

Determination of tetrabromobisphenol-A (TBBP-A) in Soil and Sediment Samples by Ultra-Performance Liquid Chromatography with Quattro Premier Mass Spectrometer

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Introduction

Brominated flame retardants (BFRs) are widely distributed in the environment, and their persistence and/or potential for bioaccumulation have caused concern ^[1]. Tetrabromobisphenol A (4,4A-isopropylidenebis(2,6-dibromophenol), TBBP-A) is the most widely used brominated flame retardant in the world with an estimated world consumption of 210 000 metric tons in 2000. It is an additive chemically bound to synthetic matrix such as plastics, textiles and electronic boards. The release of this chemical in the environment occurs through manufacturing, recycling and disposal of various fabrics and materials. TBBP-A has been found in sediments ^[2,3,4], sewage sludge ^[3,4,5], and TBBPA has also been reported in human plasma ^[6]and indoor air ^[5,7], but very few data are available for soils. The environmental distribution of TBBP-A is still scarcely known.

In China, there are a few of TBBP-A producing plants mostly lied at the east China, especially in Shandong and Jiangsu province. However, almost no studies on the TBBP-A level in China environment were reported. The objective of this research was to develop a simple and rapid method for the determination of TBBP-A level in environmental soil and sediment samples. Solid-phase extraction (SPE) offers efficient methods with lower solvent consumption, less risk of contamination, and higher selectivity. In this work, a method for sample preparation using SPE is presented. A further purpose was to investigate TBBP-A concentrations in sediments from rivers and soil surrounding the manufacturing plants.

Materials and methods

All solvents used in the extraction and analysis procedures were of HPLC-grade quality. TBBPA standard and ¹³C₁₂-TBBPA standards were obtained from Cambridge Isotope Laboratories Inc. C₁₈ SPE cartridge column (100 mg, 1.5mL) was purchased from Alltech (USA). Nitrogen gas (99.999%) was obtained from BeiWen Corporation (Beijing, China).

Four soil samples were collected around TBBP-A plants, and one sediment sample from river near the TBBP-A plants in September of 2005, in which the average pH was 7.68 and the organic carbon content was 0.89%. The environmental samples were frozen on return to Lab and kept frozen until analysis. The extraction of TBBPA from soil and sediment sample was according to the previous method with minor modifications as follows. Samples were dried with anhydrous Na₂SO₄ and 2μg of ¹³C-TBBP-A was added to each sample (30 g). The samples were extracted for 22 h using 250mL mixture acetone and dichloromethane (4:1, v/v). The solvent was evaporated, and the extracts were

transferred with methanol. The samples were then concentrated and were applied to the preconditioned C₁₈ SPE cartridge. The column was pre-conditioned with dichloromethane (2 mL) and methanol (2 mL). TBBP-A in the cartridge was eluted with 6mL of methanol, and the eluate was concentrated under nitrogen stream. The final extract is filtered through one 0.45µm syringe filter into a glass UPLC vial.

A Waters Micromass Quattro Premier XE Tandem Quadruple Mass Spectrometer (UPLC-MS/MS) system was carried out using MRM mode. A reversed-phase Waters Acquity BEH C18 (50mm × 2.1mm i.d., particle size 1.7 µm) column was used. Water (mobile phase A) and acetonitrile (mobile phase B) were used as mobile phases for the gradient elution (gradient curve:0–1 min, 50% B; 1–2min, linear change from 50 to 90% B; 2–3min, 90% B; 3–4min, linear change from 90 to 50% B; a run-time, 4min). The flow-rate of the mobile phase and the column oven temperature were set at 0.45 mL/min and 40°C, respectively. The effluent from LC column was flowed directly, without splitting, into the ion source of mass spectrometer. The UPLC–MS/MS was operated in the negative ESI mode. The cone voltage was 50 V, source temperature 120°C, collision energy 35eV. Figure 1 show the ion chromatograms for the UPLC–MS/MS analysis of TBBPA, ¹³C₁₂-TBBP-A in soil.

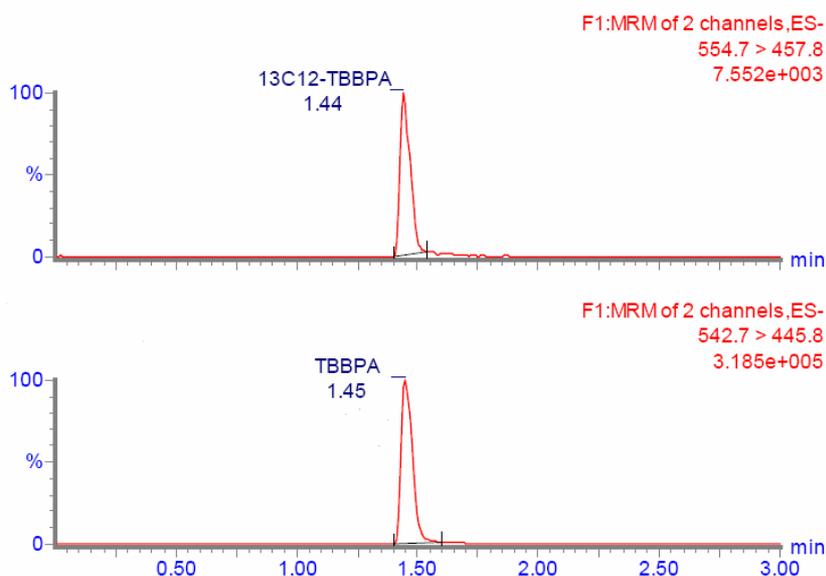


Figure 1. Ion chromatograms for the LC–MS/MS analysis of TBBPA, ¹³C₁₂-TBBPA,

Results and Discussion

The detection limit (signal-to-noise ratio (S/N) = 3) of TBBP-A in standard solution was 8.66 pg on column. Average recoveries for the extraction of TBBP-A in blank soil samples spiked at the 0.36pg to 356ng TBBP-A level ranged from 49.93 % to 91.55% and the relative standard deviation (RSD)

ranged from 0.77% to 6.49% (n=4).

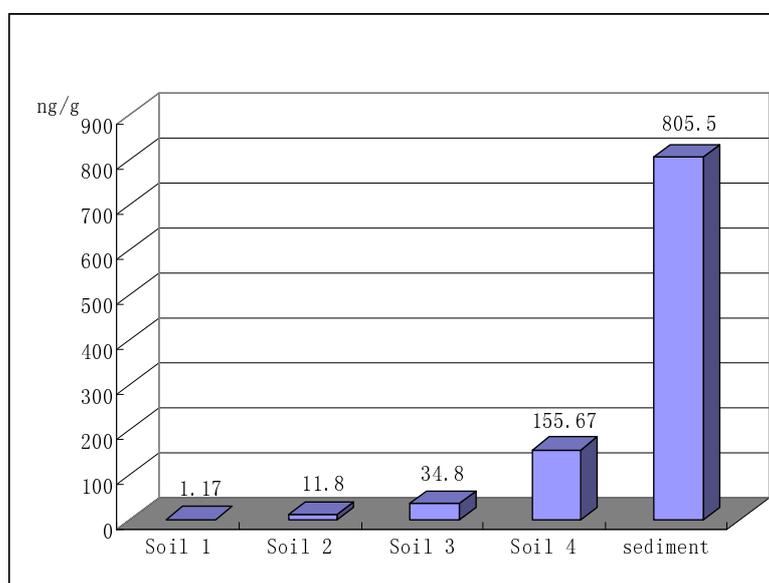


Figure 2. The concentrations of five environmental samples (ng/g)

The major concentrations difference from Figure 2 is for the different sampling site and two different types of samples, with the sediment sample showing greater level. In 1983 TBBP-A was first detected at 0.5-140 $\mu\text{g}/\text{kg}$ (dry weight) in 14 out of 19 river sediment samples in Osaka, Japan ^[8]. Sellström et al. (1990) analyzed sediment samples taken upstream and downstream from a factory in Sweden for the presence of TBBPA and its dimethylated derivative (Me2-TBBPA) ^[9]. The downstream level of TBBP-A was 430 $\mu\text{g}/\text{kg}$ and upstream was 50 $\mu\text{g}/\text{kg}$. Due to its low solubility in water and a high $\log K_{ow} = 4.5$ ^[3], TBBP-A is likely to be associated with suspended particulate matter once released in the waters and ultimately buried in sediments. However, the lack of data on its environmental fate in sediment cores precludes to establish if its input is a real on-going environmental problem. For this reason de Wit ^[2,6] has pinpointed the need for more data on TBBP-A level in sediment cores at a global level as a priority in the study of the environmental fate of this brominated flame retardant.

We detected TBBP-A in 4 soil samples surrounding the TBBP-A plants. The concentrations of soil are different from each other for the different sampling sites. Soil 1[#] was from farmland, taken windward 6 km away from plant and soil 2[#], 3[#], 4[#] samples taken surrounding the TBBP-A plants. The data show the TBBP-A may be emitted from the production sources and may be transported by air. The results presented show that there are considerable variations in the concentrations of TBBPA in soil and sediment. Further monitoring the local area will be continued to analyze TBBP-A in air, water, soil, surface sediments. Spatial and temporal variations study will give an indication of local sources as well as the effectiveness of product control measures.

Acknowledgements

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