



Determination of tetrabromobisphenol A and its brominated derivatives in water, sediment and soil by high performance liquid chromatography–tandem mass spectrometry

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Abstract

Tetrabromobisphenol A (TBBPA) was typical brominated flame retardant and potential environmental endocrine disruptor, and it had persistence, bioaccumulation and chronic toxicity. Simultaneous determination of ultra-trace TBBPA, tribromobiphenol A (tri-BBPA), dibromobiphenol A (di-BBPA), monobromobisphenol A (mono-BBPA) and bisphenol A (BPA) was developed by high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS), the parent ion charge ratios (m/z) had been optimized. The linear range was wider and the limit of detection was (LOD) $0.09 \sim 0.21 \text{ ng mL}^{-1}$, which could detect trace pollutants. The extraction efficiency was improved by optimizing the parameters, HLB cartridge was used in the water sample by solid phase extraction (SPE), the recovery rates in water samples were over 80.28% with three concentration levels, the relative standard deviations (RSD) were less than 7.12%, and the minimum detection limit of the method was $0.90 \sim 2.10 \times 10^{-3} \text{ ng mL}^{-1}$. Soil and sediment samples were extracted by accelerated solvent extraction (ASE), the recovery rates in soil and sediment were over 79.40% and 75.65%, the minimum detection limit was $0.0225 \sim 0.0525 \text{ ng g}^{-1}$, RSD was less than 7.19%. The proffered method was successfully utilized to detect actual samples, the residue of di-BBPA and mono-BBPA are detected in Naihe River and Shuxi River in Tai'an City, residue of di-BBPA and mono-BBPA was detected in the soil, and there was low residual amount of di-BBPA, mono-BBPA and BPA in the sediment of Shuxi River.

Keywords Tri-TBBPA · Di-TBBPA · Mono-BBPA · Bisphenol A · Solid phase extraction · Accelerated solvent extraction

Introduction

With the development of industry, TBBPA as the flame retardant is more and more widely used. According to statistics, the amount of TBBPA in China increases from 5.21×10^6 tons in 2014 to 6.43×10^6 tons in 2017, and it is expected to continue to increase at a significant rate [1]. Consequently, the pollution are also becoming more and more prominent. International Agency for Research on Cancer upgraded TBBPA to 2A carcinogen Class.

Due to the extensive disassembly and disposal of e-waste, TBBPA and BPA are released into the environment through many point sources and non-point sources [1, 2]. In the environment, TBBPA can be de-brominated into bromine

derivatives [3, 4]: tri-BBPA, di-BBPA, mono-BBPA and BPA by photolysis [5, 6] and microorganisms [7, 8]. Under the biological circulation, it enters the water, fish and human body, and it may even migrate to the north and south poles.

Pretreatment methods in environmental samples have been widely studied, the methods for TBBPA and bromide derivatives in water are liquid–liquid extraction [9] (LLE), solid phase extraction (SPE) [10], and ultrasonic and liquid phase extraction. Pretreatment methods in soil and sediment are Soxhlet extraction, pressurized liquid extraction (PLE), ultrasonic-assisted extraction (UAE) [11], microwave-assisted extraction (MAE) [10, 12], solid phase microextraction (SPME) [13] and accelerated solvent extraction (ASE). Supercritical fluid extraction (SFE), microwave extraction (MAE) [14], matrix solid phase dispersion extraction (SPD) and subcritical water extraction (SWE) were extraction methods applied to solid or semisolid substance. SWE was a method for extracting pollutants according to the principle of polarity [15]. Deep eutectic solvents- Micro matrix solid phase extraction was used (DES-MSPD) in soil pretreatment

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to extract nitro-toluene from soil [16]. Density-tunable liquid–phase micro extraction (DT-LPME) based on deep eutectic solvents (DES) was used to determinate polycyclic aromatic hydrocarbons in tea, medicinal herbs and liquid foods [17].

A variety of methods for the separation and detection of flame retardants and its by-products have been established, such as gas chromatography–mass spectrometry (GC–MS) [2, 18], liquid chromatography–mass spectrometry (LC–MS), liquid chromatography–secondary mass spectrometry (LC–MS/MS) [19–21]. In addition, a variety of emerging methods have gradually developed, such as capillary electrophoresis, thin layer chromatography–high performance liquid chromatography with diode array detection (TLC–HPLC–DAD), paper spray ion source mass spectrometry [22], protein analysis [23] and electrochemical method [24, 25]. Lestido-Cardama [26] reported that DART-HRMS (Direct analysis in real time ionization coupled to high resolution mass spectrometry) and XRF (X-ray fluorescence) were used as screening techniques for brominated flame retardants (BFRs) identification (Tribromophenol, Tetrabromobisphenol A and Decabromodiphenyl ether) in the food contact articles, HPLC–MS/MS was used for the determination of BFR.

The objective of this study was to develop a quick, accurate, and sensitive analytical method based on SPE (ASE)-HPLC–MS/MS for the simultaneous determination of BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA in samples at low concentrations. The mobile phase of liquid chromatography, and mass spectrometric parameters were optimized. The recovery rates, precision, accuracy and minimum detection limit of the method were assessed, and the concentrations of TBBPA and its metabolites in actual samples were analyzed by the optimized method.

Experimental

Chemicals

BPA and TBBPA (Dr. Ehrenstorfer, 99.70% and 99.45%); mono-BBPA, B-Di-BBPA (Bromide is located in different benzene), X-Di-BBPA (Bromide is located in the same benzene) and tri-BBPA were obtained from Yi Liu's lab. (98.00%, Yantai University). Methanol and acetonitrile were chromatographically pure and it was obtained from Merck Chemical Technology Co., Ltd. (Shanghai, China). The other reagents were analytical grade, and all aqueous solution were ultrapure water.

Equipment

Solid phase extraction (gx-271, Gilson, USA), UltiMate 3000 HPLC-TSQ Quantum Access Max Triple quaternary lever liquid binder (Thermo Fisher Scientific, USA), Millionth electronic balance (MSA36S, Sartorius, German), XPE26 (Mettler Totedo, Switzerland), ASE150 (Thermo Fisher Scientific, USA), Nitrogen blowing instrument (N-EVAP-34, United states Organomation).

Conditions of HPLC–MS/MS

Hypersil BDS C_{18} liquid chromatography column (4.6 mm \times 100 mm \times 2.7 μ m) was used for chromatographic separation with isocratic elution with methanol/0.1% ammonium acetate water (80:20, V:V) at a flow rate of 0.3 mL min^{-1} . The temperature of the column was set at 40 °C with an injection volume of 5 μ L, and the run time was 7 min.

Mass spectrometry conditions were optimized for maximal sensitivity in negative mode using electrospray ionization (ESI-), the operating conditions were as follows: selected reaction monitoring (SRM) was used in the mass spectrometry conditions, the collision gas pressure was 1.5 mTorr, capillary temperature was 150°C, vaporizer temperature was 400°C, sheath gas pressure was set to 40 psi, spray voltage was – 2900 V, discharge current was – 4 A. The parent of BPA, Mono-BBPA, Di-BBPA, Tri-BBPA and TBBPA was 227.10 ($[M-H]^-$), 305.00, 384.90, 462.80 and 542.50 (m/z), respectively; The product of quantifying ion was 212.10, 79.00, 79.00, 339.90 and 417.90 (m/z), respectively; The collision energy (CE) was 27, 29, 41, 39 and 40 eV, respectively; The product of confirming ion was 133.10, 81.00, 81.00, 337.90 and 419.90, respectively. And the CE was 21, 29, 41, 39 and 40 eV; Retention time of the five pollutants was 1.01, 1.09, 1.25, 1.43 and 1.64 min.

SPE for water extraction

TBBPA and its bromide derivatives in the water were extracted by SPE, the extraction conditions were optimized, two kinds of SPE cartridges were selected: Oasis HLB cartridge (6 cc/500 mg) and C_{18} (3 cc/300 mg) cartridge.

The sorbent was activated using 6 mL of methanol and 6 mL deionized water, and then 100 mL water was loaded with the flow speed of 3 mL min^{-1} and 5 mL min^{-1} . The sorbent was then washed with 6 mL distilled water to remove impurities and thereafter was allowed to dry under vacuum for 10 min to remove retained water. The comparison and selection of methanol and methanol/acetonitrile (1:1, v:v) as elution solvents has been done, the adsorbed substances were eluted with different volume methanol (8, 10, 16 and

24 mL), the eluates were then concentrated to 5 mL using a nitrogen evaporator, and it was analyzed by HPLC–MS/MS after passing through 0.22 µm organic phase microporous filter membrane.

ASE for soil and sediment extraction

ASE was selected for sample extraction. Soil and sediment samples (4.00 ± 0.02 g) were accurately weighed, and placed into extraction pools on the mechanical arm of ASE for extraction, a piece of membrane of ASE extraction filtration cellulose was laid on the top and bottom, respectively. The parameters were set as follows: the extraction pressure was 1500 psi, the heating temperature of furnace was 60, 80 and 100 °C; methanol and acetonitrile was extraction solvent, heat-up time was 5 min, and the static extraction time was set 3, 5 and 7 min, cycle index was set 1, 2 and 3 times, then, nitrogen was purged for 60 s to ensure that all the extracts flowed out of the extraction pool and that the system was clean, the operating parameters of the ASE program were more effectively optimized. The eluates were then concentrated to 1 mL using nitrogen evaporator, and it was determined by HPLC–MS–MS after passing through 0.22 µm organic phase microporous filter membrane.

Recovery rate of certified reference materials (CRM) in the samples

100 mL water sample was accurately measured, the concentrations of five substances in water samples were set to three levels, 0.5, 2.5 and 5.0 ng mL⁻¹ respectively, and each concentration was set three parallel samples. After extraction and purification according to the SPE method, the recovery rates of standard addition were determined.

4.00 g soil (sediment) samples were accurately weighed, the concentrations of five substances in the samples were set at 3.0, 6.2 and 12.5 ng g⁻¹, respectively, and each concentration was set three parallel samples, the recovery rates were calculated by extraction and purification according to the ASE method.

Sample collection

2 L Water samples were collected from Naihe River and Shuxi River in Taian City, Shandong province, China in April 2020, the water samples were filtered using GF/F filters and stored in light-protected glass bottles at 4 °C. 1 kg sediment were collected from Shuxi River. 2 kg soil were collected from experimental field of Panhe campus of Shandong Agricultural University, and it was naturally dried, the soil and sediment passed through 20 mesh sieve and was stored in -20 °C.

Data statistics and analysis

The recovery rate of samples was analyzed for significance using SPSS 22.0 (Statistical Product and Service Solutions), using one-way analysis of variance (ANOVA). Differential significance of recovery rates with different treatments was evaluated by the minimum significance difference ($p < 0.05$). The minimum detection concentration of method was calculated using the formula:

$$\text{Minimum detection limit of method} = \frac{\text{minimum detection quality (ng)} \times \text{configuration volume (mL)}}{\text{injection volume (}\mu\text{L)} \times \text{sample amount (g, L)}}$$

LOD is the limit of detection of the instrument, MDL is the minimum detection limit of the method, and ND is less than MDL.

Results and discussion

Optimization of HPLC–MS/MS

Optimization of the mass spectrometry

TBBPA and its bromine metabolites were easy to lose H⁺ and produce negatively charged ions after entering the first-order mass spectrometry. Therefore, the primary mass spectra of BPA, mono-BBPA, B-Di-BBPA, X-Di-BBPA, tri-BBPA and TBBPA single standard solution (500 ng mL⁻¹) were analyzed in negative ion mode, and the best parent ion mass charge ratio m/z of the five compounds was obtained: 227.10, 305.00, 384.90, 462.80 and 542.50 ([M-H]⁻). Then each parent ion was carried out secondary mass spectrometry analysis, and continued to optimize the collision energy of each product ion in selective reaction monitor (SRM), the ion with the strongest signal was selected for quantitative analysis and the ion with the sub strongest signal was used for qualitative analysis, m/z of TBBPA and its brominated derivatives is shown in Fig. 1a.

Then secondary mass spectrometry was used to analyze the parent ions. On the basis of the above optimization conditions, the capillary temperature, nebulizer temperature, sheath pressure, spray voltage and discharge current of the five products were optimized for the five compounds in the mixed solution (500 ng mL⁻¹) under the selective reaction monitoring mode (SRM). The parameters of other mass spectrometry conditions were the same, and total ion current (TIC) chromatograms are shown in Fig. 1b, it showed that this method was more reliable for the determination of TBBPA and its bromine derivatives.

TIC of TBBPA and its bromine derivatives was presented with high response values, and the peaks were symmetric, with no miscellaneous peaks. The retention time of the two

structural formulas of di-BBPA was 1.28 min, and two substances with different structures of di-BBPA had the same retention time, therefore, B-Di-BBPA and X-Di-BBPA were detected and analyzed together.

Optimization of the HPLC mobile phase

Under the above optimization conditions, acetonitrile/water (80:20, v:v) (Fig. 2a) and methanol/water (80:20, v:v) (Fig. 2b) were selected as the mobile phase according to the characteristics of the pollutants. Because TBBPA and its bromide derivatives are easy to ionize the H^+ in negative ionic mode, an appropriate amount of ammonium acetate was added to promote ionization of the target compounds. Therefore, ultra-pure water and 0.1% ammonium acetate water (Fig. 2c) were selected as the water phase for the selection and optimization of the mobile phase.

Comparing Fig. 2a with Fig. 2b, when the mobile phase is methanol/water (80:20, v:v), the response values of the five substances reached the maximum and the peaks were symmetrical, methanol was selected as the organic phase (Fig. 2b). Comparing Fig. 2b with Fig. 2c, it could be seen that the response value for BPA and mono-BBPA increased when 0.1% ammonium acetate aqueous solution was used as the aqueous phase, it was comprehensively considered to use methanol/0.1% ammonium acetate (80:20, v:v) aqueous solution as the mobile phase.

In this study, from Fig. 2d, it showed that the methanol/0.1% ammonium acetate aqueous solution was 70:30, although the degree of isolation of substances is relatively good, the response value was reduced, the response value was generally 10^3 , and the peak shape was asymmetric. The polarity of mobile phase decreased (Fig. 2e), the response value was high and the peak shape was better when the methanol/0.1% ammonium acetate aqueous solution was 80:20, methanol/0.1% ammonium acetate (80:20) was selected as the optimum mobile phase. Under the optimized experimental conditions, the retention time of BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA was 1.01, 1.09, 1.25, 1.43 and 1.64 min respectively. The retention time of the five substances was slightly different, the retention time was presented according to the molecular weight, and the higher the molecular weight was, and the longer the retention time was.

Linear range and detection limits of instrument

Under the optimized test conditions, the mixed standard solutions of five substances with concentrations of 0.1, 10, 25, 50, 100 and 500 $ng\ mL^{-1}$ were determined by HPLC-MS/MS. The results showed that the linear range of BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA was

$4.42 \times 10^{-13} \sim 3.23 \times 10^{-9}$ g, the linear range of substances was wide, and the correlation coefficient was greater than 0.9998, it showed good linear relationship between response value and injection amount (Fig. 3A).

LOD and limit of quantitation (LOQ) of the instrument were determined with 3 times signal-to-noise ratio ($S/N=3$) and 10 times signal-to-noise ratio ($S/N=10$) of the parent ions of the five target compounds. The LOD and LOQ of BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA were determined. The results showed that the LOD value was $0.09 \sim 0.21\ ng\ mL^{-1}$ and the LOQ value was $0.27 \sim 0.64\ ng\ mL^{-1}$, which could meet the requirements for the residue analysis of ultra-trace TBBPA and its bromine derivatives in the environment [27].

In this study, under the conditions of exploring of chromatographic method, the methanol and acetonitrile was selected as organic phase [28], and 0.1% ammonium acetate aqueous solution was chose as aqueous phase, the proportion of the two components in the mobile phases was explored to obtain higher response value and symmetrical peak shape, two proportions (80:20 and 70:30) of methanol/0.1% ammonium acetate water (V/V) were selected for optimization, and methanol/0.1% ammonium acetate water (80:20) was finally selected as the mobile phase. Isocratic elution was used in this study, because the cumbersome parameter in the gradient elution was set. In the mass spectrometry, the single standard solutions of TBBPA and its bromine derivatives were scanned to determine the parent ions of these compounds, and then the parent ions were scanned to determine the m/z of fragment ions, which was consistent with the research results [7].

Optimization of water samples pretreatment

SPE was used for the pretreatment of water samples. The SPE cartridge, sample loading speed, the type and volume of elution solvent in the solid phase extraction were optimized respectively.

Optimization of SPE cartridge

The concentration of pollutants in the water sample was set $5\ ng\ mL^{-1}$, the loading speed was $3\ mL\ min^{-1}$, 8 mL methanol was elution solvent. In the process of water sample pretreatment, it is very important to select a suitable SPE cartridge, comparing Oasis HLB cartridge with C_{18} cartridge, the results are shown in Fig. 4A, there was significant differences in the recovery rates of five compounds by C_{18} and HLB cartridge, the recovery rates by C_{18} were relatively lower, it was $49.40 \pm 0.40\% \sim 74.81 \pm 4.81\%$,

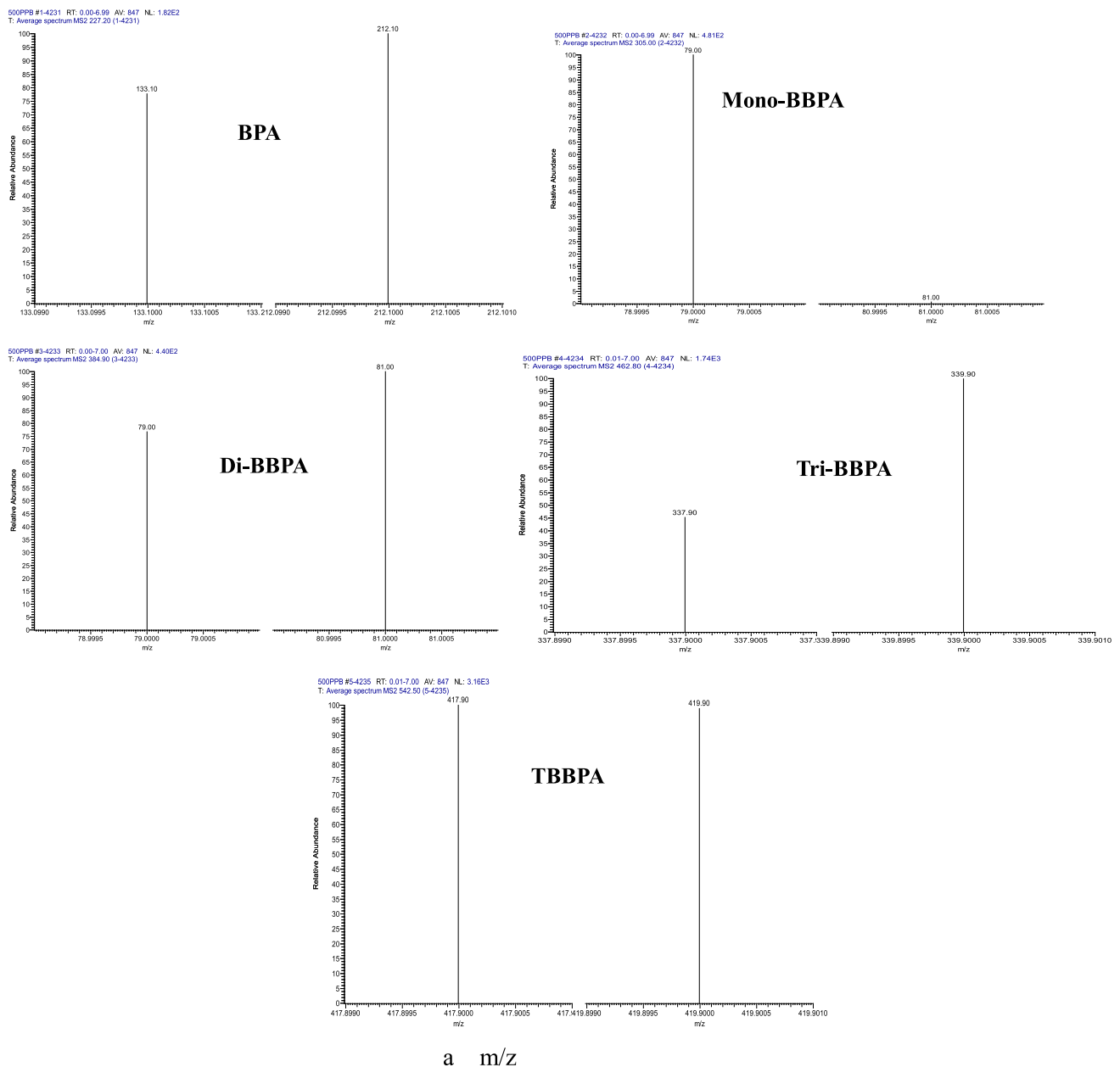


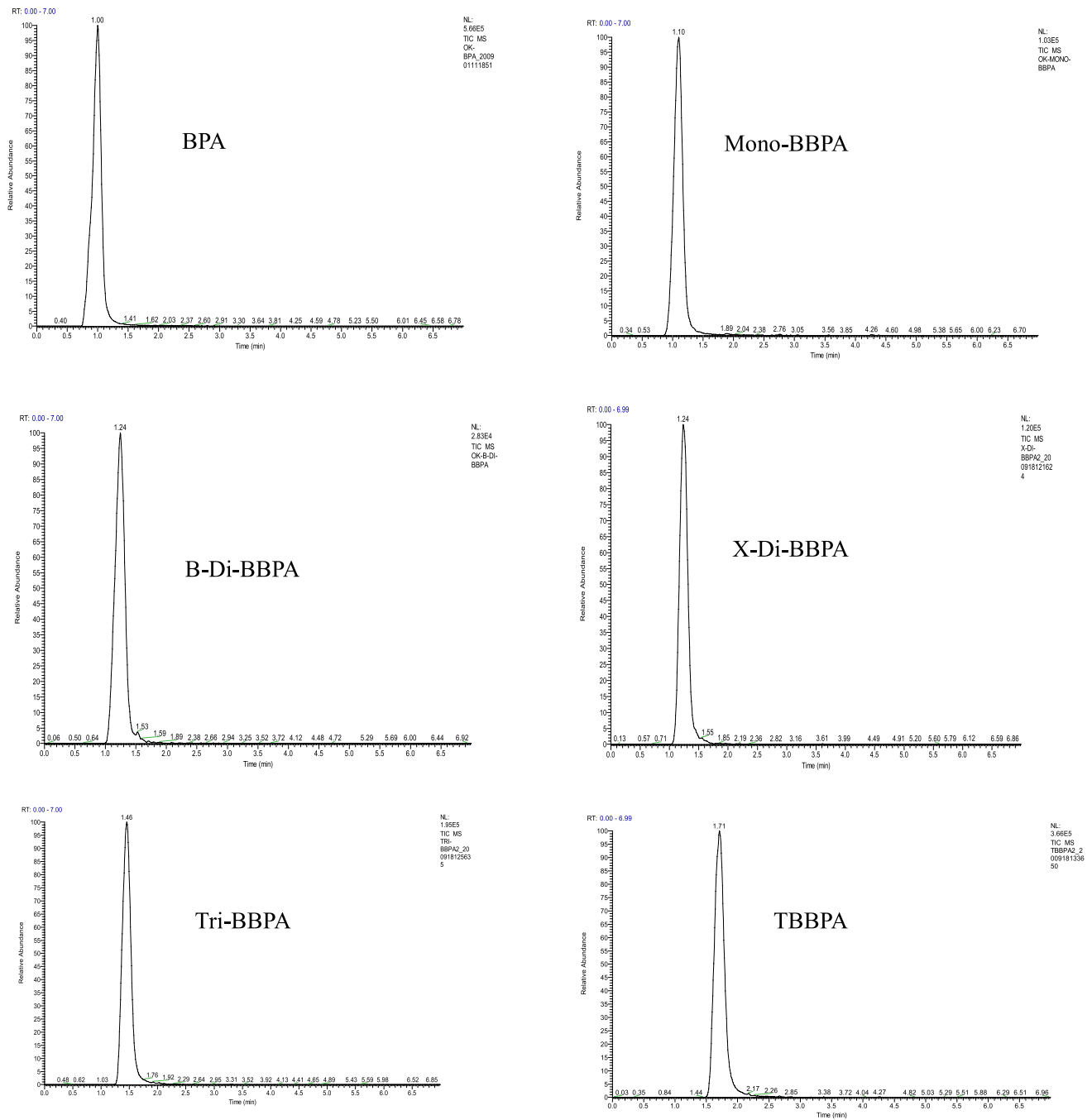
Fig. 1 m/z and Total ion current (TIC) chromatogram of TBBPA and its brominated derivatives in the concentration of 500 ng·mL⁻¹

it was indicated that C₁₈ was not suitable for the extraction; The recovery rates by HLB were higher, it was 53.97 ± 0.97% ~ 106.08 ± 2.08%, the recovery rate of BPA was 106.08%, the recovery rate gradually decreased with the increasing of molecular weight of the substance, the reason was that it was not easy to be eluted due to the large molecular weight, the initial elution volume was set 8 mL, it was indicated that increasing the volume of eluting solvent would increase the recovery rates of the compounds with

high molecular weight, it was appropriate to select the HLB cartridge as optimum SPE cartridge.

Optimization of sample loading speed

The concentration of pollutants in the water sample was set 5 ng mL⁻¹, HLB cartridge was selected, 8 mL methanol was elution solvent, and the two speeds of sample loading are compared and optimized (Fig. 4B). The recovery



b TIC

Fig. 1 (continued)

rates were $46.06 \pm 1.06\% \sim 90.13 \pm 1.13\%$ as the sample loading speed was 5 mL min^{-1} , only BPA had high recovery rate (90.13%), the reason for the high recovery rate needs further exploration, and the recovery rates of the other four substances were relatively low. The sample

loading speed was set 3 mL min^{-1} , the recovery rates were $63.97 \pm 0.97 \sim 79.10 \pm 3.10\%$, the recovery rates of five substances exceeded 60%, it was appropriate that the sampling loading speed was set 3 mL min^{-1} .

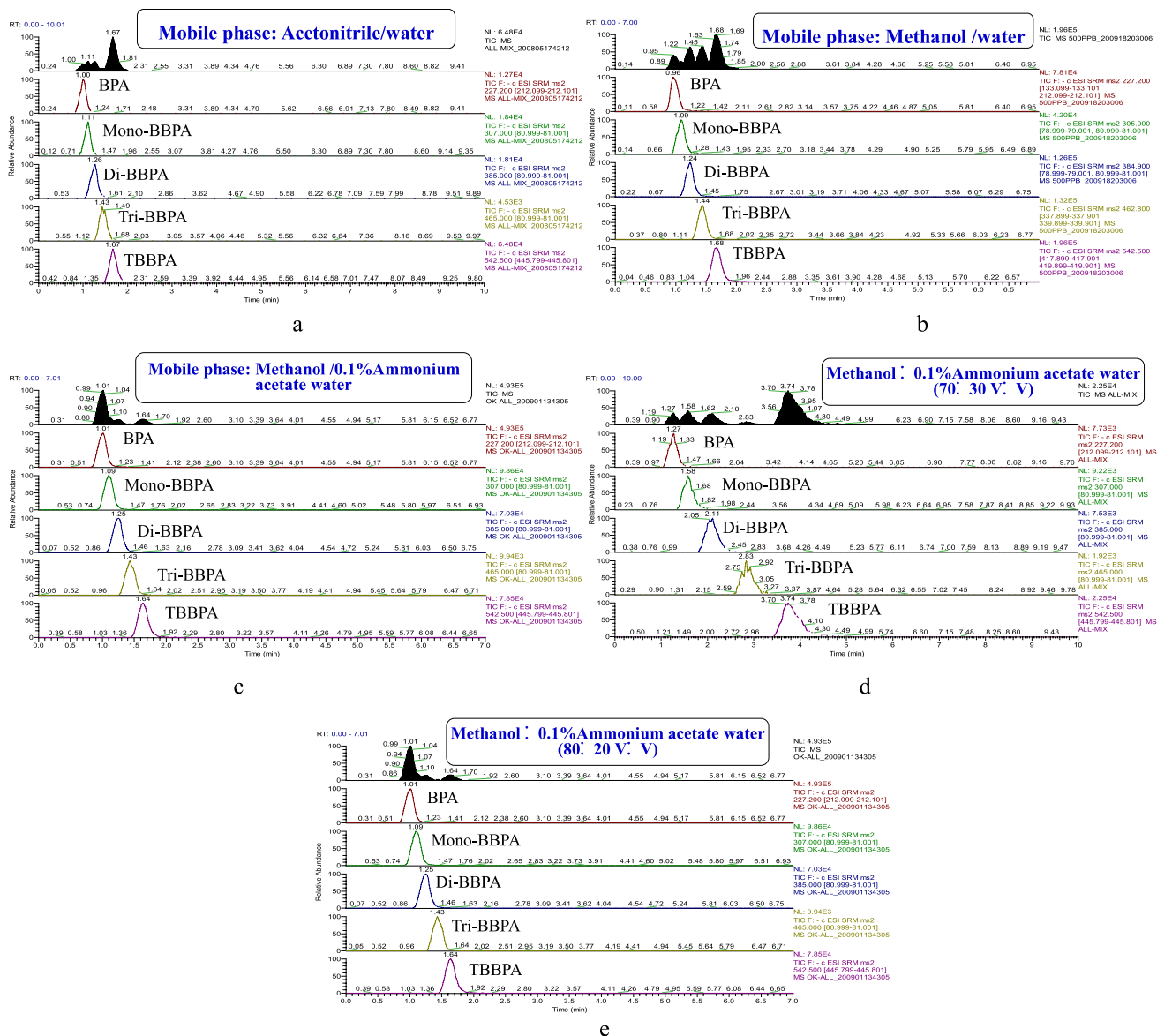


Fig. 2 TIC chromatogram of TBBPA and its brominated derivatives in the concentration of 500 ng·mL⁻¹ under the different mobile phases conditions. Note: The first diagram was TIC chromatogram,

and the other five distributaries from top to bottom are BPA, Mono-BBPA, Di-BBPA, Tri-BBPA, and TBBPA, respectively

Optimization of type and volume of eluting solvent

According to Fig. 4C, two types of solvents are used as eluting solvents. The methanol was used as the eluting solvent, and the recovery rates of five pollutants were relatively higher. The recovery rates decreased in the use of methanol/acetonitrile (1:1, V:V) as eluting solvent, and there are significant differences between the two treatments of four pollutants besides BPA, in addition, methanol/acetonitrile as

eluting solvent was unstable, so the methanol was selected as the eluting solvent.

According to Fig. 4D, the recovery rate increased gradually with the increasing of eluting volume, but recovery rate increased slightly in the volume 16~24 mL eluting solvent (methanol), it indicated that target compounds were essentially eluted by 16 mL methanol. Comprehensive consideration of cost and recovery rate, 16 mL methanol as eluting solvent was feasible.

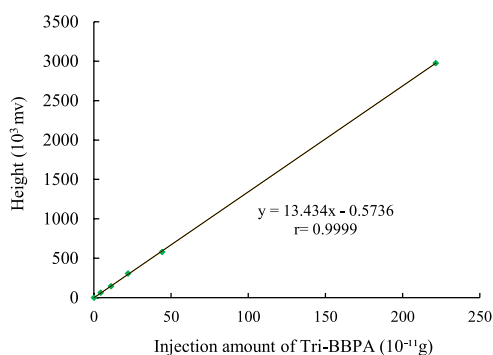
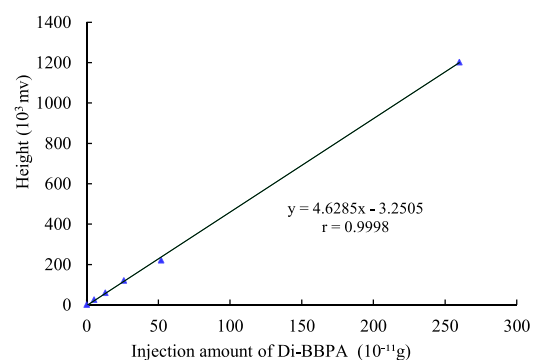
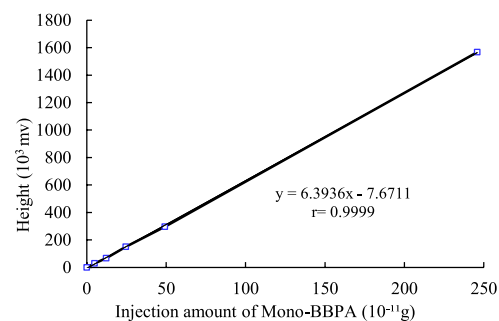
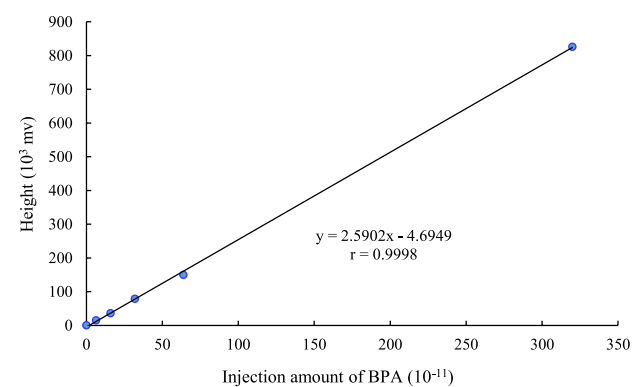


Fig. 3 Standard curve of TBBPA and its brominated metabolites

SPE and liquid–liquid extraction (LLE) are relatively feasible and it is widely used in the extraction and purification of samples [29]. SPE was selected as the pre-treatment method of water samples in this study, the method was relatively feasible, simple, rapid, efficient, solvent saving and

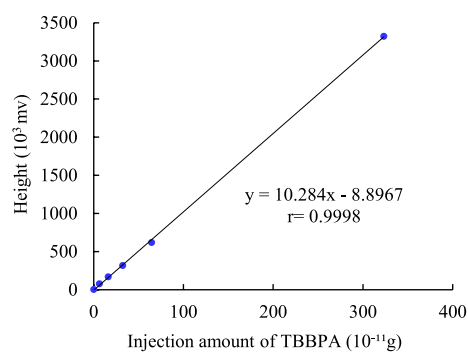


Fig. 3 (continued)

highly selective and widely applicable. The sample could be completely concentrated and purified simultaneously.

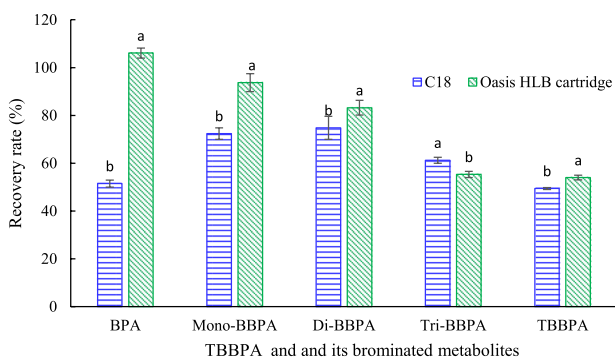
In this study, the minimum detection limit of TBBPA and its bromine derivatives was $0.90 \sim 2.10 \times 10^{-3} \text{ ng mL}^{-1}$, and the recovery rates of the water sample were $80.28 \sim 126.11\%$. Liu [4] reported that detection limit of TBBPA was 0.12 ng mL^{-1} , Xie [9] reported that detection limit of TBBPA and BPA was $0.16 \sim 0.23 \text{ ng mL}^{-1}$, compared with the reported detection methods, the established pretreatment method for TBBPA and its bromine derivatives in this study has lower detection limit, which can not only detect TBBPA and its bromine derivatives in water samples simultaneously, it also reflects the migration and transformation of brominated flame retardants in water environment.

There are many pretreatment methods for organic pollutants in water, such as Disperse Solid Phase Extraction (DSPE), Solid Phase Microextraction (SPME), Stir Bar Sorptive Extraction (SBSE), Headspace Extraction (HS) and membrane extraction. The organic pollutants such as flame retardants and its intermediate metabolites are concentrated by the adsorption principle, Membrane-assisted Solvent Extraction (MASE) was used to isolate organic contaminants from the water [30]. New adsorbent materials have also been extensively studied: metal organic frames (MOFs) and covalent organic frames material (COFs) are applied to SPE, DSPE, SPME, SBSE and membrane extraction to extract organic pollutants in the water environment [31–33], and the matrix effect has been reduced during sample pretreatment, new detection methods are also being further explored.

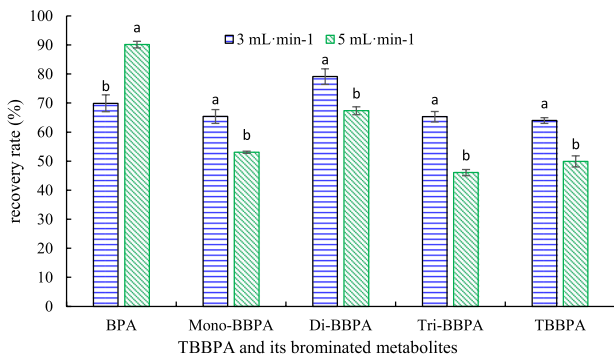
Optimization of soil and sediment samples pretreatment

Optimization of extraction temperature

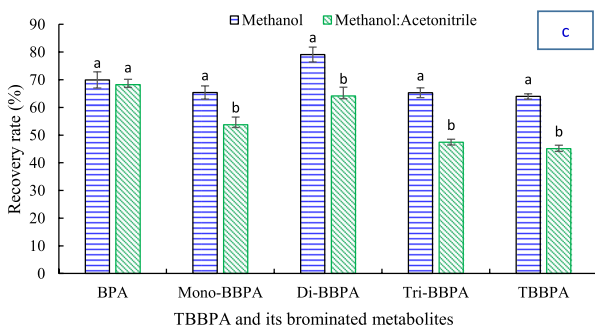
The extraction time was set 3 min and the number of cycles was one, the three extraction temperatures $60 \text{ }^\circ\text{C}$, $80 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$ were optimized, and the result is shown in Fig. 5A.



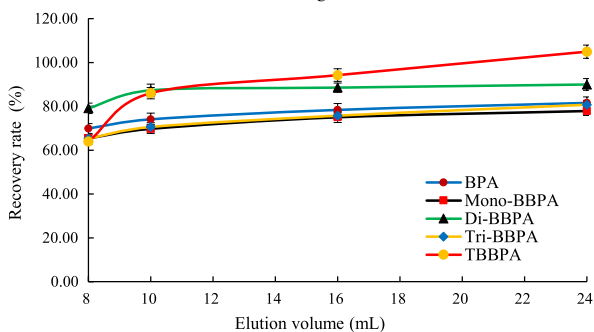
A



B



C



D

Fig. 4 Optimization of SPE parameters in the water sample. Note: The lowercase letters **a**, **b** indicate significant difference between the two treatments, the same letter indicates no significant difference

TBBPA and its brominated derivatives had the same varying tendency when the extraction temperature changed, the recovery rate first increased and then decreased in the temperature of 60, 80 and 100 °C, and the recovery rate reached the highest when the extraction temperature was 80 °C, which indicated that the extraction temperature at 80 °C was suitable for the extraction of TBBPA and its brominated derivatives. It is beneficial for TBBPA and its brominated derivatives to desorb from soil particles, and the recovery rate was increased, 80 °C was selected as the optimal extraction temperature.

Optimization of extraction time

The extraction temperature was 80°C, the number of cycles was one, and methanol was used as the extraction solvent. Three extraction times (3, 5 and 10 min) were optimized, the result is shown in Fig. 5B.

When the extraction time was set 3~10 min, the recovery rate increased to varying degrees with the extension of the extraction time, but there was no significant difference, except for BPA. Because ASE is a fast extraction instrument, and the maximum extraction efficiency would be achieved in 3 min. The recovery rates did not increase significantly with the increasing of the extraction time. The recovery rates of pollutants were higher than 90% except for BPA, the optimum extraction time was selected for 3 min according to the extraction effect and efficiency.

Optimization of cycle times

The extraction temperature was 80 °C and the extraction time was 3 min. The three extraction cycles: 1, 2 and 3 times were optimized, the results are shown in Fig. 5C.

When the number of cycles increased, the recovery rate of TBBPA and its brominated derivatives also showed obviously increasing trend. When the number of cycles was one, the recovery rates of five pollutants were relatively low, the possible reason was that the target substances were not completely extracted after one cycle; The recovery rates increased significantly after two cycles, and the rates were higher than 90%; However, when the number of cycles was three cycles, the recovery rates were not significantly increased, two cycles was the best extraction condition by comprehensive analysis.

Soxhlet extraction, solid phase extraction, ultrasonic assisted extraction (UAE) and pressurized solvent extraction (PLE) are widely used in the pretreatment methods of soil and sediment. As pretreatment method of solid sample, ASE was used in the extraction of veterinary drug/ pesticide residues in livestock and poultry excrement [34], and it was also used in the extraction of antibiotics

in poultry muscles and pork [35]. In this study, ASE was used in the extraction of TBBPA and its bromine derivatives from the soil and sediment, the extraction efficiency could meet the requirements of residue analysis.

ASE was used to pretreat soil and sediment samples in this research, and the parameters such as extraction temperature, extraction time and cycle times were optimized. It was determined that the extraction parameters were set as: the temperature was 80 °C, according to the properties of the sample and the extraction solvent, extraction temperatures of 60, 80, 100 and 120 °C were selected in the ASE, the thiamphenicol, florfenicol and florfenicol amine residues in poultry meat and pork samples were extracted by ASE in the temperature 80 °C [36], the extraction recovery of each target was above 80%. The extraction time for 3 min (short extraction time) and two cycles, which was consistent with literature [37, 38]. Guerra [39] reported that the minimum detection limits of TBBPA and its bromine metabolite in sediments was in the range 0.6 ~ 3.7 ng g⁻¹dw (dry weight), while method detection limit (MDL) of soil and sediment in this study were 0.0225 ~ 0.0525 ng g⁻¹, the sensitivity of the method was higher, the developed methodology will be applied to study the ultra-trace concentration levels in soil and sediment samples.

The accuracy and precision of method

The results are shown in Table 1. Three addition levels were set in the water sample, the recovery rates of TBBPA and its brominated derivatives were 80.28 ± 2.32% ~ 126.11 ± 8.98%, and the relative standard deviation (RSD) was 2.64 ~ 7.12%. When the addition concentrations of TBBPA and its brominated derivatives in the soil were 3.025, 6.250 and 12.500 ng g⁻¹, the recoveries were 79.40 ± 3.37% ~ 121.23 ± 5.93%, and RSD was 0.39 ~ 7.19%. The recovery rates of TBBPA and its brominated derivatives were 75.65 ± 4.18% ~ 109.07 ± 4.11% under the three concentrations in the sediment, and the relative standard deviation was 2.41 ~ 7.17%, MDL was 0.0225 ~ 0.0525 ng g⁻¹. The results showed that this method could meet the requirements of trace detection and analysis of TBBPA and its brominated derivatives in actual samples.

Determination of the actual samples

The established detection and analysis methods were used to detect actual water (Shuxi River and Naihe River), soil and sediment samples. TIC chromatogram of TBBPA and its brominated derivatives in the actual water, soil and sediment sample are shown in Fig. 6. The results showed that its impurities in the sample had little impact on the determination of the sample, and the impurities in the water, soil and

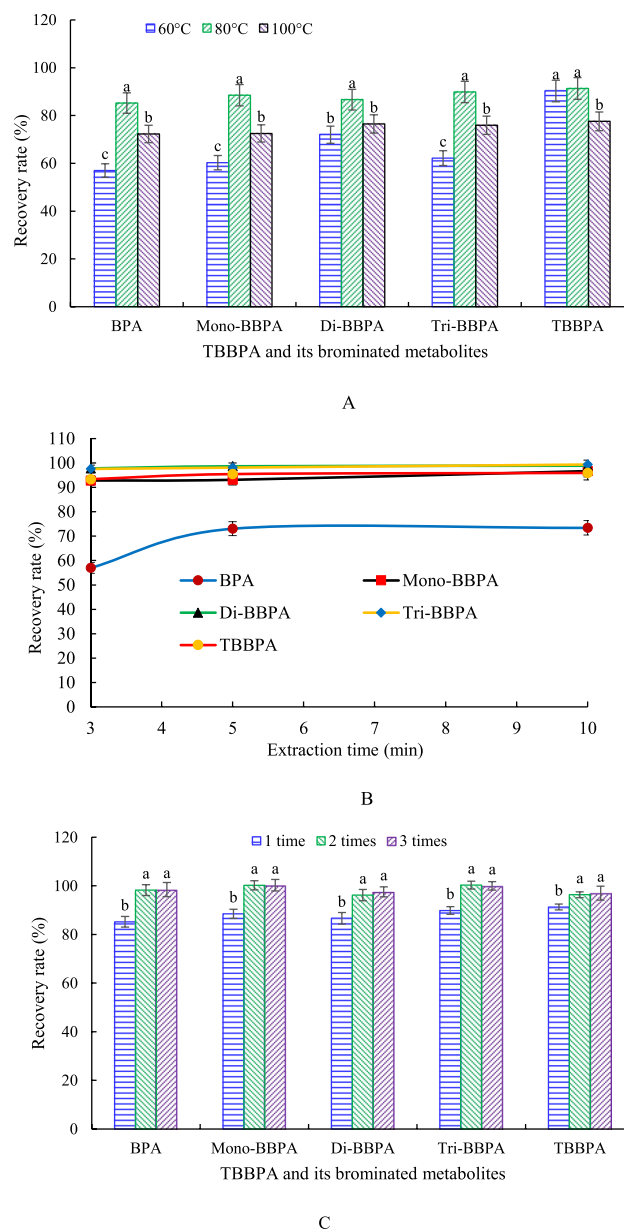


Fig. 5 Optimization of ASE condition in the soil. Note: The lower-case letters **a**, **b** and **c** indicate significant difference in the three treatments, the same letter indicates no significant difference

sediment did not significantly interfere with the determination of TBBPA and its brominated derivatives. It showed that this method was more suitable for the analysis of TBBPA, tri-BBPA, di-BBPA, mono-BBPA and BPA residues in the actual water, soil and sediment samples.

The residual concentrations of TBBPA and its brominated derivatives in the actual water, soil and sediment are shown in Table 2. It indicated that the other four brominated derivatives were all detected except that the parent TBBPA was not detected in the Naihe River (the Tai'an city, Shandong province in China), the concentration of BPA, mono-BBPA,

di-BBPA, tri-BBPA was 0.17 ± 0.02 , 3.74 ± 0.07 , 3.38 ± 0.05 and 1.48 ± 0.07 ng mL⁻¹. The residual amount of di-BBPA and mono-BBPA was detected in Shuxi River in Tai'an City, the concentration was 2.23 ± 0.07 and 3.78 ± 0.03 ng mL⁻¹, the other three pollutants were not detected, and the possible cause was the migration and transformation of these pollutants from other places, not from the local source of pollution. The trace residual amount of di-BBPA and mono-BBPA was detected in soil, the concentration was 1.93 ± 0.09 and 2.45 ± 0.09 ng·g⁻¹. The residual amount of di-BBPA, mono-BBPA and BPA was detected in the sediment of Shuxi River, the concentration was 2.37, 1.27 and 1.36 ± 0.02 ng·g⁻¹, the BPA in the sediment come from the de-brominating of mono-BBPA and di-BBPA derivatives, TBBPA was not detected in the soil and sediment samples, it confirmed that there was no pollution source of TBBPA nearby, brominated derivatives come from the migration and transformation of TBBPA elsewhere.

In the Xiaoqing River (Zhangseng River) near the estuary to Bohai Sea in Shouguang City, Shandong Province, China, the maximum residual level of tri-BBPA, di-BBPA, mono-BBPA and BPA was 0.205, 0.148, 0.0131 and 0.559 ng mL⁻¹ in water, respectively. The residual level of tri-BBPA, di-BBPA, mono-BBPA and BPA was 116~253, 149~971, <MDL~523 and $1.03 \sim 5.45 \times 10^3$ ng g⁻¹dw in sediment. The residual level of tri-BBPA, di-BBPA, mono-BBPA and BPA was $1.05 \times 10^2 \sim 2.23 \times 10^4$, $7.60 \sim 3.28 \times 10^3$, <MDL~ 2.81×10^3 and $1.85 \times 10^2 \sim 1.87 \times 10^4$ ng kg⁻¹ dw in soil [40]. Shouguang City in Shandong Province is the largest production bases for brominated flame retardants in China, therefore, high concentration of tri-BBPA, di-BBPA, mono-BBPA and BPA was detected in the sediment, soil, and water samples. TBBPA were generally less

than 23.9×10^{-3} ng mL⁻¹ in water, but the concentrations of TBBPA in Chaohu Lake (Anhui province in China, industry concentration site) reached 0.85~4.870 ng mL⁻¹ [41]. The Chinese criterion maximum concentration (CMC) and criterion continuous concentration (CCC) of aquatic life criteria for TBBPA are estimated to be 0.1475 mg L⁻¹ and 0.0126 mg L⁻¹ in terms of aquatic exposure [27], the concentrations of TBBPA in the most aquatic environment in China were below the thresholds.

The concentrations of TBBPA in soil were ND~7758 ng g⁻¹ dry weight in China, there were significant differences in residues in different regions [42], and it showed that it had less environmental risk by the risk assessment. TBBPA was not detected in the soil in this research, there was no pollution source of TBBPA in the nearby area according to the field investigation and analysis, brominated derivatives of TBBPA originated from the migration and transformation of TBBPA in other areas. TBBPA was de-brominated and reduced to its bromine derivatives in the environment and migrated to the nearby area, so the residual level was relatively low. TBBPA and its brominated derivatives in soil, sediment and water have been detected and analyzed by HPLC-MS/MS in the present studies, and it proved that it was a highly sensitive and low minimum detection limit method. This study provided scientific detection method for exploring the migration and transformation of TBBPA in the environment, and it is of great significance to explore the environmental behavior of ultra-trace TBBPA and its bromine derivatives in the environment.

Table 1 Recovery rates and MDL in the water, soil and sediment samples

Samples	Additive concentration	BPA	Mono-BBPA	Di-BBPA	Tri-BBPA	TBBPA
Water (ng·mL ⁻¹)	0.50	108.85 ± 8.29	82.78 ± 4.11	96.75 ± 3.67	116.16 ± 6.99	126.11 ± 8.98
	2.50	86.80 ± 7.89	83.74 ± 4.47	80.28 ± 2.32	83.45 ± 5.15	115.69 ± 5.91
	5.00	114.26 ± 9.81	84.62 ± 7.55	83.74 ± 4.68	87.69 ± 2.32	105.07 ± 5.63
	MDL (ng·mL ⁻¹)	0.0021	0.001	0.001	0.0009	0.0013
Soil (ng·g ⁻¹)	3.125	79.40 ± 3.37	120.10 ± 3.02	112.33 ± 3.94	103.58 ± 1.34	83.03 ± 2.31
	6.250	99.45 ± 3.34	121.23 ± 5.93	92.88 ± 5.52	109.04 ± 3.22	89.18 ± 3.51
	12.500	89.83 ± 6.46	99.61 ± 1.69	98.63 ± 0.38	93.54 ± 3.48	102.19 ± 2.99
	MDL (ng·g ⁻¹)	0.0525	0.025	0.025	0.0225	0.0325
Sediment (ng·g ⁻¹)	3.125	104.03 ± 3.52	109.07 ± 4.11	103.36 ± 6.26	106.98 ± 3.63	96.77 ± 3.68
	6.250	98.23 ± 5.59	76.95 ± 2.26	77.62 ± 5.63	75.65 ± 4.18	83.50 ± 3.87
	12.500	96.42 ± 6.06	93.85 ± 4.03	85.06 ± 2.05	96.43 ± 7.80	106.70 ± 7.65
	MDL (ng·g ⁻¹)	0.025	0.025	0.025	0.025	0.025
LOD (ng·mL ⁻¹)		0.21	0.10	0.10	0.09	0.13
LOQ (ng·mL ⁻¹)		0.64	0.30	0.31	0.27	0.39

Results are expressed as $\bar{x} \pm s$

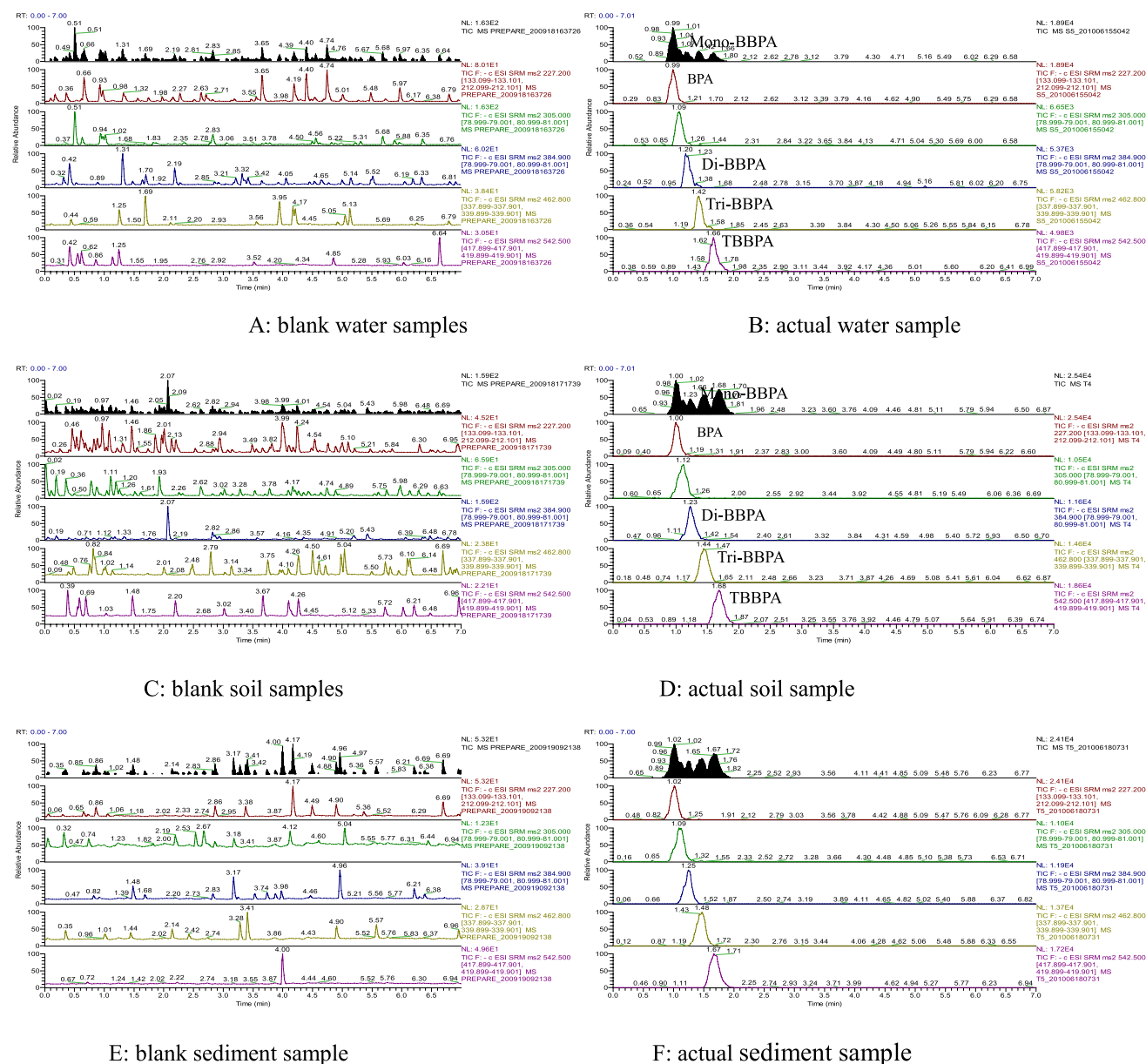


Fig. 6 TIC chromatogram of TBBPA and its brominated derivatives in the actual samples. **A** blank water samples. **B** actual water sample. **C** blank soil samples. **D** actual soil sample. **E** blank sediment sample. **F** actual sediment sample

Table 2 Concentration of TBBPA and its brominated metabolites in actual samples

Practical Samples	Site	BPA	Mono-BBPA	Di-BBPA	Tri-BBPA	TBBPA
Water (ng·mL ⁻¹)	Naihe River	0.17 ± 0.02	3.74 ± 0.07	3.38 ± 0.05	1.48 ± 0.07	ND
	Shuxi River	ND	3.78 ± 0.03	2.23 ± 0.07	ND	ND
Soil (ng·g ⁻¹)	Panhe campus of Shandong Agricultural University	ND	1.93 ± 0.09	2.45 ± 0.09	ND	ND
Sediment (ng·g ⁻¹)	Shuxi River	1.36 ± 0.02	1.27 ± 0.11	2.37 ± 0.11	ND	ND

Results are expressed as $\bar{x} \pm S$, ND was less than the minimum detection limit

Conclusions

SPE for water sample treatment, ASE for soil and sediment treatment and the simultaneous detection of TBBPA and its bromine derivatives was developed by HPLC–MS/MS, which provided a highly sensitive method for confirming and analyzing trace BPA, mono-BBPA, di-BBPA, tri-BBPA and TBBPA in the water, soil and sediment samples. ASE has the advantages of rapid extraction, less impurity interference and high degree of automation in the pretreatment of soil and sediment. The preferred method was successfully utilized to detect actual samples, and the concentration of bromine derivatives in river, soil and sediment samples were in a range of $< \text{LOD} \sim 3.78 \text{ ng mL}^{-1}$, $< \text{LOD} \sim 2.45 \text{ ng g}^{-1}$ and $< \text{LOD} \sim 2.37 \text{ ng g}^{-1}$, the residual level of TBBPA bromine derivatives was low, TBBPA was not detected in the actual samples, therefore, TBBPA and its bromine derivatives have low potential ecological risks to the organisms.

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Author contributions HX: Conceptualization, Funding acquisition, Methodology, Supervision, Writing-review & editing. Data, associated metadata, and calculation tools are available from the corresponding author (huixie@sdaq.edu.cn). YX: Conceptualization, formal analysis. FS: Formal analysis, data curation, software. JL: Investigation, supervision. RL: Editing.

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Data availability The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no competing interests.

Ethical approval Not applicable.

Consent to participate All authors have given consent to their contribution.

Consent to publish All authors have agreed with the content and all have given explicit consent to publish.

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