Analytical Methods

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Optimization of selective pressurized liquid extraction and ultrasonication-assisted QuEChERS methods for the determination of polybrominated diphenyl ethers in sediments

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Two fast analytical methods, selective pressurized liquid extraction (SPLE) and ultrasonication-assisted QuEChERS method (Quick, Easy, Cheap, Effective, Rugged and Safe) followed by GC-MS/MS, were optimized for the determination of polybrominated diphenyl ethers (PBDEs) in sediments. Ultrasonication was used to improve the extraction efficiency of QuEChERS. The experimental parameters of SPLE and ultrasonication-assisted QuEChERS, such as sorbents type, composition and elution solvents, were optimized in detail. The obtained recoveries of both methods were satisfactory for PBDEs analysis. The inter/intra-day RSDs were <7%. The limits of quantification (LOQ) were ≤0.1 ng/g dry weight (d.w.). The figures of merit were at same level as former reported results. The proposed methods were validated to the analysis of PBDEs in standard reference materials (SRM 1944 and 2585). The results indicated that both optimized methods were feasible for analysis and monitoring of PBDEs. Besides, the comparison between two methods revealed that elevated temperature and pressure could weaken the interaction between PBDEs and sediment matrix, resulting in improvement of extraction efficiency. Both proposed methods were successfully applied to the analysis of 3 sediment samples and the determination of BDE 47, 99, 100 and 153 suggested both methods practical and suitable for PBDEs analysis in real sediments samples.

Introduction

Polybrominated diphenyl ethers (PBDEs) are largely produced and used as brominated flame retardants (BFRs) in polycarbonate plastics, plastic lining, and fire-resistant polymers which exhibited potential endocrine disrupting properties and developmental neurotoxicity arousing great concerns of the whole society[1-3].

Solid matrices such as sediment, soil and indoor dust are considered as major sinks of PBDEs in the environment and the relative analytical methods have been well studied[4, 5]. Conventional Soxhlet extraction, pressurized liquid extraction (PLE), ultrasonic liquid extraction (ULE) and microwave assisted extraction (MAE) have already been used for the extraction of PBDEs from these solids[6-11]. Besides, various micro-extraction techniques including solid phase micro-extraction (SPME), and dispersive liquid–liquid micro-extraction (DLLME) have also been developed[12-14]. Due to the various concentration levels of PBDEs in sediments (from pg/g to μg/g dry weight (d.w.)), highly efficient extraction and purification are crucial for the accurate determination[15-17]. Up to date, PLE and column chromatography/gel permeation chromatography (GPC) were believed to be one of the most valid methods for PBDEs analysis[17, 18].

Analytical methods are developing to be more straightforward, less toxic solvent consumption and less time/labor cost. Selective pressurized liquid extraction (SPLE) and QuEChERS method (acronymic name from quick, easy, cheap, effective, rugged and safe) are developed based on typical extraction techniques with novel modifications which have received increasing interests from analysts. SPLE is a technique introducing clean-up steps into PLE extraction cycles by filling sorbents in extraction cells to remove undesired co-eluted substances[19, 20]. The selectivity is achieved by different adsorption affinity between filled sorbents and various extracted chemicals. SPLE could save more time compared to traditional PLE with complex purification steps and it has been successfully applied for the detection of PBDEs[21, 22]. QuEChERS was initially applied as pretreatment process for the detection of pesticides from fruits and vegetables has been proved to be plausible as sample preparation procedure[23]. Based on QuEChERS methodology, modifications including novel sorbent applications and combination with assistant techniques, have been made to improve the method performance for specific groups of chemicals[24, 25]. Although QuEChERS method is a universal pretreatment procedure available for a wide polarity range of chemicals[26, 27], it has been applied for limited types of environmental matrices such as plants, soil, etc.[26, 28, 29]. As PBDEs were bounded to sediments stronger than vegetables, assistant techniques are needed to be introduced into conventional QuEChERS for sufficient extraction.

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ARTICLE

Hence, taking full advantages of SPLE and QuEChERS methods to achieve fewer and simpler pretreatment steps while improving analysis efficiency is of great significance for simultaneously analysis of PBDEs in sediments.

Capillary gas chromatography-negative chemical ionization mass spectrometry (GC-NCI-MS) could obtain a great sensitivity for PBDEs by monitoring bromide ions (m/z=79 and 81). As a result, a complete elimination of interferences during the pretreatment which demands complicated procedures were required[4, 22]. To overcome the disadvantage at selectivity of GC-NCI-MS, gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) could provide a positive identification and the possibility of using [13]C- mass-labeled standards for isotope dilution quantification[30].

The aim of this work was to optimize and apply two analytical methods for the simultaneous determination of selected PBDEs from sediment matrices. QuEChERS/SPLE methods were applied and the performance of the proposed methods were verified by the analysis of standard reference material (SRM) 1944 and SRM 2585. Besides, real sediment samples collected from polluted were also analyzed.

Experimental

Chemicals and Materials

Chemical name, abbreviation and structures are shown in Figure 1. BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 were obtained from Accustandard (New Hevan, CT). Mass-labeled ^{13}C-BDEs (BDE-28，BDE-47，BDE-100，BDE-99，BDE-153，BDE-154) were purchased from Cambridge Isotope Laboratories (Andover, MA). HPLC-grade dichloromethane isooctane and hexane were supplied by J.T. Baker (Phillipsburg, NJ). Ultrapure water (18.3 MΩ) was generated by a Milli-Q system (Millipore, Billerica, MA). QuEChERS sorbents including primary–secondary amine (PSA), C18, $MgSO_4$ and graphitized carbon black (GCB) were purchased from Agilent Technologies (Santa Clara, CA). Alumina were from Sigma-Aldrich (St. Louis, MO). Sediments were collected from a polluted area around a manufacturing plant in Shandong province, China. All sediment samples were freeze-dried and sieved through a stainless steel 2-mm sieve, stored at −20 °C until analysis. SRM-2585 & 1944 were purchased from NIST (National Institute of Standards and Technology, MD), detailed information is presented in Table S1†.

Instruments

Sediments were extracted by an ASE 350 (Dionex Co.) and analyzed on an Agilent 7000 B Triple Quadrupole GC/MSMS System (EI−MS/MS). Each 2 microliters of sample was loaded onto a DB-5 (15 m × 0.25 mm × 0.10 μm) capillary column in splitless injection mode. The temperature program initiated from 90℃ (held for 3 min) to 280℃ (held for 5min) at 20℃/min. Carrier gas was helium at 1.0 mL/min. Multiple reaction monitoring (MRM) mode with the electron impact ion source (EI+) was applied for the identification and quantification of target chemicals. Detailed MRM parameters were provided in Table S2†.
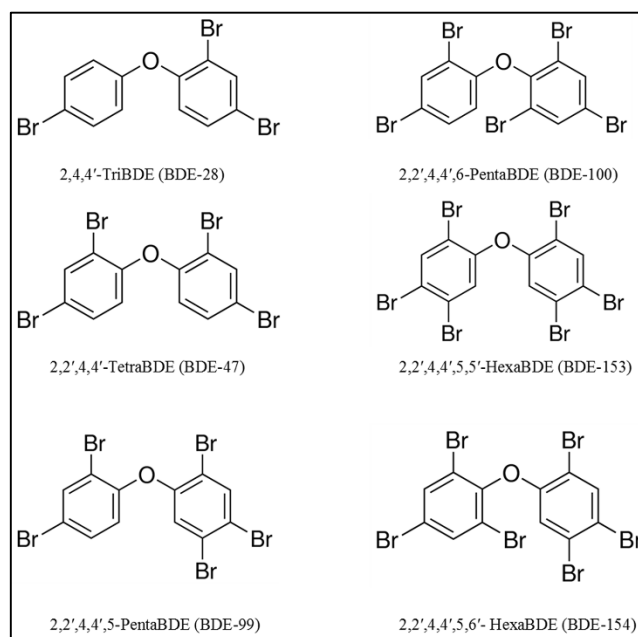

Fig.1. Chemical name, abbreviation and structure of six PBDEs.

SPLE method

SPLE was carried out with several modifications based on published reports[21, 22]. Briefly, 1.0 g sediment samples were spiked with ^{13}C-labeled standards, well mixed with 5.0 g alumina and 1.0 g diatomaceous earth in extraction cells. The extraction parameters were set as follows: solvent composition was hexane–dichloromethane (1:1) mixture; the pressure was set at 1500 psi, and temperature was 100 °C; after optimization, 3 cycles extraction was sufficient for sediments. Approximately 40 mL extracts were collected and rotary evaporated to about 2 mL. After filtration with a 0.2 μm GHP membrane and concentration by gentle nitrogen stream, solvent was substituted to isooctane for instrument analysis.

QuEChERS method

QuEChERS method with modifications was applied[31]. Detailed optimization information including extraction solvent proportion and extraction time was summarized in Supplementary Materials. Similar as SPLE, 1.0 g sediment was spiked and placed into a 15 mL polyethylene terephthalate centrifuge tube (Corning Inc., NY). Extraction solvent was 5 mL mixture of hexane and dichloromethane (1:1). The extraction cycle was kept for 5 min in ultrasonic bath and the supernatant was collected. The procedure was repeated for three times and all supernatant was combined and concentrated to about 5 mL under a gentle nitrogen stream. The concentrated extracts together with 5 mL dichloromethane were placed into another 15 mL centrifuge tube (Corning Inc., NY) where sorbents for clean-up were already mixed thoroughly. PSA, C18, $MgSO_4$ and GCB are most popular materials used in QuEChERS method. Efficiency of different compositions of these materials were evaluated by investigating the spiked recoveries. After ultrasonication assisted water bath for 15

minutes, the centrifugation was done at 4500 rpm for 5 min. The supernatant was collected for further concentration leaving the undesired matrix components adsorbed on the sorbents. The collected liquid was passed through a 0.2 μm GHP membrane, dried under a gentle nitrogen stream at room temperature and reconstituted into 0.5 mL isooctane for instrument analysis.

Quality Assurance/Quality Control

For the positive identification and quantification of the PBDEs, confirmation criteria given elsewhere was applied with minor modifications[32]. To avoid contamination and background concentrations interference, labelled standards were applied for recovery, LOD and LOQ, matrix effect investigations. The linearity was assessed by the performances of seven point standard curves and the linear dynamic range of instrument response ($r^2 > 0.99$) were achieved. Limit of quantification (LOQ) and limit of detection (LOD) represented the concentrations when the signal to noise ratios were 10 and 3, respectively. Matrix effects were calculated by the differences between extracts from sediment samples spiked with labelled standards and extracts from solvent-washed diatomaceous earth spiked with equivalent labelled standards (Dionex, Sunnyvale, CA). The quantification was based on an external calibration method and corrected according to the mass-labelled IS recoveries. Two procedural blank of 1.0 g solvent-washed diatomaceous earth was included for each batch. All of the PBDEs in the blanks were under LOD.

Results and discussion

Modifications of SPLE

SPLE is highlighted for its relative high extraction efficiency and less solvent/time consumption. Some parameters were evaluated to improve the method performance based on former reports[21]. The sorbents compositions added into cells were evaluated by recoveries and matrix effects. An aliquot of 5.0 g alumina, acid silica gel (ASG, 40 %), and florisil were separately added as sorbent with 1.0 g sediment and 10 ng ^{13}C-labelled standards also spiked in. The data illustrated that alumina and florisil had higher recoveries than ASG while alumina showed better efficiency than florisil for BDE-99 and BDE-100 under given conditions (Figure 2). Alumina was believed to be more active for cleaning up during analysis of sediment samples because of its strong adsorption energy for aromatic carbons and selectivity in molecular structure of aromatic chemicals[33]. Matrix effect was estimated by comparing the response of 5 extracts from sediment samples spiked with labelled standards and extract from solvent-washed diatomaceous earth spiked with equivalent labelled standards. Results showed no obvious matrix effect (< 10 %) for alumina which indicated the added mass and sorbent capable of purifying the extracts. After experimenting adding more alumina, no improvement in recoveries or matrix effect was observed. Two alumina addition ways were also compared. One was mixed with samples in the cells and the other was set as one layer below the samples. Similar extraction efficiencies were obtained by both
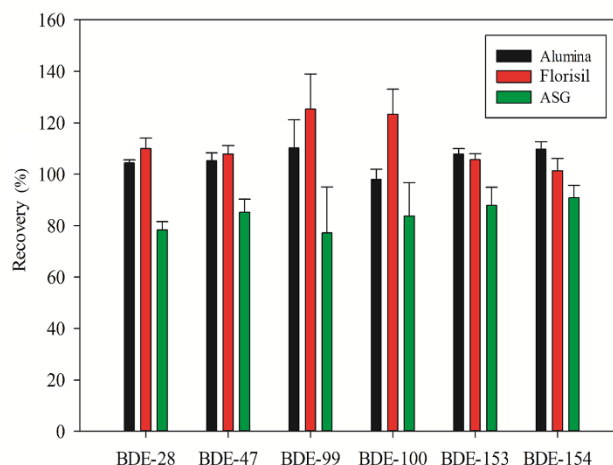

Fig. 2. Recoveries and relative standard deviations for selected PBDEs by using three different sorbent in SPLE. Each was run in replicate (n=3). ASG: Acid silica gel.

methods under same extraction conditions (Table 1). More parameters were also considered including PLE conditions. As thorough investigations has been done to improve its extraction efficiency including extraction time, temperature, flush volume, and extraction cycles[32-34], in this work, a spiked diatomaceous earth control (10 ng) using PLE was analyzed using a temperature at 100℃, pressure at 1500 psi, flush volume at 100 % and 3 extraction cycles . Another spiked sediment was subjected to SPLE under same conditions. Results showed the recoveries of control ranged from 95 % to 103 % while for SPLE the recoveries of sediments were from 85 % to 110 % which is satisfying for PBDEs analysis. After the extraction cycles were increased to 4 for SPLE, the recoveries were 83 % to 113 %, no PBDEs were obviously detected in the fourth cycle. Therefore, the SPLE method was processed following the parameters as temperature at 100℃, pressure at 1500 psi, flush volume at 100 % and 3 extraction cycles with 5.0 g alumina mixed with 1.0 g sediment.

### Optimization of ultrasonication-assisted QuEChERS method

Traditional QuEChERS consisted of extraction and clean-up processes assisted by shaking. Dr. Anastassiades and Dr. Lehotay (the developer of QuEChERS) noticed that shaking mode would be the inadequacy for extracting chemicals from soils/sediments as chemicals are bounded to environmental matrices much stronger than vegetables/fruits[37]. Ultrasonic extraction could achieve satisfying efficiency based on cavitation phenomenon[38]. The penetration of solvent into solid matrices were promoted by the increasing pressure aroused by bubble implosion. Therefore, we introduced ultrasonication into QuEChERS to improve the performance of extraction. Similar mechanism was also reported by Dr. Xu for the analysis of organophosphate and halogenated flame retardants in food matrices[39].

**Table 1** Recoveries for selected PBDEs under two alumina addition ways in SPLE (10 ng standards spiked, n=3).

Chemicals	Recovery（%）	
	Mixture	Layer
BDE-28	102 ±2.81	98.0 ±5.21
BDE-47	101 ±4.01	104 ±1.07
BDE-99	113 ±10.2	107 ±5.26
BDE-100	104 ±5. 27	105 ±1.17
BDE-153	110 ±3.74	114 ±7.07
BDE-154	106 ±8.86	104 ±6.20

Besides, the clean-up efficiency of QuEChERS were influenced mainly by the composition of liquid solvents and sorbents. The most popular sorbents used in QuEChERS method are $MgSO_4$, C18, PSA and GCB. Specific optimization was carried out by determining the proportions of $PSA/C18/GCB/MgSO_4$ according to a 4-factor at 3-level Taguchi Orthogonal Arrays (Table 2)[40]. Levels of each variable were defined as follows: C18, GCB and PSA were 0.1, 0.3 and 0.5 g, respectively, $MgSO_4$ was 1.0, 1.5 and 2.0 g. The evaluation criteria of this optimization was the recovery of 20 ng labelled PBDEs spiked in 1 g sediment (Figure 3). According to data analysis, the influence of investigated 4 sorbents were in following sequence: GCB>C18>PSA>MgSO4. GCB presented a negative effect on recovery which could be due to the insufficient elution of adsorbed PBDEs. Based on the evaluation of each sorbent , a mixture of 0.5 g C18, 0.3 g PSA, 0.1 g GCB and 1.5 g $MgSO_4$ could give the optimum performance.

A further investigation was designed to ascertain whether GCB feasible as sorbent for PBDEs analysis. Two kits, $PSA/C18/MgSO_4$ (0.3 g/0.5 g/1.5 g) and $PSA/C18/MgSO_4/GCB$ (0.3 g/0.5 g/1.5 g/0.1 g), were used for this assessment. The results were summarized in Figure 4. Among these two groups of sorbents, the combination of $PSA/C18/MgSO_4$ obtained better recovery and no obvious matrix effects were observed (<10%) which indicated GCB unnecessary for the analysis. As a result, the purification with $PSA/C18/MgSO_4$ (0.3 g/0.5 g/1.5 g) were proved to be practicable for the PBDEs analysis in sediments.
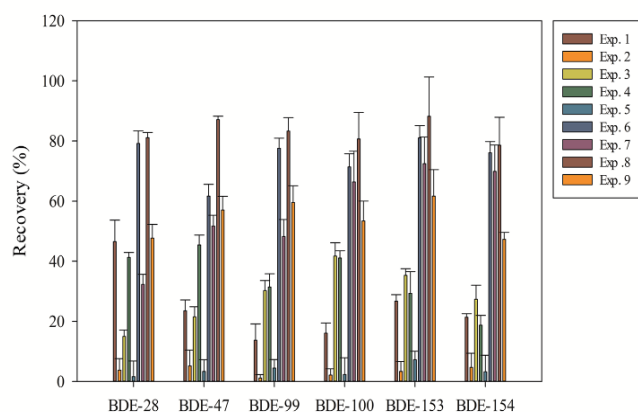
Fig. 3. Recoveries and relative standard deviations for selected PBDEs according to a 4-factor at 3-level Taguchi Orthogonal Arrays using ultrasound-assisted QuEChERS. Each was run in replicate (n=3).

Table 2 Recoveries for selected PBDEs using different sorbent proportions. Experiment design according to a 4-factor at 3-level Taguchi Orthogonal Arrays.

Experiment	C18 (g)	PSA (g)	GCB (g)	$MgSO_4$ (g)
1	0.1	0.1	0.1	1.0
2	0.1	0.3	0.3	1.5
3	0.1	0.5	0.5	2.0
4	0.3	0.1	0.3	2.0
5	0.3	0.3	0.5	1.0
6	0.3	0.5	0.1	1.5
7	0.5	0.1	0.5	1.5
8	0.5	0.3	0.1	2.0
9	0.5	0.5	0.3	1.0
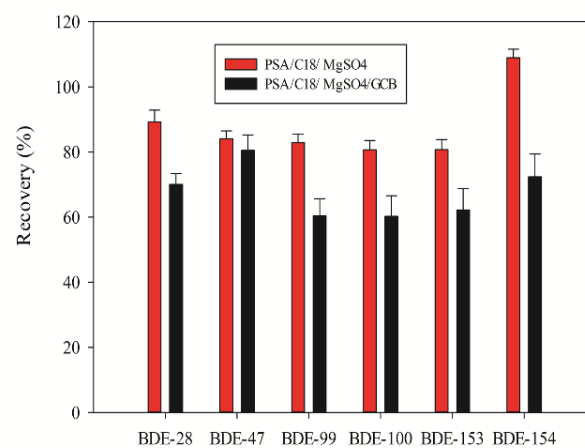
Fig. 4. Recoveries and relative standard deviations for selected PBDEs by using different compositions of sorbents in QuEChERS. Each was run in replicate (n=3).

Validation and comparison of SPLE and ultrasonication-assisted QuEChERS

Detection limits, linearity, precision and trueness were used for the validation and comparison between ultrasonication-assisted QuEChERS and SPLE methods (Table 3). The linearity range was obtained using ultrasonication-assisted QuEChERS and SPLE under optimized conditions. For spiked sediment, the linearity of calibration curve was in the range of 0.5–200 ng/g d.w.. The coefficients or correlation (r^2) were >0.99. Three replicated results showed that the relative deviations (RSDs, inter/intra-day) for both method were quite similar (<7%) at spiked concentration of 10 ng/g d.w.. For SPLE, the LODs and LOQs were slightly better than ultrasonication-assisted QuEChERS which could be attributed to its elevated temperature and pressure resulting as stronger extraction and clean-up ability. The sensitivity of both methods was at the same level as former reported results [22, 41, 42].

Table 3. The linearity, LODs, LOQs and RSDs of ultrasound-assisted QuEChERS (UA-Q) and SPLE for selected PBDEs.

Chemicals	r^2	Line range (ng/g d.w.)	Intra-day RSD (%, n=3)		Inter-day RSD (%, n=3)		LOD (ng/g d.w.)		LOQ (ng/g d.w.)	
			UA-Q	SPLE	UA-Q	SPLE	UA-Q	SPLE	UA-Q	SPLE
BDE-28	0.991	0.5-200	3.8	2.6	5.2	4.1	0.03	0.02	0.1	0.05
BDE-47	0.994	0.5-200	3.6	1.9	6.1	3.5	0.05	0.02	0.1	0.05
BDE-99	0.996	0.5-200	2.5	1.4	3.2	3.1	0.03	0.01	0.1	0.05
BDE-100	0.992	0.5-200	4.4	4.3	5.3	4.1	0.03	0.01	0.1	0.05
BDE-153	0.991	0.5-200	3.8	1.2	3.3	3.3	0.03	0.01	0.1	0.05
BDE-154	0.998	0.5-200	3.4	2.7	5.1	4.1	0.03	0.01	0.1	0.05

On the other hand, SPLE employed high pressure and temperature, less than 90 mL solvent and 45 minutes for each sample during the analysis process. Ultrasonication-assisted QuEChERS consumed less than 20 mL solvent for each sample and more than 6 samples could be conducted during one process in about 2 hours which is better time-saving than SPLE. However, more human labors were needed for ultrasonication-assisted QuEChERS as SPLE was a highly automatic system.

In summary, both methods were found suitable for analyzing PBDEs in sediments. Meanwhile, the precision and accuracy for the SPLE method were slightly higher than the ultrasonication-assisted QuEChERS method. Other figures of merit as LODs and LOQs of SPLE method were also better than those of the ultrasonication-assisted QuEChERS method. With consideration about other method characteristics, the ultrasonication-assisted QuEChERS method consumed less solvent and saved more time than SPLE which deserved further development and optimization.

Performances of ultrasonication-assisted QuEChERS and SPLE on SRM 1944 and 2585

The ultrasonication-assisted QuEChERS and SPLE methods were applied for the analysis of SRM 1944 and 2585. SRM 1944 is a mixture of marine sediment collected in New York and New Jersey with selected PBDEs concentrations at ng/g d.w. (Table S1†). SRM 2585 is used for evaluating analytical methods for selected chemicals in house dust and similar matrices. The certified concentrations for selected PBDE congeners in SRM 2585 are at μg/g d.w. which would be appropriate for assessing the performance of these two methods for PBDEs at high concentrations in high organic carbon (TOC) contained matrices. All extracts from SRM 2585 were 10 times diluted into isooctane for instrument analysis.

Ultrasonication-assisted QuEChERS method (86%-113%) and SPLE (91%-104%) both showed high efficiency on SRM 1944 which were relatively coincident with the reference mass fraction values (Figure 5). The performances were slightly better than reported research employed SPLE followed by ultrahigh pressure liquid chromatography–tandem mass spectrometry with a recovery as 65%-112 % from SRM 1944[43]. The results presented in Figure 5 also indicated both methods capable of PBDEs detection in sediments. While for SRM 2585, SPLE were more coincident with given values. The relative high TOC content of dusts may enhanced combination between PBDEs and matrices resulting the insufficient extraction by ultrasonication-assisted QuEChERS and more co-elution interferes

demanding stronger clean-up efficiency. The results confirmed the feasibility of ultrasonication-assisted QuEChERS and SPLE in the analysis of PBDEs in sediments.

Application of ultrasonication-assisted QuEChERS and SPLE on real samples

The two optimized methods were applied to measure the six PBDEs in field sediment samples collected from areas around a flame retardants manufacture plant in Shandong province (Figure S1). BDE 47, 99, 100 and 153 were detected in sample 1 and 3. The occurrence profiles were showed in Figure 6 and Table S3†.
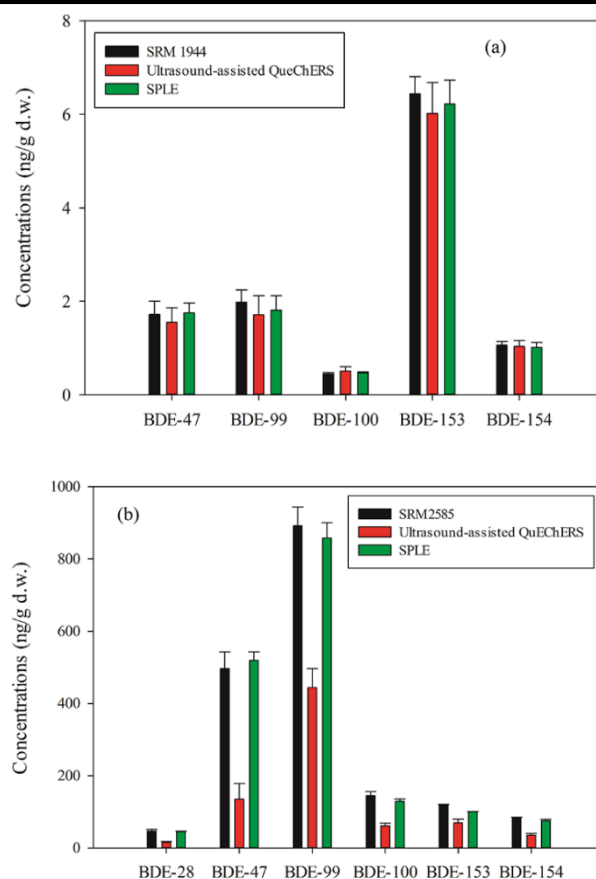
Fig.5 Detected concentrations of PBDEs in SRM 1944 &2585 by SPLE and ultrasound-assisted QuEChERS (n=3). (a) SRM 1944; (b) SRM 2585.
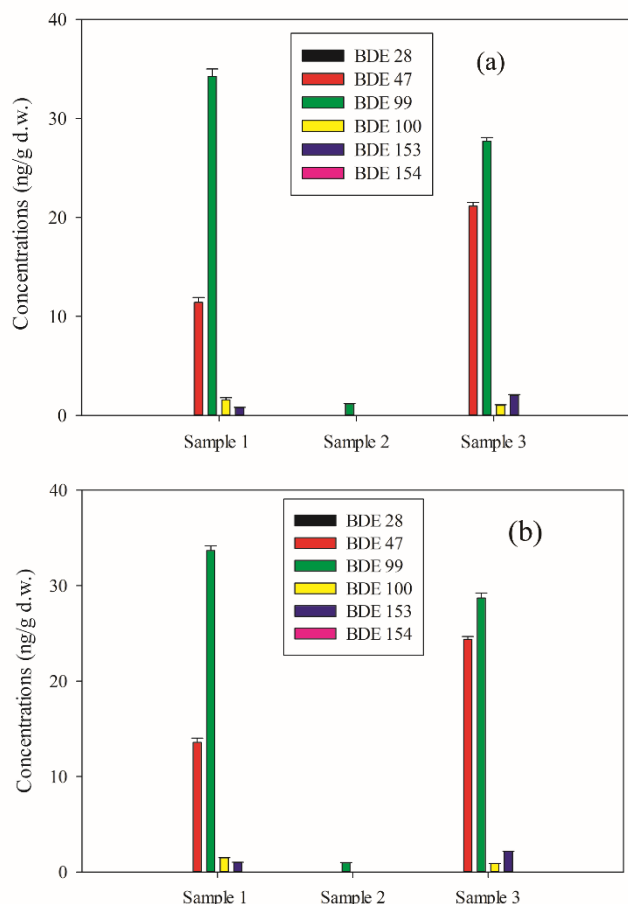
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Fig. 6. Detected concentrations of PBDEs in three sampling locations around a flame retardants manufacture plant using ultrasonication-assisted QuEChERS (a) and SPLE (b). (Sample 1&2 were collected from wastewater canals of the plant in use; Sample 3 were collected from an impounding reservoir which was abandoned several years ago. Detailed mapping was in Figure S1)

Total PBDEs concentrations were 47.9 ±0.861 ng/g d.w. and 49.7 ±0.907 ng/g d.w. using ultrasonication-assisted QuEChERS and SPLE in sample 1, 51.9 ±0.871 ng/g d.w. and 56.1 ±0.676 ng/g d.w in sample 3. BDE 99 were detected in sample 2 at levels of 1.15 ±0.051 ng/g d.w. and 0.947 ±0.684 ng/g d.w. while no other PBDEs were above LOQ. BDE 47 and 99 were the predominant congeners representing 94 % of total PBDEs levels in sample 1 and 3 which were in coincidence with former reports as these PBDEs are major congeners in commercial BDE mixtures [15].

PBDEs levels in sample 1 and 2 implied PBDEs discharged through wastewater from the plant could be efficiently eliminated by the treatment unit. Although impounding reservoir was out of use for several years, the levels in sample 3 were still comparable with that in sample 1 could be due to the persistence and accumulation of PBDEs in sediments.

Conclusions

Two fast methods, SPLE and QuEChERS, for simultaneous analysis of six PBDEs in sediment samples were optimized. The method performances were compared and validated by SRMs. Ultrasonication was introduced into QuEChERS to improve its extraction efficiency and the composition of sorbents used in clean-up step was optimized as a mixture of PSA/C18/ $MgSO_4$ (0.3 g/0.5 g/1.5 g). The method performance on sediment was at same level as former reported applications on food and biological matrices which indicated the extension of method application scopes[44-46]. For SPLE, the sorbents filled in extraction cells were compared and evaluated. Alumina was selected for its good adsorb capacity and selectivity for aromatic carbons. Under the improved parameters, both methods showed good efficiency for PBDEs analysis in SRM 1944 while for indoor dusts or similar high TOC containing matrices, SPLE with elevated temperature and pressure exhibited better applicability than ultrasonication-assisted QuEChERS. Meanwhile, both methods were applied for real samples analysis. The results showed BDE 47 and 99 were predominant congeners among investigated PBDEs ranging from 0.92 to 35.1 ng/g d.w. Both methods were proved practical and suitable for PBDEs determination in sediments. It is also noteworthy that, MRM scanning enhancing detection selectivity strongly supported these two methods to achieve satisfying sensitivity. More considerations are needed for applying these methods in different matrices such as elevating experiment intensity while avoiding degradation of higher brominated congener and be more environmental friendly.

Acknowledgements

Notes and references

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1. Y. Wang, H. Liu, C. Zhao, H. Liu, Z. Cai and G. Jiang, *Environ. Sci. Technol.*, 2005, **39**, 4961-4966.
2. M. Alaee, P. Arias, A. Sjodin and A. Bergman, *Environ Int*, 2003, **29**, 683-689.
3. L. G. Costa, R. de Laat, S. Tagliaferri and C. Pellacani, *Toxicol Lett*, 2014, **230**, 282-294.
4. H. M. Stapleton, *Anal Bioanal Chem*, 2006, **386**, 807-817.
5. A. Covaci, S. Voorspoels, L. Ramos, H. Neels and R. Blust, *Journal of Chromatography A*, 2007, **1153**, 145-171.
6. X. Peng, C. Tang, Y. Yu, J. Tan, Q. Huang, J. Wu, S. Chen and B. Mai, *Environ Int*, 2009, **35**, 303-309.
7. A. O. W. Leung, W. J. Luksemburg, A. S. Wong and M. H. Wong, *Environ. Sci. Technol.*, 2007, **41**, 2730-2737.

8. J. L. Sun, Z. X. Chen, H. G. Ni and H. Zeng, *Chemosphere*, 2013, **92**, 471-476.

9. P. Wang, Q. Zhang, Y. Wang, T. Wang, X. Li, L. Ding and G. Jiang, *Anal Chim Acta*, 2010, **663**, 43-48.

10. Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng, N. Zhu and G. Jiang, *Analytica Chimica Acta*, 2011, **708**, 61-68.

11. X. Li, X. M. Li, X. X. Yang, Q. Li, B. Huang and X. J. Pan, *Anal. Methods*, 2014, **6**, 9658-9666.

12. X. Liu, J. Li, Z. Zhao, W. Zhang, K. Lin, C. Huang and X. Wang, *Journal of Chromatography A*, 2009, **1216**, 2220-2226.

13. F. Jia, X. Cui, W. Wang, L. Delgado-Moreno and J. Gan, *Environ Pollut*, 2012, **167C**, 34-40.

14. G. Zhang, X. Zang, Z. Li, Q. Chang, C. Wang and Z. Wang, *Analytical Methods*, 2014, **6**, 2756.

15. B. Gevao, E. A. Boyle, A. A. Aba, G. G. Carrasco, A. N. Ghadban, D. Al-Shamroukh, H. Alshemmari and M. Bahloul, *Sci Total Environ*, 2014, **491-492**, 148-153.

16. Z.-W. Zhang, Y.-X. Sun, K.-F. Sun, X.-R. Xu, S. Yu, T.-L. Zheng, X.-J. Luo, Y. Tian, Y.-X. Hu, Z.-H. Diao and B.-X. Mai, *Chemosphere*, 2015, **123**, 26-32.

17. J. Guo, Z. Li, A. L. Sandy and A. Li, *Journal of chromatography. A*, 2014, **1370**, 1-8.

18. S. Krol, B. Zabiegala and J. Namiesnik, *Talanta*, 2012, **93**, 1-17.

19. Q. Zhang, T. Liang, L. Wang and H. Cao, *Analytical Methods*, 2012, **4**, 2441.

20. Q. Wang, J. Yin, H. Pan, F. Xu and Y. Yang, *Analytical Methods*, 2014, **6**, 7335.

21. A. de la Cal, E. Eljarrat and D. Barceló, *Journal of Chromatography A*, 2003, **1021**, 165-173.

22. E. Baron, E. Eljarrat and D. Barcelo, *Anal Bioanal Chem*, 2014, **406**, 7667-7676.

23. M. Á. González-Curbelo, B. Socas-Rodríguez, A. V. Herrera-Herrera, J. González-Sálamo, J. Hernández-Borges and M. Á. Rodríguez-Delgado, *TrAC Trends in Analytical Chemistry*, 2015, **71**, 169-185.

24. A. L. Capriotti, C. Cavaliere, P. Foglia, R. Samperi, S. Stampachiacchiere, S. Ventura and A. Laganà, *TrAC Trends in Analytical Chemistry*, 2015, **71**, 186-193.

25. M. Anastassiades, S. J. Lehotay, D. Stajnbaher and F. J. Schenck, *J Aoac Int*, 2003, **86**, 412-431.

26. C. Lesueur, M. Gartner, A. Mentler and M. Fuerhacker, *Talanta*, 2008, **75**, 284-293.

27. C. Lesueur, P. Knittl, M. Gartner, A. Mentler and M. Fuerhacker, *Food Control*, 2008, **19**, 906-914.

28. M. M. Aguilera-Luiz, J. L. Vidal, R. Romero-Gonzalez and A. G. Frenich, *Journal of chromatography. A*, 2008, **1205**, 10-16.

29. D. Drozdzynski and J. Kowalska, *Anal Bioanal Chem*, 2009, **394**, 2241-2247.

30. B. Binici, M. Bilsel, M. Karakas, I. Koyuncu and A. C. Goren, *Talanta*, 2013, **116**, 417-426.

31. R. Perez-Burgos, E. M. Grzelak, G. Gokce, J. Saurina, J. Barbosa and D. Barron, *Journal of chromatography. B, Analytical technologies in the biomedical and life sciences*, 2012, **899**, 57-65.

32. Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai and G. Jiang, *Journal of chromatography. A*, 2011, **1218**, 197-204.

33. L. R. Snyder, *Marcel Dekker, Inc.*, 1968.

34. M. Gorga, E. Martinez, A. Ginebreda, E. Eljarrat and D. Barcelo, *Sci Total Environ*, 2013, **444**, 51-59.

35. F. Mercier, E. Gilles, G. Saramito, P. Glorennec and B. Le Bot, *Journal of Chromatography A*, 2014, **1336**, 101-111.

36. X. Zheng, F. Xu, K. Chen, Y. Zeng, X. Luo, S. Chen, B. Mai and A. Covaci, *Environ Int*, 2015, **78**, 1-7.

37. M. A. Ronald E. Majors, Steven J. Lehotay, *LCGC*, 2010, **13**.

38. N. B. Lana, P. Berton, A. Covaci, A. G. Atencio, N. F. Ciocco and J. C. Altamirano, *Journal of chromatography. A*, 2013, **1285**, 15-21.

39. F. Xu, A. Garcia-Bermejo, G. Malarvannan, B. Gomara, H. Neels and A. Covaci, *Journal of chromatography. A*, 2015, **1401**, 33-41.

40. J. I. Cacho, N. Campillo, P. Vinas and M. Hernandez-Cordoba, *Journal of chromatography. A*, 2015, **1380**, 156-161.

41. J. Sun, J. Liu, Q. Liu, G. Qu, T. Ruan and G. Jiang, *Talanta*, 2012, **88**, 669-676.

42. X. T. Wang, L. Chen, X. K. Wang, Y. Zhang, J. Zhou, S. Y. Xu, Y. F. Sun and M. H. Wu, *Chemosphere*, 2015, **133**, 22-30.

43. G. Mascolo, V. Locaputo and G. Mininni, *Journal of chromatography. A*, 2010, **1217**, 4601-4611.

44. A. R. Fontana, A. Camargo, L. D. Martinez and J. C. Altamirano, *Journal of chromatography. A*, 2011, **1218**, 2490-2496.

45. Y. Sapozhnikova and S. J. Lehotay, *Anal Chim Acta*, 2013, **758**, 80-92.

46. L. J. Han, Y. Sapozhnikova and S. J. Lehotay, *Analytica Chimica Acta*, 2014, **827**, 40-46.
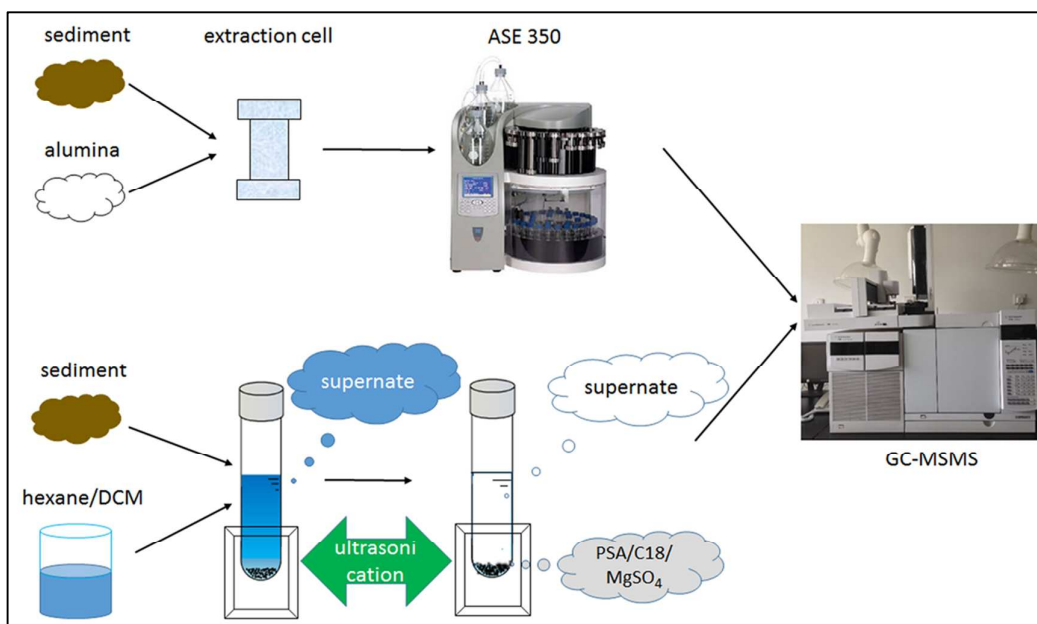
SPLE and ultrasonication-assisted QuEChERS were optimized or the analysis of PBDEs in sediments. Both SPLE and ultrasonication-assisted QuEChERS were validated by SRMs and applied on real samples. Both methods provided good LODs and LOQs, precision and recoveries. SPLE showed better performance than ultrasonication-assisted QuEChERS for dusts and more complex environmental matrices.