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Development of an analytical method for the determination of polybrominated diphenyl ethers in sewage sludge by the use of gas chromatography coupled to inductively coupled plasma mass spectrometry

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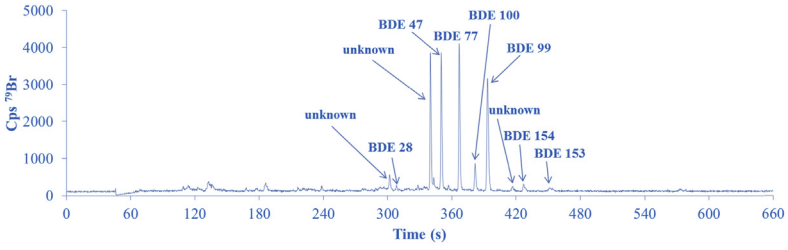
HIGHLIGHTS

- A new analytical procedure for the determination of six PBDEs in sewage sludge was developed.
- PBDEs were extracted with HCl/MeOH, and addition of Tris-citrate buffer and iso-octane.
- Concentrations of PBDEs in the organic phase (iso-octane) were determined by GC-ICP-MS.
- The procedure developed is simple, accurate, repeatable, reproducible and sensitive.
- BDE 47 and BDE 99 were the most abundant BDE congeners in sludge samples analysed.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are flame retardants. As a consequence of their widespread use, they have been released into the environment. PBDEs are lipophilic organic contaminants that enter wastewater treatment plants (WWTPs) from urban, agricultural and industrial discharges. Because of their low aqueous solubility and resistance to biodegradation, up to 90% of the PBDEs are accumulated in the sewage sludge during the wastewater treatment. To assess the possibilities for sludge re-use, a reliable determination of the concentrations of these PBDEs is of crucial importance. Six PBDE congeners (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154) are listed as priority substances under the EU Water Framework Directive. In the present work a simple analytical method with minimal sample-preparation steps was developed for a sensitive and reliable determination of the six PBDEs in sewage sludge by the use of gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP-MS). For this purpose an extraction procedure was optimised. Different extracting agents (methanol (MeOH), acetic acid (AcOH)/MeOH mixture (3:1) and 0.1 mol L^{-1} hydrochloric acid (HCl) in MeOH) followed by the addition of a Tris-citrate buffer (co-extracting agent) and iso-octane were applied under different modes of extraction (mechanical shaking, microwave- and ultrasound-assisted extraction). Mechanical shaking or the microwave-assisted extraction of sewage sludge with 0.1 mol L^{-1} HCl in MeOH and the subsequent addition of the Tris-citrate buffer and the iso-octane extracted the PBDEs from the complex sludge matrix most effectively. However, due to easier sample manipulation during the

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extraction step, mechanical shaking was used. The PBDEs in the organic phase were quantified with GC-ICP-MS by applying a standard addition calibration method. The spike recovery test (recoveries between 95 and 104%) and comparative analyses with the species-specific isotope-dilution (ID) GC-ICP-MS confirmed the accuracy of the developed analytical procedure. The procedure is sensitive (limits of detection (LODs) for PBDEs congeners between 0.2 and 0.3 ng g^{-1}), repeatable and reproducible (RSDs 2.2–5.7%) and was applied for the determination of PBDEs in sewage sludge samples collected three times at the municipal WWTP over a period of 16 years.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in a variety of commercial products, like polyurethane foams, electronic equipment, plastics, building materials and textiles [1,2]. When such materials are used, recycled, disposed on landfills or incinerated, PBDEs can be released into the environment by leaching and volatilization. Consequently, their presence has been confirmed in the terrestrial and aquatic environment and, to a lesser extent, in the air [3–5]. PBDEs have a high binding affinity to particles and organic matter [6] and have been found in sediments [1,7], soils [6,9], sewage sludge [1,7,9], house dust [7–9], and in outdoor and indoor air [1,7–9]. Studies have also shown that they can be present in different living organisms, including humans, where they were detected in human blood, adipose tissue and breast milk [10–12]. Increasing concentrations of PBDEs in human tissues have caused health concerns due to the tendency of PBDEs to disrupt the functioning of thyroid hormones and the reproductive organs [13,14]. Because of their environmental persistence, capability for long-range atmospheric transport, bio-accumulation and health-hazard potential, six PBDE congeners (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154) have been registered as priority hazardous substances by the European Union Water Framework Directive (WFD) [15]. They were manufactured in penta-, octa- and deca-BDE commercial formulations, which were mixtures of tetra-to deca-congeners in various proportions. The European Union banned the use of penta- and octa-BDE formulations in 2004 and the use of deca-BDE in 2008 [16,17].

PBDEs, like other lipophilic organic contaminants, enter wastewater treatment plants (WWTPs) from different sources, including urban and agricultural runoffs, household domestic wastewater and industrial discharges [18]. Because of their low aqueous solubility (high hydrophobicity) and resistance to biodegradation, PBDEs preferentially partition into the sludge during wastewater treatment [9]. Therefore, the determination of PBDEs in sewage sludge is a useful strategy for assessing the environmental fate of PBDEs originally present in wastewaters. There is evidence that municipal sewage may be a significant source of PBDEs. In municipal wastewater treatment plants, up to 90% of the PBDEs from wastewater end up in sewage sludge [19,20].

In Europe the majority of sewage sludge is disposed in landfills or applied to the land. When sewage sludge is used as fertilizer, such an application can contribute to the release of PBDEs into the environment. Consequently, PBDEs may accumulate and transfer via the food chain, threatening the environment and human health [21,22]. Currently there is no guideline, either within Europe or internationally, that regulates or proposes permissible levels of PBDEs in sewage sludge used for land application. The analysis of sewage sludge for PBDEs provides valuable information about the risks associated with the re-use of sewage sludge as biosolids for land application. Thus, reliable analytical methods are needed in order to evaluate the contribution of contaminated sewage sludge to the PBDEs' pollution of the terrestrial environment.

Most analytical procedures for the determination of PBDEs in sewage sludge developed in recent years employ the time- and solvent-consuming Soxhlet extraction method [22–27], accelerated solvent extraction (ASE) [28–30], microwave-assisted extraction (MAE) [31] or ultrasound-assisted extraction [7]. Those based on the separation of PBDEs by gas chromatography (GC) [32] coupled with different highly developed detector systems, such as high resolution mass spectrometry (HR-MS) [25,27,28], mass spectrometry operating in the negative chemical ionization mode (NCI-MS) [22–24,30,31,33] or electron capture detectors (ECNI-MS) [26,29] are applied almost exclusively. All these analytical procedures are comprised of extraction, clean-up and instrumental analysis. Despite the fact that inductively coupled plasma mass spectrometry (ICP-MS) is a versatile and sensitive detector, it is not commonly used for the detection of separated PBDEs [33–36].

The aim of this study was to develop a simple analytical procedure with minimal sample preparation for a sensitive and reliable determination of the six PBDEs in sewage sludge samples by GC-ICP-MS. For this purpose the influence of different extracting agents (methanol (MeOH), acetic acid (AcOH)/MeOH mixture (3:1) and 0.1 mol L^{-1} HCl in MeOH) and the subsequent addition of the Tris-citrate buffer (co-extracting agent) and iso-octane on the extraction efficiency was studied when applying different modes of extraction (mechanical shaking, microwave- and ultrasound-assisted extraction). For the quantification of the PBDEs a standard addition calibration method was applied. In order to check the accuracy of the developed analytical procedure, the spike recovery test and the species-specific isotope-dilution (ID) GC-ICP-MS analysis were used. Finally, the PBDEs were determined in sewage sludge samples from municipal WWTP collected in 1998, 2000 and 2014.

2. Experimental

2.1. Instrumentation

The analysis of PBDEs was carried out on an Agilent 6890 gas chromatograph (GC) Agilent Technologies (Santa Clara, CA, USA) equipped with an Agilent 6890 Series Autosampler Injector. The GC was coupled to an Agilent 7700× ICP-MS via a heated transfer line and fitted with a 15 m × 0.25 mm DB-5MS capillary column (film thickness 0.25 μm) coated with 5% phenylmethylpolysiloxane Agilent J&W Scientific (Palo Alto, CA, USA). The control and operation of the coupled system were performed using Agilent MassHunter software.

For the separation of the PBDEs on a 15-m column the following GC temperature program was applied: at the start the column temperature was raised from 120 °C to 300 °C at a heating rate of 30 °C min^{-1} and held there for 5 min. The inlet temperature and