeting of the Convention of the Parties (COP4) of the Stockholm Convention on Persistent Organic Pollutants (POPs), Stockholm Convention on Persistent Organic Pollutants (POPs). <http://chm.pops.int/>.
[6] Y. Luo, X.J. Luo, Z. Lin, S.J. Chen, J. Liu, B.X. Mai, and Z.Y. Yang, Sci. Total Environ. **407**, 1105 (2009).
[7] D.L. Wang, Z.W. Cai, G.B. Jiang, A. Leung, M.H. Wong, and W.K. Wong, Chemosphere **60**, 810 (2005).
[8] A. Leung, Z.W. Cai, and M.H. Wong, J. Mater. Cycles Waste Manag. **8**, 21 (2006).
[9] Z.W. Cai and G.B. Jiang, Talanta **70**, 88 (2006).
[10] A.O.W. Leung, W.J. Luksemburg, A.S. Wong, and M.H. Wong, Environ. Sci. Technol. **41**, 2730 (2007).
[11] A. de la Cal, E. Eljarrat, and D. Barceló, J. Chromatogr. A **1021**, 165 (2003).
[12] Y.J. Jhong and W.H. Ding, J. Chinese Chem. Soc. **55**, 335 (2008).
[13] S. Lacorte and M. Guillamon, Chemosphere **73**, 70 (2008).
[14] U. Sellström, C.A. de Wit, N. Lundgren, and M. Tysklind, Environ. Sci. Technol. **39**, 9064 (2005).
[15] R.H. Rieck, LC GC N. Am. **21**, 992 (2003); **22**, 914 (2004).
[16] P. Korytár, A. Covaci, J. de Boer, A. Gelbin, and U.A. Th. Brinkman, J. Chromatogr. A. **1065**, 239 (2005).
[17] Y.W. Wang, A. Li, H.X. Liu, Q.H. Zhang, W.P. Ma, W.L. Song, and G.B. Jiang, J. Chromatogr. A **1103**, 314 (2006).
[18] E. Eljarrat, S. Lacorte, and D. Barceló, J. Mass Spectrom. **37**, 76 (2002).
[19] W.Y. Qu, X.H. Bi, G.Y. Sheng, S.Y. Lu, J.M. Fu, J. Yuan, and L.P. Li, Environ. Int. **33**, 1029 (2007).
[20] M.J. La Guardia, R.C. Hale, and E. Harvey, Environ. Sci. Technol. **40**, 6247 (2006).
[21] A. Christiansson, J. Eriksson, D. Teclechiel, and Å. Bergman, Environ. Sci. Pollut. Res. **16**, 312 (2009).

[22] Integrated Spectral Database System of Organic Compounds. <http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi>
[23] E. Hoh, L.G. Zhu, and R.A. Hites, Environ. Sci. Technol. **39**, 2472 (2005).
[24] WHO/ICPS. Environmental Health Criteria 162: Brominated diphenyl ethers (World Health Organization, Geneva, Switzerland, 1994).
[25] A. Hassanin, K. Breivik, S.N. Meijer, E. Steinnes, G.O. Thomas, and K.C. Jones, Environ. Sci. Technol. **38**, 734 (2000).