



Original article

Determination of polybrominated diphenyl ethers in river water by combination of liquid–liquid extraction and gas chromatography–mass spectrometry



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ABSTRACT

In this work, a reliable and sensitive method for detecting polybrominated diphenyl ethers (PBDEs) has been developed by the combination of liquid–liquid extraction and gas chromatography–mass spectrometry. PBDEs were extracted from a large volume of water by liquid–liquid extraction and purified by silica gel chromatography. In order to reduce the deviation, dibromobiphenyl was exploited as the internal standard to minimize differences among the injections. The quantification was performed using an external standard. Good linear correlation coefficients (>0.991) and a wide linearity range (1.0–500.0 ng/L) indicated the steadiness of the proposed method. Moreover, the satisfactory recovery ($>75\%$) suggested that successful determination of PBDEs in river water had been achieved. Furthermore, the deduction behavior of PBDEs in river water could be inferred according to the results.

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1. Introduction

Over the past 50 years, polybrominated diphenyl ethers (PBDEs) were widely used as flame retardant in building materials, electronics, furnishings, foods, airplanes, plastics, polyurethane foams, and textiles [1–5]. The core structure of PBDEs was a diphenyl ether scaffold, which contains 10 hydrogen atoms. Every hydrogen atom can be replaced by a bromine atom, resulting in 209 congeners. PBDEs are stable, highly persistent, and easily bioaccumulated. Most PBDEs are difficult to degrade naturally [6,7]. Moreover, they can migrate over a long distance, and integrate into food chains [5,8]. Therefore, they have attracted increasing attention in the ecosystems because of the health hazards of these chemicals. PBDEs have been found in the environment, animal tissues and bloods, as well as in humans [9,10]. Many studies have shown that PBDEs can reduce human fertility and display neurotoxicity [11]. Because of their toxicity and persistence, four kinds of PBDEs (TeBDE, PeBDE, HxBDE and HpBDE) were restricted under the Stockholm Convention, a treaty to control and phase out major persistent organic pollutants (POPs).

PBDEs are widely used in various products and can easily diffuse into the surrounding, especially in waters. For example, PBDEs from the fabrication and application of plastics, electronics, textiles, automotive, furniture, etc., can all get into water [8,12]. On the other hand, PBDEs can be resorbed by the environment through the discharge and disposal of sewage and sludge, becoming another source of PBDEs in the environment [13]. Large amount of persistent pollutants are poured into aquatic systems, which is the most important natural solvent. It is reported that PBDE concentrations in discharged effluent range from 4 pg/L to 20,000 pg/L [14]. Therefore, determination of PBDEs in water is of great importance and the results may be alarming. However, little is known about PBDEs in water because PBDEs are difficult to process by traditional technologies due to their congeners and degradation [15,16]. Highly brominated diphenyl ethers such as NoBDE and DeBDE can easily lose one, two or even more bromine atoms to form lower brominated diphenyl ethers in the complex environment by biodegradation or photodegradation [17–19]. Moreover, little PBDEs would diffuse into water because they prefer sludge rather than sewage due to their high octanol–water partition coefficient [6,13]. Rayne's group has reported that the total concentration of lower brominated PBDEs (except BDE-209, as expressed as PBDEs) was 140 ng/L in the sewage plant influent [15]. However, it is only about 2.9–46 ng/L in the effluent. The

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influent concentration of BDE-209 was 169 ng/L. In contrast, the effluent concentration was 6 ng/L. Therefore, a large volume of sample was required.

Large volumes of sample can enhance matrix influence and suppress the signal. Thus, various sample pretreatment methods were developed. Soxhlet extraction, a traditional sample pretreatment for PBDEs, was usually laborious and time-consuming. Many researchers reported that PBDEs can be extracted by solid phase extraction/solid phase microextraction (SPE/SPME) [20,21]. However, it has some drawbacks, such as high cost, sample carry-over, and time-declining performance. More importantly, SPE/SPME was not suitable for large volume extraction because the sample would be overloaded, and extra instrument such as a pump was needed. Dispersive liquid-liquid microextraction (DLLME) was also developed because it was simple and highly effective, but it was easy to over-extraction and some matrix could easily condensed [22,23]. Therefore, liquid-liquid extraction (LLE) as a reliable and simple method was often used to pretreat water samples in large volumes [14,24]. Moreover, due to the extremely low level of the targeted compounds and the large number of interfering substances, analytical methods for PBDEs determination are difficult to develop. To overcome these difficulties, highly selective detection methods and/or tedious pretreatment methods are demanded [25,26]. GC was used to separate the targets. A mass spectrometer that enabled the identification of chemical structure [27–29] was used as a detector. Thus, an internal standard coupled with GC-MS is developed to provide a reliable quantification and to accurately determine the concentrations of these targets.

The purpose of this work is to establish an accurate and reliable method for the determination of PBDEs in water. Ten PBDEs with different degrees of bromination were analyzed by liquid-liquid extraction coupled with GC-MS (Fig. 1). The developed method was successfully applied to analyze PBDEs in river water. Moreover, the possible behavior of PBDEs in environment was proposed.

2. Experimental

2.1. Chemicals

Acetone and hexane (HPLC grade) were purchased from J. K. Baker Corporation. Water was obtained by purification of de-ionized water through a Milli-Q system (Millipore, Bedford, MA, USA). All PBDEs were purchased from Wako (Osaka, Japan, purity 98%). Mixtures of PBDEs except DeBDE were made in a

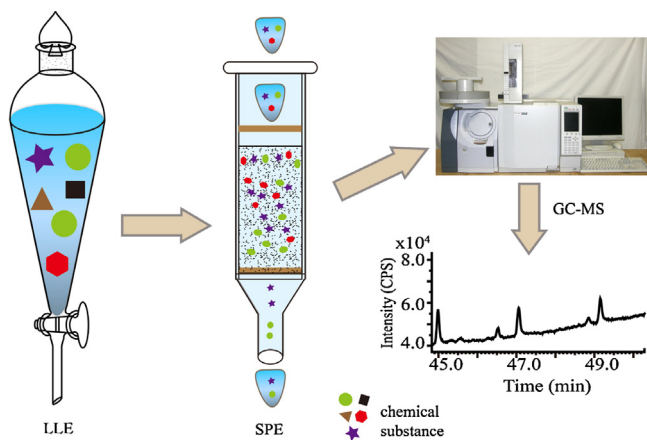


Fig. 1. Procedure for the determination of PBDEs in river water based on LLE-SPE and GC-MS. LLE indicated liquid-liquid extraction. SPE depicted solid phase extraction by silica gel column.

concentration range of 0.1–500.0 ng/L. DeBDE was prepared in the concentration range of 1.0–5000.0 ng/L.

2.2. Sample collection and pretreatment

Water samples were collected in glass bottles at the position above 60 cm above the riverbed. The river is located at the east of YuanMingYuan. To validate the LLE method, a 100 mL water sample spiked with 2.00 ng/L PBDEs was used. The solution was filtered through a 0.45 μm membrane, and then extracted with 3 \times 20 mL petroleum ether-hexane (1:2). The elute solution was dried over Na_2SO_4 . Then the extraction solvent was condensed to 2 mL by nitrogen blowing.

The extraction solution was subjected to column chromatography by packing 6.0 g of silica gel particle in a column (15 cm \times 10 mm I.D.). 0.5 cm^3 of absorbent cotton was placed at the top and the bottom of the column. Before using, the silica gel was activated at 140 $^\circ\text{C}$ overnight. The column was equilibrated with 30 mL of petroleum ether-hexane (1:2) solvent. Then the sample was introduced. The column was eluted with 2 \times 15 mL of the petroleum ether-hexane (1:2) solvent. All elution solvents were combined and dried over anhydrous Na_2SO_4 . Then, the eluted solvent was condensed to 500 μL by the usage of 1 mL/min nitrogen gas. Finally, 1 μL of the extraction was injected into the GC-MS. The pretreatment procedures were the same as those for the un-spiked samples.

2.3. GC-MS system for the determination of PBDEs

The ten PBDEs were determined using a Shimadzu GC/MS QP2010 system. The GC system was equipped with an electronic pressure controller, a programmable-temperature vaporizer (PTV) and an autosampler. A 30 m \times 0.25 mm I.D. Rtx-ris capillary column with a film thickness of 0.25 μm was selected as the GC column. In these cases, the stationary phase of the analytical columns was 5% phenyl, 95% dimethylpolysiloxane. The PVT started from 110 $^\circ\text{C}$ for the initial 1 min, was increased to 250 $^\circ\text{C}$ with a rate of 12 $^\circ\text{C}/\text{min}$ and maintained at 250 $^\circ\text{C}$ for 1 min. After that, the temperature was increased at a rate of 1.5 $^\circ\text{C}/\text{min}$ to 320 $^\circ\text{C}$, and was kept at 320 $^\circ\text{C}$ for 5 min. The mass spectrometer was operated in electron ionization (EI) in the scan mode at the m/z range from 100 to 1000 for all PBDEs. Dwell times were set at 50 ms. Helium was used as mobile phase. The temperatures of ion source, injection, and interface were set at 250, 320 and 320 $^\circ\text{C}$, respectively. The electron energy was 70 eV. The style of injection was splitless and the injected volume was 1 μL . A quantitative analysis of PBDEs was carried out by selecting a specific mass for each analyte, that is, the selected-ion monitoring (SIM) mode. Table 1 listed the retention times and m/z ratios of the quantification and confirmation ions of all PBDEs.

3. Results and discussion

3.1. GC-MS conditions and characteristics of ionic fragments

PBDEs with different chemical structures and polarity allowed us to separate them using column chromatography. Therefore, the mixture of ten congeners of PBDEs from mono- to decabromination were separated by GC-MS. Temperature of vaporizing was the key element for GC resolution. Three PVT programs were studied (Fig. 2A). Fig. 2B–D showed the total ion chromatograms (TIC) corresponding to the three PVTs of standard PBDEs at 2 ng/mL (expect DeBDE). The DeBDE was at 20 ng/L. The peaks of NoBDE and DeBDE disappeared in Fig. 2B, and DeBDE lost in Fig. 2C. But, Fig. 2D displayed the peaks of NoBDE and DeBDE. It was deduced that the accelerating programming rate of temperature will lead to

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