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Selective pressurized liquid extraction of replacement and legacy brominated flame retardants from soil

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardant registered as UN POPs due to their persistence in the environment, bioaccumulation potential and toxicity. Replacement novel brominated flame retardants (NBFRs) have exhibited similar health hazards and environmental distribution, becoming recognized as significant contaminants. This work describes the development and validation of a sensitive and reliable method for the simultaneous quantitation of PBDEs and NBFRs in environmental soil samples using selective pressurized liquid extraction (S-PLE) and gas chromatography coupled to triple quadrupole mass spectrometry (GC-(EI)-MS/MS). Under optimal conditions, extraction of eight PBDEs (−28, −47, −99, −100, −153, −154, −183 and −209) and five NBFRs; pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis(2,4,6-tribromophenoxy)ethane (BTBPE) was performed at 100° C and 1500 psi using a 1:1 mixture of hexane and dichloromethane. The method utilized 33 mL capacity PLE cells containing, from bottom to top, a single cellulose filter, 3 g activated Florisil, 6 g acid silica (10% w/w), 3 g Na_2SO_4, another cellulose filter, 2 g activated copper powder and 3 g soil sample dispersed in 2 g Na_2SO_4 and 1 g of Hydromatrix. The method was evaluated by repeated extraction and analysis of all analytes from 3 g soil at three spike concentrations. Good recoveries were observed for most analytes at each of the spiking levels with RSD values generally below 20%. MDLs ranged from 0.01 to 4.8 ng/g dw for PBDEs and 0.01–0.55 ng/g dw for NBFRs. The described one-step combined extraction and cleanup method reduces sample processing times compared with traditional procedures, while delivering comparable analytical performance. The method was successfully applied to environmental soil samples (n = 5), detecting PBDEs in each sample and providing the first account of NBFR contamination in Australian soils.

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1. Introduction

A range of brominated flame retardants (BFRs) have been incorporated into plastics, electronic equipment, foams and textiles. The most common of these, polybrominated diphenyl ethers (PBDEs), have come under a great deal of scientific and regulatory scrutiny due to their long-range atmospheric transport potential [1], persistence in the environment [2,3], and toxicity [4]. Ubiquitous environmental contamination has been indicated in studies from around the world, with PBDEs frequently detected in air, soils and sediments [3]. Toxicological reports have shown a range of adverse effects in humans and animals from exposure to the substance at environmentally relevant concentrations [4], such as endocrine disruption [5] and developmental neurotoxicity [6]. In light of environmental and human health hazards, specific PBDEs have been classified as United Nation's Persistent Organic Pollutants [7], and subject to legislated bans and voluntary withdrawal by manufacturers in North America [8,9], Europe [10,11] and Australia [12]. Restriction and regulation of PBDEs, however, has driven a rise in production and use of "novel" brominated flame retardants (NBFRs). As many as 75 NBFRs have been commercially produced to replace PBDEs [13]. A subset of these have similar chemical properties to banned PBDEs and have also been shown to be toxic and capable of environmental mobility, and have been detected in a range of environmental matrices [14–16]. A number of NBFRs have been recorded in atmospheric samples from Europe, USA, Asia and Africa at concentrations similar to and exceeding those of PBDEs [17–20]. As with PBDEs, evidence suggests that most NBFRs are undergoing net atmospheric deposition to land [21–23]. Processes are poorly understood, however, and current global soil contamination levels have rarely been studied.

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Gas chromatography coupled to mass spectrometry (GC–MS) has been the most commonly employed instrumental technique for quantifying BFRs. While single ion monitoring (SIM) mode using electron capture negative ionization (ECNI) has provided excellent sensitivity for BFR analysis, the complex chromatographic elution profile of combined PBDE and NBFR measurement benefits from the enhanced selectivity of triple quadrupole mass spectrometry in electron ionization mode (GC–(EI)–MS/MS) [24,25]. Even with the selectivity of such detectors, instrumental sensitivity and reproducibility are highly reliant on sample preparation steps and extract purity [26]. Traditional methods of organohalogen separation from solid matrices have typically utilized Soxhlet extraction, solid phase extraction (SPE), ultrasonic assisted extraction or pressurized liquid extraction (PLE) followed by chromatographic cleanup using a range of adsorbents [14]. These processes have been employed successfully for the extraction of various combinations of PBDEs and NBFRs from soil [27–29] but can be slow and inefficient due to the multiple processes involved. Recently, methods described as "selective" pressurized liquid extraction (S-PLE) have been developed for extraction of analytes of interest with minimal co-extraction of interfering compounds [30,31]. This is achieved by incorporating appropriate cleanup adsorbents into the PLE cell below the sample, and refining parameters such as extraction temperature and solvent composition [32]. S-PLE methods also achieve faster sample preparation with lower risk of operator error or accidental sample contamination [33]. The commercially available Accelerated Solvent Extraction (ASE) system (Dionex, Thermo Scientific) is the most common way to perform PLE or S-PLE. While cell sizes up to 100 mL are available for all later models of the ASE system (ASE 150, ASE 300, ASE 350), the popular early version of the instrument (ASE 200) has a maximum cell capacity of 33 mL. Unlike regular gel permeation chromatography, the volume of adsorbent that can be used for in S-PLE cleanup is limited by the capacity of the instruments extraction cell. This means selection of solvent composition, adsorbent mixture and ratio of sample to adsorbent is critical. Development of an S-PLE method that can be performed using 33 mL cells is ideal as it can be applied to all currently available ASE platforms. Smaller PLE cell sizes also require the use of less chromatographic material and lower solvent volumes.

S-PLE has been shown to be an appropriate technique for the extraction of PBDEs and other established flame retardants from a variety of matrices, including soils [34]. To date, S-PLE has rarely been used to extract NBFRs and has only been applied for combinations of 2 or 3 of the new compounds [35]. The objective of this study is to develop a sensitive, rapid and repeatable method for the simultaneous quantification of PBDEs and NBFRs in environmental soil samples using one-step S-PLE and GC-(EI)-MS/MS. The S-PLE method will be limited to an ASE cell capacity of 33 mL such that it can be applied to all current ASE systems and reduce solvent and adsorbent usage. Furthermore, this work aims to validate the optimized method by repeated analysis of spiked soil, and to apply the process to real environmental samples.

2. Methods and materials

2.1. Reagents and standards

Individual standard solutions were purchased from AccuStandard Inc. (New Haven, CT, USA):,1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE), bis(2-ethylhexyl) tetrabromophtalate (BEH-TEBP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 2,3,4,5,6-pentabromotoluene (PBT), 2,3,4,5,6-pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB), (each 100 μg/mL in toluene), 3,4,4′-tribromodiphenyl ether (BDE-37) and 3,3′,4,4′-tetrabromodiphenyl ether (BDE-77) (each 50 ng/mL in isooctane), and a mixed solution of 2,4,4′-tribromodiphenyl ether (BDE-28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183) and decabromodiphenyl ether (BDE-209) (each 20 μg/mL, except BDE-209; 200 μg/mL, in isooctane:toluene 80:20). Internal surrogate standards comprised a mixed solution of mass-labeled [$^{13}C_{12}$] BDEs (^{13}C-BDE-28, ^{13}C BDE-47, ^{13}C BDE-99, ^{13}C BDE-100, ^{13}C BDE-153, ^{13}C BDE-154, ^{13}C BDE-183) (2 μg/mL in toluene) and a solution of ^{13}C BDE-209 (25 μg/mL in toluene), each from Wellington Labs. (Guelf, ONT, Canada).

All solvents used in extraction, cleanup and analysis were of chromatographic analysis grade unless otherwise stated. isooctane, toluene, *n*-hexane and dichloromethane (DCM) were obtained from Honeywell Burdick & Jackson (Muskegon, MI, USA), and acetone (AR grade) from Chem Supply (Gilman, SA, Australia). Sodium hydroxide (NaOH) and hydrochloric acid (HCl, 32%) were from Rowe Scientific (Doveton, VIC, Australia) and concentrated sulfuric acid (H_2SO_4, 98%) from Merck (Kilsyth, VIC, Australia). Florisil (60–100 mesh $MgSiO_3$), copper powder and anhydrous sodium sulfate (Na_2SO_4) were from Sigma Aldrich (St Louis, MO, USA), Davisil silica (200–425 mesh amorphous SiO_2) from Grace Davison Discovery Science (Rowville, VIC, Australia), Hydromatrix diatomaceous earth from Varian Inc. (Santa Clara, CAL, USA).

2.2. Adsorbent preparation

In order to test different chromatographic clean-up procedures, adsorbent media were prepared to a range of specifications. Florisil, silica and sodium sulfate were each activated by heating to 130 °C for 16 h in a conventional fan-forced oven. Deactivated Florisil (5% w/w) was prepared by gravimetric addition of Milli-Q water to freshly activated Florisil powder, followed by vigorous mixing in a closed container on a rotary shaker at 320 rpm for 4 h. Acid silica (5 and 10% w/w) and a basic silica (20% w/w) were produced according to USEPA Method 1614 [36] by addition of concentrated H_2SO_4 or 1 M NaOH to freshly activated silica. Thorough homogenization was achieved via the same process as used for mixing deactivated Florisil.

Copper powder was activated immediately prior to use by sonication in concentrated HCl for 20 min. In an Erlenmeyer flask, acid was rinsed from the copper thoroughly using Milli-Q water, which was in-turn rinsed with acetone. A final rinse of *n*-hexane was used to remove residual acetone and provide a protective barrier against oxidation.

All glassware used for storing or transferring solvents, adsorbents and samples was heated to 500 °C in a muffle-furnace for 12 h to eliminate trace contamination before use.

2.3. Sample preparation

Five soil samples were taken from the Greater Melbourne region; four samples from industrial areas and a single sample from a university campus. Samples were taken to a depth of 0–100 mm using a stainless steel hand trowel pre-cleaned with a 1:1 mixture of hexane/acetone. Samples were stored in amber glass jars with PTFE lined lids at below 4 °C until analysis. Prior in-house screening studies determined ubiquitous PBDE contamination in soil samples (n = 30), which poses a challenge for sourcing a natural blank soil for spiking and recovery experiments. However, a soil sample from a large parkland region approximately 20 km northeast of Melbourne's center was selected for use in preliminary

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