2005

# Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility

Dongli Wang

Zongwei Cai
*Hong Kong Baptist University*, zwcai@hkbu.edu.hk

Guibin Jiang

Anna Leung

Ming H. Wong
*Hong Kong Baptist University*, mhwong@hkbu.edu.hk

*See next page for additional authors*


Link to published article: http://dx.doi.org/10.1016/j.chemosphere.2005.04.025

**Analysis of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling area by using gas chromatography/tandem mass spectrometry**

Dongli Wang[1], Zongwei Cai*[1], Guibin Jiang[2], Anna Leung[3], Ming H. Wong[3], Wai Kwok Wong[1]

[1]Department of Chemistry, [3]Institute for Natural Resources and Environmental Management, Hong Kong Baptist University, Kowloon, Hong Kong SAR, China

[2]Research Center for Eco-environmental Sciences, the Chinese Academy of Sciences, Beijing, China

*Correspondence:

Department of Chemistry

Hong Kong Baptist University

Kowloon

Hong Kong

Tel. 00852-34117070; Fax: 34117348

Email: zwcai@hkbu.edu.hk

**Abstract**

A gas chromatography/ion trap mass spectrometry method was developed to determine polybrominated diphenyl ethers (PBDEs) in soil and sediment collected in the vicinity of an open electronic waste disposal and recycling site located in South China. The samples were prepared by using Soxhlet extraction and column chromatographic clean-up with silica gel and alumina. Average recoveries of 81 to 98% were obtained for the $^{13}C$-labeled PBDE internal standards spiked in the samples prior to sample preparation. The method detection limits ranged from 0.013 to 0.25 ng/g for the PBDEs. The analysis of four standard sea sand samples with a known amount of spiked PBDEs gave relative analytical errors of -26.0 to 30.8 % and relative standard deviations of 13.8 to 36.1 %. The PBDEs were detected in the soil and sediment samples at levels of 0.26 to 824 ng/g, which were 10-60 times higher than those reported in other PBDEs contaminated sites in the world.

## Introduction

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been extensively used as flame-retardants. The compounds are incorporated into many types of polymers used in electric circuit boards, computer and TV housing, furniture, building materials, textiles, carpets and vehicles. The concern with PBDEs is that the chemicals can be released into the environment from the products since they are not chemically bound to the materials, and more importantly, they are persistent with a high bioaccumulation potential. Various PBDEs have been detected with significant levels in environmental matrices such as air (1, 2), sediment (3-6) and sewage sludge (7, 8) as well as biological samples such as biota (9-11), human blood (12), adipose tissues (13-17) and breast milk (18, 19). In a study on Swedish breast milk, the levels of PBDEs were found to increase from the year of 1972 to 1997 (18).

Recent studies indicate that several PBDE congeners may interfere with the aryl hydrocarbon (Ah) receptor (20). In rats and mice, 2, 2', 4, 4'-tetraBDE (BDE-47) was found to transform to hydroxylated metabolites (21), which competed with thyroxin for the binding site on transthyretin (22). Some hydroxylated PBDE metabolites were also found to bind directly to the thyroid receptor (23). The observations suggested that several PBDEs and/or their metabolites might have disrupted the endocrine system (24-26) although the toxicities of PBDEs were considered to be low (27, 28). These findings indicate the importance and the urgency to accurately identify and determine PBDE levels in the environment.

It was reported that illegal and unsafe recycling operations of electronic wastes (e-wastes) have been conducted in the town of Guiyu in Guangdong, China. The town located northeast of Hong Kong includes a cluster of small villages that have become a booming recycling

center for electronic waste arriving from various regions around the world since 1995 (29). Villagers separate and recover metals from printed circuit boards, PVC-coated wire and cable by open burning. The amounts of scrap computers, monitors and printers are alarming, overflowing in large piles in the front and back yards of villagers. The wires are burned in heaps right in front of the houses, releasing cancer-causing fumes. The unsafe e-waste recycling causes severe environmental pollution from heavy metals, fire retardants, and the formation of polyhalogenated dibenzo-*p*-dioxins and dibenzofurans (30). However, little information on the PBDE congener profiles and concentrations in the environment around the e-waste recycling site has been reported. The present study aims to develop a capillary gas chromatography/ion-trap mass spectrometry method to analyze PBDEs in sediment and soil samples collected from the town of Guiyu.

## Experimental

*Chemical reagents and standard solutions*

Dichloromethane, hexane and acetone of Absolve grade were purchased from Tedia Company Inc. (Fairfield, OH, USA). Nonane and sea sand were purchased from Fluka (Milwaukee, USA). Granular anhydrous sodium sulfate (Tedia, Fairfield, USA), silica gel 60 (0.063-0.200 mm, Merck, Whitehouse Station, USA) and neutral alumina (Brockmann I, Standard Grade, ~150 mesh, Aldrich Chemical Co., Milwaukee, USA) were activated at 170 $^{o}$C for more than 24 h. Copper powder was supplied from UniChem (Surrey, UK). Concentrated sulfuric acid was purchased from BDH Laboratory Supplies (Dorset, England). Sulfuric acid-impregnated silica gel (w/w) was prepared by combining concentrated sulfuric acid (30%) with activated neutral silica gel.

All PBDE standard solutions were purchased from Wellington Laboratories (Ontario,

Canada). Two individual native standard solutions of 4-bromodiphenyl ether (BDE-3) and 2, 4-dibromodiphenyl ether (BDE-7) were used at concentration of 50 μg/mL. Mixed native standard solution of PBDEs contained 2, 2', 4-tribromodiphenyl ether (BDE-17), 2, 2', 4, 4'-tetrabromodiphenyl ether (BDE-47), 2, 3', 4, 4'-tetrabromodiphenyl ether (BDE-66), 2, 2', 4, 4', 6-pentabromodiphenyl ether (BDE-100), 2, 2', 4, 4', 5, 5'-hexabromodiphenyl ether (BDE-153), 2, 2', 3, 4, 4', 5', 6-heptabromodiphenyl ether (BDE-183) at 5 μg/mL and decabromodiphenyl ether (BDE-209) at 10 μg/mL. A composite native PBDE standard solution containing BDE-3, BDE-7, BDE-17, BDE-47, BDE-66, BDE-100, BDE-153, BDE-183 with a concentration of 100 pg/μL and BDE-209 with a concentration of 200 pg/μL was prepared in nonane and used for adjusting GC/MS-MS parameters and for determining method precision and recovery. A $^{13}C$-labeled internal standard solution containing $^{13}C_{12}$-BDE-3, $^{13}C_{12}$-BDE-15, $^{13}C_{12}$-BDE-28, $^{13}C_{12}$-BDE-47, $^{13}C_{12}$-BDE-99, $^{13}C_{12}$-BDE-153, $^{13}C_{12}$-BDE-154, and $^{13}C_{12}$-BDE-183 at 5 μg/mL was diluted to 5 pg/μL in acetone. Diluted $^{13}C_{12}$-labeled PBDEs solution (1.0 mL) was spiked into the sea sand and the samples prior to the extraction. A recovery standard solution of $^{13}C_{12}$-BDE-139 at 5 μg/mL, was diluted to 100 pg/μL with nonane. A set of 5 PBDE calibration standard solutions (CS-1 to CS-5) contained 19 native PBDEs and 10 $^{13}C$-labeled PBDEs. The concentrations of mono- to heptabrominated diphenyl ethers ranged from 1 to 400 pg/μL, and decabromodiphenyl ether ranged from 10 to 4000 pg/μL, while the $^{13}C$-labeled standards were maintained constantly at 100 pg/μL (Table 1). Another calibration standard solution (CS-6) containing native BDE-3, BDE-7, BDE-17, BDE-47, BDE-66, BDE-100, BDE-153, and BDE-183 at 2500 pg/μL, native BDE-209 at 5000 pg/μL and $^{13}C_{12}$-BDE-3, $^{13}C_{12}$-BDE-15, $^{13}C_{12}$-BDE-28, $^{13}C_{12}$-BDE-47, $^{13}C_{12}$-BDE-99, $^{13}C_{12}$-BDE-153, $^{13}C_{12}$-BDE-154, $^{13}C_{12}$-BDE-183, $^{13}C_{12}$-BDE-139 at 100 pg/μL was used for

quantifying PBDEs in the collected samples at high levels. The composition and concentration of the calibration standard solutions are presented in Table 1.

*Insert Table 1 here*

*Sample collection and preparation*

Three samples were collected in the vicinity of an open e-waste recycling site located in Guiyu, Guangdong, China in August 2003. One of the soil samples (soil 1) was collected at a site for open dumping of burnt plastic [23 18.98 N, 116 21.70 E]. The other soil sample (soil 2) was collected at a site for dumping and disposal of waste printer rollers [23 21.18 N, 116 21.66 E]. A sediment sample was collected from the bank of the Lianjiang River [23 20.04 N, 116 21.61 E] that flows through the town of Guiyu. The samples were placed in glass bottles and stored at –20 $^{o}$C until analyses.

After being air-dried at ambient temperature, samples were thoroughly mixed and ground with a mortar and pestle before being passed through a 250-μm sieve to obtain a homogeneous matrix. Four grams of each sample were precisely weighed, spiked with 5 ng of mixed $^{13}$C-labeled PBDE internal standard, and mixed with approximately 20 g anhydrous sodium sulphate and 15 g of acid washed copper powder. The prepared samples were transferred to the thimbles for Soxhlet extraction with a solvent mixture of hexane and acetone (1:1, v/v) for 18 h. The extract was concentrated to approximately 1 mL with rotary evaporator followed by evaporation under a gentle stream of nitrogen. The sample was then transferred to a glass chromatography column packed with 6 g of acidic silica gel (30 %, w/w). PBDEs in the sample extract were eluted with 20 mL of hexane. The hexane fraction was concentrated to about 1 mL under a gentle stream of nitrogen. The sample extract was further cleaned-up on a chromatography column packed with 6 g of activated neutral alumina. The column was

subsequently eluted with 20 mL of hexane and 20 mL of a solvent mixture of hexane and dichloromethane (3/2, v/v). The latter fraction containing PBDE congeners was concentrated to 50 μL under a gentle stream of nitrogen. Recovery standard $^{13}C_{12}$-BDE-139 (5 ng) was added into the extract prior to the GC/ion-trap MS analysis.

*GC/MS-MS analysis*

The sample extracts were analyzed by GC/MS-MS on a ThermoQuest Trace GC/PolarisQ ion trap mass spectrometer (Austin, TX, USA). The GC system was operated in splitless injection mode, and the purge valve was activated 2 min after the sample injection. A 30 m DB-5 column (0.25 mm i.d., 0.25 μm film thickness) was used for PBDEs separation with the following temperature program: 110 $^{o}$C for 1 min, 8 $^{o}$C/min to 180 $^{o}$C and hold for 1 min, 2 $^{o}$C /min to 240 $^{o}$C and hold for 5 min, 2 $^{o}$C /min to 280 $^{o}$C and hold for 6 min. Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min with vacuum compensation. The GC injector temperature was maintained at 290 $^{o}$C. The temperatures of the MS ion source and transfer line were kept at 250 $^{o}$C and 300 $^{o}$C, respectively. Sample extract (1 μL) or standard solution was manually injected with a solvent delay set at 6 min. The mass spectrometer was operated with electron impact ionization (EI) mode with electron energy of 70 eV. Xcalibur software was used for the instrument parameters optimization as well as the data acquisition and analysis.

The GC/MS and MS-MS method development began with injecting the calibration standard solution (CS-5) with a concentration of 400 pg/μL in full-scan mode in order to establish the chromatographic retention time segments and to select an appropriate precursor ion for each PBDE congener. The chromatographic segment or window was established for the PBDEs based on their retention times and the selected quantitative ions. The most

abundant ion from the full-scan mass spectrum of each congener was selected as the precursor ion for MS-MS analysis. Subsequently, default parameter values for the MS-MS experiment were set as follows: 1.0 μ for the isolation width, 8 ms for isolation time, 15 ms for excitation time, 1.00 V for resonant excitation voltage, 0.45 for "q" value, 50 for AGC target value, 70 eV for electron energy and 250 mA for the emission current. Collision-induced dissociation (CID) MS-MS experiments were conducted on the selected precursor ions, and MS-MS spectra were obtained for the PBDE congeners. Two characteristic ions were selected for each congener on the basis of highest abundance in the resultant CID MS-MS spectrum.

Four important instrumental parameters, i.e. the "q" value, resonant excitation voltage (REV), excitation time (ET), and isolation time (IT), were optimized to achieve the best ion trap MS analytical performance for the PBDEs analysis. Injections of the native PBDE mixture containing BDE-3, BDE-7, BDE-17, BDE-47, BDE-66, BDE-100, BDE-153, BDE-183 and BDE-209 at 100 pg/μL were used to investigate the method sensitivity by changing each of the four instrument parameters. For BDE-47, the operating parameters were constantly set at the default values in order to obtain the relative signal intensity related to other PBDE congeners.

Identification of the PBDEs in the soil samples and sediment was performed with the following criteria: retention time matching with the corresponding authentic standards, signal-to-noise of greater than 3 for the selected ions, bromine isotope ratio of at least two characteristic ions matching the theoretical values within 20 % deviation. Quantitation of the PBDEs was performed by using isotope dilution MS technique. $^{13}C$-labeled PBDEs internal standards were spiked into the environmental samples and recovered using the same method as the native analytes during the sample preparation and GC/MS-MS analysis. $^{13}C_{12}$-BDE-139

was used to determine the recoveries of the internal standards. The isotopic dilution MS method provides better accuracy and precision for the quantification of the analytes at ultra-trace levels in complex matrices (9, 31). Instrument calibration was performed from the analysis of the mixtures of 19 native PBDEs and 10 $^{13}$C-labeled PBDEs over the concentration range of 1 to 400 pg/μL. A wider calibration range of 1 to 2500 pg/μL for BDE-3, BDE-7, BDE-17, BDE-47, BDE-66, BDE-100, BDE-153 and BDE-183 was investigated in order to analyze the soil samples due to high levels of the PBDEs. Relative response factors (RRFs) of the native PBDEs to the corresponding $^{13}$C-labeled internal standards were also determined. RRFs were used to quantify the PBDEs levels in the samples. For those PBDE congeners whose RRF could not be determined due to the lack of authentic standards, estimations of their levels were made by using the RRF value of the most closely eluted PBDE in the same chromatographic window.

*Quality assurance and quality control*

The quality assurance and quality control (QA/QC) samples included solvent blank, matrix blank and spiked matrix, all of which were analyzed together with the collected soil and sediment samples. The commercially available cleaned sea sand, that was tested and demonstrated to be free of PBDEs, was used for the matrix blank and matrix spiked samples. Five ng of each of the nine native PBDE standards were spiked into 4 g of sea sand at a concentration of 1.25 ng/g to prepare the matrix-spiked samples for evaluation of the method performance. Relative errors and standard deviations obtained from the analyses of four matrix-spiked samples were used to evaluate the accuracy and precision of the analytical method.

## Results and discussion

*GC-ion trap MS analysis of the PBDE standards*

The method development commenced with the determination of retention time of the 19 native PBDEs and the selection of characteristic ions from the GC/ion trap MS analyses in full-scan EI-MS mode. Baseline separation was achieved for all PBDE congeners except for BDE-209 that was not measured under the present gas chromatography conditions. The analysis of BDE-209 usually involves a special GC approach such as pressure programming or a short chromatography column due to its higher boiling point (32). Optimization of the EI-MS conditions occurred at source temperature of 250 $^{o}$C and electron energy of 70 eV. Under the EI-MS conditions, mass spectrometric fragmentation of the PBDE congeners was found to depend on the number of bromine substitution. For the mono-, di- and tri-PBDEs, the molecular ions ($[M]^+$ or $[M+2]^+$) were observed to be the most intensive peaks and thus were selected as the precursor ions for the subsequent tandem mass spectrometric analysis (Table 2). Different fragmentation patterns, however, were obtained for the PBDE congeners containing more bromines, i.e., the tetra- to hepta-PBDEs. For all ortho-substituted tetra- through hepta-PBDEs, predominant ion clusters resulting from the loss of $Br_2$ (i.e., $[M- Br_2+2]^+$ or $[M-Br_2+4]^+$) were selected, while the most intensive molecular ion clusters were observed for those non-ortho-substituted tetra- through hepta-PBDEs (e.g., BDE-77 and BDE-126). The observation agrees with the data published by Marsh *et al.* (23) and Alaee *et al.* (29) who reported that PBDEs with ortho-substituted bromine favored the formation of the $[M-Br_2]^+$ over the $[M]^+$ species when analyzed by EI-MS.

*Insert Table 2 here*

The predominant ion peak for each congener obtained from its full-scan spectrum was

selected as the precursor ion for the MS-MS analysis (Table 2). Because two different types of precursor ions were selected for the tetra-DBE and penta-DBE standards, two corresponding chromatographic segments were established for each of their determinations. The selected PBDE precursor ions were isolated in the ion trap and fragmented by using collision-induced dissociation (CID) mass spectrometry. The MS-MS spectra of all 19 native PBDE standards were initially recorded under the default MS-MS parameters. The MS-MS fragmentation was found to significantly depend on the congeners. For BDE-3, the most abundant $[M\text{-}COBr]^+$ ion at *m/z* 141 was selected as the quantification ion and the $[M\text{-}Br]^+$ at *m/z* 169 was selected as the confirmation ion. The dibrominated diphenyl ether BDE-15 that had no bromine atom existing at ortho position showed the most intensive ion peak corresponding to the loss of $Br_2$ at *m/z* 168. The MS-MS of BDE-7, however, showed the most intensive peak corresponding to the loss of COBr at *m/z* 219 due to the presence of one bromine at the ortho position. Thus, the quantification ions were selected at *m/z* 168 and *m/z* 219 for BDE-5 and BDE-17, respectively. Similarly, the $[M\text{-}COBr]^+$ ion was observed as the base peak for ortho-substituted tri- to heptabrominated PBDEs, while the fragmentation ion with the loss of $Br_2$ was the base ion for non-ortho substituted congeners such as BDE-77 and BDE-126. The quantitative ions were selected based on the criteria of peak intensity and ion specificity as well as potential interference from other compounds. Consideration was given primarily to the peak intensity in order to achieve the best sensitivity. The selected quantitative ions are summarized in Table 2.

The next step for MS-MS method development was to optimize the ion-trap MS parameters in series to obtain the best sensitivity for the PBDEs analysis. These parameters included “q” value, resonant excitation voltage, isolation time and excitation time. One micro liter of the native PBDEs standard solution (100 pg/μL for each congener) was injected for

optimizing each of the above parameters. The obtained peak intensity was compared to a selected reference compound BDE-47, whose parameters were constantly set in default values. The use of the relative response of each optimized PBDE congener to BDE-47 reduced the error resulting from the sample injection. The optimized "q" value, isolation time and excitation time were found to be 0.45, 8 and 15 ms, respectively, for each of the testing PBDE congeners. The optimized value of resonant excitation voltage, however, varied significantly from congener to congener. Figure 1 demonstrated the variation of relative response for several PBDE congeners as a function of the CID voltage.

*Insert Figure 1 here*

The calibration standards were analyzed under the optimized MS-MS parameters. The signal-to-noise ratio (S/N) for the GC peak of the selected ion was better than 5 for all calibration points. Linear calibration was obtained within the range of 5-400 pg for mono-BDE, di-BDE and penta-BDE congeners as well as 20-400 pg for hexa-BDE and hepta-BDE congeners. For tri-BDE congeners, the linear calibration range was from 1 to 400 pg. Good correlation coefficients ranging between 0.9853 and 0.9999 were achieved for the calibration curves of all tested PBDE congeners.

*Method development for PBDEs in solid samples*

Sample preparation procedure for PBDEs in solid samples was performed by using Soxhlet extraction and column chromatographic clean-up. It was reported that Soxhlet extraction provided good efficiency for extracting brominated flame-retardants from sediment and biota samples (33). Elimination of interferences was achieved by applying the chromatographic clean-up steps with acid silica gel and alumina. No detectable levels of PBDEs were found in matrix and method blanks. The accuracy and precision of the method

were evaluated by analyzing the standard sea sand samples in which PBDEs were spiked at 1.25 ng/g. The data of recovery and relative standard deviation were determined and presented in Table 3. The analysis of the spiked matrix samples containing 5 ng of the PBDE congeners gave average results ranging from 3.20 to 6.55 ng/g (dry weight) with relative standard deviation from 13.8 to 36.1 % (n=4). Higher relative standard deviation was found for the PBDE congeners that contained more bromines such as BDE-153 and BDE-183. Quantitative recoveries of 91.4 to 107.1 % were achieved for the extraction and clean-up procedures for $^{13}C$-labeled internal standards, except for the mono-BDE congener (BDE-3) which had an average recovery of 37.8 %. The poor recovery of BDE-3 was probably due to its relatively low boiling point, resulting in losses during the concentration procedure (34). Method detection limits obtained with the developed sample preparation procedure and with the optimized GC/MS-MS parameters ranged from 0.013 to 0.25 ng/g (dry weight) for the PBDEs (Table 3).

*Insert Table 3 here*

*Analysis of PBDEs in soil and sediment samples*

The developed GC/ion trap MS method was applied for analyzing the soil and sediment samples collected in the vicinity of open e-waste treatment sites located in Guiyu, Guangdong, China. Characteristic ion chromatograms of seven PBDE groups obtained from the analysis of one of the soil samples (soil 2) are shown in Figure 2. A total of 43 PBDE congeners with the mono- to hepta-brominated substitutions were detected in the developed chromatographic windows. The identification of the PBDEs in the sediment and soil samples was based on the examination of the characteristic MS-MS fragment ions and by comparing their retention times with those of the available authentic standards. Since only 19 native PBDE standards

were available, the detection of some of the PBDE congeners could not be conclusively confirmed. Table 4 presents the quantitative results of those identified PBDE congeners whose standards were available as well as the total levels of each isomeric group. The total PBDE levels included the estimated results of those PBDEs whose authentic standards were not available. The obtained data indicated that the PBDEs existed in the soil and sediment samples with concentrations ranging from 0.02 to 824 ng/g (dry weight). The recoveries of the $^{13}$C-labeled internal standards averaged from 81 to 98 % with relative standard deviation ranging from 2.0 to17.9 %, except for $^{13}$C-BDE-3 that had a low recovery of 40 % with RSD of 37.3 %.

*Insert Figure 2 and Table 4 here*

The concentration of mono-BDE (BDE-3) was 1.01 and 0.34 ng/g in the sediment and one of the soil samples (soil 2), respectively. To our knowledge, this is the first time to report BDE-3 detection in soil and sediment samples. At least two other peaks were observed in the retention segment designed for mono-BDE at 8.02 and 10.09 min (Figure 2A). The bromine isotope ratio obtained from these two peaks, however, did not match the theoretical isotope contribution within the identification criteria. Furthermore, the peak at 8.02 min was also observed in the chromatogram of method blank sample, clearly indicating that it was not from an isomer of mono-BDE. Two di-BDEs, BDE-7 and BDE-15, were detected at concentrations from 0.26 to 0.52 ng/g in the environmental samples. The detected levels were comparable to those reported in river and coastal sediments from Portugal (6). Two tri-BDEs (BDE-17 and BDE-28) were detected at concentrations varying from 0.34 to 5.15 ng/g in the two soil samples and from 1.05 to 1.09 ng/g in the sediment sample, respectively. Detection of BDE-17 and BDE-28 has been previously reported in crab tissue samples (35) and in air sample (36),

whereas only trace levels of BDE-28 were found in ringed seals' serum samples (37). The major PBDE congeners detected in the soils and river sediment were BDE-71, BDE-47, BDE-66, BDE-99, BDE-100, BDE-154, BDE-153, BDE-139, BDE-138 and BDE-183, whose concentrations varied from 0.80 to 824 ng/g. In all samples, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153 and BDE-183 were the dominant congeners. The concentrations of BDE-47, BDE-99, BDE-100 in the two soil samples were in the range of 2.70 to 615 ng/g, which were several times higher than the levels in the sediment collected from Lianjiang River. The levels of common congeners BDE-47, BDE-99 and BDE-100 in the sediment were 3.94, 0.89, 6.87 ng/g, respectively, which were comparable to those reported in Swedish river sediments (3), in the upper layer of a sediment core collected in the Baltic Sea (38) and in Portugal river and coastal sediments (6). Higher levels of BDE-47, BDE-99 and BDE-100 in sediments were reported in a downstream area of a manufacturing plant in the United Kingdom (39) and a downstream area of industry sites in Swedish (3).

Two tetra-BDEs, BDE-66 and BDE-71, were detected in all three samples with the highest concentrations up to 16.1 ng/g for BDE-71 in the soil sample collected near the e-waste recycling site (soil 2). BDE-66 was previously detected in human blood samples in Sweden and German (40, 41) and in sediments from Portugal (6). BDE-153, BDE-154 and BDE-138 were detected in the sediment and soil samples at concentrations of 1.23 to 210 ng/g. These three congeners of hexa-BDE were previously found at high levels in blood plasma of workers at a computer disassembly plant (12) as well as in Swedish human liver and adipose tissues (15). BDE-138 and BDE-139 were also detected in the two soil samples with concentration ranging from 2.35 to 39.9 ng/g, however, they were not detected in the sediment sample collected from Lianjiang River.

Table 4 presents total PBDE concentrations from mono-BDEs to hepta-BDEs groups in the sediment and soil samples. The results of total PBDE concentrations consist of those identified PBDE congeners whose standards were available and those congeners whose authentic standards were unavailable. When the authentic standards were unavailable, concentrations of those PBDEs were estimated by using the RRF of a reference congener that had closest retention time in the same window segment. The estimated result was obtained based on the assumption that the MS response of the targeted PBDE was same as that of the reference PBDE. Nevertheless, the data of total PBDEs showed different levels of pollutants between the sediment and soil samples. The total mono-BDE concentrations were 0.34 and 1.01 ng/g for soil 2 and the sediment, respectively. For di-BDE, total congener concentrations were 2.73 ng/g in the sediment, and 2.86 and 2.35 ng/g in the two soil samples, respectively. For tri-BDE congeners, total congener levels in the sediment and soil 1 were of the same magnitude, but the concentration of total tri-BDE in soil sample 2 (11.2 ng/g) was nearly 4 times higher. For the sediment sample, tetra- and penta-BDEs were the predominant congeners with concentrations at 8.41 and 8.52 ng/g, respectively, while hexa- and hepta-BDEs were also detected at higher levels of 5.27 and 3.81 ng/g, respectively. This distribution pattern was similar to the data that were previously reported on sediment samples from Portugal (6).

Although the two soil samples showed comparable levels of total PBDEs, their isomer patterns were significantly different. While the highest level was observed for the sole hepta-BDE isomer or BDE-183 in the sample of soil 1, penta-BDE isomers existed in soil 2 with the highest concentrations. The level of BDE-183 in soil 1 was nearly 70 times of that in soil sample 2. However, the concentrations of the total tetra-BDE and penta-BDE in soil 2 were approximately 20 and 40 times, respectively, higher than those in soil 1. For soil 2, tetra-,

penta-, and hexa-BDE were the predominant isomers and its congener pattern was similar to a commercial penta-BDE formulation, in which tetra-BDEs, penta-BDEs and hexa-BDEs account for 24-38%, 50-60% and 4-8%, respectively (42). Soil sample 2 was collected in the vicinity of a site for dumping and dismantling printer rollers. The high levels of the PBDE congeners probably resulted from the commercial penta-BDE product used in the fire retardants for printers. Soil sample 1, on the other hand, was collected near the site of burnt plastic. Hexa-BDE and hepta-BDE isomers were predominantly detected in soil 1 with total concentrations of 277 and 824 ng/g, respectively. This PBDE isomer profile has not been reported previously. The concentration ratio of the hexa-BDE to hepta-BDE isomer was similar to that reported in the octa-PBDE-based flame retardant. The octa-BDE product contains 10-12%, 44%, 31-35%, 10-11% and <1% of hexa-BDEs, hepta-BDEs, octa-BDEs, nona-BDEs and deca-BDEs, respectively (27). Unfortunately, the octa-BDEs, nona-BDEs and deca-BDEs could not be analyzed under the current chromatographic conditions.

The levels of total PBDEs in the soil samples collected near the e-waste dumps were apparently higher than those in sediment taken from the Lianjiang River. It appears that the river sediment was contaminated from e-waste activities such as the dumping, dismantling and burning of e-wastes, however, the data was limited and the samples collected for this study was not comprehensive. A number of PBDEs congeners detected at lower levels in the soil and sediment samples were not conclusively identified or confirmed. The presence of these PBDEs demonstrated the importance of extending the current analytical method to other PBDE congeners. Nevertheless, the PBDEs data obtained from the analysis of the environmental samples by the developed GC/ion trap MS method provided useful information on PBDE contamination in the town of Guiyu. PBDE concentrations in soils near the dumping

sites in Guiyu were approximately 10-60 times higher than those reported for other PBDE-contaminated locations in the world. The obtained isomer profiles of PBDEs from the two soil samples collected from different contamination sites were found to be similar to various technical formulations of fire retardant products. Uncontrolled recycling and disposal of e-wastes by simple dismantling, acid treatment, and open burning have apparently resulted in soil contamination and migration of PBDEs into river sediment.

**Acknowledgement**

Financial support for this work was sponsored by the Faculty Grant (FRG/01-02/II-34) and the special fund for Dioxin Laboratory from Hong Kong Baptist University. Zongwei Cai and Guibin Jaing would like to thank the Research Fund for Chinese Young Scholars in Overseas, Hong Kong and Macao - Distinguished Young Scholar Award (B) of National Science Foundation of China (#20329701). The authors would also like to thank Mr. Jingchun Duan, Ms. Xiangli Li, Dr. Yan Liang, Ms. Li Lin, Dr Tiangang Luan, and in particular, Dr Xiaoxuan Liu for field assistance.

**References**

(1) Dodder, N. G.; Strandberg, B.; Hites, R. A. *Organohalogen Compd*. **2000**, *47*, 69-72.

(2) Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. A. *Environ. Sci. Technol*. **2001**, *35*, 1078-1083.

(3) Sellström, U.; Kierkegaard, A.; de Wit, C.; Jansson, B. *Environ. Toxicol. Chem.* **1998**, *17*, 1065-1072.

(4) Christensen, J. H.; Platz, J. *J. Environ. Monit*. **2001**, *3*, 543-547.

(5) de Boer, J.; Wester, P. G.; van der Horst, A.; Leonards, P. E. *Environ. Pollut*. **2003**, *122*, 63-74.

(6) Lacorte, S.; Guillamon, M.; Martinez, E.; Viana, P.; Barcelo, D. *Environ. Sci. Technol.* **2003**, *37*, 892-898.

(7) Sellstrom, U.; Kierkegaard, A.; de Wit, C.; Jansson, B.; Asplund, L.; Bergander; L.; Bignert, A.; Odsjo, T.; Olsson, M. *Organohalogen Comp.* **1996**, *28*, 526-529.

(8) Hartonen, K.; Bφwardt, S.; Hawthorne, S. B.; Riekkola, M-L. *J. Chromatogr. A* **1997**, *774*, 229-242.

(9) Alaee, M.; Sergeant, D. B.; Ikonomou, M. G.; Luross, J. M. *Chemosphere* **2001**, *44*, 1489-1495.

(10) Akutsu, K.; Obana, H.; Okihashi, M.; Kitagawa, M.; Nakazawa, H.; Matsuki, Y.; Makino, T.; Oda, H.; Hori, S. *Chemosphere* **2001**, *44*, 1325-1333.

(11) Herzke, D.; Gabrielsen, G. W.; Evenset, A.; Burkow, I. C. *Environ. Pollut.* **2003**, *121*, 293-300.

(12) Sjodin, A.; Hagmar, L.; Klasson, W. E.; Kronholm, D. K.; Jakobsson, E.; Bergman, A. *Environ. Health Perspect*. **1999**, *107*, 643-648.

(13) Guvenius, T.; Meironyte, D.; Koidu, N. *Organohalogen Compd.* **1999**, *40*, 379-382.

(14) She, J.; Petreas, M.; Winkler, J.; Visita, P.; McKinney, M.; Kopec, D. *Chemosphere* **2002**, *46*, 697-707.

(15) Meironyte, D.; Bergman, A.; Noren, K. *Arch. Environ. Contam. Toxicol*. **2001**, *40*, 564-570.

(16) Covaci, A.; de Boer, J.; Ryan J. J.; Voorspoels, S.; Schepens, P. *Anal. Chem*. **2002**, *74*, 790-798.

(17) Choi, J. W.; Fujimaki, T. S.; Kitamura, K.; Hashimoto, S.; Ito, H.; Suzuki, N., Sakai, S., Morita, M. *Environ. Sci. Technol*. **2003**, *37*, 817-821.

(18) Meironyte, D.; Noren, K.; Bergman, A. *J. Toxicol. Environ. Health*, *Part A*, **1999**, *58*, 329-341.

(19) Ohta, S.; Ishizuka, D.; Nishimura, H.; Nakao, T.; Aozasa, O.; Shimidzu, Y.; Ochiai, F.; Kida, T.; Nishi, M.; Miyata, H. *Chemosphere* **2002**, *46*, 689-696.

(20) Meerts, I.; Luijks, E.; Marsh, G.; Jakobsson, E.; Bergman, A. A.; Brouwer, A. *Organohalogen Compd*. **1998**, *37*, 147–150.

(21) Orn, U.; Klasson-Wehler, E. *Xenobiotica* **1998**, *28*, 199 –211.

(22) Meerts, I.; Marsh, G.; van Leeuwen-Bol, I.; Luijks, E.; Jakobsson, E.; Bergman, A. A.; Brouwer, A. *Organohalogen Compd*. **1998**, *37*, 309–312.

(23) Marsh, G.; Bergman, A. A.; Bladh, L. G.; Gillner, M.; Jakobsson, E. *Organohalogen Compd*. **1998**, *37*, 305–308.

(24) Fowles, J. R.; Fairbrother, A.; Baecher-Steppan, L.; Kerkvliet, N. I. *Toxicology* **1994**; *86*, 49-61.

(25) Darnerud, P. O.; Sinjari, T. *Organohalogen Comp*. **1996**, *29*, 316-319.

(26) Meerts, I.; van Zanden, J. J.; Luijks, E.; van Leewen-Bol, I.; Marsh, G.; Jakobsson, E.; Bergman, A. A.; Brouwer, A. *Toxicol. Sci*. **2000**, *56*, 95–104.

(27) WHO/ICPS. Environmental Health Criteria 162: Brominated diphenyl ether, World Health Organization, Geneva. **1994**.

(28) Hornung, M.W.; Zabel, E. W.; Peterson, R. E. *Toxicol. Appl. Pharmacol*. **1996**, *140*, 227-234.

(29) Texas Campaign for the Environment, Guiyu village in China where many US computers are stripped down & pollute the village air, water and land, http://www.texasenvironment.org/e-waste/guiya_china.htm

(30) Soderstrom, G.; Marklund, S. *Environ. Sci. Technol*. **2002**, *36*, 1959-1964.

(31) Eljarrat, E.; Lacorte, S.; Barcelo, D. *J. Mass Spectrom*. **2002**, *37*, 76-84.

(32) de Boer, J.; Allchin, C.; Law, R.; Zegers, B.; Boon, J. P. *Trends Anal. Chem*. **2001**, *20*, 591-599.

(33) Hyotylainen, T.; Hartonen, K. *Trends Anal. Chem*. **2002**, *21*, 13-29.

(34) Tittelmier, S. A.; Tomy; G. T. *Organohalogen Compd*. **2000**, *47*, 206-209.

(35) Ikonomou, M. G.; Rayne, S.; Fischer, M.; Fernandez, M. P., Cretney, W. *Chemosphere* **2002**, *46*, 649-663.

(36) Gouin, T.; Thomas, G. O.; Cousins, I.; Barber, J.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol*. **2002**, *36*, 1426-1434.

(37) Ikonomou, M. G.; Rayne, S.; Addison, R. F. *Environ. Sci. Technol*. **2002**, *36*, 1886-1892.

(38) Nylund, K.; Asplund, L.; Jansson, B.; Jansson, P.; Litzen, K.; Sellström, U. *Chemosphere* **1992**, *24*, 1721-1730.

(39) Allchin, C. R.; Law, R. J.; Morris, S. *Environ. Pollut*. **1999**, *105*, 197-207.

(40) Klasson, W. E.; Hovander, L.; Bergman, A. *Organohalogen Comp*. **1997**, *33*, 420-425.

(41) Schroter-Kemani, C.; Helm, D.; Herrmann, T.; Papke, O. *Organohalogen Compd*. **2000**, *47*, 49-52.

(42) de Wit, C. *Chemosphere* **2002**, *46*, 583-624.

**Table 1.** Concentrations of native and $^{13}$C-labeled PBDEs in calibration standard solutions (pg/μL).

| Compounds | CS[a] -1 | CS-2 | CS-3 | CS-4 | CS-5 | CS-6 |
|---|---|---|---|---|---|---|
| *native PBDEs* | | | | | | |
| BDE-3 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-7 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-15 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-17 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-28 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-47 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-49 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-66 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-71 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-77 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-85 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-99 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-100 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-119 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-126 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-138 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE153 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-154 | 1.0 | 5.0 | 20 | 100 | 400 | -- |
| BDE-183 | 1.0 | 5.0 | 20 | 100 | 400 | 2500 |
| BDE-209 | 10 | 50 | 200 | 1000 | 4000 | 5000 |
| *$^{13}$C-labeled PBDEs* | | | | | | |
| $^{13}C_{12}$-BDE-3 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-15 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-28 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-47 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-99 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-153 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-154 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-183 | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-BDE-209 | 100 | 100 | 100 | 100 | 100 | -- |
| $^{13}C_{12}$-BDE-139 | 100 | 100 | 100 | 100 | 100 | 100 |

[a]: calibration standard.

**Table 2.** The GC/ion-trap conditions and the monitored precursor and fragment ions for the PBDEs analysis.

| Compounds | Segment (min) | IUPAC No. | Precursor ions (m/z) | Characteristic fragment ions (m/z) | Br isotopic intensity ratio |
|---|---|---|---|---|---|
| Mono-BDE | 6.00-12.10 | 3 | 248 $[M]^+$ | 141,169 | -- |
| | | 3L[a] | 260 $[M]^+$ | 152,181 | |
| Di-BDE | 12.10-18.00 | 7, 15 | 328 $[M+2]^+$ | 168, 219/221 | 82.9/100 |
| | | 15L[a] | 340 $[M+2]^+$ | 180, 231/233 | 82.9/100 |
| Tri-BDE | 18.00-28.00 | 17, 28 | 406 $[M+2]^+$ | 246/248 | 96.4/100 |
| | | 28L[a] | 418 $[M+2]^+$ | 258/260 | |
| Tetra-BDE | 28.00-34.50 | 47, 49, 66, 71 | 326 $[M-Br_2+2]^+$ | 217/219 | 89.9/100 |
| | 34.50-37.00 | 77 | 486 $[M+4]^+$ | 326/328 | 100/62.3 |
| | 28.00-34.50 | 47L[a] | 338 $[M-Br_2+2]^+$ | 228/230 | |
| Penta-BDE | 37.00-46.00 | 85, 99, 100,119 | 404 $[M-Br_2+2]^+$ | 295/297 | 55.8/100 |
| | 46.00-47.50 | 126 | 564 $[M+4]^+$ | 404/406 | 72.8/100 |
| | 37.00-46.00 | 99L[a] | 416 $[M+Br_2+2]^+$ | 306/308 | |
| Hexa-BDE | 47.50-59.50 | 138, 153, 154 | 484 $[M-Br_2+4]^+$ | 375/377 | 76.5/100 |
| | | 153L, 154L, 139L[a] | 496 $[M-Br_2+4]^+$ | 386/388 | |
| Hepta-BDE | 59.50-62.00 | 183 | 562 $[M-Br_2+4]^+$ | 455/457 | 100/94.7 |
| | | 183L[a] | 574 $[M-Br_2+4]^+$ | 466/468 | |

[a]: $^{13}C$-labeled PBDE congeners.

**Table 3.** Recovery, accuracy and precision data from 4 replicate analysis of spiked standard sea sand samples.

| | Add level (ng) | Found average level (ng) | Relative error (%) | Recovery (%) | RSD[a] (%) |
|---|---|---|---|---|---|
| Native congeners | | | | | |
| BDE-3 | 5.00 | 3.75 | -25.4 | -- | 20 |
| BDE-7 | 5.00 | 3.95 | -21.5 | -- | 13 |
| BDE-17 | 5.00 | 4.35 | -12.7 | -- | 23 |
| BDE-47 | 5.00 | 4.30 | -13.8 | -- | 18 |
| BDE-66 | 5.00 | 4.30 | -13.8 | -- | 26 |
| BDE-100 | 5.00 | 3.20 | -26.0 | -- | 20 |
| BDE-153 | 5.00 | 6.55 | 30.8 | -- | 32 |
| BDE-183 | 5.00 | 4.60 | -8.2 | -- | 36 |
| Labeled congeners | | | | | |
| $^{13}C_{12}$-BDE-3 | 5.00 | 1.90 | -- | 38 | 47 |
| $^{13}C_{12}$-BDE-15 | 5.00 | 4.55 | -- | 91 | 28 |
| $^{13}C_{12}$-BDE-28 | 5.00 | 4.95 | -- | 99 | 16 |
| $^{13}C_{12}$-BDE-47 | 5.00 | 5.35 | -- | 107 | 10 |
| $^{13}C_{12}$-BDE-99 | 5.00 | 4.65 | -- | 93 | 6 |
| $^{13}C_{12}$-BDE-153 | 5.00 | 4.10 | -- | 82 | 21 |
| $^{13}C_{12}$-BDE-154 | 5.00 | 4.60 | -- | 92 | 10 |

[a] Relative standard deviation (n = 4).

**Table 4**. Concentrations of PBDEs in the sediment and soil samples (ng/g, dried weight).

| Congener | Sediment | Soil 1 | Soil 2 |
|---|---|---|---|
| BDE-3 | 1.01 | nd [a] | 0.34 |
| *total mono-BDE* [b] | *1.01* | *nd* | *0.34* |
| BDE-7 | 0.26 | 0.43 | 0.40 |
| BDE-15 | 0.40 | 0.34 | 0.52 |
| *total di-BDE* | *2.73* | *2.86* | *2.35* |
| BDE-17 | 1.09 | 0.34 | 5.15 |
| BDE-28 | 1.05 | 0.78 | 5.15 |
| *total tri-BDE* | *2.51* | *2.71* | *11.2* |
| BDE-71 | 2.27 | 1.93 | 16.1 |
| BDE-49 | nd | nd | nd |
| BDE-47 | 3.94 | 5.89 | 244 |
| BDE-66 | 0.80 | 0.96 | 10.7 |
| BDE-77 | nd | nd | nd |
| *total tetra-BDE* | *8.41* | *14.9* | *280* |
| BDE-85 | nd | nd | nd |
| BDE-100 | 0.89 | 2.70 | 89.4 |
| BDE-99 | 6.87 | 13.3 | 615 |
| BDE-119 | nd | nd | nd |
| BDE-126 | nd | nd | nd |
| *total penta-BDE* | *8.52* | *18.4* | *725* |
| BDE-154 | 1.23 | 32.0 | 48.9 |
| BDE-153 | 3.36 | 210 | 44.1 |
| BDE -139 | nd | 3.56 | 39.9 |
| BDE-138 | nd | 9.91 | 2.35 |
| *total hexa-BDE* | *5.27* | *277* | *139* |
| BDE-183 | 3.81 | 824 | 12.3 |
| *total hepta-BDE* | *3.81* | *824* | *12.3* |
| **Total PBDEs** | **32.3** | **1140** | **1169** |

[a]: Not detected.

[b]: Total results were the sum of levels from both identified and unidentified PBDE congeners. The concentrations of the unidentified PBDEs were estimated because the corresponding authentic standards were not available.

Figure legends:

Figure 1. Optimization of the ion-trap MS parameter (resonant excitation voltage) for 7 selected PBDEs from each of the isomer groups of mono- to hepta-BDE.

Figure 2: Extracted MS-MS chromatograms of mono- to hepta-BDEs obtained from the analysis of soil 2 collected in the vicinity of e-waste dumping site (A: mono-BDE; B: di-BDE; C: tri-BDE; D: tetra-BDE; E & F: penta-BDEs; G: hexa-BDEs; H: hepta-BDEs). The confirmed PBDEs with the corresponding authentic standards are labeled with their IUPAC identification numbers near the chromatographic peaks. Peaks of other PBDE congeners were detected, but not confirmed through the comparison with authentic standards due to the lack of the standards.

Figure 1

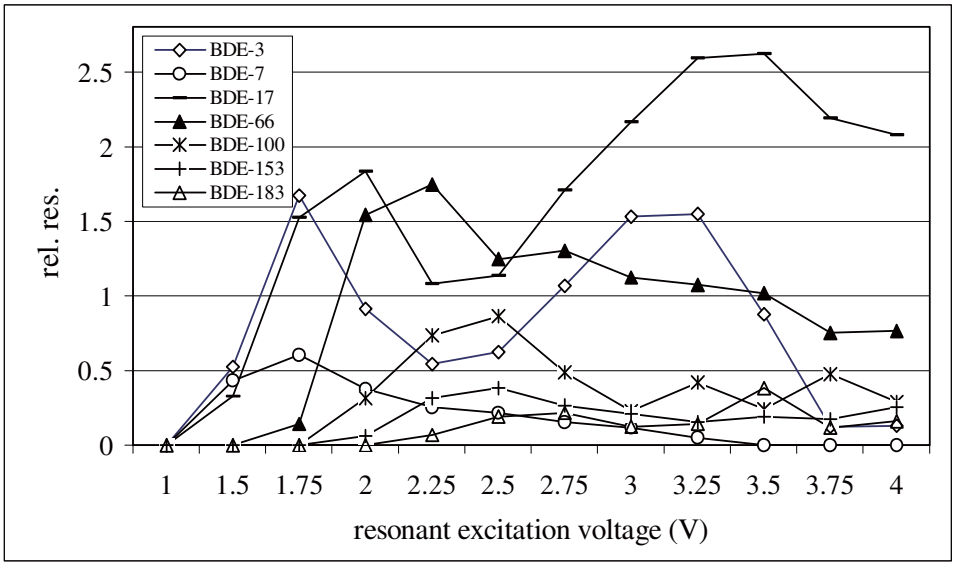
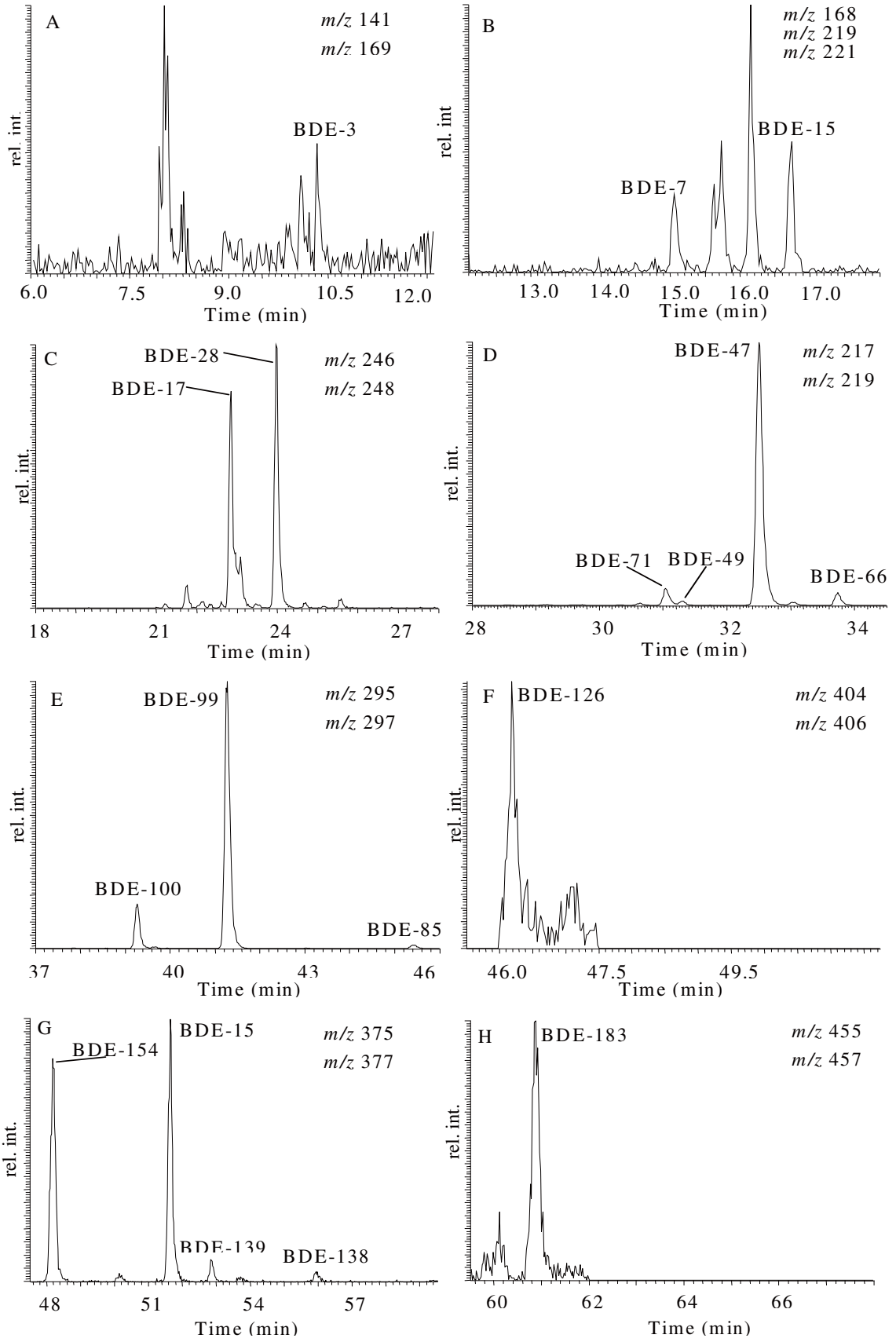

BDE-3
BDE-7
BDE-17
BDE-66
BDE-100
BDE-153
BDE-183
rel. res.
2.5
2
1.5
1
0.5
0
1
1.5
1.75
2
2.25
2.5
2.75
3
3.25
3.5
3.75
4
resonant excitation voltage (V)

Figure 2


A
m/z 141
m/z 169
BDE-3
rel. int.
6.0
7.5
9.0
10.5
12.0
Time (min)
B
m/z 168
m/z 219
m/z 221
BDE-15
BDE-7
rel. int
13.0
14.0
15.0
16.0
17.0
Time (min)
C
BDE-28
BDE-17
m/z 246
m/z 248
rel. int.
18
21
24
27
Time (min)
D
BDE-47
m/z 217
m/z 219
BDE-71
BDE-49
BDE-66
rel. int.
28
30
32
34
Time (min)
E
BDE-99
m/z 295
m/z 297
BDE-100
BDE-85
rel. int.
37
40
43
46
Time (min)
F
BDE-126
m/z 404
m/z 406
rel. int.
46.0
47.5
49.5
Time (min)
G
BDE-154
BDE-15
m/z 375
m/z 377
BDE-139
BDE-138
rel. int.
48
51
54
57
Time (min)
H
BDE-183
m/z 455
m/z 457
rel. int.
60
62
64
66
Time (min)