

POLYBROMINATED DIPHENYL ETHERS IN THE ENVIRONMENT OF E-WASTE RECYCLING

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Abstract

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants (BFRs) in a wide variety of applications including plastics, resins, electronic and electrical product. They are ubiquitous environmental contaminants due to their extensive use. Structurally, PBDEs resemble environmental contaminants such as PCBs and PCDD/Fs. The analysis of PBDE congeners by GC/MS was studied in terms of their potential interferences. Different MS approaches were normally used for the PBDE analyses: quadrupole and ion trap mass (EI-MS). Carbon-13 isotope dilution method was used to quantify fish samples collected from electronic waste recycling region.

E-waste containing PBDEs may be incinerated and emitted into the atmosphere, deposited in field and river, where they may move into water and sediment. Through these environmental pathways, exposure to wildlife and humans occurs. Focus will be placed on the fish because PBDEs have a persistent and high binding affinity to adipose and a tendency to accumulate in fish. It is expected that the environment in Guiyu, Guang Dong is significantly contaminated by PBDEs due to the e-waste recycling activities.

Introduction

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been extensively used as flame retardants in furniture, building materials and electronic components. PBDEs can be released into the environment, persistent with a high bioaccumulation potential and thus affect human health. The flame retardant have been detected with significant levels in environmental (1-3) and biological (4-5) samples. Recent toxicological studies suggested that several PBDEs and/or their metabolites might have disrupted the endocrine system (6-7). Thus, trace analysis of PBDEs is important.

Illegal recycling operations of electronic wastes (e-wastes) have been reported to cause severe environmental pollution of PBDEs (8). However, little information on the PBDE congener profiles and concentrations in the environment around the e-waste recycling site has been reported. This study aims to develop and apply a capillary gas chromatography/ion-trap mass spectrometry method for analyzing PBDEs in environmental samples collected from an e-waste disposal site. Various contamination sources of PBDEs were discussed based on the obtained analytical results.

Experimental

Chemical reagents and standard solutions

Chemicals used in this study were Analytical or higher grade. The PBDE standard solutions were purchased from Wellington Laboratories (Ontario, Canada). Cleaned sand was purchased from Fluka (Milwaukee, USA) and used for method development. A set of 5 PBDE calibration standard solutions

(CS-1 to CS-5) contained 19 native PBDEs and 10 ¹³C-labeled PBDEs. The concentrations of mono- to heptabrominated diphenyl ethers ranged from 1 to 400 pg/μL while the ¹³C-labeled standards were maintained constantly at 100 pg/μL.

Sample preparation and analysis

Cleaned sand was spiked with known levels of PBDE standards prior to the sample preparation for evaluating method accuracy and precision. Environmental soil samples were collected from six sampling points around an approximate 30-m² disposal site of e-wastes. The samples were thoroughly mixed and ground prior to the sample preparation. One gram of each of the sand and field soil sample was mixed with 10 g anhydrous sodium sulphate and 5 g of acid washed copper powder. After one nanogram of ¹³C-labeled PBDE internal standard was added, the sample was Soxhlet extracted with a solvent containing hexane and acetone (1:1, v/v) for 12 hours. The sample was cleaned-up with columns of acidic silica gel and activated neutral alumina for the GC/MS/MS analysis. One microliter of the sample extract was injected into a DB-5 column (60 m, 0.25 mm i.d., 0.25 μm film thickness) with injector temperature of 280 °C and splitless injection mode on a ThermoQuest Trace GC/PolarisQ ion trap mass spectrometer. The column temperature was programmed from 110 °C (1 min) to 180 °C at rate of 8 °C/min; from 180 °C (1 min) to 280 °C at 2 °C /min and finally hold for 10 min at 280 °C. Ion-trap was used for the electron impact ionization (EI) MS/MS analysis.

Results and discussion

Sample preparation procedure for PBDEs in solid samples was performed by using Soxhlet extraction and column chromatographic clean-up (9). Quantitative recoveries (more than 65 %) were achieved for the sample preparation procedure, except for the mono-BDE congener (BDE-3) which had an average recovery of 40 %. The accuracy and precision of the method were evaluated by analyzing the cleaned sand samples spiked with known amount PBDEs. The obtained relative errors and relative standard deviations were less than 30% (n=6) when the added PBDE levels were 1 ppb. Calibration standards were analyzed under the optimized MS/MS parameters. Linear calibration was obtained within the range of 1-400 pg for the PBDE congeners. For the ion trap MS/MS analysis, the most intensive ion peak of each PBDE congener was selected as the parent ion. The selected parent ions were isolated in the ion trap and fragmented by using CID mass spectrometry. MS/MS spectra of all analytes were recorded, from which a characteristic ion was selected as quantitative ion. The quantitative ions were selected based on the criteria of peak intensity and ion specificity as well as potential interference from other compounds. The [M-COBr]⁺ fragment ion was observed as the base peak for PBDEs with ortho-substituted bromine, while the fragmentation ion with the loss of Br₂ ([M-Br₂]⁺ ion) was the base ion for non-ortho substituted congeners.

Identification of the PBDEs in soil samples was performed with the criteria of chromatographic retention time, selected characteristic ion and bromine isotope ratio. Isotope dilution MS technique was applied for the PBDE quantitation. Relative response factors of the native PBDEs to the corresponding ¹³C-labeled internal standards were measured and used to quantify the PBDE levels in the samples. Only the PBDEs, whose ¹³C-labelled internal standards were available, were quantitatively analyzed.

The recoveries of the ^{13}C -labeled internal standards were better 60% with relative standard deviation ranging from 8 to 26 %. Both individual and averaged concentrations of the PBDEs are presented for the soil samples. Because the soil samples were collected from the sampling points around the same e-wastes disposal site, the detected PBDE levels were similar with a standard deviation of less than 30%. The data indicated that the PBDEs existed in the soil samples with concentrations ranging from sub-ppb to about 600 ppb (dry weight). Mono-BDE (BDE-3) was not detected in the collected soil samples. BDE-15 (di-BDE) was detected at concentrations from 0.60 to 0.92 ppb in the soil samples. The average concentration of the tri-BDE (BDE-28) was 5.01 ppb with a standard deviation of 0.62. Other PBDE congeners detected in the soils were BDE-47, BDE-99, BDE-139, BDE-153, BDE-154, and BDE-183, whose averaged levels varied from 12.3 to 552 ppb. Tetra- (BDE-47), penta- (BDE-99) and hexa-BDE (BDE-139, BDE-153, BDE-154), were the predominant isomers and its congener pattern was similar to a commercial penta-BDE formulation (10). Thus, the high levels of the PBDE congeners probably resulted from the commercial penta-BDE product used in the fire retardants because the soil samples were collected in the vicinity of a site for the e-wastes disposal. Uncontrolled disposal and recycling have apparently resulted in the soil contamination with the PBDEs.

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