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Determination of phthalates and organophosphate esters in particulated material from harbour air samples by pressurised liquid extraction and gas chromatography–mass spectrometry

M. Aragón, R.M. Marcé *, F. Borrull

Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, Sescelades Campus, Tarragona 43007, Spain

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ABSTRACT

A method based on gas chromatography–mass spectrometry (GC–MS) combined with a pressurised liquid extraction (PLE) to determine four organophosphates, seven phthalate esters and bis(2-ethylhexyl) adipate in particulated material of harbour air samples has been developed. Some studies show that these compounds may cause hormone disrupting effects on human health. Moreover, the U.S. Environmental Protection Agency (EPA) has classified benzyl butyl phthalate and di(2-ethylhexyl) phthalate as possible human carcinogens.The chromatographic time per run analysis is less than 15 min and the complete separation of all compounds is achieved. The PLE was optimised with recoveries above 90% and the repeatability of the method with real samples is less than 11% (%RSD, $n=4$). The MDLs (0.004–0.4 ng m^{-3}) and MQLs (0.02–2 ng m^{-3}) are limited by the fact of some compounds are present in low levels in sampling blank filters.The method was successfully applied in several samples and most of the compounds under study were found. The most relevant values were the high concentration of di-iso-butyl phthalate (between 28 and 529 ng m^{-3}) and the significant concentration of di(2-ethylhexyl) phthalate (between MQL and 22 ng m^{-3}). In addition, benzyl butyl phthalate was also detected in some samples but at low concentration levels (between MQL to 0.2 ng m^{-3}).

1. Introduction

Phthalate and organophosphate esters are a group of organic compounds that are widely used as plastic additives to alter the physical properties such as the malleability and flame resistance of synthetic materials. Moreover, organophosphate esters are typically used as flame retardants [1], stabilisers and plasticisers in a variety of products such as building materials, furnishing fabrics and textiles. Phthalate and bis(2-ethylhexyl) adipate (DEHA) additives are mainly used as plasticisers in polymeric materials, such as cellulose esters and vinyl chloride copolymers (PVC) [2], although some studies have shown that these compounds may cause hormone disrupting effects on human health [3]. They can increase developmental abnormalities in animals, for instance, cleft palate, skeletal malformations and foetal death. These studies have been performed with rats, mice and other rodents [4]. The U.S. Environmental Protection Agency (EPA) has also classified benzyl butyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP) as possible human carcinogens [4]. In addition, some phthalates (BBP, DBP, DEHP and DiBP) have been included in the "registration, evaluation, authorisation and restriction of chemicals" (REACH) regulation (EC) 1907/2006 [5].

The widespread use of bis(2-ethylhexyl) adipate, phthalate and organophosphate esters and increasing public concern has encouraged the study of these compounds worldwide in a variety of environmental samples, including wastewater [6–8], surface water [9], indoor and outdoor air and dust [10–13], and even in other human matrices such as urine and blood [14].

It is also common to find some phthalate esters such as diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), dibutyl phthalate (DBP), BBP, DEHP and di-n-octyl phthalate (DnOP) in particulated material from outdoor air collected with a quartz filter of PM10 at maximum concentrations of 610 ng m^{-3} for DEP [15]. Organophosphate esters (TBP and TPP) have been determined in indoor air at maximum concentrations between 18 and 172 ng m^{-3} and 0.8 and 40 ng m^{-3}, respectively [16]. In addition, Sjödin et al. analysed air samples in different work environments using polyurethane foams (PUFs) to collect samples and they found TPP and TBP at concentrations between 12 and 180 ng m^{-3} and 9 and 24 ng m^{-3}, respectively [17].

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* Corresponding author. Tel.: +34 977 55 81 70; fax: +34 977 55 84 46.
E-mail address: rosamaria.marce@urv.cat (R.M. Marcé).

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Phthalate and organophosphate esters are usually determined by gas chromatography [1–3,8,15,18–22] because these compounds are volatile and thermally stable. NPD is a commonly used detector for organophosphate esters, although this detector does not offer confirmation of the analytes [2]. Mass spectrometry allows sensitive and selective detection, particularly when operating in selected ion monitoring (SIM) [12]. Gas chromatography coupled to mass spectrometry is the best choice for the study of both group of compounds because this technique makes their determination easier than when HPLC–MS/MS is used, although there are some studies in which this technique is applied [9,11,23].

Extended problems appear when these compounds are determined. Phthalate esters can be found anywhere, including common laboratory equipment and reagents. It is necessary to clean all the materials used very well and to avoid all kinds of plastics during the experimental procedure. It is also necessary to minimise the number of steps during the analytical process [12].

Several methods have been reported to extract different pollutants from particulated air material or other similar matrices such as indoor or outdoor dust [9–12]. Soxhlet extraction [24], microwave-assisted extraction (MAE) [23], ultrasound assisted extraction (USAE) [12], matrix solid-phase dispersion (MSPD) [12] or pressurised liquid extraction (PLE) [12,25] are different extraction techniques used when organophosphate or phthalate esters are determined.

In recent years [6,25] it has been established that pressurised liquid extraction (PLE) is an efficient extraction technique to determine phthalate esters, DEHA and organophosphate in different matrices using an automated process with a reduced consumption of organic solvent and less time needed for sample treatment prior to the analysis. Many organic solvents have been used for this extraction technique such as hexane, ethyl acetate, dichloromethane, acetone, methanol and toluene [12,23].

The aim of this paper is to develop a reliable method to determine the presence of DEHA, phthalate and organophosphate esters in harbour air particulated material. This is an important area of study for the daily manipulation of several products in every loading and unloading shipping process and it is necessary to control these compounds in the environmental air pollution. Up to now, these compounds have not been studied in harbour air particulated material, and this fact makes this study of relevant interest because the harbour area is situated near the city centre and it could be a potential zone where some of these pollutants are found.

2. Experimental

2.1. Chemical standards

The standards used were bis(2-ethylhexyl) adipate (DEHA), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), dimethyl phthalate (DMP), di-n-octyl phthalate (DnOP), tributyl phosphate (TBP), triethyl phosphate (TEP), tri-iso-butyl phosphate (TiBP), triphenyl phosphate (TPP) and the internal standard d_4-diethyl phthalate (d_4-DEP). All were purchased from Sigma-Aldrich (St. Louis, USA). Fig. 1 shows the chemical structure of the target compounds. Stock solutions of individual standards were prepared by dissolving each compound in ethyl acetate (GC grade with $>99\%$ purity, SDS, Peypin, France) at a concentration of 1000 mg L^{-1}. The working mixed solution of

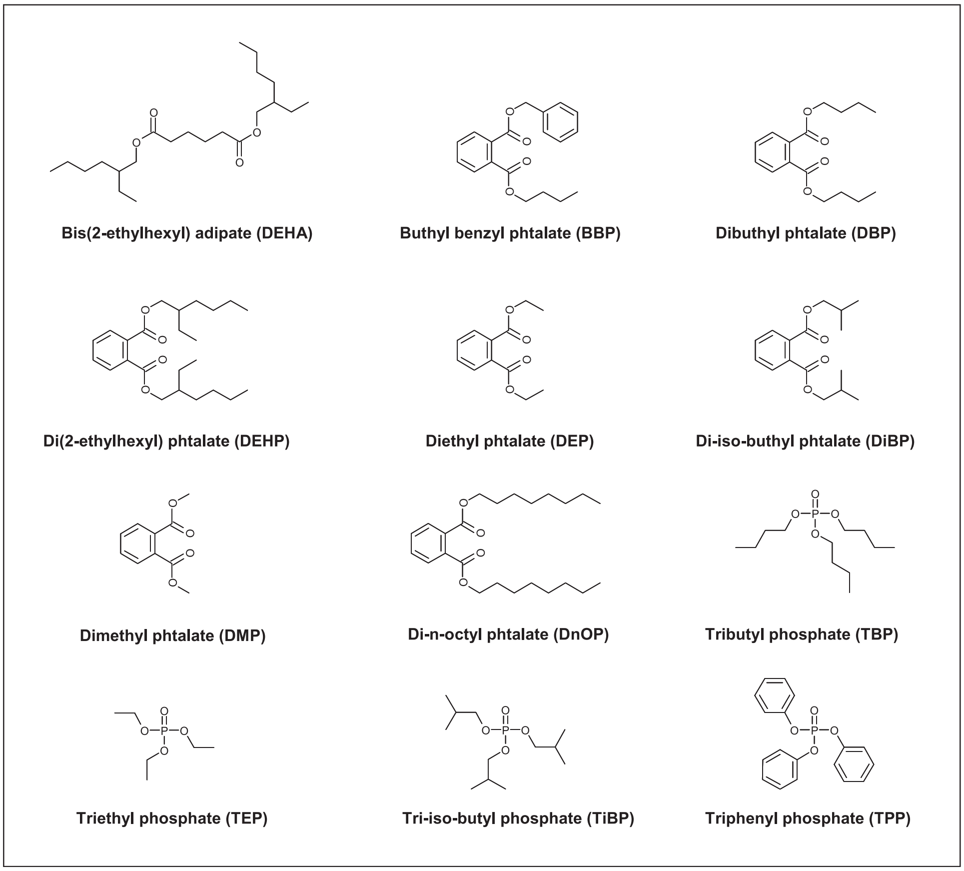

Fig. 1. Chemical structure of phthalates esters: organophosphates and DEHA.

10 mg L^{-1} was prepared freshly by diluting previous solution with ethyl acetate. All solutions were stored at 4 °C.

Other solvents used in this study (acetone, cyclohexane, dichloromethane and methanol) were also GC grade from SDS. Hyflo Super Cel diatomaceous earth for filling the extraction cells of the pressurised liquid extraction equipment was supplied by Sigma Aldrich. Helium gas with 99.999% purity (Carburos Metálicos, Barcelona, Spain) was used for the chromatographic analysis.

2.2. Sample collection

The samples were collected using a TE-6070 PM10 High Volume Air Sampler (Tisch Environmental, Inc., Village of Cleves, Ohio, USA). The samples were taken for 24 h at a flow rate of ca. 0.83 m^3 min^{-1} on PM10 Micro-fibre quartz filter (media 8 in. × 10 in.) by Munktell (Acefesa, S.A.U, Gavà, Spain) twice a week from Tarragona's harbour during the months of November and December 2011 from two sampling zones shown in Fig. 2. During this period, a total of 10 samples of air particulated material were taken. The QFFs samples were wrapped in aluminium foil, protected with a sealable plastic bag and kept at −18 °C in the freezer until analysis.

2.3. Pressurised liquid extraction

Particulated material from air samples was extracted using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) equipped with an 11 ml stainless steel extraction cell. To optimise the method, one quarter of the particulated material filters from air were spiked with all the compounds dissolved in ethyl acetate before the extraction. Each PM10 filter was spiked with all the compounds and placed in cell filled with cellulose filter, placed at the bottom of the cell, followed by 1 g of diatomaceous earth.

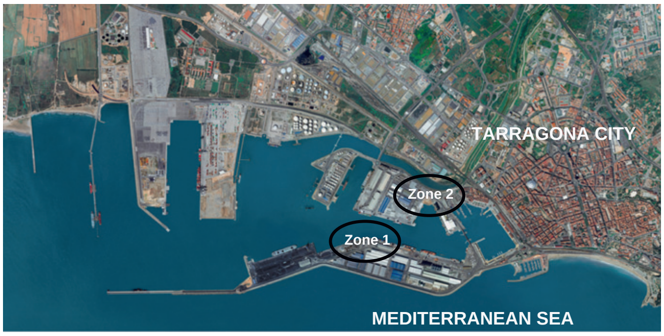

Fig. 2. Tarragona's harbour sampling zones.

The extraction solvent was dichloromethane:ethyl acetate (50:50, v/v) and the operating conditions were as follows: extraction temperature, 80 °C; extraction pressure, 1500 psi; preheating period time, 5 min; static extraction time, 10 min; number of extraction cycles, 1; final extraction volume ~22 ml; flush volume, 60% and nitrogen purge, 120 s.

The extracts were evaporated to dryness with a rotary evaporator and the residue was redissolved with 1 ml of ethyl acetate containing 5 μg mL^{-1} of internal standard d$_4$-DEP. The final extract was filtered with a 0.45 μm PTFE micro filter (Teknokroma, Barcelona, Spain) prior to analysis by gas chromatography–mass spectrometry.

2.4. Chromatographic analysis

The chromatographic instrument was a GCMS-QP2010 Ultra High Performance Gas Chromatograph Mass Spectrometer with an EI detector and an automatic injector (Shimadzu Corporation, Izasa S.A., Madrid, Spain). For the GC–MS analysis, the column used was Zebron ZB-5 (30.0 m × 0.25 mm × 0.25 μm) provided by Phenomenex (Le Pecq Cedex, France). The inlet was set at 250 °C and automatic injections of 1 μl of extracts were performed in a splitless mode. The helium carrier gas flow was set at 1 mL min^{-1}. The oven temperature programme began at 60 °C and it was increased to 260 °C at 20 °C min^{-1}, and then to 300 °C at 25 °C min^{-1} and kept at that temperature for 5 min. The GC–MS interface was set at 280 °C. The MS detection was in selective ion monitoring operating mode (SIM) at an electron impact energy of 70 eV. Two or three mass fragments were selected for each compound. The most intense ion was used for quantification and the other ions were used for confirmation the presence of the compounds. The quantitative and qualitative ions and their relative ratios are showed in Table 1.

3. Results and discussion

3.1. Gas-chromatography

Two columns (30.0 m × 0.25 mm × 0.25 μm) provided by Phenomenex (Le Pecq Cedex, France) with different contents of

Table 1
Target compounds, in chromatographic elution order, their retention times (tr), quantifier and qualifier ions, method detection (MDL) and quantification limits (MQL; expressed in ng m^{-3}), repeatability (expressed as relative standard deviation (%RSD, $n=4$)) and recoveries in real samples.

Compound	tr (min)	Quantifier ion	Qualifier ions		MDL (ng m^{-3})	MQL (ng m^{-3})	Repeatability (%RSD, $n=4$)	Recoveries (%, $n=4$, 20 ng m^{-3})
TEP	4.58	99	127(70)	155(50)	0.04	0.2	9.8	99
DMP	7.19	163	77(35)	194(10)	0.04	0.2	0.5	95
TiBP	7.54	99	155(10)		0.02	0.04	2.3	104
DEP	8.12	149	177(30)		0.2	0.4	10.8	95
TBP	8.39	99	155(15)		0.04	0.2	–[a]	100
DiBP	9.77	149	57(45)	223(10)	0.4	2.0	8.2	110
DBP	10.28	149	223(6)		0.4	2.0	–[a]	96
BBP	12.21	149	91(90)	206(25)	0.02	0.04	–[a]	97
DEHA	12.28	129	57(45)	147(12)	0.04	0.2	6.5	90
TPP	12.50	326	77(75)		0.004	0.02	3.4	97
DEHP	13.07	149	57(50)	167(30)	0.2	0.4	11.1	98
DnOP	14.15	149	279(13)	57(48)	0.004	0.02	4.4	95
DEP-d$_4$	8.11	153	181(30)					

[a] Compounds not found in the samples.

phenyldimethylsiloxane (5% and 50%) were tested to optimise the separation of these compounds. Zebron ZB-5 gives shorter analysis time and better peak shape than Zebron ZB-50. For this reason, Zebron ZB-5 was chosen as optimal for the chromatographic separation of these compounds.

The oven temperature programme was optimised to obtain a complete resolution between every compound and reduce the time per run analysis. Under optimised conditions the time analysis was less than 15 min.

Instrumental validation parameters were evaluated. For TiBP, DEP, DiBP, DBP, DEHA and DEHP, their instrumental detection limit (IDL) was 0.5 ng ml^{-1}. For TEP, DMP, TBP, BBP, TPP and DnOP, their IDL was 1 ng ml^{-1}. The method was linear up to 10 μg ml^{-1} with a determination coefficient (R^2) higher than 0.999 for all compounds, except for DEP which it was 0.995.

3.2. *PLE optimisation*

To optimise the extraction procedure of PLE, initial conditions were selected from previous studies in which some phthalate and organophosphate esters had been determined in different environmental solid samples. Quintana et al. [1] used ethyl acetate in PLE to determine organophosphate esters in outdoor particulated samples of PM10, obtaining recovery values higher than 80% for most of the compounds. Reid et al. [25] determined some plasticisers and phthalate esters (DBP, DEHP and DiBP) in sediments, sludges and leachate soils with dichloromethane:acetone (50:50, v/v) as PLE solvent obtaining recovery values of nearly 95%. Cortazar et al. [23] compared microwave-assisted extraction and pressurised solvent extraction for the determination of phthalate esters in sediment samples and tested methanol, acetone and n-hexane as extraction solvents and methanol was finally chosen such as optimal for the extraction procedure due to better results obtained.

Based on previous papers [1,7,23,25], initial PLE conditions were fixed at 80 °C extraction temperature, 10 min of static time, 1 cycle, 60% flush volume and 120 s of purge time. Ethyl acetate, dichloromethane, acetone and methanol were chosen as suitable solvents for the extraction of these compounds.

Firstly, a quarter part of blanks filters was tested with the initial conditions to determine the presence of the studied compounds. In this part of the PLE optimisation, all of these compounds except TPP and DnOP, were found in the conventional PM10 filter used (Micro-Quartz filter media 8 in. × 10 in. TE-QMA 20 × 25 cm^2 from Whatman, Maidstone, UK) at concentration corresponding to a level in air between 16.6 and 0.05 ng m^{-3}. Precalcinated filters were then tested (Munktell Micro-fibre quartz filter 203 × 254 mm^2) to evaluate the concentration of these compounds in the blanks. The results showed lower concentration values, between 0.8 and 0.004 ng m^{-3} for all compounds, except for DiBP which was found at concentration level of 3.7 ng m^{-3}. The highest value in the non-precalcinated filter was for DEP with a concentration of 16.6 ng m^{-3} and it was reduced to 0.8 ng m^{-3} with precalcinated filters. Consequently, precalcinated filters were chosen as optimal for the following experiments.

To find the optimal extraction solvent, the experiments were carried out with 5 μg mL^{-1} spiked blank filters and mixed with 1 g of diatomaceous earth and it was extracted under initial conditions, as previously described. Extracts were evaporated to dryness and the residue was redissolved with 1 ml of ethyl acetate containing 5 μg mL^{-1} of internal standard d$_4$-DEP prior to the analysis by GC–MS.

Table 2 shows the recoveries obtained with different extraction solvents and the mixture tested. The results obtained when acetone or methanol were used were below 60% for most of them, except for DiBP and DBP, which had not been extracted when methanol was used, and with acetone, they showed low recovery values. However, when acetone was used DEHA, DEHP and DnOP showed recovery values between 75% and 99%. On the other hand, when dichloromethane or ethyl acetate was used, the recovery values were between 60% and 100% for most of compounds, except for DMP, TiBP and TBP which showed slightly lower recoveries. Nevertheless, when a mixture of dichloromethane and ethyl acetate (50:50) was used as extraction solvent, the results were significantly increased obtaining recovery values above 80% for all compounds and then it was chosen as the extraction solvent.

Table 2
PLE recoveries expressed in % of each compound obtained with different extraction solvents. For extraction conditions see text.

Compound	Acetone	Methanol	Dichloromethane	Ethyl acetate	DCM:EtOAc (50:50)
TEP	31	37	98	81	115
DMP	48	47	47	54	111
TiBP	52	46	47	56	94
DEP	55	151	116	138	89
TBP	46	42	52	59	95
DiBP	4	–	66	60	92
DBP	23	–	76	67	85
BBP	77	54	99	78	112
DEHA	75	60	95	72	94
TPP	67	47	109	78	83
DEHP	76	59	93	72	102
DnOP	99	68	104	77	105

%RSD ($n=3$) $<10\%$ when $\%R>30\%$.

The second parameter optimised was the extraction temperature. The extraction was tested at three different temperatures (60, 80 and 100 °C). According to results obtained, best recovery values (> 80%) were obtained at 80 °C except for DMP and TiBP, which showed higher recoveries at 60 °C. When 100 °C was applied, the recovery values for TEP, DMP, TiBP and DBP were lower than 50%. For these reasons, 80 °C was selected as the extraction temperature.

The third parameter optimised was the extraction time. The results were obtained at three different extraction times (5, 10 and 20 min). When 5 min was tested the recovery of DMP, TiBP, DEP and TBP decreased significantly compared to the results obtained at 10 min. When 20 min was applied for the extraction time, the recoveries of all compounds did not improve and, therefore, 10 min was selected in line with the recoveries obtained and the reduced extraction time.

The fourth parameter optimised was the number of extraction cycles. Two consecutive simple extractions were applied with dichloromethane:ethyl acetate (50:50, v/v), at 80 °C and 10 min of static extraction time. The recoveries with these PLE conditions were higher than 80% for all compounds and the recoveries were considered negligible (lower than 4%) in the second cycle. For this reason, one cycle was selected as optimal.

Initially, this experimental part was tested with a quarter of precalcinated blank filters to found the optimal parameters in the extraction procedure according to the best results. Next, these optimised parameters were tested in sample filters to confirm the recovery values obtained previously. To calculate the recoveries, the sample filters were divided into four parts. Two of them were spiked at 20 ng m^{-3} and the other two were used to subtract the concentration present in the sample. The recovery values obtained with real samples are shown in Table 1.

The recoveries obtained were higher than 90% for all compounds and they were similar to obtained with the extracts of standards.

3.3. *Method validation*

In order to validate the method, the linear range, the MDL, the MQL and the repeatability (expressed as relative standard deviation) for DEHA, phthalate and organophosphate esters, were evaluated under optimised PLE conditions for particulated material air samples collected in Tarragona's harbour. All validation parameters are shown in Table 1 and a chromatogram from fortified blank filter is shown in Fig. 3.

The calibration curve has been obtained with seven precalcinated blank filters spiked at different levels between 0.004 ng m^{-3} and 40 ng m^{-3}, and subjected to the extraction procedure. The method was lineal from MQL to 40 ng m^{-3}. Due to the fact that blank filters contain some of these compounds, MDL corresponds with a signal response of approximately three times higher than a signal blank filter.

Repeatability was evaluated analysing every part of a sample filter divided into four parts and this value was expressed as the relative standard deviation (%RSD) for each compound. The repeatability ($n=4$) is less than 11%, except in the case of TBP, DBP and BBP of which the values were not calculated because these compounds were not detected in the sample.

3.4. Application of harbour air samples

The PLE/GC–MS method developed was used to determine DEHA, four organophosphate and seven phthalate esters in particulated material of air samples from Tarragona's harbour. The compound signals obtained were confirmed with quantifier and qualifier mass fragments.

Two different sampling places were studied and they are shown in Fig. 2. Zone 1 is considered an important sampling place due to its loading and unloading of shipped products and Zone 2 is an area of heavy traffic.

DEP, DiBP and DEHP were present at elevated concentration values in all samples, in contrast to TBP and DBP, which were not found in any samples.

In Zone 1, TiBP, DEP, DiBP, DEHA, TPP and DEHP were found in most of the samples (Table 3). In contrast, DMP was found in only one sample and TBP, DBP and BBP were not detected in any samples. The highest concentration values of these compounds were found for DiBP, DEHP and DEP. A Total Ion Chromatogram (TIC) corresponding to a sample (M7) in Zone 1 is shown in Fig. 4.

In Zone 2, the concentration of TEP, DMP, TiBP, DEP, DiBP, DEHA, TPP, DEHP and DnOP was identified. TBP and DBP were detected in only one and two samples below MQL. The lowest concentration values were found for DnOP and, in contrast, the highest concentration values of these compounds were found for DiBP, DEHP and DEP. The results of samples taken in Zone 2 are shown in Table 4.

Comparing the two zones, the concentration of these compounds in Zone 2 is higher than in Zone 1. Nevertheless, there is no significant difference between the maximum levels of concentrations of the two zones. However, DiBP, which was usually found in concentrations below 100 ng m^{-3}, in one sample in Zone 2 was identified at a concentration of higher than 500 ng m^{-3}.

The compounds found in the present study are the same found in a previous paper by Rudel et al. [15] who reports the presence of phthalate esters in outdoor air (consisting of <7 μm particulated and vapour phase) with other semivolatile endocrine

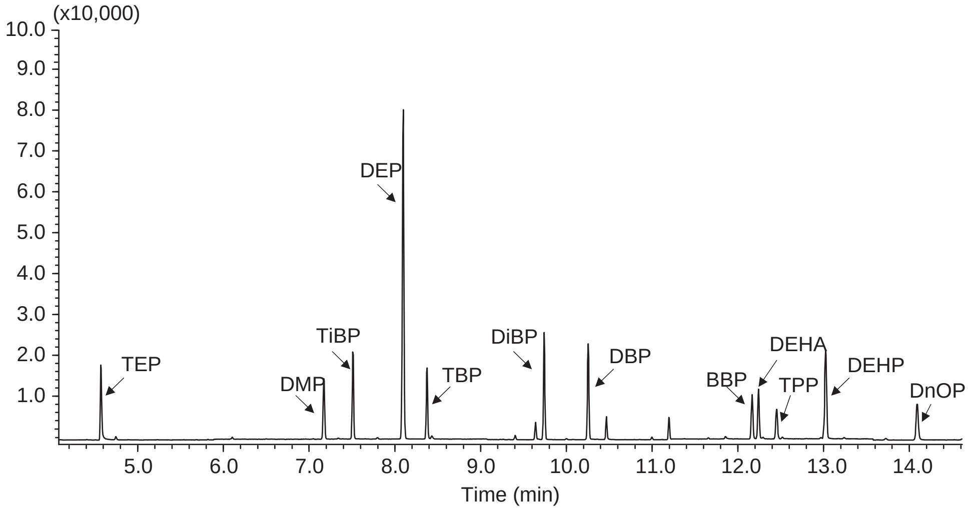

Fig. 3. TIC GC–MS chromatogram from fortified blank filter at 2 ng m^{-3}.

Table 3
Concentrations (ng m^{-3}) and average of phthalates esters, organophosphates and DEHA in sampling Zone 1.

Compound (ng m^{-3})	M1	M2	M3	M4	M5	M6	Average
TEP	< MDL	0.68	< MDL	0.47	< MDL	< MDL	–
DMP	< MDL	< MDL	< MDL	< MDL	1.05	< MDL	–
TiBP	0.05	0.21	0.10	0.13	< MDL	< MDL	0.09
DEP	7.85	1.38	1.93	1.23	< MDL	1.54	2.34
TBP	< MDL	< MQL	< MDL	< MDL	< MDL	< MDL	–
DiBP	145.76	93.53	48.14	64.23	28.09	100.74	80.08
DBP	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL	–
BBP	< MDL	< MDL	< MQL	< MDL	< MDL	< MDL	–
DEHA	0.36	1.08	0.53	0.46	< MDL	< MDL	0.41
TPP	0.15	0.14	0.15	0.40	0.13	0.15	0.19
DEHP	2.60	3.79	7.56	3.19	< MQL	1.67	3.15
DnOP	0.05	0.09	0.09	0.12	0.05	0.06	0.08

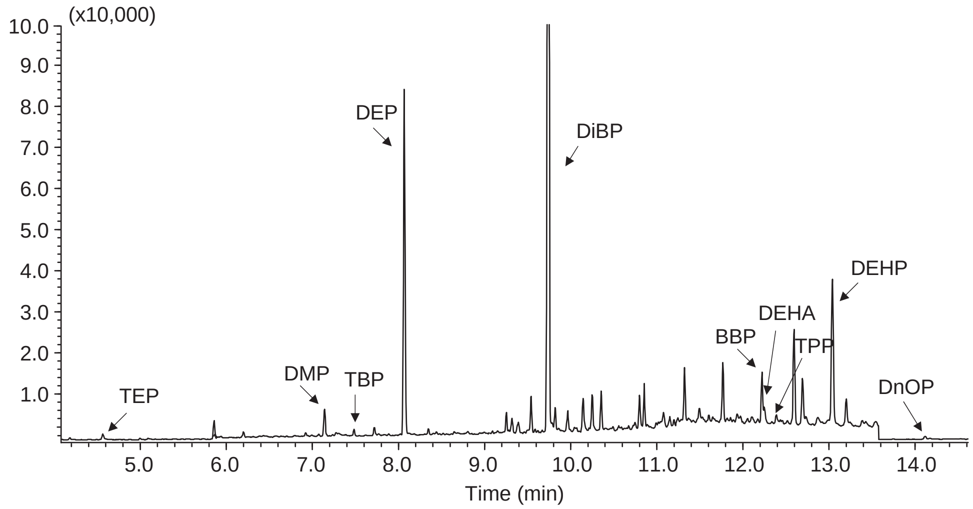

Fig. 4. TIC GC–MS chromatogram obtained of a sample: sample M7, Zone 1.

Table 4
Concentrations (ng m^{-3}) and average of phthalates esters, organophosphates and DEHA in sampling Zone 2.

Compound (ng m^{-3})	M7	M8	M9	M10	Average
TEP	2.30	0.49	0.83	1.21	1.21
DMP	0.74	1.17	0.26	0.91	0.77
TiBP	0.81	0.11	0.21	0.18	0.33
DEP	2.96	0.99	2.47	1.28	1.93
TBP	< MQL	< MDL	< MDL	< MQL	–
DiBP	43.52	31.28	529.54	64.23	167.14
DBP	< MQL	< MDL	< MDL	< MDL	–
BBP	0.08	0.01	0.01	0.21	0.08
DEHA	0.92	0.43	0.29	0.46	0.53
TPP	0.26	0.18	0.19	0.40	0.26
DEHP	21.78	1.95	2.10	8.86	8.67
DnOP	0.20	0.08	0.12	0.12	0.13

disrupting compounds. The study was located in urban and rural cities in Northern California and the authors found DEP, DiBP, DBP, BBP and DEHP at maximum concentrations of 610, 18, 32, 8.5 and 230 ng m^{-3}, as the sum of concentrations in both phases. This fact corroborates that these compounds are the most abundant in air samples. In addition, DnOP, TEP, TiBP, TPP and DEHA were also determined. No data about the presence of organophosphates in outdoor air samples were found in literature.

4. Conclusions

A method was developed by using pressurised liquid extraction and GC–MS to determine the presence of DEHA, phthalate and organophosphate esters jointly in the particulated material from Tarragona's harbour. The method developed provides a time extraction and chromatographic analysis in 30 min per sample with few experimental steps, avoiding possible contamination in the procedure and obtaining recovery values higher than 90% for all compounds in the samples.

The most commonly detected compounds were TEP, DMP, TiBP, DEP, DiBP, DEHA, TPP and DEHP. Concentration levels for phthalate esters were between MQL and 529.5 ng m^{-3}, organophosphate esters were between MQL and 2.3 ng m^{-3} and DEHA was between 0.3 and 1.1 ng m^{-3}.

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