



Pressurized liquid extraction of organophosphate triesters from sediment samples using aqueous solutions

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ABSTRACT

A novel procedure for the extraction of seven organophosphate triesters (OPs), used as flame retardants and plasticizers, from sediment samples has been developed. It is based on the pressurized liquid extraction of the analytes with aqueous solutions, combined with a further concentration step using solid-phase extraction (SPE) and followed by gas chromatography coupled to mass spectrometry (GC-MS) determination. The effects of different variables on the yield and selectivity of the sample preparation process are systematically evaluated. The optimal responses were observed extracting 2 g of sediment with a water:acetonitrile (75:25) solution at 90 °C and 1500 psi for 5 min. The obtained extract was made up to 200 mL with ultrapure water and passed through an OASIS HLB, 60 mg cartridge. Analytes were recovered with 2 mL of ethyl acetate and this extract concentrated to a lower volume, ca. 0.2 mL. Recoveries of the proposed extraction method ranged from 77 to 111%, with relative standard deviations below 10%, for spiked river and marine sediment samples with total carbon contents (TC) up to 4.0%. The limits of quantification (LOQs) of the method varied between 0.5 and 5 ng g⁻¹. Analysis of non-spiked sediment samples revealed the presence of low levels for some of the investigated species, with the highest concentration (47 ng g⁻¹) corresponding to tris(2-chloroethyl) phosphate (TCEP).

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1. Introduction

Organophosphate triesters (OPs) are frequently used flame retardants and plasticizers. Varnishes, hydraulic fluids, polyurethane foams and textiles are some of the products they are added to [1]. Their extensive use as additives is responsible for their occurrence in the environment, mainly in surface water, wastewater, air and dust [2–4]. This fact added to the persistence of some species, particularly the chlorinated OPs [5,6], limited water solubility and high adsorption to particulate matter of others [2] might lead to their accumulation in environmental solid samples, such as sediments. Up to the present moment, just a few studies have dealt with the determination of OPs in sediment samples [7–10]. In most of these works, sample preparation is time-consuming, requires large amounts of organic solvents and/or presents a limited selectivity, which makes necessary including further clean-up steps in the sample preparation scheme.

The use of water as extractant is an appealing alternative due to its low cost, environmental friendliness and selectivity [11]. At room temperature and atmospheric pressure, the polarity of water

is too high to efficiently extract most non-ionic organic species which are associated with soil particles. However, its dielectric constant can be lowered down to values similar to those of organic solvents by increasing the temperature at moderate pressures to keep water in the liquid state [12]. This modality has been named as subcritical water extraction (SWE) or pressurized hot water extraction (PHWE). Typical applications of this technique to recover low polar compounds from medium complexity matrices, e.g. sediments, require the use of temperatures in the range from 250 to 325 °C [11,13,14]. Practical drawbacks of operating at such high temperatures are related to the risk of analytes degradation and the lack of commercially available extraction devices [11].

Alternatively to pure water, its binary mixtures with miscible organic solvents, e.g. methanol, isopropanol, acetone, and acetonitrile, usually provide acceptable extraction yields operating at temperatures below 200 °C, achieving a good selectivity and reducing the risk of analytes thermal decomposition. An additional advantage of employing aqueous solutions instead of pure water is that extractions can be automated using commercially available instrumentation, such as pressurized liquid extractors able to operate in the range of temperatures from 40 to 200 °C. Up to now, pressurized aqueous solutions have been successfully applied to the extraction of organochlorine pesticides, chlorobenzenes, chlorophenols and polycyclic aromatic hydrocarbons from soil and sediment samples [15–17].

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As far as we could trace, only two methods based on the use of pressurized solvents have been applied to the extraction of OPs from sludge [18] and dust [19], respectively. In both cases, ethyl acetate was used as extractant and a very limited selectivity was obtained in the extraction process; consequently, an extra clean-up was necessary. Additionally to the above referred studies, some OPs have also been included in multi-residue methods for the determination of anthropogenic pollutants in sediments, using pressurized, heated mixtures of isopropanol: water [20]. However, in the above work the percentage of isopropanol represented up to 80% of the extraction solution and the yield of the process for several chlorinated OPs remained below 50%.

The aim of this research work was to evaluate the possibilities and limitations of pressurized aqueous mixtures, containing moderate percentages (up to 25%) of different organic solvents, for the extraction of seven OPs compounds, showing large differences among their polarities ($\log K_{ow}$ values from 1.4 to 4.6 units), from sediment samples. The obtained extract was diluted with ultrapure water and further concentrated using the SPE technique. Alternatively, the feasibility of employing solid-phase microextraction (SPME), under previously optimized conditions for the extraction of OPs from water samples [21], to concentrate the raw extract from sediments, is also discussed. After extraction, analytes were determined by gas chromatography with mass spectrometry (GC-MS) detection.

2. Experimental

2.1. Reagents, material and standards








Ultrapure water, obtained from a Milli-Q system purchased from Millipore (Bedford, MA, USA), was employed throughout this study. HPLC-grade acetonitrile, acetone and methanol, as well as trace analysis ethyl acetate and *n*-hexane were purchased from Merck (Darmstadt, Germany). Sodium chloride was provided by VWR (Leuven, Belgium). Silicon dioxide acid-washed was acquired from Riedel-de Haën (Seelze, Germany). Tripropyl phosphate (TPPrP), triisobutyl phosphate (TiBP), tributyl phosphate (TnBP), tris(2-chloroethyl) phosphate (TCEP), tris(dichloropropyl) phosphate (TDCP) and triphenyl phosphate (TPP) were acquired from Aldrich (Milwaukee, WI, USA). Tris(2-chloropropyl) phosphate (TCPP), as a technical mixture of isomers, was provided by Dr. Ehrenstorfer (Augsburg, Germany). Tripentyl phosphate (TPeP) was purchased from TCI Europe (Zwijndrecht, Belgium) and used as internal standard (IS). Chemical structures and octanol–water partition coefficients of target analytes are summarized in Table 1. Individual stock solutions of each species and the IS were prepared in acetone. Diluted standards and mixtures of OPs were made in *n*-hexane, when used to spike sediment samples, and in ethyl acetate, when employed to assess the performance of the GC-MS system. The stock solution of the IS was also diluted with ethyl acetate and added to calibration standards and sample extracts.

Reversed-phase Oasis HLB (60 mg) cartridges were provided by Waters (Milford, MA, USA). Cellulose and glass fiber filters, placed at the bottom and top of PLE cells, were purchased from Restek (Bellefonte, PA, USA). A manual SPME holder and poly(dimethylsiloxane)-divinylbenzene (PDMS-DVB, 65 μm film thickness) fibers were obtained from Supelco (Bellefonte, PA, USA).

2.2. Samples

River and marine sediments were used throughout this study. All samples were obtained from small rivers and marine estuaries located in Galicia (Northwest Spain). Samples were air dried in a hood and sieved to increase their homogeneity. The fraction

Table 1
Structures and octanol–water (K_{ow}) partition coefficients of selected species.

	Substituents	^a Log K_{ow}
TPPrP	$R_1=R_2=R_3=$ 	1.87
TiBP	$R_1=R_2=R_3=$ 	3.60
TnBP	$R_1=R_2=R_3=$ 	4.00
TCEP	$R_1=R_2=R_3=$ 	1.44
TCPP	$R_1=R_2=R_3=$ 	2.59
TDCP	$R_1=R_2=R_3=$ 	3.65
TPP	$R_1=R_2=R_3=$ 	4.59

^a Values taken from Ref. [2].

with a particle size below 0.3 mm was employed for analysis. Optimization of extraction and concentration processes was carried out with a pool of five sediments spiked at the 500 ng g^{-1} level. For the method performance evaluation, discrete sediment samples with different total carbon (TC) contents, spiked at 200, 50, and 20 ng g^{-1} for each OPs, were employed. The spiking procedure consisted of mixing an accurately weighed fraction of sediment with a standard solution of OPs in *n*-hexane, using a volume of solvent which guaranteed that the sample was completely covered. This slurry was thoroughly stirred and left in a hood until complete evaporation of the solvent. Then, it was stored in amber glass vessels at 4 °C, for at least 2 weeks before extraction.

2.3. Sample preparation

A Dionex (Sunnyvale, CA, USA) ASE 200 system, equipped with 11 mL capacity stainless steel cells, was used to extract OPs from sediments. A cellulose filter followed by a glass fiber one were placed at the bottom of each extraction cell, then 2 g of acid-washed silicon dioxide and the same mass of sediment were loaded into the cell. The remaining free space was filled with silicon dioxide. Finally, one cellulose filter was placed on top. Under optimized conditions, water containing a 25% of acetonitrile was employed as extractant. Extractions were performed at 90 °C and 1500 psi, using a single static extraction cycle of 5 min. Flush volume and purge time were set at 60% and 300 s, respectively.

Raw extracts provided by the PLE system (ca. 16 mL) were made up to 200 mL with ultrapure water and concentrated using a 60 mg OASIS HLB cartridge, previously pre-conditioned with ethyl acetate, methanol and water:acetonitrile (98:2), 3 mL each. Then, the sorbent was dried with a stream of nitrogen for 20 min and analytes were recovered with 2 mL of ethyl acetate. After addition of the internal standard (TPeP), the extract was either injected directly in the GC-MS system, without any additional clean-up, or concen-

Table 2
Linearity, repeatability ($n = 5$ replicates) and instrumental limits of quantification (LOQs), defined for a S/N of 10, of the GC-MS system.

Compound	Quantification ions (m/z)	Correlation coefficient (R^2)	Repeatability (RSD%)		LOQ (ng mL ⁻¹)
			40 ng mL ⁻¹	400 ng mL ⁻¹	
TPrP	99	0.996	5	3	5
TiBP	99	0.993	2	6	6
TnBP	99	0.996	6	4	6
TCEP	249 + 251	0.999	6	1	8
TCPP	277 + 279	0.997	5	2	10
TDCP	379 + 381 + 383	0.995	5	5	8
TPP	325 + 326	0.994	6	4	4

trated with a gentle stream of nitrogen to a lower volume, ca. 0.2 mL, in case of samples fortified at low concentration levels and also to investigate the concentrations of target OPs in real life sediment samples.

2.4. Determination

Analytes were determined by GC-MS, using a Varian (Walnut Creek, CA, USA) CP 3900 gas chromatograph connected to an ion trap mass spectrometer (Varian Saturn 2100). Separations were carried out using a HP-5 MS type capillary column (30 m × 0.25 mm i.d., d_f : 0.25 μ m) supplied by Agilent (Wilmington, DE, USA). Helium (99.999%) was used as carrier gas at a constant flow of 1.2 mL min⁻¹. The GC oven was programmed as follows: 70 °C (held for 1 min), at 15 °C min⁻¹ to 270 °C (held for 10 min). The GC-MS interface and the ion trap temperatures were set at 280 and 220 °C, respectively. Injections (2 μ L volume) were made in the splitless mode (1 min splitless time), with the injector port at 270 °C. The mass spectrometer was operated in the electron-impact ionization mode (70 eV). Electron-impact mass spectra were recorded in the range of m/z from 90 to 400 units. Most intense ions, used to quantify the concentration of each compound in sediment samples are given in Table 2. Quantification was carried out using standard addition over final extracts obtained from SPE cartridges, in order to compensate for differences in the efficiency of mass transfer from the injector to the capillary column, in the GC system, between pure standards and sample extracts [10].

3. Results and discussion

3.1. Performance of GC-MS

Table 2 summarizes some relevant data related to the determination step. The linearity in the responses of the GC-MS system was evaluated with standards, in ethyl acetate, at six different concentration levels from 10 to 2000 ng mL⁻¹. Correlation coefficients from 0.993 to 0.999 were obtained within the above interval. Relative standard deviations for five consecutive injections of standards at two different concentration levels, 40 and 400 ng mL⁻¹, ranged from 1 to 6%. Instrumental limits of quantification (LOQs) of the GC-MS system, calculated as the concentration of analyte giving a signal 10 times the standard deviation of the background noise, for chromatograms monitored using the most intense ions for each OPs, ranged from 4 ng mL⁻¹ for TPP up to 10 ng mL⁻¹ for TCPP.

3.2. Optimization of extraction conditions

3.2.1. Preliminary assays

Initially, two spiked sediments with different total carbon (TC) contents (ca. 1 and 3%) and three extraction solutions: water, acetonitrile and water:acetonitrile (90:10) were considered. Water and water:acetonitrile extractions were carried out in the range of temperatures from 120 to 200 °C; whereas, a value of 120 °C

was fixed when extractions were performed with pure acetonitrile. In all cases, a single static extraction cycle of 10 min at 1500 psi was employed. Flush volume and purge time were set at default values: 60% and 1 min, respectively. The extracts in pure water were directly concentrated using an OASIS HLB cartridge (60 mg). Those corresponding to water:acetonitrile (90:10) were first diluted to 100 mL with ultrapure water and those obtained with 100% of acetonitrile were first evaporated to about 10 mL and then diluted to 500 mL with ultrapure water. After that, they were concentrated using same SPE conditions as those reported for water and water:acetonitrile extracts [21]. Cartridges were eluted with 2 mL of ethyl acetate and extracts injected in the GC-MS system. Operating within the above range of temperatures, water alone failed to extract TPP, the most hydrophobic of the considered OPs (Table 1), even from the sediment with the lower carbon content. For the most complex one, just TPrP and TCEP, the most polar of the considered compounds, were noticed in the corresponding chromatograms. On the other hand, all OPs were found in water:acetonitrile (90:10) and acetonitrile extracts from both sediments. Chromatograms corresponding to extractions performed at 120 °C are shown in Fig. 1. As appreciated from total ionic current (TIC), Fig. 1A, and selected ions chromatograms, Fig. 1B, acetonitrile provided much more complex extracts than its binary mixture with water. Consequently, the signal to noise (S/N) ratio of OPs peaks was considerably higher in the latter situation. On the basis of the above comments, it is evident that the mixture of water with acetonitrile provides favorable features, in terms of efficiency and selectivity, when compared to any of both solvents used individually. Therefore, extraction conditions were systematically optimized considering aqueous solutions containing up to 25% of different organic solvents as modifiers.

3.2.2. Pressurized liquid extraction parameters

Systematic optimization of PLE extraction conditions was carried out with 2 g fractions from a pooled (river and marine) sediment sample. This matrix, showing a TC of 6.2%, was fortified with target compounds at 500 ng g⁻¹, using the procedure reported in Section 2.2, and then, aged for 1 month before extraction. The effects of temperature, type and percentage of organic solvent on the efficiency of the extraction were simultaneously evaluated using a mixed level 3¹ × 2² experimental factorial design, with 2 central points. The variable temperature was evaluated at three levels in the range from 90 to 150 °C. Higher values were not considered since they are expected to reduce the selectivity of the extraction. The percentage of organic solvent was varied between 5 and 25% and two solvents with different polarities: methanol and acetonitrile were considered as modifiers, Table 3. Extracts were diluted, prior to the concentration step, with the amount of water necessary to maintain the percentage of organic solvent below 2%, otherwise TPrP, TCEP and TCPP might be partially lost in the SPE concentration step.

Responses (analyte peak area/IS peak area) obtained in the 14 experiments involved in the above design were processed with

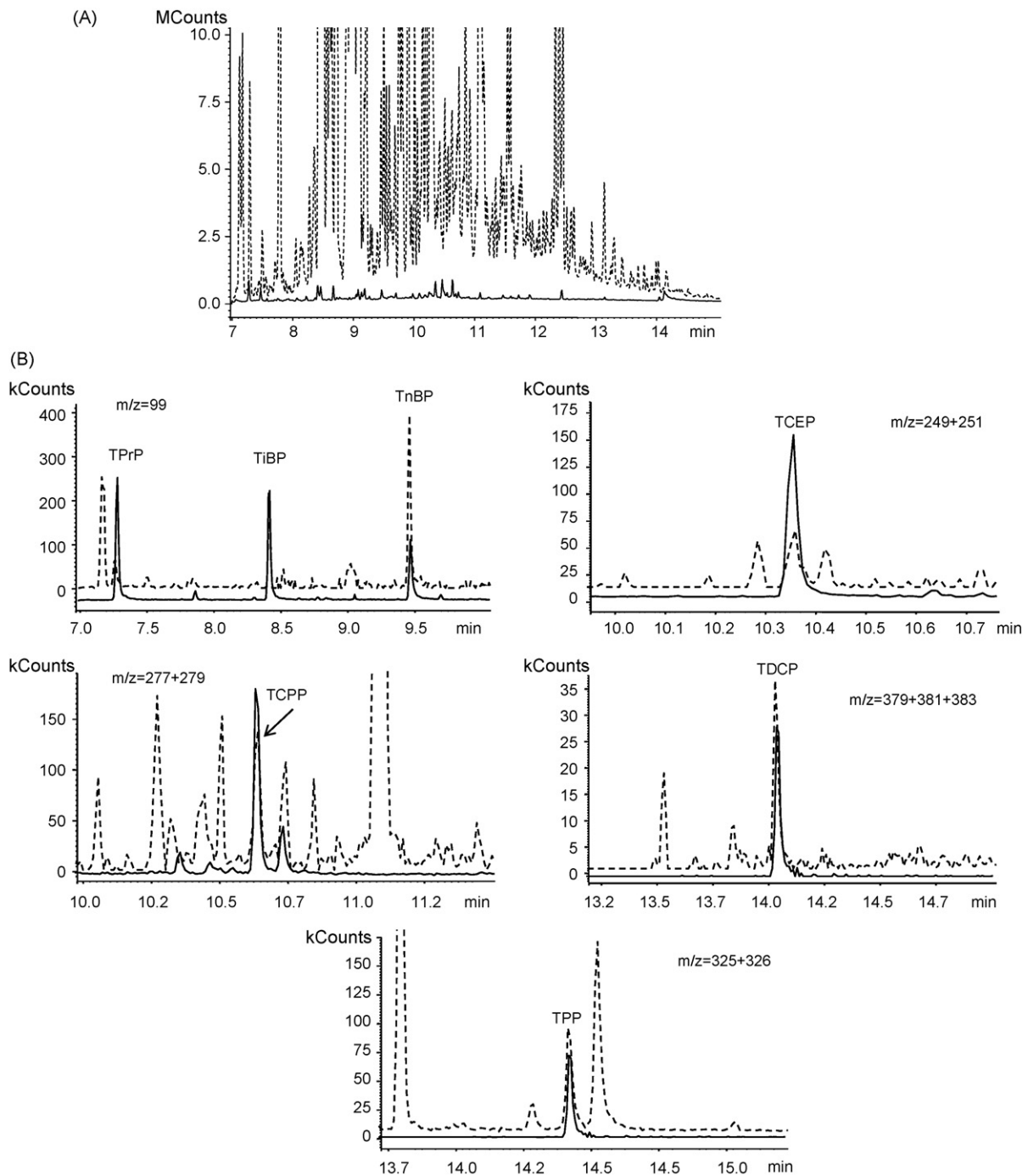


Fig. 1. Overlay of GC-MS chromatograms for a spiked sediment sample (3% of carbon, addition level 500 ng g^{-1}) using acetonitrile (dotted line) and water:acetonitrile, 90:10 (solid line) as extractants. TIC (A) and selected ions chromatograms (B).

the Statgraphics Centurion XV (Manugistics, Rockville, MD, USA) software. Main effects and two-factor interactions for some of the investigated OPs are graphically depicted in Fig. 2. The behavior of TnBP was similar to that of TPrP and TiBP, whereas TCPP and TCEP

both followed a similar trend. The length of the lines in main effect plots (Fig. 2A) is proportional to the variation in the efficiency of the extraction, for a given compound, when the considered factor changes from the lower to the upper level, within the domain of the design. The sign of the slope indicates whether the extraction yield increases (positive slope) or decreases (negative slope) with the investigated factor.

The percentage of modifier (variable C, Table 3) affected positively to the extraction of all species, except TCPP and TCEP. Moreover, its effect was statistically significant (95% confidence level) for those OPs showing $\log K_{ow}$ values over 3 units, Table 1. On the other hand, the type of modifier (methanol or acetonitrile) was the less important of the investigated factors and the

Table 3
Domain of the $3^1 \times 2^2$ experimental factorial design.

Factor	Code	Lower	Level medium	Upper
Temperature ($^{\circ}\text{C}$)	A	90	120	150
Organic modifier	B	Methanol	–	Acetonitrile
Modifier percentage (%)	C	5	–	25

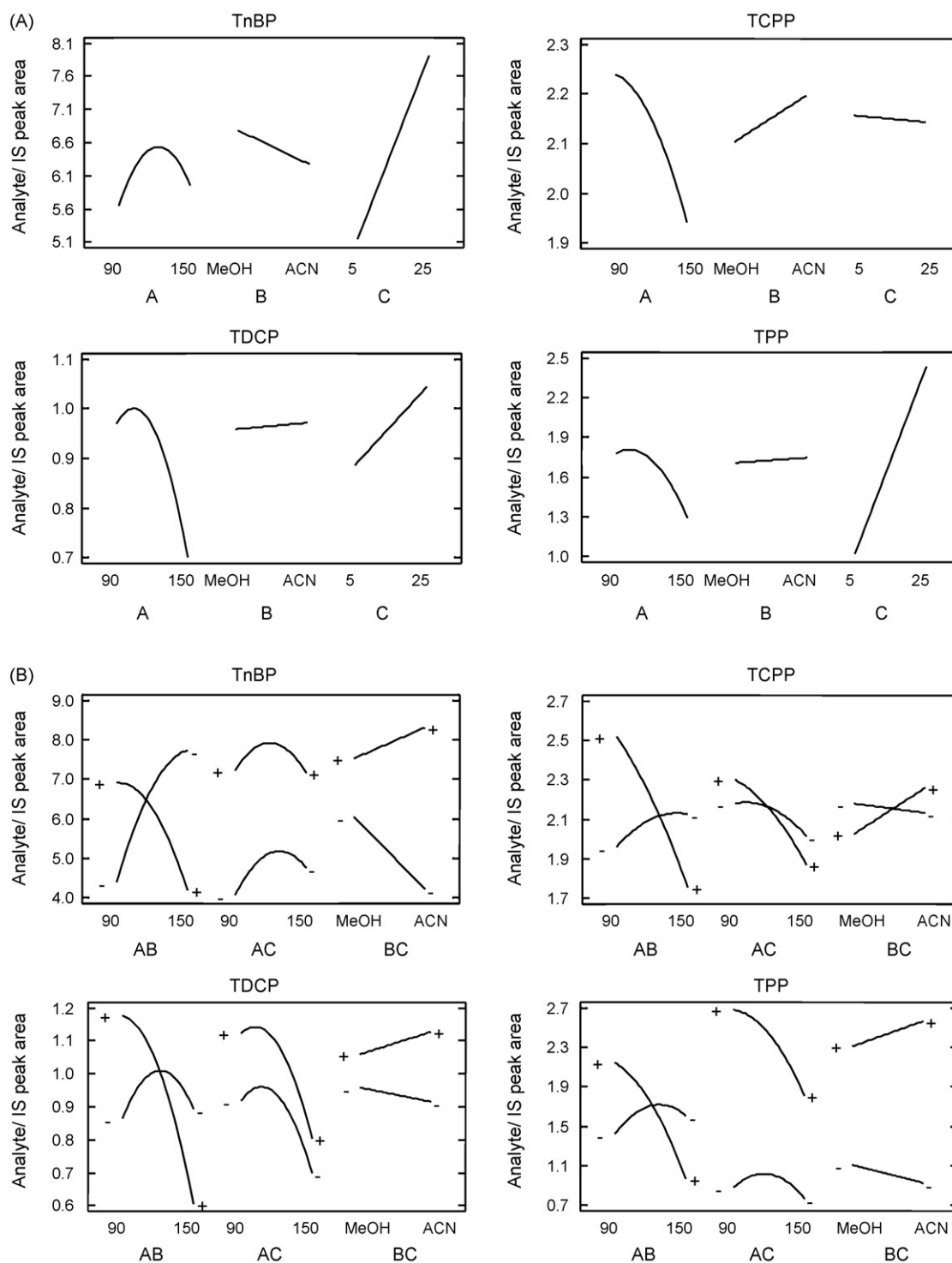


Fig. 2. Graphics for main effects (A) and two-factor interactions (B) obtained from the $3^1 \times 2^2$ experimental factorial design.

sign of its effect was compound dependant. For TPP and the three chlorinated OPs, the variable temperature affected negatively to the extraction yield, being statistically significant for TDCP and TCPP. This behavior points that these compounds might be partially decomposed at high temperatures, which matches with previously reported results for some pesticides using similar extraction conditions [15]. In the case of TnBP (TiBP and TPrP followed a similar trend), the main effect associated to the extraction temperature (code A, Table 3) showed an important curvature, with a maximum at 120 °C (Fig. 2A), the medium level fixed for this variable in the

experimental factor. In spite of this, neither the temperature nor the quadratic term of this variable, were of statistical significance for any of these three species.

Two factor interactions graphs (Fig. 2B) provided some relevant conclusions, particularly as regards temperature (code A, Table 3) and type of modifier (code B, Table 3) variables. For all compounds, a cross-shaped graph was noticed for the AB interaction, meaning that at 90 °C higher responses were achieved using acetonitrile as modifier; whereas, at 150 °C the use of methanol was more favorable. Except for TCPP and TCEP, the standardized value of the AB

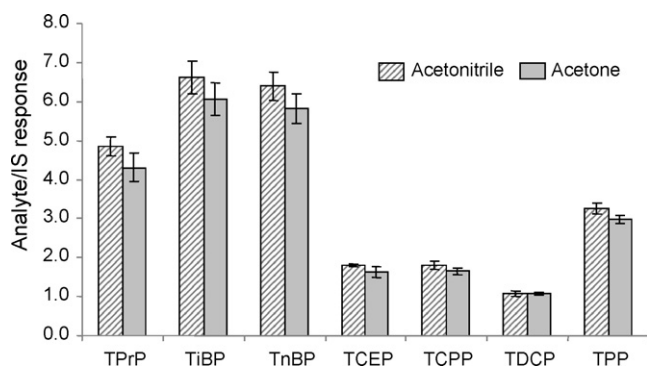


Fig. 3. Comparison of responses obtained using acetonitrile and acetone as organic modifiers (25%) in the extraction process. PLE at 90 °C and 1500 psi. A single static cycle of 10 min was used, $n=4$ replicates.

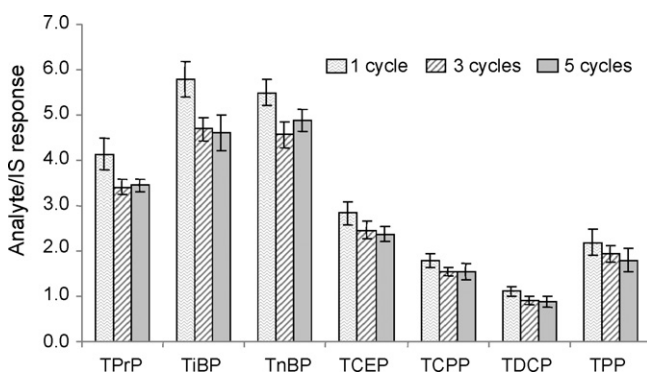


Fig. 4. Comparison of responses as function of the number of extraction cycles, 5 min each, at 90 °C using water:acetonitrile (75:25) as extractant, 60% of flush volume.

interaction overpassed the 95% confidence bound. Finally, the other two factor interactions (temperature–percentage of modifier, AC, and type–percentage of modifier, BC) played a negligible effect on the yield of the extraction, Fig. 2B.

On the basis of above comments, further extractions were carried out at 90 °C using water containing a 25% of acetonitrile as organic modifier. Moreover, some additional assays were performed using acetone as alternative to acetonitrile. The former solvent had been previously employed in the extraction of OPs from dust [3,22] and it presents a lower polarity than acetonitrile. For TPrP, TiBP and TnBP slightly higher responses were observed using acetonitrile than with acetone, whereas for the rest of species no significant differences were observed between both modifiers, Fig. 3. Thus acetonitrile was kept as modifier in the extraction solution.

Other variables, potentially affecting to the performance of PLE, such as the number of static extraction cycles, their duration, flush volume and purge time were also thoroughly investigated. Fig. 4

shows the responses obtained for 1, 3 and 5 extraction cycles of 5 min. For non-chlorinated, alkyl OPs (TPrP, TiBP and TnBP) obtained responses were slightly higher with one cycle than with more. For the rest of species, smaller differences were noticed; however, the trend was also a diminution in their responses with the number of extraction cycles. Therefore, one cycle was selected for further assays, which is advantageous in terms of extraction duration. After that, the duration of the static extraction cycle was varied between 5 and 25 min, data not shown. Responses obtained for triplicate extractions were independent of the extraction time, so it was kept at the lower value to speed up as much as possible the extraction process.

As regards the volume of extraction solution (flush volume, referred as a percentage of the cell volume: 11 mL) values between 60 and 150% were evaluated. Increasing the flush volume leads to an increase in the final volume of the obtained extract. Bearing this in mind, extracts were diluted, prior to the concentration step, with the amount of water necessary to maintain the percentage of acetonitrile below 2%, as previously remarked. Again, compounds responses were unaffected by this parameter (data not shown), thus 60% was selected in order to reduce the solvent consumption. The purge time controls the period during which nitrogen is passing through the stainless steel cell to sweep away all the solvent wetting the sample and the cell filling, at the end of the static extraction cycle. It can be changed between 0 and 300 s. In order to completely recover the aqueous–organic mixture employed in the extraction, the maximum allowed purge time was employed. Shorter periods were insufficient for complete solvent removal and thus, the cell filling remained wet once the extraction was concluded.

3.3. SPME versus SPE concentration

Alternatively to SPE, SPME was also considered for the concentration of OPs. In this case, extracts were made up to 25 mL with ultrapure water and an aliquot of 20 mL submitted to optimal SPME conditions previously reported for water samples [21]. In brief, a PDMS-DVB fiber was exposed to the extract, in the direct sampling mode, for 40 min at room temperature under magnetic stirring (1100 rpm), using a Teflon covered magnetic stir bar. Sodium chloride (2 g) was added to the extracts in order to improve the efficiency of the extraction, particularly for the most polar compounds. Higher salt concentrations could not be used since they promoted the separation of phases (water and acetonitrile) in the SPME vessel. Under the above conditions, responses (peak areas) obtained by SPME were between 2 and 15 times higher than those achieved using SPE as concentration technique considering a final extract volume of 2 mL, Fig. 5. The exception to this behavior corresponded to the highly polar TCEP, for which the response attained by SPME was 3-folds lower than using SPE, Fig. 5. Taking into account that (1) TCEP is one of the most environmentally concerning organophosphorous flame retardants, (2) SPE extracts can be concentrated to a lower volume ca. 0.2 mL without notice-

Table 4

Recoveries of the proposed method with their standard deviations (SD) and LOQs of the overall method, $n=3$ replicates.

Sediment type	Recovery (%) ± SD				LOQ (ng g ⁻¹)	
	River (TC: 2.3%)		River (TC: 1.2%)			
	50 ng g ⁻¹	200 ng g ⁻¹	20 ng g ⁻¹	200 ng g ⁻¹		
TPrP	88 ± 7	95 ± 7	104 ± 4	94 ± 5	90 ± 3	0.5
TiBP	87 ± 8	107 ± 8	106 ± 5	98 ± 4	77 ± 6	3
TnBP	85 ± 9	82 ± 3	107 ± 6	90 ± 6	87 ± 4	0.6
TCEP	103 ± 7	100 ± 7	109 ± 7	87 ± 6	92 ± 6	0.8
TCPP	98 ± 4	109 ± 5	96 ± 8	100 ± 4	81 ± 7	5
TDCP	95 ± 8	110 ± 6	89 ± 5	99 ± 7	98 ± 8	0.8
TPP	95 ± 5	110 ± 2	81 ± 5	79 ± 6	111 ± 4	4

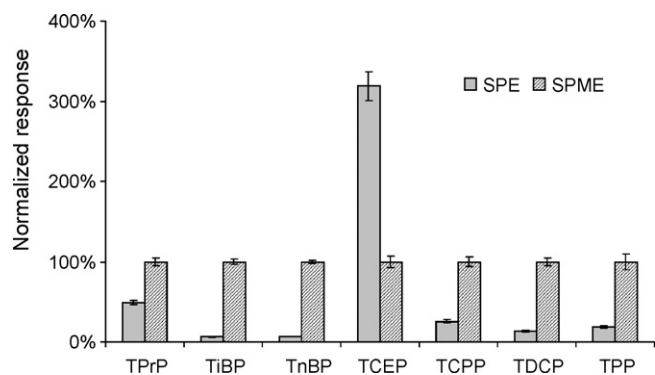


Fig. 5. Relative efficiencies for SPE (final extract volume 2 mL) and SPME as concentration techniques for sediment extracts, $n=3$ replicates. Depicted values correspond to the pooled sediment matrix used in the experimental factorial design.

able losses of target species, and (3) SPE extractions, at difference to SPME ones, can be performed simultaneously, the former was maintained as the concentration technique in the proposed sample preparation approach.

3.4. Method performance

Recoveries of the proposed method were evaluated with river and marine sediment samples, with different TC contents, spiked with target compounds at several concentrations in the range from 20 to 200 ng g^{-1} . Spiked fractions of each sample were aged for 2 weeks before extraction; moreover, non-fortified ones were also processed. Table 4 summarizes the obtained results for triplicate extractions. Recoveries from 77 to 111%, with standard deviations below 10, were attained for all compounds in the three considered samples. GC-MS traces for the lower level spiked sample (20 ng g^{-1}) are presented in Fig. 6. In order to assess the yield of the proposed method with more complex matrices, an indoor dust sample, TC 25.1%, was processed using the method developed in this work

Table 5

Comparison of OPs concentrations (ng g^{-1}) found in a non-spiked dust sample (TC 25.1%) using two different extraction approaches, $n=3$ replicates.

Analyte	PLE (water:acetonitrile, 75:25)		MAE (acetone) [Ref. [3]]	
	Mean	SD	Mean	SD
TiBP	186	9	176	10
TnBP	222	7	n.q.	–
TCEP	6200	200	4100	200
TCPP	65	3	64	2
TPP	330	19	330	22

n.q., not quantified.

and a microwave assisted extraction (MAE) protocol, specifically designed to deal with dust samples, using acetone as extractant [3]. Results obtained with both approaches are compared in Table 5. TPrP and TDCP remained under the LOQ of the method, whereas values for the rest of species ranged from 64 to 6200 ng g^{-1} . A good agreement was noticed between the measured concentrations of TiBP, TCPP, and TPP using both extraction procedures; however, TnBP could not be quantified in MAE extracts due to co-elution with an interference showing the same m/z ratio. Finally, the protocol developed in this work provided a significantly higher concentration of TCEP, the most polar of the investigated species, than MAE.

Procedural blanks often showed the presence of TiBP, TCPP and TPP at concentrations between 1 and 2 ng g^{-1} . The exact source of this contamination could not be identified; although, in case of TPP, it could be associated with the ultrapure water used in the extraction step and also to dilute the primary extract from sediment samples. Whatever the source of this contamination was, procedural blanks have to be periodically performed to avoid false positives during analysis of real, non-spiked, sediment samples. Limits of quantification (LOQs) of the proposed method were estimated considering a sample intake of 2 g and a final extract volume of 0.2 mL. Values from 0.5 to 5 ng g^{-1} were achieved, Table 4. These LOQs are in the same range of values to those provided by LC-MS/MS (0.48–11 ng g^{-1}) and GC-ICP-MS (2–4 ng g^{-1}) [8,10].

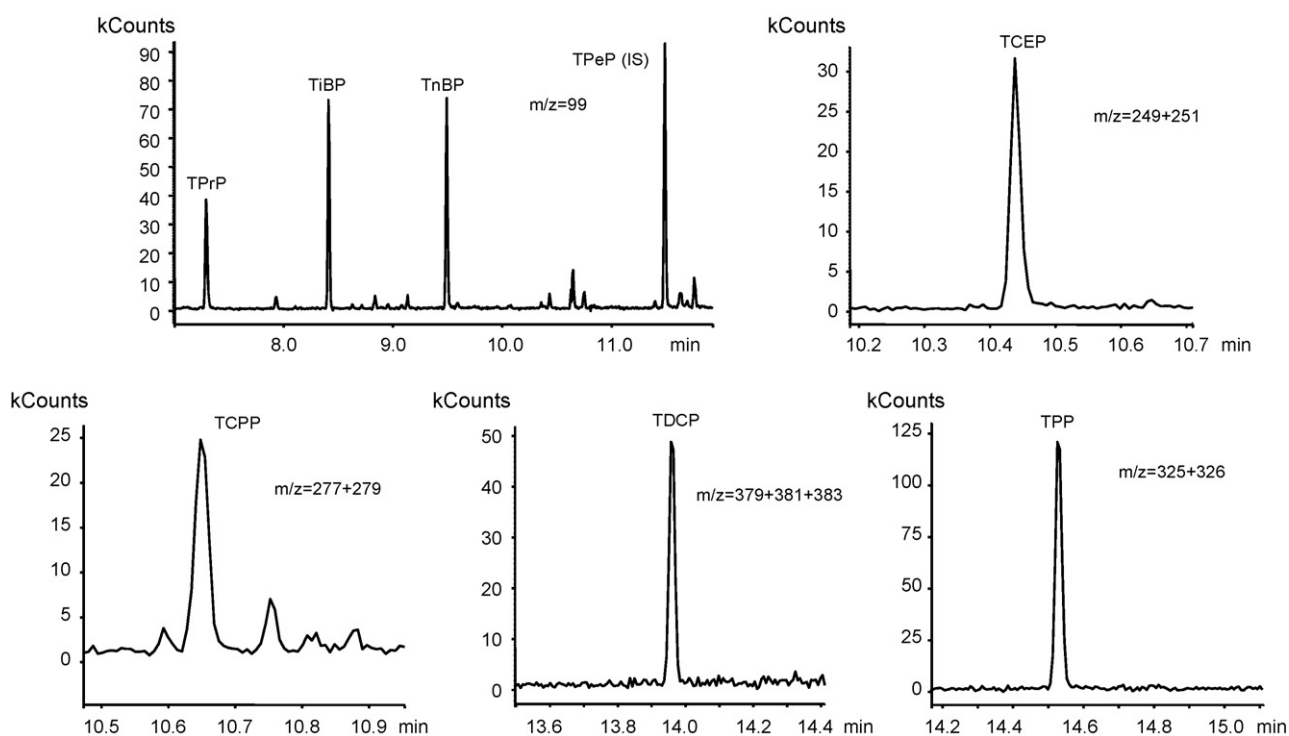


Fig. 6. Selected ion chromatograms for a river sediment spiked at the 20 ng g^{-1} level.

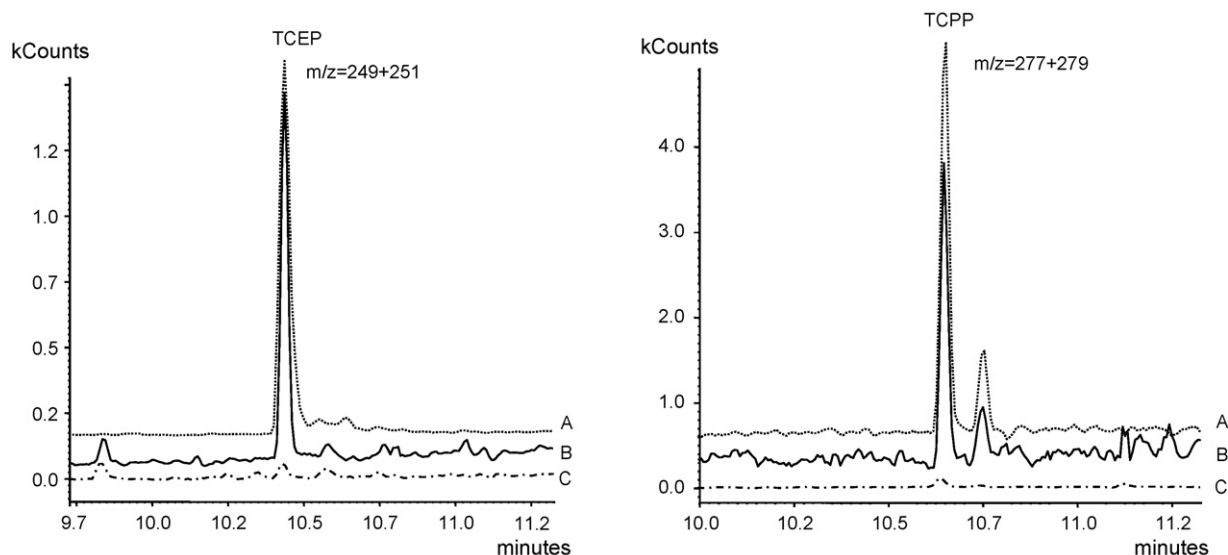


Fig. 7. Overlay of GC-MS chromatograms for TCEP and TCPP in sediment samples. (A) OPs standard (20 ng mL^{-1}); (B) un-spiked sediment; (C) procedural blank.

Several sediments were subjected to the optimized procedure and in most of them, OPs remained below the LOQs of the method; however, relatively low levels of some target analytes were detected in two of the analyzed samples: TiBP ($7.80 \pm 0.05 \text{ ng g}^{-1}$), TCEP ($45.9 \pm 0.1 \text{ ng g}^{-1}$) and TPP ($6.4 \pm 0.3 \text{ ng g}^{-1}$) were found in one of them and TCPP ($38 \pm 2 \text{ ng g}^{-1}$) was present in the other, Fig. 7. Above values are significantly lower than maximum concentrations of OPs measured in sediments from highly industrialized areas in Germany [23], urban areas in Austria [8] and a waste disposal site in Japan [9]. They are also one order of magnitude lower than concentrations found in solid samples from indoor environments, e.g. dust [1–3].

4. Conclusions

A valuable sample preparation method for the extraction of seven OPs from sediment samples has been proposed. Pressurized liquid extraction using aqueous solutions, with a 25% of acetonitrile, provided recoveries over 77% for spiked sediment samples with different carbon contents, it required a very low consumption of organic solvents (ca. 4 mL in the extraction step) and it presented an improved selectivity versus the use of organic solvents as extractants. Optimization studies showed that maximum extraction yields were achieved at relatively low temperatures, which minimized the risk of analytes decomposition and also allowed to automate the extraction process by using commercially available PLE instrumentation. Real life sample analysis pointed to the existence of just very low levels of OPs in environmental sediments probably due to the high water solubility of certain species and the rapid hydrolysis of the most hydrophobic ones. Preliminary results suggest the possibility of broadening the application field of the developed method to more complex matrices, such as indoor dust where OPs levels reach the $\mu\text{g per g}$ level.

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