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Evaluating the blank contamination and recovery of sample pretreatment procedures for analyzing organophosphorus flame retardants in waters

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ABSTRACT

Organophosphate esters (OPEs), used as flame retardants and plasticizers, are widely present in environmental waters. Development of accurate determination methods for trace OPEs in water is urgent for understanding the fate and risk of this class of emerging pollutants. However, the wide use of OPEs in experimental materials results in blank interference, which influences the accuracy of analytical results. In the present work, blank contamination and recovery of pretreatment procedures for analysis of OPEs in water samples were systematically examined for the first time. Blank contaminations were observed in filtration membranes, glass bottles, solid phase extraction cartridges, and nitrogen blowing instruments. These contaminations could be as high as 6.4–64 ng/L per treatment. Different kinds of membranes were compared in terms of contamination levels left after common glassware cleaning, and a special wash procedure was proposed to eliminate the contamination from membranes. Meanwhile, adsorption of highly hydrophobic OPEs on the inside wall of glass bottles was found to be 42.4%–86.1%, which was the primary cause of low recoveries and was significantly reduced by an additional washing step with acetonitrile. This work is expected to provide guidelines for the establishment of analysis methods for OPEs in aqueous samples.

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Introduction

As one of the most commonly used organophosphorus flame retardants (OPFR), organophosphate esters (OPEs) are widely used as flame retardants or plasticizers in plastics, electronic equipment, furniture, textiles, construction and transportation (Marklund et al., 2003; Reemtsma et al., 2008; Wang et al., 2010). Given that OPFR are considered to be suitable alternatives for polybrominated diphenyl esters, which have been

restricted under restriction of the use of certain hazardous substances (RoHS) 2011 (European Union, 2011), and penta- and octabromodiphenyl ethers, which were banned by the European Union (Leung et al., 2007), the general production and consumption of OPEs is expected to increase in the coming years.

The widespread application of OPEs may lead to their diffusive spread into the environment by volatilization, leaching and abrasion (Sundkvist et al., 2010). As a result, OPEs are now

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widely present in indoor and outdoor environments, such as in surface water (Wang et al., 2011; Bacaloni et al., 2008), ground water (Regnery et al., 2011), and wastewater (Rodil et al., 2005; Marklund et al., 2005), as well as in airborne particles (Möller et al., 2011, 2012), indoor dust (Marklund et al., 2003; Van den Eede et al., 2012; Yang et al., 2014) and soils (Fries and Mihajlovic, 2011). Moreover, OPEs in the environment can enter the bodies of animals and humans via skin (Möller et al., 2012), the respiratory system, and diet. Currently, OPEs have already been detected in marine and fresh water biota (Sundkvist et al., 2010; Kim et al., 2011), human milk (Sundkvist et al., 2010), and human plasma (Shah et al., 2006), and their metabolites were also found in human urine (Reemtsma et al., 2011).

OPEs have been found to pose potential risks to human health. The main toxic effects included eye and skin irritation, carcinogenicity, dermatitis, and neurotoxicity (Möller et al., 2012; Van den Eede et al., 2012). For example, tricresyl phosphate (TCrP) shows delayed neurotoxicity (Craig and Barth, 1999), and chlorinated OPEs are considered to be potentially carcinogenic (Ni et al., 2007). Their potential PBT (persistence, bioaccumulation, toxicity) properties and increasing production have made OPEs a new research hotspot in recent years.

A reliable analysis method is the basis for related studies, such as on the occurrence, fate and effects of pollutants. However, OPEs are widely present in blank tests due to their

broad range of applications in instruments and materials used in analytical laboratories. Tri(2-butoxyethyl) phosphate (TBEP) was found in Teflon-layered silicone septa (Rodríguez et al., 2006) and hydrophilic lipophilic balanced (HLB) cartridges (Wang et al., 2011), whereas tris(2-chloroisopropyl) phosphate (TCPP), triphenyl phosphate (TPhP), triisobutyl phosphate (TiBP) and tri-n-butyl phosphate (TnBP) were also detected in blank tests for analysis of OPEs in water samples (Cristale et al., 2013; Bacaloni et al., 2007). Nevertheless, few comprehensive studies on the blank contamination of OPEs during the pretreatment of aqueous samples have been reported. Additionally, though commercially available isotope-labeled internal standards for some OPEs (TMP-d9, TEP-d15, TPrP-d21, TPhP-d15, TnBP-d27 in Table 1) can be adopted to improve the method recoveries, good absolute recovery is still pursued as the guarantee for method detection limits and quantification limits.

In this study, the pretreatment procedures for analysis of OPEs in water samples were systematically examined, to test possible blank contaminations and develop corresponding protocols. In addition, the pretreatment procedure was optimized to eliminate the interference of blank contamination, reduce the loss and improve the recovery of OPEs. This work will provide effective guarantees for accurate analysis methods for OPEs in water samples.

Table 1 – Abbreviations and UPLC-MS/MS (ultra-performance liquid chromatography-tandem mass spectrometry) detection parameters for the studied organophosphate esters (OPEs).

Compounds	Abbreviation	Retention time (min)	Transitions	Collision energy (eV)	Transition ratio (%) ^b
Trimethyl phosphate	TMP	1.49	141.0 → 79.3 141.0 → 109.1 ^a	23 17	18.05
Triethyl phosphate	TEP	2.24	183.0 → 81.3 183.0 → 99.2 ^a	24 18	30.65
Tris(2-chloroethyl) phosphate	TCEP	3.33	284.9 → 99.2 ^a 286.9 → 99.2	30 29	90.02
Tri-n-propyl phosphate	TPrP	4.91	225.1 → 99.2 ^a 225.1 → 141.1	18 10	46.08
Tris(2-chloroisopropyl) phosphate	TCPP	5.55	326.9 → 99.1 ^a 328.9 → 99.1	30 29	98.70
Tris(2-chloro-1-(chloromethyl)ethyl)phosphate	TDCEP	7.89	430.9 → 99.2 ^a 432.9 → 99.1	28 29	82.70
Triphenyl phosphate	TPhP	8.43	327.0 → 152.1 ^a 327.0 → 214.9	33 25	86.76
Triisobutyl phosphate	TiBP	8.57	267.1 → 99.1 ^a 267.1 → 155.0	18 6	11.28
Tri-n-butyl phosphate	TnBP	8.75	267.1 → 99.2 ^a 267.1 → 155.1	18 10	45.65
Cresyldiphenyl phosphate	CDPP	9.49	341.0 → 152.1 341.0 → 229.0 ^a	33 27	97.84
Tri(2-butoxyethyl) phosphate	TBEP	9.83	399.1 → 199.0 ^a 399.1 → 299.0	15 12	66.92
Tri-3-cresyl phosphate	TCrP	10.74	369.1 → 165.1 ^a 369.1 → 243.0	43 27	56.94
2-Ethylhexyl diphenyl phosphate	EHDPP	11.04	363.1 → 243.0 ^a 363.1 → 152.1	39 12	13.48
Tri(2-ethylhexyl) phosphate	TEHP	13.48	435.2 → 99.1 ^a 435.2 → 113.2	30 12	23.13

^a Quantification transition.

^b Transition ratio between the qualitative transition and the quantification transition.

1. Materials and methods

1.1. Chemicals and materials

All OPE standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) except for TiBP, which was purchased from Adamas-beta (Shanghai, China), and detailed information is shown in Table 1. Acetonitrile (ACN, Optima grade) was purchased from Fisher Scientific (Shanghai, China). Ultra-pure water (18.3 M Ω) produced with a Milli-Q Gradient system (Millipore, Bedford, USA) was used throughout.

Individual OPE stock solutions (1000 mg/L) were prepared in ACN. A mixed stock solution containing 10 mg/L each of the fourteen OPEs was prepared by dilution of the stock solutions with water/ACN (60/40). All the stock solutions were stored in the dark at 4°C.

Filtration of water was conducted with a solvent filtration/degassing system (1000 mL) obtained from Jinteng (Tianjin, China). Two kinds of cartridges, Oasis HLB cartridges (6 mL, 200 mg) purchased from Waters (Milford, MA, USA) and ENVI C18 cartridges (6 mL, 500 mg) obtained from Supelco (Bellefonte, PA, USA), were used for solid phase extraction (SPE). The eluent from SPE cartridges was collected in glass bottles (8 mL) purchased from CNW (Düsseldorf, German), and further concentrated with a nitrogen evaporator (N-EVAP 112) from Organomation (Berlin, MA, USA) or rotary evaporator (RV 10) from IKA (Staufen, Germany).

1.2. Ultra-performance liquid chromatography-tandem mass spectrometry (UPLC–MS/MS) analysis

A triple quadrupole mass spectrometer (TSQ Quantum Access, Thermo Scientific, USA) was interfaced to an ultra-performance liquid chromatography system (ACQUITY UPLC, Waters, USA) for the determination of the 14 OPEs. Separation of the OPEs was accomplished using the UPLC system equipped with a Waters BEH C18 column (2.1 mm $\times$ 100 mm, 1.7 μ m). The injection volume was 10 μ L, and the column temperature was 45°C. Eluent A was 0.1% (V/V) formic acid, and B was ACN. The gradient was as follows: 0 min, 40% B; 0.5 min, 40% B; 3 min, 50% B; 4.5 min, 55% B; 8.5 min, 70% B; 9 min, 100% B; 13.8 min, 100% B; 13.9 min, 40% B; and 15.5 min, 40% B. The ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) chromatogram of each analyte is shown in Fig. 1.

1.3. Water sample pretreatment procedures

Water sample pretreatment procedures included membrane filtration, SPE and further concentration with nitrogen flushing or rotary evaporation. After filtration by pressure with membranes, water samples were concentrated by SPE cartridges previously conditioned with 6 mL ACN and 6 mL water. When sample loading was finished, the cartridges were rinsed with 6 mL ultrapure water and then eluted with 6 mL ACN. Finally, the extracts were concentrated to near dryness with nitrogen flushing or rotary evaporation, and redissolved in 1 mL water/ACN (3/2) before determination.

Fig. 1 – UPLC–MS/MS (Ultra-performance liquid chromatography–tandem mass spectrometry) chromatogram of a standard solution containing 100 μ g/L each of the 14 organophosphate esters (OPEs). TMP, TEP, TCEP, TPrP, TCPP, TDCP, TPhP, TiBP, TnBP, CDPP, TBEP, TCrP, EHDPP and TEHP refer to Table 1.

2. Results and discussion

High levels of TEP, TiBP and TnBP were detected in the blank tests, with a total amount of 6.4–64 ng/L per treatment, which may come from the equipment and materials used in sample pretreatment due to their wide application as plasticizers and lubricants (Van der Veen and De Boer, 2012). To understand the source of blank contamination and to test the OPE recovery, sample pretreatment procedures including membrane filtration, SPE and concentration (nitrogen flushing and rotary evaporation) were comprehensively examined.

2.1. Membrane filtration

Before SPE, membrane filtration was conducted to remove the particles and microorganisms from water samples, which can protect the instruments and columns from blocking. Therefore, it is necessary to test the blank contamination of OPEs from membranes and the adsorption of OPEs on the membranes and the inside glass surface of the filtering apparatus.

Blank contamination from three kinds of membranes, including a GF/C membrane (glass fiber, 1.2 μ m, 45 mm, Whatman, UK), nylon membrane (0.45 μ m, 45 mm, Jiuding, China), and mixed cellulose esters membrane (MCE, 0.45 μ m, 45 mm, Jiuding, China) were tested by respectively dipping them in 5 mL water and 5 mL acetonitrile (ACN) for 30 min, which were then injected into the UPLC–MS/MS system for OPE analysis. TEP and TnBP were detected in all three membranes, while TiBP was only detected in the GF/C and MCE membranes (Fig. 2). The total amount of these three compounds was in the range of 0.78–26 ng/L per treatment, which is high in comparison to their relatively low concentrations in environmental water samples (5–1510 ng/L for surface water, groundwater and drinking water; Wang et al.,

Fig. 2 – UPLC-MS/MS chromatograms for 5 µg/L mixed standard solution (a) and blank contaminations of filtration membrane. Nylon membrane dipped in acetonitrile (ACN) (b1) or water (b2); MCE (mixed cellulose esters) membrane dipped in ACN (c1) or water (c2); GF/C (glass fiber) membrane dipped in ACN (d1) or water (d2); GF/C membrane successively immersed in ACN and pure water for 30 min (both three times) and dried in a vacuum oven (d3).

2010). Fortunately, the blank contamination of OPEs in the GF/C membrane was well eliminated by successively immersing in ACN and pure water for 30 min (three times each), and then drying in a vacuum oven (Fig. 2), while the two other membranes partially dissolved in ACN. Thus, a GF/C membrane pretreated with a wash procedure as described above is recommended for filtering samples.

The loss of OPEs caused by the adsorption on the inside glass wall of the filtering apparatus and membrane was evaluated. Significant adsorption on the inside wall of the filtering apparatus was observed when 40 mL ultrapure water spiked with 25 µg/L each of the OPEs passed directly through the filtering apparatus (without a membrane), especially for highly hydrophobic OPEs such as TiBP, TnBP, CDPP, TBEP, TCrP, EHDPP and TEHP (see Table 1), with an adsorption of 42.4%–86.1% (Filter group, Fig. 3). Meanwhile, the adsorption of OPEs on the membrane was evaluated by the recovery difference between the group with membrane and the “Filter group” without membrane (Fig. 3). Compared with the “Filter group”, significant adsorption (5.0%–85.4%) on nylon and MCE membranes was also observed for these highly hydrophobic OPEs, while adsorption on the GF/C membrane was not significant (<8%). To solve this problem, after filtration of the sample, the glass filtering apparatus and containers were washed with 6 mL ACN and the resulting ACN was then used for elution of OPEs in the following SPE procedure. A test of 200 mL ultrapure water spiked with 100 ng/L each of OPEs showed that the method recoveries of these highly hydrophobic OPEs were significantly improved by this approach compared to the control group (Fig. 4).

2.2. Solid phase extraction

SPE is commonly used in purification and concentration of OPEs in aqueous samples (Wang et al., 2011; Bacaloni et al.,

Fig. 3 – Recoveries of filtration by different membranes from 40 mL ultrapure water spiked with 25 µg/L each of the OPEs.

2007; Bollmann et al., 2012; García-López et al., 2010; Quintana et al., 2008), due to its advantages of lower consumption of solvents, time-saving operation and high reproducibility compared to the classical liquid–liquid extraction.

The blank contamination in the SPE procedure may come from SPE cartridges and bottles used for collecting eluent. The Oasis HLB cartridge (6 mL, 200 mg, Waters) and ENVI C18 (6 mL, 500 mg, Supelco), the two most commonly used SPE cartridges for OPE analysis in previous works (Wang et al., 2011; Rodil et al., 2005; García-López et al., 2010), were examined by washing the SPE cartridges twice with 1 mL ACN each time, and the ACN was respectively collected for OPE analysis. TnBP was found in the ENVI C18 cartridges, while TEP, TCPP, TiBP, TnBP and TBEP were found in HLB cartridges with a total OPE amount of 0.15–1.7 ng/L per

Fig. 4 – Method recoveries under different conditions for 200 mL ultrapure water spiked with 100 ng/L each of the OPEs. Control: GF/C membrane, hydrophilic lipophilic balanced (HLB) cartridges (6 mL, 200 mg), nitrogen blowing (40°C); Wash: the same conditions as control group, while filtering apparatus and containers were washed with 6 mL ACN.

Fig. 5 – SPE (solid phase extraction) recoveries using different cartridges and different sample volumes. Ultrapure water spiked with 0.5 $\mu\text{g/L}$ each of the OPEs was tested.

treatment. However, none of these contaminants was detected in either cartridge after they were conditioned with 6 mL ACN and 6 mL water (Fig. S1), indicating that the activation step for SPE cartridges could effectively eliminate the blank contamination.

To test if the new glass bottles (8 mL, CNW) used for collecting the SPE eluents contain blank OPEs, the plastic bottle cap and glass bottle were washed with 1 mL ACN and the OPE concentrations in the ACN washings were analyzed. High levels of TiBP (4.3–35 ng/L) were detected in the ACN after washing the glass bottle (Fig. S2), indicating that the inside wall of the glass was contaminated with TiBP, and that the contamination can be eliminated by washing with ACN. So, new glass bottles should be well washed before use.

De-ionized water spiked with 0.5 $\mu\text{g/L}$ each of the OPEs was used to assess the OPE recoveries of the two SPE cartridges and the influence of sample volume. After sample loading and rinsing, the cartridges were eluted with 6 mL ACN, which was well mixed and directly injected into the UPLC–MS/MS system for OPE analysis. When 200 mL of sample was treated, HLB cartridges (6 mL, 200 mg) showed better recoveries than ENVI C18 cartridges (6 mL, 500 mg) especially for TMP, TBEP and TEHP (Fig. 5). Both SPE cartridges showed a breakthrough phenomenon for TMP (Fig. S3), possibly owing to the weak retention of polar TMP. However, this problem could be well solved by isotope dilution methods, as the isotope-labeled internal standard of TMP (TMP-d9) is commercially available.

2.3. Concentration

After SPE, the eluent was further concentrated under a gentle stream of nitrogen (40°C) or with a rotary evaporation procedure (40°C, 18,000 Pa, 100 r/min) before redissolving it in 1 mL water/ACN (3/2) for determination. To test the potential blank contamination caused by nitrogen flushing and rotary evaporation, 6 mL ACN was used to carry out the same procedure. Low levels of TEP, TiBP and TnBP were detected in blank experiments using nitrogen flushing, with a total amount of these OPEs in the range of 1.2–1.4 ng/L per

treatment, while no target compound was detected for rotary evaporation (Fig. S4). The contamination by OPEs possibly comes from the OPE volatilization from plastic connecting tubes in the apparatus used for blowing nitrogen. Fortunately, the contamination from nitrogen blowing was relatively stable (Table S1) and the blank contamination could be subtracted during sample analysis.

Experiments showed that for most of the target OPEs, recoveries for nitrogen blowing and rotary evaporation were similar, by concentrating to the extent of leaving a spot of eluent on the bottom of the bottles (Fig. S5). However, in view of the time cost, nitrogen blowing was considered the first choice for concentration.

After optimization, the procedural blank was reduced to 2.2–5.3 ng/L per treatment, and the procedural absolute recoveries of target OPEs for 200 mL ultrapure water spiked with 100 ng/L each of OPEs were in the range of 54.9%–122%, except for TMP and TEHP, which were 25.4% and 44.7%, respectively (Fig. 4). Meanwhile, the method developed in this study also showed good performance for wastewater. For 100 mL influent and effluent of a wastewater treatment plant, both spiked with 1 $\mu\text{g/L}$ each of the OPEs, the procedural absolute recoveries of target OPEs were between 51.5%–110% and 51.3%–115%, except for TMP, which was 31.7% and 34.9%, respectively (Fig. S6).

3. Conclusions

For the first time, pretreatment procedures for analysis of OPEs in water samples were systematically examined for blank contamination and recovery of OPEs. Blank contamination was observed widely, including filtration membranes, glass bottles used for receiving the eluent, SPE cartridges, and nitrogen blowing apparatus. These contaminations were well eliminated by common cleaning of glassware and a special wash procedure for membranes. Meanwhile, adsorption on the inside wall of glass bottles was proved to be the primary cause of low recoveries for highly hydrophobic OPEs, and the loss could be significantly reduced by an additional washing step with organic solvent. GF/C membranes and HLB cartridges are recommended for membrane filtration and SPE in water sample pretreatment. This work is expected to improve the quality assurance of the analysis methods for OPE measurement in aqueous samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.01.022>.

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