



Matrix solid-phase dispersion of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogues in lettuce, carrot and soil[☆]



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ABSTRACT

In the present work, a novel analytical method for the simultaneous determination of ten polybrominated diphenyl ethers (PBDEs), eight methoxylated PBDEs (MeO-PBDEs) and seven hydroxylated PBDEs (OH-PBDEs) in soil, lettuce and carrot samples was developed. The procedure was based on matrix solid-phase dispersion (MSPD) followed by gas chromatography coupled to negative chemical ionization-mass spectrometry (GC–NCI–MS). Under optimum conditions, 0.5 g of sample (freeze-dried in the case of lettuce and carrot samples) was dispersed with 0.5 g of octadecyl-functionalized silica (C₁₈) and 1.75 g of acidified silica (10% H₂SO₄, w/w) was used as clean-up sorbent. A two-step fractionated elution was carried out. First, PBDEs and MeO-PBDEs were eluted in 75:25% (v/v) n-hexane/dichloromethane mixture and, then, the retained OH-PBDEs were eluted in pure dichloromethane. Both extracts were analyzed by GC–NCI–MS separately, in the case of OH-PBDEs after derivatization with N-methyl-N-(trimethylsilyl) trifluoroacetamide. The developed method was validated in terms of accuracy for soil, lettuce and carrot matrices, spiked at two fortification levels (5 and 25 ng g⁻¹). After correction with the corresponding surrogate, apparent recovery values (defined as the recovery obtained after correction with the corresponding surrogate) were in the 80–129% range. Precision (as relative standard deviation) in the 1–21% range and method detection limits (MDLs) in the 0.003 and 0.3 ng g⁻¹ range for soil and in the 0.003–0.4 ng g⁻¹ range (dry weight) for lettuce and carrot samples were obtained. For PBDEs the method was also validated with a standard reference material (SRM-2585) of house dust. Finally, the method was applied for the determination of target analytes in soil, lettuce and carrot.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of halogenated flame retardants that have been widely used as additives in many manufactured items in order to delay or inhibit the initial step of the development of fires and combustion processes. In the past decade, the production and the use of these polybrominated compounds was regulated and

restricted [1–4] due to their ubiquitous environmental distribution, persistence, bioaccumulation and toxicity potentials [5,6].

In the last years attention has also been focused on some structural analogues of PBDEs, namely hydroxy-PBDEs (OH-PBDEs) and methoxy-PBDEs (MeO-PBDEs). Those two groups of compounds could be natural bio-products produced in the marine environment by some invertebrates [7,8] or biotransformation metabolites of PBDEs. Although the origin, fate, biotransformation behavior and bioaccumulation mechanism of these compounds is not well established yet, ortho-substituted MeO-PBDEs and OH-PBDEs seem to be natural products, while meta- and para-substituted are more likely to be biotransformation metabolites [9].

Recent studies have shown that OH-PBDEs can interact with estrogen receptor and exhibit estrogenic activity [10,11].

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The presence of a hydroxy group increases the endocrine disruptor potential of polybrominated compounds and, therefore, those metabolites could be even more toxic than the PBDEs [12–14]. Moreover, the presence of OH-PBDEs could interfere also in the thyroid hormone system, by interacting with thyroid hormone receptor, due to their structural similarities with the thyroid hormones [9,14]. OH-PBDEs and MeO-PBDEs have been detected both in controlled animal exposure experiments [15–18] and, more recently, in many different matrices, such as marine organisms [7,8,19–23], humans [24–28], plants and soil [29–31], as well as in surface water, rain and snow samples [32].

One way to study the introduction of organic contaminants to humans via the food chain is to study the uptake of target and related compounds by different crop plants. Although the agricultural application of sewage sludge has been recommended by the European Union (EU) authorities as an economical alternative of disposal [33], concern has increased due to the confirmed presence of heavy metals, organic contaminants and pathogenic bacteria. Acceptance limits concerning metal contents [34] have been already legislated and some organic contaminants, including PBDEs, are suggested for regulation [35]. Within this scenario, the measurement of PBDEs in sludge amended soils and crops has gained importance.

Although few studies have been reported, according to existing literature, solid–liquid extraction [7,21,31], ultrasound assisted solid–liquid extraction [30,36,37], pressurized liquid extraction (PLE) [22,38,39] and Soxhlet extraction [29,40] have been mostly employed for the determination of PBDEs, OH-PBDEs and MeO-PBDEs in solid samples. The above-mentioned extraction methodologies are based on a solid–liquid extraction that requires further clean-up and fractionation steps [7,21,22,29–31,36–40].

Liu et al. [20] also published a method based on matrix solid-phase dispersion (MSPD). However, the analysis of OH-PBDEs was performed by liquid chromatography–tandem mass spectrometry (LC-MS/MS).

In the case of PBDEs and MeO-PBDEs separation and detection has been typically carried out by GC-MS, both in negative chemical ionization (NCI) [24,25,41,42] or electron impact (EI) [29,43–46] mode. Analysis of PBDEs and related compounds based on NCI allows the quantification of trace amounts, since it provides a high sensitivity in comparison with EI, which, on the other hand, offers more structural information, facilitating compound identification [47,48]. For OH-PBDEs both LC [15,20,28,49] and GC analysis are employed. In the case of GC analysis of OH-PBDEs, they are usually determined after derivatization with diazomethane [16,25,32,42], which is a time consuming reaction (approx. 4 h) and implies the use of a toxic and explosive reagent.

Within this scenario, the aim of the present work was to develop a simple method based on MSPD followed by GC-NCI-MS for the determination of 10 PBDEs, 8 MeO-PBDE and 7 OH-PBDE analogues in soil, lettuce and carrot. The simplicity, efficiency, low cost and the opportunity to carry out a simultaneous extraction and clean-up were the reasons to choose MSPD as extraction technique. Moreover, low solvent and sample amounts were required. This extraction technique offered us the possibility to obtain a fractionated extraction of PBDEs and MeO-PBDEs from OH-PBDEs. Apart from the MSPD optimization, a thorough study of the GC-NCI-MS separation/detection step was performed. Different derivatization reagents, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), N-methyl-N-(tert-butylidimethylsilyl) trifluoroacetamide (MTBSTFA), N-methyl-bis-trifluoroacetamide (MBTFA), acetic anhydride and ethyl chloroformate (EtCF), were tested. Finally, the developed method was applied to soil, lettuce and carrot samples.

2. Experimental

2.1. Chemicals and materials

Standard individual solutions 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), 2,2',3,3',4,4',6,6'-octabromodiphenyl ether (BDE-197) and decabromodiphenyl ether (BDE-209) in isooctane ($50 \mu\text{g mL}^{-1}$ each) were provided by AccuStandard (New Haven, CT, USA).

The solution of MeO-PBDEs ($5 \mu\text{g mL}^{-1}$ each in isooctane) containing a mixture of 2,2',4,4'-tetrabromo-5-methoxydiphenyl ether (5-MeO-BDE-47), 2,2',4,4'-tetrabromo-6-methoxydiphenyl ether (6-MeO-BDE-47), 2,2',4',5-tetrabromo-4-methoxydiphenyl ether (4-MeO-BDE-49), 2',3,4',5-tetrabromo-2-methoxydiphenyl ether (2-MeO-BDE-68), 2,2',4,4',5-pentabromo-5'-methoxydiphenyl ether (5'-MeO-BDE-99), 2,2',4,4',6'-pentabromo-5-methoxydiphenyl ether (5-MeO-BDE-100), 2,2',4,5,5'-pentabromo-4'-methoxydiphenyl ether (4'-MeO-BDE-101) and 2,2',4',5,6'-pentabromo-4-methoxydiphenyl ether (4-MeO-BDE-103) was obtained from Wellington Laboratories (Guelph, Canada).

Individual solutions of 3'-hydroxy-2,4,4'-tribromodiphenyl ether (3'-OH-BDE-28), 5-hydroxy-2,2',4,4'-tetrabromodiphenyl ether (5-OH-BDE-47) and 3-hydroxy-2,2',4,4'-tetrabromodiphenyl ether (3-OH-BDE-47) at $50 \mu\text{g mL}^{-1}$ each, and 4'-hydroxy-2,2',4,5'-tetrabromodiphenyl ether (4'-OH-BDE-49), 6'-hydroxy-2,2',4,4',5-pentabromodiphenyl ether (6'-OH-BDE-99), 4-hydroxy-2,2',3,4'-tetrabromodiphenyl ether (4-OH-BDE-42) and 5'-hydroxy-2,2',4,4',5-pentabromodiphenyl ether (5'-OH-BDE-99) at $10 \mu\text{g mL}^{-1}$ each in acetonitrile were acquired from AccuStandard.

As surrogate standards 3,3',4,4'-tetrabromodiphenyl ether (BDE-77) and 2,2',3,4,4',5,6'-heptabromodiphenyl ether (BDE-181) in isooctane ($50 \mu\text{g mL}^{-1}$ each) were acquired from AccuStandard, [$^{13}\text{C}_{12}$]-decabromodiphenyl ether ($^{13}\text{C}_{12}$ -BDE-209), $25 \mu\text{g mL}^{-1}$ in toluene, from Wellington Laboratories, and [$^{13}\text{C}_{12}$]-triclosan ($^{13}\text{C}_{12}$ -TCS, $100 \mu\text{g mL}^{-1}$ in nonane, 99%) from Cambridge Isotope Laboratories (Andover, MA, USA).

The empirical formula and molecular weight of all the target analytes and their corresponding surrogates are listed in Table 1. Mixtures of all PBDEs and MeO-PBDEs were prepared at $1 \mu\text{g mL}^{-1}$ in isooctane (chromatographic grade, Merck, Darmstadt, Germany) and stored in the dark at -20°C . In the case of OH-PBDEs and $^{13}\text{C}_{12}$ -TCS diluted standard solutions were prepared in ethyl acetate (EtOAc, chromatographic grade, Merck, Darmstadt, Germany).

Solid standard of BDE-209, used to fortify the amended soil, was purchased from AccuStandard. Pentabromodiphenylether (technical mixture) containing a mixture of tetra-, penta- and hexa-BDE congeners, used also to fortify amended soil was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). n-hexane, (chromatographic grade), ethanol (EtOH) and H_2SO_4 (95–97%) were purchased from Merck (Darmstadt, Germany) and dichloromethane (DCM) from VWR Prolabo (Fontenay-sous-Bois, France). Florisil and octadecyl-functionalized silica (C_{18}) were provided by Sigma-Aldrich (Steinheim, Germany). Primary-secondary amine bonded silica (PSA) was acquired from Supelco (Bellefonte, PA, USA) and silica from Merck. Ultrapure water was obtained from a Milli-Q water purifier ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore, Billerica, MA, USA) in the laboratory. Silica and Florisil were activated at 130°C overnight and deactivated with controlled percentages of H_2SO_4 or Milli-Q water. Pyridine (99.5%) was obtained from Riedel de Haën (Seelze, Germany).

The derivatization reagents used in this work, MSTFA, MBTFA and MTBSTFA were purchased from Sigma-Aldrich. Acetic

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