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# **Reliable quantification of phthalates in environmental matrices (air, water, sediment and soil): A review**

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## Abstract

Because of their widespread application, phthalates are ubiquitous in the environment. Their presence in the environment has attracted considerable attention due to their potential impacts on ecosystem functioning and on public health, and their quantification has become a necessity. However, PAEs are ubiquitous in the laboratory environment/products; analysis of real samples with a low PAE background can be difficult. Therefore, accurate analysis of PAEs in environmental matrices is a challenging task. This paper is a synthesis of the extensive literature data on the most performance methods for extraction/pretreatment and quantification recently developed for quantifying PAEs in different environmental matrices (air, water, sediment and soil). The procedures of quality control and quality assurance are also presented to overcome the problem of sample contamination and the problems encountered due to matrix effects. This paper also provides useful information about the material preparation, sample pretreatment and the quantification to avoid overestimating PAE concentrations in environmental matrices.

**Keywords:** phthalates, DEHP, environmental matrices, quantification, derivatization, GC/MS, LC/MS.

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## Introduction

Phthalates or phthalic acid esters (PAEs) are widely used since 1920s in the manufacture and processing of plastic products as plasticizers. To date, PAEs are used in a very broad range of industrial applications (Serôdio et al., 2006; Simoneit et al., 2005). Not chemically but only physically bound to the polymeric matrix, PAEs can easily be released into the environment directly and/or indirectly, during manufacture, use, and disposal (Cadogan et al., 1993). PAEs can be eliminated from several environmental matrices by different biotic and abiotic pathways and are not expected to be highly persistent in most media (Barreca et al., 2014; Cartwright et al., 2000; Yuan et al., 2010). However, their extensive use and permanent emissions have resulted in their ubiquitous presence in the environment. PAEs have been widely detected throughout the worldwide environment, including atmospheric aerosols and air (Barreca et al., 2014; Fu et al., 2009; Wang et al., 2014; Xie et al., 2007), in municipal solid waste compost (Farrell et al., 2009), sludge from sewage and wastewater treatment (Dargnat et al., 2009; Reid et al., 2009), river and marine waters/sediments (Blair et al., 2009; Net et al., 2014; Xie et al., 2007), wastewater (Gao et al., 2014) and in drinking water (Gao et al., 2014; Liou et al., 2014). Indoor air where people spend 65-90% of their time is also highly contaminated by various PAEs released from plastics, consumer products within homes, suspended particulate matters and house dusts (Pei et al., 2013; Wang et al., 2014).

A large variety of field and laboratory studies reveal high exposure and evident toxicity of PAEs affecting human health and ecosystems functioning (Cartwright et al., 2000; Kolena et al., 2014). Due to their potential health and environmental risk, PAEs have become a matter of worldwide concern. The use of PAEs is now subject to stricter control and some PAEs have been prohibited or their reduction in numerous products has been recommended (Bette, 2007; Official Journal of the European Communities, 1999). The constraint on industrial wastewater discharges and stricter regulation on the release of PAEs, the quantification of their contamination levels in the environment has become a necessity. In addition, for removal purposes, for the protection of water resources and in the general environment, different environmental matrices should be monitored. However, PAEs are ubiquitous in the laboratory (air, products, reagents, solvents); analysis of real samples with a low PAE background can be difficult. This review provides a summary of the literature data on the most performance methods of pretreatment and quantification recently developed for analysis of PAEs in different environmental matrices. It provides also some useful information to avoid overestimating PAE concentrations. A list of acronyms and abbreviations used in this review is provided in Table 1S in Supporting Information.

### 1. Quality control and quality assurance

Several methods of extraction and analysis that can be applied with good efficiency for determination of PAE concentrations in environmental matrices are briefly presented in Table 1. One of the main problems for PAEs analysis is the risk of contamination, as PAEs are ubiquitous and could be present in water, organic solvents, air, glassware and in the plastic material used for the analysis. Thus, the primary issue for the quantification of PAEs is not the trace analysis itself but the risk of contaminating the environmental samples during the analytical procedure, which can often lead to false positive or overestimated results (Fankhauser-Noti et al., 2007; Marega et al., 2013). Contamination can occur at different stages including during field sampling, sample preparation and up to the chromatographic analysis itself. In real samples, a high background can be observed for the analysis of PAEs. Sample contamination can occur throughout the different steps of the procedures as well (e.g., extraction, transfer or storage). All the steps must be subjected to strict quality control procedures. There are not reliable methods to carry out in situ analysis of PAEs in the environment. All samples should be transported to the laboratory within 24 h. Water samples should be stored at 4°C, and solid matrix samples (i.e., sediment, sludge, suspended solid matter (SSM), atmospheric particle retained on filter, soil, etc.) should be kept at

-20°C. The analysis should be performed as soon as possible. In this section, some useful information about the material preparation, procedural blanks, recoveries studies and the quantification of PAEs are presented.

### **1.1. Materials and chemical preparation**

Contamination from the ambient air of the laboratory can be significant. Concentrations of DnBP, DiBP and DEHP in laboratory air have been reported between 0.37 and 3.0  $\mu\text{g}/\text{m}^3$  (Baram et al., 2000; Fankhauser-Noti et al., 2007), which can cause contamination of glassware and solvents. To avoid overestimating PAE concentrations during sampling and the experiment, it is recommended to avoid the personal use of hand creams, perfumes, deodorants, and any cosmetic products that contain PAEs (Félix-Cañedo et al., 2013). Ideally, a room dedicated to the analysis of PAEs with a purified air filter should be used. All the materials handled during sampling and sample treatment should be made of glass, Teflon, polytetrafluoroethylene, aluminum or stainless steel. To minimize PAEs contamination, rigorous control measures are required to prevent sample contamination and to maintain a low background concentration. These procedures include prewashing the laboratory material and equipment. All laboratory glassware should be washed with an appropriate organic solvent such as cyclohexane, n-hexane, isooctane, methanol or 2,2,4-trimethylpentane (Hashizume et al., 2002; Tienpont et al., 2004). An acidic solution such as hydrochloric acid, sulfochromic mixture or mixture of ammonium persulfate and sulfuric acid (Cincinelli et al., 2001; Dagnat et al., 2009; Mousa et al., 2013) or a 1 M potassium hydroxide solution (Baram et al., 2000) can also be used.

The glassware should be calcinated at 450-550°C overnight to remove organic materials. The use of plastic materials throughout the procedure is absolutely prohibited (Teil et al., 2007). Moreover, the adsorption of PAEs on the glassware walls can be minimized by calcination (Blair et al., 2009; Dévier et al., 2013; Fankhauser-Noti et al., 2007; Félix-Cañedo et al., 2013; Marega et al., 2013; Teil et al., 2007). The glassware should be washed and kept in an appropriate box with a lid (glass or PTFE) and/or calcinated aluminium to avoid the adsorption of PAEs from ambient air (Tienpont et al., 2004). Possible sources of contamination can also be derived from SPE cartridges, filters, vial caps, syringes and septa.

PAEs have been reported in some commercial organic solvents. For example, DnBP and DEHP have been measured on the order of 100  $\mu\text{g}/\text{L}$  in hexane (Fankhauser-Noti et al., 2007). For this reason, all solvents used should be of high purity and should be pre-checked for the presence of PAEs. To increase its purity, organic solvents can be distilled (Cincinelli et al., 2001) or pre-baked aluminum oxide can be added at 3% (w/v) (Fankhauser-Noti et al., 2007; Luo et al., 2012; Wu et al., 2013). Attention should also be given to the use of deionized water, which can sometimes contain a significant amount of PAEs (Cao et al., 2008; Hashizume et al., 2002). Other chemical products, such as salts (e.g., aluminium oxide, silica, sodium carbonate, sodium chloride, sodium sulfate) should be decontaminated by calcination at 400-550°C from 4h to overnight (Cao et al., 2008; Teil et al., 2007).

### **1.2. Procedural blank**

The first step of PAEs quantification is quality control and quality assurance. Quality control should be routinely implemented to minimize the risk of sample contamination. Analytical blanks for each step of the procedure should be performed to track the source of sample contamination and thus find an appropriate solution, if required. The blank should be free of targeted compounds or they should be present at low levels. A blank must be used at each step of the sample treatment (i.e., extraction, purification and pre-concentration) or, at the very least, one blank for the entire analytical procedure could be used in triplicate. The blank should be free from any targeted PAEs to ensure that no significant contamination occurs during the procedure. Moreover, to minimize the error of quantification, procedural blanks should be extracted together

with each set of the samples measured in triplicate. Method blanks and field blanks are strongly recommended for each environmental sample batch. DnBP and DEHP are found frequently in procedural blanks. If they are present at low concentrations, which account for less than a few % of those in the targeted sample, it is not necessary to subtract them from the sample measurement. However, if they are present at significant levels, they must be eliminated or subtracted from the sample measurement. It is also noteworthy that deionized water from purification systems (e.g., Milli-Q RG, Millipore, USA) can contain PAEs. The common background contamination was estimated at 0.02, 0.15, 0.005 and 0.49  $\mu\text{g/L}$  for DEP, DnBP, BBzP and DEHP, respectively (Prokúpková et al., 2002). The DEHP concentrations in blanks can be up to 90-1640  $\text{ng/L}$ , with a mean value of approximately 500  $\text{ng/L}$  (11 laboratories) (INERIS, 2009).

### **1.3. Quantification of concentration**

The quantification of PAEs can be performed either with an external or internal standard. Nevertheless, the use of internal standard(s) is strongly recommended because of the many steps required between the initial sampling and final analysis. The loss of targeted compounds could be significant during the different experimental steps (i.e., extraction, purification, pre-concentration, transfer, storage). For example, PAEs with short alkyl chain lengths (i.e., DMP, DEP) are quite volatile, and thus their loss during the pre-concentration step could be significant. Using an internal standard allows one to correct for the eventual loss of each targeted compound. Additionally, it allows one to correct for the error caused by variations of the injected volume and the response of the detector, especially when the analysis is performed using the GC-MS. In addition to the advantages mentioned, the internal standard allows one to monitor matrix effects. The choice of an appropriate internal standard is important for precise quantification. For these reasons, the use of deuterated analogs of the targeted compounds as internal standards is generally recommended. The internal standards that are most often used and proved to be efficient for the GC quantification of PAEs are: DiPhP, DnPhP, DnBzP, dimethyl isophthalate DMIP, benzyl benzoate or deuterated PAEs (DMP-d<sub>4</sub>, DEP-d<sub>4</sub>, DnBP-d<sub>4</sub>, BBzP-d<sub>4</sub>, DEHP-d<sub>4</sub>, DiDP-d<sub>4</sub>, BEHP-d<sub>4</sub>, DHxP-d<sub>4</sub>, DnPhP-d<sub>4</sub>, DnOP-d<sub>4</sub> and DiNP-d<sub>4</sub>) (Table 1).

The linear range and limits of detection/quantification (LOD/LOQ) should be studied initially. Generally, the LOD of PAEs using the performance methods cited in table 1 gives satisfactory values, ranging from less than 1  $\mu\text{g/kg}$  to dozens of  $\mu\text{g/kg}$  dw for solid matrices (i.e., soil, sludge and sediment) and from less than 10  $\text{ng/L}$  to dozens  $\text{ng/L}$  for liquid matrices (i.e., surface water, wastewater). For more precise measurements, a procedural blank and a spiked matrix sample are strongly recommended, and both should be performed in duplicate (at least) with each set of samples.

### **1.4. Recoveries studies**

Recoveries of targeted PAEs and internal standards (if any) in the matrix of interest should be evaluated initially by spiking a certain amount of standard mixture, with a concentration similar to those in the real samples, into the matrix and performing the entire analytical procedure. Spike recovery rates should be within acceptable limits to ensure either good efficiency and no significant loss or interference during the procedure. The recoveries of PAEs in real sample can be different for one PAE to another, which might be affected by the organic contents of blank matrices and the extraction efficiency of the method used. To date, many performance methods for quantifying PAEs in different environmental matrices have been developed, and the extraction yield are generally very satisfactory as presented in table 1.

### **1.5. Sample storage and transport**

After sampling, the water samples are stored and transported in aluminium or stainless steel containers at 4°C (Caroli et al., 2011; Furtmann, 1994; Wu et al., 2013). PAEs are biodegradable in aqueous media. Nevertheless, many authors have reported superior preservation of water samples by stabilizing them and by limiting bacterial growth following the addition of either sodium azide (500 mg/L sample) (Fromme et al., 2002; Tienpont, 2004) or an acid (e.g., hydrochloric acid to pH 2, commercial formic acid to pH 2.5, nitric acid 0.01 M, or sulfuric acid at 3 % to pH 2-3) (Blair et al., 2009; Félix-Cañedo et al., 2013; Huang et al., 2008; Vogelsang et al., 2006). Liquid samples should be stored in a refrigerated chamber at 4°C ( $\pm$  3°C) in darkness and treated (i.e., extraction, analysis) as soon as possible within a maximum period of 14 days to reduce losses by adsorption on the walls of the container (EPA, 1995). While solid sample should be stored at -20°C until the treatment can be performed (He et al., 2013; Liou et al., 2014; Wang et al., 2013).

## **2. Extraction or pretreatment techniques**

### **2.1. Water sample**

Many different methods could be applied to determine the concentration of PAEs in water. To collect wastewater from WWTP, 1 L aluminium sample bottles were chosen (Dargnat et al., 2009). Amber glass bottles can also be used. To collect seawater, it is strongly recommended to use a Go-Flo bottle that is coated with Teflon rather than a Niskin bottle. Using Teflon minimizes the degree of contamination. Moreover, when collecting the water sample at a depth of 10 m (Dargnat et al., 2011; Wurl, 2009), for example, the sample should be kept in a closed system, which limits its interaction with the atmosphere.

Among the large variety of extraction methods, the methods most often used and that have shown good efficiency are liquid-liquid extraction (LLE), solid-phase micro-extraction (SPME) and solid-phase extraction (SPE). Other recent extraction methods for PAEs from aqueous matrices have been developed; for example, the LLE associated with a large volume injection (LVI), the liquid phase microextraction (LPME) (Farahani et al., 2008), and the microextraction by liquid-liquid dispersion (DLLME) (Yan et al., 2010). PAEs are adsorbed on SSM, approximately 70 % of DnOP, 55 % of DEHP and 10-20 % of other PAEs (Furtmann, 1994). Consequently, the quantification should be performed both on the dissolved and particulate phases to better represent the global contamination and their distribution in the water column.

#### **2.1.1. Liquid-liquid extraction (LLE)**

The LLE technique consists of adding organic solvent (approximately 50 to 200 mL) into the aqueous sample (500 to 1000 mL, in general) and shaking the contents. This step collects the maximum of PAEs in the organic phase following the decantation step. Cai et al. (2007) reported that propanol was the best solvent for the extraction of PAEs from water. In this case, organic salts must be added to the mixture to separate the two phases (i.e., the water and organic solvent) because propanol is soluble in water. To allow the best phase separation, ammonium sulphate should be added (Cai et al., 2007). However, good efficiency can also be obtained by using hexane and/or DCM, which are non-miscible with water (Gao et al., 2014; Liu et al., 2013; Net et al., 2014). Furthermore, the addition of an organic modifier (e.g., 50 % methanol) can be necessary for the extraction of the most apolar PAEs such as DEHP and DnOP (Bergström et al., 2007). For successive extractions of the same sample ( $n=1-3$ ), recovery yields above 80 % are generally obtained (Table 1).

In the presence of SSM, the LLE technique is feasible without separating SSM from water. The resulting emulsion involving water and SSM can be removed by various techniques (e.g., EPA-Method 506 (EPA, 1995)) including centrifugation, the addition of salts (e.g., 20-150 g of NaCl per liter of water) (Adewuyi et al., 2012; Hashizume et al., 2002), ultrasound, freezing or

vigorous stirring. However, the presence of emulsions can affect the extraction efficiency of the compounds present in the SSM. With for exception of DMP, Farahani et al. (2008) showed that the addition of salt (NaCl) does not always improve the efficiency of the extraction of analytes.

Using non-miscible organic solvent allows one to avoid the addition of organic salt. This approach saves time and involves less preparatory steps, which could be a source of sample contamination. In this regard, Method 8061 of the US-EPA is the most often used approach (Gao et al., 2014; Liu et al., 2013; Zeng et al., 2008a, b). For this method, 2 L of water should first be filtered with 0.7  $\mu\text{m}$  glass fiber filters, spiked with the internal standard, and then extracted with 3 $\times$ 100 mL of DCM. Traces of water can be eliminated with sodium sulphate and then solvent exchanged with 1 mL hexane prior to GC-MS analysis. Overall, the LLE technique is simple to implement but requires the use of a large volume of organic solvents (up to 500 mL) and thus expensive. Additionally, the LLE technique is very labor intensive and time consuming. It requires the use of many pieces of glassware, which further increases the potential for sample contamination.

### **2.1.2. Solid phase micro extraction (SPME)**

The SPME technique is a solvent-free method. It involves the use of a fiber coated with an extracting phase, which can be a liquid (polymer) or a solid (sorbent) that extracts PAEs from water. After extraction/concentration, the SPME fiber is transferred to the injection port of the separating instruments, such as GC, where thermal desorption of PAEs occurs and analysis is performed. The extraction involves the equilibrium sorption of analytes onto a microfiber coated with a hydrophilic polymer. There are numerous fiber coatings available based on the solid sorbents. Poly(dimethylsiloxane) (PDMS), which is relatively non-polar, is the most frequently used fiber. Among a large variety of fiber coatings, polydimethylsiloxane and divinyl benzene (PDMS-DVB), hand-made polyaniline, and polyacrylate fibers has been successfully used to analyze the 6 PAEs listed in the priority list of the US-EPA (Li et al., 2006a, b, c; Polo et al., 2005; Prokúpková et al., 2002). The advantage of the SPME is organic solvents-free technique, which avoids the risk of secondary contamination that may occur during the pretreatment step. Further, the fiber can be reused (for 100-300 cycles). However, it appears that the SPME method for the quantification of PAEs remains in the development phase. To date, very few data are available in the literature that have used this technique and most did not report good efficiency for all of the selected PAEs.

### **2.1.3. Solid phase extraction (SPE)**

SPE is another extraction technique that is an alternative method to LLE. SPE has received increasing attention because of its ease of implementation, its ability to save time and solvent, and to eliminate the emulsions. In addition, high enrichment factors are usually obtained with SPE technique. To date, SPE has been shown to be a powerful method for the extraction, pre-concentration and cleanup of water samples. Furthermore, SPE is semi-automatic and allows for the simultaneous extraction of up to 12 or 24 water samples. Briefly, PAEs are transferred from the water sample (100-1000 mL) to a previously activated solid phase. PAEs are recovered by elution with an appropriate solvent. Typical cartridge devices consist of short columns; conventionally, an open syringe barrel contains the sorbent with different particulate sizes, usually between 50-60  $\mu\text{m}$ . Cartridges that have been reported to provide good extraction efficiency for PAEs are: C18, HLB, and a mixture of LiChrolut RP18 and Lichrolut EN (2.5/1 by weight) (Fromme et al., 2002; He et al., 2013; Liou et al., 2014; Zheng et al., 2014). The water sample can be extracted directly without filtration, but in most cases, filtration is a necessity step to avoid clogging, especially when the sample contains a high level of SSM. Internal standards (if any) should be spiked into the sample prior to extraction. MeOH, DCM, hexane and acetone are commonly used as eluting solvent, either as individual solvents or as mixtures (Table 1).



Magnetic SPE (MSPE) using iron-based magnetic nanotubes of carbon can be used as an alternative to SPE for the extraction of PAEs in mineral and tap waters (Luo et al., 2012). Two examples of the SPE method for the extraction and cleanup of PAEs from water samples are presented in Figure 1S in Supporting Information.

## **2.2. Sludge, sediment, SSM and soil samples**

Based on the literature data, the extraction of PAEs from solid matrices such as sludge, SSM, sediment and soil can be performed with common methods. Common methods have been reported that extract with good efficiency PAEs in both SSM and sediment (Zheng et al., 2014), soil and sediment (Zeng et al., 2008a, b, 2009), sediment, sludge and soil (Reid et al., 2009). The analysis of PAEs in a solid matrix generally includes extraction, clean up, column fractionation and chromatographic separation. A large variety of solvents, such as acetone, acetonitrile, DCM, hexane, ethyl acetate can be used to extract PAEs with good efficiency (Table 1). The extraction of PAEs from solid environmental matrices is conventionally performed by the Soxhlet extraction technique (Meng et al., 2014; Wang et al., 2008, 2014). Soxhlet technique offers good extraction yields. However, it is time and solvent consuming and thus expensive.

Other extraction techniques have also been developed for PAEs not only to reduce the volume of solvents and extraction times but also to improve the precision of the recovery of the analytes. Such techniques include microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), ultrasonic and accelerated solvent extraction (ASE) (Table 1). Among these techniques, ASE, also known as pressurized liquid extraction (PLE), has received increased attention because of its ease to implement and its ability to save time. Further, this approach allows one to extract with high pressure. This means that solvents can be heated to temperatures above their boiling points, which make them much more efficient to dissolve target compounds from their matrix. Moreover, this technique maintains constant extraction conditions and its automation provides reliable repeatability (Hubert et al., 2001; Schantz, 2006). In general, solid matrices should be dried, finely ground and sieved at 0.2-2 mm prior to extraction for better efficiency (Ma et al., 2014; Meng et al., 2014; Wang et al., 2013; Zeng et al., 2008a). For coastal and port samples, the optimum extraction yield was obtained when sediments were sieved at 0.2 mm (Muñoz-Ortuño et al., 2014). Indeed, reducing the particle size improves the extraction yield by providing better contact of the solvent with the sample. A hydromatrix or diatomaceous earth dispersing agent can be added to the sample to prevent aggregation of sample particles when using the ASE technique (Reid et al., 2009). Two protocols for analyzing PAEs from solid matrices are presented in Figure 2S in Supporting Information.

## **2.3. Air samples (gas and particulate phases)**

Air samples can be collected on quartz fiber filters (QFFs) (25×25 cm) previously calcinated (450°C), and then stored at -20°C until the analysis is performed (Fu et al., 2013). PAEs can be collected either by pumping an air sample through ethylene glycol or directly through an activated Florisil column, with a detection limit of 10 ng per injection using GC-ECD. Passive sampling on charcoal, which is less expensive than active sampling but requires much longer sampling times, can also perform measurements in air. In this case, the detection limit is 200 ng/m<sup>3</sup>. PAEs in the gas phase can be collected on polyurethane foam plugs (PUFs). QFFs and PUFs should be then wrapped in aluminum foil and stored in Teflon bags and kept at -20°C until the analysis is performed. PAEs in QFFs and PUFs can be extracted using the many different techniques as previously reported for solid matrices.

## **3. Chromatographic analysis**

### **3.1. Direct analysis of PAEs**

The identification and quantification of PAEs in environmental matrices require an appropriate pre-treatment step, as reported previously, followed by an analysis using different separation and detection techniques. PAEs can be quantified using chromatographic techniques such as liquid chromatography (LC) or gas chromatography (GC). GC equipped with mass spectrometry (MS) is the most common technique used for the determination of PAEs (Table 1). However, LC is a useful technique for analyzing non-volatile PAEs and their degradation products (Silva et al., 2004a, b). A mass spectrometer is the most common detector used; it is an efficient tool for the identification and quantification of each targeted PAE with low LOD (ng/L or <μg/kg). To achieve accurate quantification, compounds must be fully resolved from each other with a low signal-to-noise background.

### **3.1.1. Gas chromatography**

PAEs are weakly polar compounds. The columns most commonly used for PAEs separation in GC/MS are non-polar capillary columns such as DB-5MS and HP-5MS (Table 1). Other columns such as DB-XLB, Rxi-5MS, SLB-5MS, Phenomenex XLB, Ultra-2 and DB-35 can be also used with good efficiency (Table 1). After the separation step, each compound is transported into a MS detector where compounds can be ionized with electronic impact (EI) or chemical ionization (CI) and can be detected in full scan, SIS, SIM, MS/MS or MRM mode. Programming the temperature at 50°C for 1 min until 320°C for 2 min (ramp 10°C/min) with a HP-5MS column is typical for the determination of PAEs by the GC/MS technique. These conditions are a good compromise between resolution and the run time for the PAE analysis. With a non-polar column, the separation of analytes is based on the low boiling point of the analytes (Tienpont, 2004). Table 2 presents the quantifier/qualifier ions of PAEs using a Rxi®-5ms capillary column.

### **3.1.2. Liquid chromatography (LC)**

According to the literature data, PAEs can also be quantified using the LC. However, compared to GC/MS, a lower sensitivity is obtained with LC/MS. Indeed, LC is more appropriate for analyzing mono phthalate esters (MPEs) and degradation products of PAEs than PAEs themselves. With LC, PAEs separation is commonly achieved on an apolar C18 (octadecyl-silicagel, ODS) analytical column, using a mobile phase containing an organic solvent such as methanol or ACN and Milli-Q water, both generally buffered (e.g. with 10 mM ammonium formate, ammonium acetate) or acidified (0.05-0.1 % AcOH or TFA). However, a C8 column provides better separation peaks for the isomeric mixtures, well defined and narrower peaks than on a classical C18. Better separation can be obtained when the column is thermostated between room temperature to 80°C. Table 2S presents the columns commonly used in LC for the analysis of PAEs. MS or UV detector can perform the detection of PAEs using LC. Table 3 presents the quantifier and qualifier ions of PAEs with MS detector. By MS, PAEs can be analyzed by electrospray (ESI) (Masia et al., 2013) or atmospheric pressure chemical (APCI) (Castillo and Barcelo, 2001) ionization in positive mode.

## **3.2. Derivatization method**

Generally, PAEs can be easily identified and quantified by direct analysis as reported in the previous section. PAEs are sufficiently volatile to be analyzed directly by GC/MS. Nevertheless, their derivatization can make them more volatile. Although this step facilitates their analysis by GC, it is used very little. The peaks of silylated derivatives in the GC chromatograms are more symmetrical and thinner than those of corresponding PAEs, and the retention times are shorter. For the derivatization technique, PAEs are first hydrolyzed using an alkaline solution of

NaOH or KOH. Following by the acidification step and the obtained phthalic acid (PA) are then extracted with organic solvents and then derivatized (e.g., by silylation as showed in Figure 1) prior to GC/MS analysis.

For the derivatization of PAEs, first, alkaline hydrolysis can be performed with 1 M NaOH, or at  $\text{pH} \geq 12$ , at  $90^\circ\text{C}$  for 30 min or at room temperature (Kim et al., 2007; Peng et al., 2013). Following alkaline hydrolysis, the solution can be acidified with HCl to  $\text{pH} \leq 2$  and convert carboxylates into carboxylic acids. PA and alcohols obtained are usually extracted with ethyl acetate according to Kim et al. (2007). Under anhydrous conditions, these analytes can be derivatized by silylation. The derivatizing agent most commonly used is pentafluorobenzyl chloride (PFBCl). However, other derivatization reagents such as *N*-Methyl-*N*-*tert*-butyldimethylsilyltrifluoroacetamide (MTBSTFA) and *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) can be used (Ballesteros et al., 2006; Félix-Cañedo et al., 2013; Fu et al., 2013; Schreiber et al., 2011). The quantifier and qualifier ions of silyl derivatives of phthalic esters are presented in Table 4. This method allows to quantifying the total PAEs with good efficiency and low LOQ. However, this technique does not allow the determination of the contamination level of individual PAE. Indeed, this derivatization technique gives the sum of concentration of PA, mono-alkyl phthalate esters, and PAEs. Thus, to determine the real contamination level PAEs, other measurement should be performed to quantify the concentration of PA and mono-alkyl phthalate ester present initially in the sample.

## Conclusions

To date, PAEs are the most common chemicals that humans are in contact with daily. They are ubiquitous in all environmental compartments including urban and industrial effluents. In order to answer to the constraint on industrial wastewater discharges, stricter regulation on the release of PAEs and especially to minimize the health and environmental risk, the quantification of their contamination levels in the environment should be monitored. During these last few decades, there has been considerable improvement in PAEs extraction and analysis techniques. Numerous pretreatment techniques and detection methods can be now applied for identifying and quantifying these compounds in different environmental matrices throughout the worldwide environment, including atmospheric aerosols, indoor and outdoor air, in municipal solid waste compost, sludge, river and marine waters/sediments, SSM and drinking water. Generally, these compounds present in the environmental matrices at the concentration level that can be easily identified and quantified by common techniques of extraction (i.e., LLE, SPE, SPME, ASE, Soxhlet, sonication...) and analysis (i.e., GC/MS, LC/MS). However, the problem is not the trace analysis itself but the risk of contamination during the analytical procedure due to its ubiquity in the laboratory environment/products/solvents/reagents, which can often lead to false positive or overestimated results. This paper is a synthesis of the extensive literature data on the most performance methods of pretreatment and quantification recently developed for analysis of PAEs in different environmental matrices. Some useful information to avoid overestimating PAEs is also reviewed. To get reliable results, stricter quality control and quality assurance must be respected.

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## Table and Figure Captions

### Table Captions

**Table 1:** Extraction technique and quantification method for the measurement of PAEs in environmental matrices.

**Table 2:** Ions for selected ion monitoring (SIM) of PAEs by GC/MS-EI

**Table 3:** Ions for selected ion monitoring (SIM) or MRM transitions of PAEs by LC/MS in positive and negative modes.

**Table 4:** Ions for SIM of the corresponding silyl derivatives of phthalic esters by GC/MS-EI (Kim et al., 2007).

### Figure Captions

**Figure 1:** Hydrolysis reaction and the derivatization of PAEs by silylation (Kim et al., 2007).

**Table 1:** Extraction technique and quantification method for the measurement of PAEs in environmental matrices.

Target PAEs	Extraction/Pretreatment		Identification and quantification				
	Solvent (Eluent)	Technique	Internal standards /Surrogate	Column	Analyse	Yields (%)	Ref.
<b>Water samples</b>							
7PAEs <sup>a</sup>	DCM	LLE	-	DB-5	GC-FID GC-MS	-	[1]
16PAEs <sup>b</sup>	DCM	LLE	DiPhP, DnPhP, DnBzP, Benzyl benzoate	DB-5MS	GC-MS	78-113	[2]
15PAEs <sup>c</sup>	DCM	LLE	DiPhP, DnPhP, DnBzP, Benzyl benzoate	DB-35MS	GC-MS	62-112	[3]
DMP, DEP, DnBP, DEHP	DCM	LLE	Butyl benzoate	Col-Elite 5	GC-FID	82-91	[4]
15PAEs <sup>d</sup>	DCM	LLE	External calibration	DB-5MS	GC-MS	81-104	[5]
6PAEs <sup>e</sup>	DCM/Hexane	LLE	Benzyl benzoate	XLB	GC-MS	72-108	[6]
DnBP, DcHxP, DEHP	Ethyl acetate	LLE	DnBP-d4	DB-5MS	GC-MS	> 75	[7]
6PAEs <sup>e</sup>	Hexane	LLE	DnPhP-d4	-	GC-MS	86-114	[8]
DMP, DEP, BBzP	n-Tetradecane, can	HF- LLME	-	Ascentis-ODS	LC-UV	91-102	[9]
7PAEs <sup>f</sup>	1-Dodecane	LPME	Benzyl benzoate	DB-5MS	GC-MS	84-115	[10]
DnBP, BBzP, DEHP, DnOP	Toluene	MMLLE	-	DB-5	GC-FID	54-110	[11]
16PAEs <sup>b</sup>	Acetone	MSPE	External standard	RXi®-5MS	GC-MS	80-125	[12]
DnBP, DEHP, BBzP	Acetone	SPE	DnBP-d4, BBzP-d4, DEHP-d4	DB-XLB	GC-MS	82-106	[13]
15PAEs <sup>d</sup>	Acetone	DSPE	Triphenyl phosphate	HP-5MS	GC-MS	71-117	[14]
15 PAEs <sup>d</sup>	DCM/Acetone/MeOH	SPE	-	DB-5MS	GC-MS	71-98	[15]
6PAEs <sup>e</sup>	DCM/Hexane	SPE	DEP-d4, DnBP-d4, DnOP-d4	HP-5MS	GC-MS	61-108	[16]
11PAEs <sup>g</sup>	Ethyl acetate	SPe	DAIP	HP-1	GC-MS	91-108	[17]
8PAEs <sup>h</sup>	MeOH	SPE	DMP-d4, DEP-d4, DnBP-d4, BBzP-d4, DEHP-d4, DiNP-d4, DnOP-d4, DiDP-d4	Eclipse-plus- C18	UHPLC- ESI- MS/MS	65-135	[18]
8PAEs <sup>h</sup>	MeOH	SPE	External calibration	C18	LC-ESI- MS/MS	-	[19]
BBzP, DEHP	MeOH/DCM	SPE	DBP, DnOP	RP-18	LC-UV	99-104	[20]
DMP, DAIP, DnBP, BBzP, DcHxP, DEHP	C <sub>6</sub> H <sub>5</sub> Cl	DLLME	-	DB-5MS	GC-MS	68-89	[21]
DnBP	Solvent-free	SPME	Benzyl benzoate	DB-5MS	GC-FID	-	[22]
6PAEs <sup>e</sup>	Solvent-free	SPME	External calibration	DB-35	GC-ECD	0-116	[23]
6PAEs <sup>e</sup>	Solvent-free	SMPE	External calibration	DB-35	GC-ECD GC-MS	-	[24]
6PAEs, 4MPes <sup>i</sup>		SPME	MEP-d4, MBP-d4, DEP-d4, DBP-d4	HP-5MS	GC-MS	-	[25]
11PAEs <sup>j</sup>	-	SPME	DMP-d4, DEP-d4, DnPrP-d4, DnBP-d4, DnHxP-d4, BBzP-d4, DEHP-d4, DBzP-d4	HP-5MS-UI	GC-MS	-	[26]
6PAEs <sup>k</sup>	DCM/ Hexane	SPME	3,5-Di- <i>tert</i> -butyl- 4-hydroxyanisol	DB-5	GC-FID	78-116	[27]
DnBP	Without pre-treatment		Benzyl benzoate	C18	LC-UV	-	[28]
<b>Groundwater and drinking water (tap, bottled water)</b>							
6PAEs <sup>e</sup>	DCM	LLE	DnOP-d4	Rtx-5MS	GC-MS	70-94	[29]
5PAEs <sup>l</sup>	DCM	LLE	-	TG-5MS	GC-MS	-	[30]
6PAEs <sup>e</sup>	DCM, hexane	LLE, SPE	-	DB1, DB-5	GC/FID		[31]
BBzP, DEHP	Acetone	SPE	Internal calibration	DB1	GC-MS	-	[32]
5PAEs <sup>m</sup>	Ethyl acetate	SPE	DEHP-d4	Rxi-5MS	GC-MS	-	[33]

8PAEs <sup>n</sup>	-	SPME	DMP -d4; DEP-d4, DnBP d4 ; DEHP d4 ; DnOP-d4	DB-5MS	GC-MS	-	[34]
<b>Wastewater samples</b>							
6PAEs <sup>c</sup>	Hexane/DCM	LLE	External calibration	HT8	GC-ECD	68-84	[35]
6PAEs <sup>c</sup>	Hexane/DCM	LLE	External calibration	HT8	GC-ECD	68-84	[36]
5PAEs <sup>o</sup>	DCM	LLE	n-Butyl benzoate	Zorbax Eclipse XDB C18	LC-UV	57-97	[37]
6PAEs <sup>e</sup>	MeOH/Diethylether	SPE	Internal calibration	ZB-5MS	GC-MS	95-106	[38]
6PAEs, 4 MPES <sup>i</sup>	-	SPME	MEP-d4; MBP-d4; DEP- d4; DBP-d4	HP-5MS	GC-MS	-	[25]
DEP, DEHP	Hexane, DCM, MeOH	SSPE	External calibration	Hypersil Green ENV	LC-MS	69-71	[39]
<b>Seawater samples</b>							
DnBP, DHxP, DcHxP, DEHP	Ethyl acetate	LLE	DnBP-d4, DEHP-d4	DB5-MS	GC-MS	> 75	[7]
DEP, MEP	Hexane	LLE	-	HP-5	GC- FID/GC- MS	-	[40]
15PAEs <sup>c</sup>	Acetone	DSPE	Triphenyl phosphate	HP-5MS	GC-MS	71-117	[14]
DEP, DnPrP, DiBP, DcHcanACN	SPE	-	Zorbax Eclipse XDB C8	LC-UV	80-104	[41]	
10MPES <sup>p</sup>	Ethyl acecane, ACN	SPE	MEP- <sup>13</sup> C4, MnBP- <sup>13</sup> C4, MEHP- <sup>13</sup> C4, MiNP- <sup>13</sup> C4	Synergi RP- MAX C12	LC-MS	50-72	[42]
DEHP	Methanol	SPE	-	C18	LC-UV	70	[43]
DEP, DnBP, BBzP	-	EE-SPME	-	HP-1	GC-MS	74-93	[44]
<b>Sediment</b>							
5PAEs <sup>q</sup>	DCM/Acetone	ASE	-	Pinnacle <sup>TM</sup> II Phenyl	LC-6AD	83-92	[45]
6PAEs <sup>c</sup>	Ethyl acetate	ASE	DBzP, Benzyl benzoate	DB-5MS	GC-MS	77-102	[46]
10MPES <sup>p</sup>	AcOH /MeOH	ASE/SPE	MEP- <sup>13</sup> C4, MnBP- <sup>13</sup> C4, MEHP- <sup>13</sup> C4, MiNP- <sup>13</sup> C4	Synergi RP- MAX C12	LC-MS	83-99	[42]
15PAEs <sup>c</sup>	-	MAE	-	DB-5MS	GC-MS	84-109	[15]
DnBP, DEHP BBzP	Cyclohexane/Ethyl acetate	Soxhlet	DnBP-d4, BBzP-d4, DEHP-d4,	DB-XLB	GC-MS	71-102	[13]
16PAEs <sup>b</sup>	DCM	Soxhlet	DiPhP, DnPhP, DnBzP, Benzyl benzoate	DB-5MS	GC-MS	71-108	[2]
DMP, DEP, DnBP, DEHP	DCM	Soxhlet	Butyl benzoate	-	GC	89-90	[4]
16PAEs <sup>b</sup>	DCM	Soxhlet	DiPhP, DnPhP, DnBzP, benzyl benzoate	DB-5MS	GC/MS	77-109	[47]
6PAEs <sup>c</sup>	Hexane/DCM	USE	DMP-d4, DnBP-d4, DnOP-d4	C8 DB-5	LC/ESI- MS GC/MS	71-106	[48]
<b>Sludge samples</b>							
5PAEs <sup>o</sup>	DCM/Acetone	ASE	-	Pinnacle <sup>TM</sup> II Phenyl	LC-6AD	83-92	[45]
DEHP	Hexane	Sonication -assisted	<i>tert</i> -butylphenol	HP-5MS	GC-MS	105±8	[49]
DnBP, BBzP, DEHP	Cyclohexane/Ethyl acetate	Soxhlet	DnBP-d4, BBzP-d4, DEHP-d4	DB-XLB	GC-MS	71-102	[13]
16PAEs <sup>b</sup>	DCM	Soxhlet	DMP-d4, DEP- d4, DnBP-d4, DEHP-d4	HP-5MS	GC-MS	74-100	[50]
6PAEs <sup>c</sup>	DCM	Volatilisation/ condensation	External calibration	HT8	GC-ECD	68-84	[36]
<b>Soil samples</b>							
12PAEs <sup>r</sup>	ACN	ASE	2-Methylantracene	LiChroCART RP-18	LC-UV	82-92	[51]
DEHP	DCM	ASE	DEHP-d4	ZB-5MS	GC-MS	90	[52]
5PAEs <sup>o</sup>	DCM/Acetone	ASE	-	Pinnacle <sup>TM</sup> II Phenyl	LC-6AD	83-92	[44]
DiNP, DEHP	n-Hexane	ASE	DEHP-d4	Rxi-5ms	GC-MS	99±11	[53]
6PAEs <sup>c</sup>	Acetone/Hexane	Centrifuga	DnBP-d4	DB-5	GC-MS	80-113	[54]

		tion					
7PAEs <sup>w</sup>	DCM	SLE	DnBP-d4, BBzP-d4, DEHP-d4, DnOP-d4	DB5-MS	GC-MS	-	[55]
16PAEs <sup>b</sup>	DCM	Soxhlet	DiPhP, DnPhP, DnBzP	DB-5MS	GC-MS	76-111	[56,57]
DnBP, DEHP	DCM/Acetone	USE	-	DB-5MS	GC-FID	≥ 98	[58]
<b>Air</b>							
DEHP, BBzP	DCM	Soxhlet	-	DB-5MS	GC-MS	-	[21]
DiBP, DEHP, DNP	DCM	Soxhlet (QFFs, PUFs)	DiPhP, DnPhP, DnBzP, Benzyl benzoate	HP-5	GC-MS	> 71	[59]
6PAEs <sup>c</sup>	DCM	Soxhlet	DEHP-d4	HP-5MS	GC-MS	75	[60]
16PAEs <sup>b</sup>	DCM	Soxhlet	DiPhP, DnPhP, DnBzP, Benzyl benzoate	DB-5MS	GC-MS	72-121	[61]
17PAEs <sup>s</sup>	DCM	Soxhlet	-	HP-5MS	GC-MS	73-94	[62]
6PAEs <sup>t</sup>	DCM <sup>**</sup>	Soxhlet	DBzP	HP-5MS	GC-MS	86-118 <sup>**</sup>	[63]
	Hexane/Diethylether <sup>*</sup>					80-140 <sup>*</sup>	
14PAEs <sup>u</sup>	Hexane/DCM/MeOH	Soxhlet	DnBP-d4, DEHP-d4	HP-5MS	GC-MS	72-105 <sup>*</sup>	[64]
						82-105 <sup>**</sup>	
6PAEs <sup>t</sup>	Acetone	SPE air sampling	<sup>13</sup> C-DnPeP	DB-5MS	GC-MS <sup>2</sup>	>90-100	[65]
DnBP, DEHP	Acetone/Hexane/MeOH/Carbon disulfide	Sep-Pak PS Air cartridge	External calibration	HP-5MS	GC-MS	94-102	[66]
6PAEs <sup>c</sup>	DCM	USE	Benzyl benzoate	HP-5MS	GC-MS	78-116	[67]
6PAEs <sup>c</sup>	DCM/Acetone	USE	-	DB-5	GC	92-115	[58]
15PAEs <sup>c</sup>	DCM/Acetone	USE	External calibration	DB-5MS	GC-MS	84-107	[5]
15PAEs <sup>c</sup>	Hexane	USE	DEP-d4, DHxP-d4, DEHP-d4	SLB-5MS	GC-MS	-	[68]
BBzP, DEHP	Adsorption tubes (glass, 300mg Tenax TA)		-	DB-1701	TD-GC-MS	-	[69]
7PAEs <sup>v</sup>	Adsorption tubes (Tenax TA)		External calibration	ZB-5	TD-GC-MS	-	[70]
<b>Marine aerosols</b>							
DEHP	DCM/MeOH	LLE	C13 n-alkane	DB-5MS	GC-MS		[71]

\*Gas-phase ; \*\* Particulate phase

- 7PAEs : DMP, DEP, DiPrP, DnBP, DEHP, DnOP, DiOP
- 16PAEs : DMP, DEP, DiBP, DnBP, DMGP, DMPP, DEEP, DnAlP, DnHxP, BBzP, HEHP, DBEP, DcHxP, DEHP, DnNP, DnOP
- 15PAEs : DMP, DEP, DiBP, DnBP, DMEP, BMPP, DEEP, DnPeP, DHxP, BBzP, DBEP, DcHxP, DEHP, DnOP, DNP
- 15PAEs : DMP, DEP, DPrP, DiBP, DnBP, DAIP, DHxP, BBzP, DEHP, DnOP, BMEP, BMPP, DEEP, DBEP, DcHxP
- 6PAEs : DMP, DEP, DnBP, BBzP, DEHP, DnOP
- 7PAEs : DMP, DEP, DAIP, DnBP, BBzP, DcHxP, DEHP
- 11PAEs : DMP, DEP, DPrP, DnBP, DAIP, BBzP, DcHxP, DEHP, DnOP, BMPPrP, DMPPrP
- 8PAEs : DMP, DEP, DnBP, BBzP, DEHP, DnOP, DiNP, DiDP
- 6PAEs : DMP, DEP, DnBP, BBzP, DEHP, DOP and 4MPEs : MMP, MEP, MBP, MEHP
- 11PAEs : DMP, DEP, DiPrP, DnPrP, DnBP, DnHxP, BBzP, DcHxP, DEHP, DnOP, DBzP
- 6PAEs : DMP, DEP, DiPrP, DiBP, DnBP, DEHP
- 5PAEs : DEP, DiBP, DnBP, BBzP, DEHP
- 5PAEs : DMP, DEP, DiBP, DnBP, DEHP
- 8PAEs : DMP, DEP, DiBP, DnBP, BBzP, DHxP, DEHP, DnOP
- 5PAEs : DMP, DEP, DnBP, DPhP, DEHP
- 10MPEs : MMP, MEP, MnBP, MBzP, MEHP, MnOP, MiHxP, MiHpP, MiNP, MiDP
- 5PAEs : DMP, DnBP, DEHP, DiNP, DiDP
- 12PAEs : DMP, DEP, DiPrP, DnBP, BBzP, DnPeP, DHxP, DHpP, DEHP, DnOP, DNP, DDP
- 17PAEs : DMP, DEP, DiBP, DnBP, DMEP, BMPP, DEEP, DnPeP, DHxP, BBzP, DBEP, DcHxP, DEHP, DnNP, DiNP, DPhP, DnOP
- 6PAEs : DMP, DEP, DiBP, DnBP, BBzP, DEHP
- 14PAEs : DMP, DEP, DAIP, DiBP, DnBP, DnPeP, BBzP, BOP, DHxP, DiOP, DnOP, DEHP, DiNP, DiDP
- 7PAEs : DMP, DEP, DiBP, DnBP, BBzP, DEHP, DnOP
- 7PAEs : DnBP, DnPeP, BBzP, DEHP, DnOP, DnNP, DiNP

References: <sup>[1]</sup>Espadaler et al., 1997; <sup>[2]</sup>Zeng et al., 2008a; <sup>[3]</sup>Liu et al., 2013; <sup>[4]</sup>Fatoki et al., 2010; <sup>[5]</sup>Das et al., 2014; <sup>[6]</sup>Net et al., 2014; <sup>[7]</sup>Kim et al., 2007; <sup>[8]</sup>Gao et al., 2014; <sup>[9]</sup>Chao et al., 2013; <sup>[10]</sup>Farahani et al., 2008; <sup>[11]</sup>Bergström et al., 2007; <sup>[12]</sup>Luo et al., 2012; <sup>[13]</sup>Fromme et al., 2002; <sup>[14]</sup>Wu et al., 2013; <sup>[15]</sup>Zheng et al., 2014; <sup>[16]</sup>He et al., 2013; <sup>[17]</sup>Furtmann, 1994; <sup>[18]</sup>Liou et al., 2014; <sup>[19]</sup>Yang et al., 2014; <sup>[20]</sup>Jara et al., 2000; <sup>[21]</sup>Farahani et al., 2007; <sup>[22]</sup>Li et al., 2006a; <sup>[23]</sup>Prokūpková et al., 2002; <sup>[24]</sup>Holadová et al., 2007; <sup>[25]</sup>Alzaga et al., 2003; <sup>[26]</sup>Dévier et al., 2013; <sup>[27]</sup>Batlle and Nerín, 2004; <sup>[28]</sup>Li et al., 2006b; <sup>[29]</sup>Amiridou and Voutsas, 2011; <sup>[30]</sup>Dumitrascu, 2013; <sup>[31]</sup>EPA, 1995; <sup>[32]</sup>Félix-Cañedo et al., 2013; <sup>[33]</sup>Bach et al., 2013; <sup>[34]</sup>Cao, 2008; <sup>[35]</sup>Teil et al., 2007; <sup>[36]</sup>Dargnat et al., 2009; <sup>[37]</sup>Adewuyi, 2012; <sup>[38]</sup>Ballesteros et al., 2006; <sup>[39]</sup>Castillo and Barcelo, 1999; <sup>[40]</sup>Peng et al., 2013; <sup>[41]</sup>Cai et al., 2003; <sup>[42]</sup>Blair et al., 2009; <sup>[43]</sup>Bell and Barsh, 2010; <sup>[44]</sup>Mousa et al., 2013; <sup>[45]</sup>Reid et al., 2009; <sup>[46]</sup>Huang et al., 2008; <sup>[47]</sup>Sun et al., 2013; <sup>[48]</sup>Lin et al., 2003; <sup>[49]</sup>Aparicio et al., 2007; <sup>[50]</sup>Meng et al., 2014; <sup>[51]</sup>hang et al., 2010; <sup>[52]</sup>Rhind et al., 2013; <sup>[53]</sup>Cousins et al., 2014; <sup>[54]</sup>Wang et al., 2013; <sup>[55]</sup>Vikelsøe et al., 2002; <sup>[56]</sup>Zeng et al., 2008b; <sup>[57]</sup>Zeng et al., 2009; <sup>[58]</sup>Xu et al., 2008; <sup>[59]</sup>Huang et al., 2013; <sup>[60]</sup>Xie et al., 2005; <sup>[61]</sup>Zeng et al., 2010; <sup>[62]</sup>Wang et al., 2014; <sup>[63]</sup>Xie et al., 2007; <sup>[64]</sup>Wang et al., 2008; <sup>[65]</sup>Bergh et al., 2011; <sup>[66]</sup>Toda et al., 2004; <sup>[67]</sup>Kong et al., 2013; <sup>[68]</sup>Barreca et al., 2014; <sup>[69]</sup>Choi et al., 2010; <sup>[70]</sup>Aragon et al., 2013; <sup>[71]</sup>Fu et al., 2013; <sup>[72]</sup>Serôdio et al., 2006; <sup>[73]</sup>Tienpont, 2004; <sup>[74]</sup>Schiedek, 1995; <sup>[75]</sup>Guo et al., 2013; <sup>[76]</sup>Bergé, 2012; <sup>[77]</sup>Litz et al., 2003; <sup>[78]</sup>Schreiber et al., 2011; <sup>[79]</sup>Khedr, 2013; <sup>[80]</sup>Castillo and Barcelo, 2001.

**Table 2:** Ions for selected ion monitoring (SIM) of PAEs by GC/MS-EI.

Analyte	Quantifier ion (abundance)	Qualifier ions (abundance)	Reference	Analyte	Quantifier ion (abundance)	Qualifier ions (abundance)	References
DMP	163 (100)	194, 135, 77	[12]	DEHP	167 (36) 149 (100)	279 (9.8), 149 (100)	[7]
		194(15), 135(15)	[29]			279, 167, 113	[12]
		194, 133	[38]			279 (8.8), 167 (34)	[13,29,32,34]
		194, 77	[34]			279	[10,38]
		194	[10,25,73]			167, 57	[30]
		77	[33,72,75]			167	[26,33,25]
DEP	149 (100)	222, 177, 121	[12]	DPhP	225	197, 153, 77	[12]
		222 (1.6), 177 (23)	[76,77]	DBzP	149	108	[26]
		177, 76	[34]	BBzP	149 (100)	312(1), 206(22)	[77]
		177 (28)	[10,25,26,29,38,72,73,75]			238, 206, 91	[12]
		177, 65	[30]			238 (5), 206 (25)	[76]
BMEP	59	251, 193, 149	[12]			206, 91	[34,73]
						206	[10,13]
						205 (21.5), 91 (71.5)	[29]
						205	[38]
						91, 65	[30]
						91	[26,72,75]
BEEP	45	149, 121, 72	[12]	DiHP	149	265	[73]
BBEP	149	249, 193, 57	[12]				
DnPrP	149 (100)	209 (5.9), 191 (6.9)	[77]	DnOP	149 (100)	279, 261, 179	[12]
DiPrP	149		[26]			279 (6.6), 207 (4.4)	[77]
DnBP	149 (100)	278 (1.0), 223 (7.4), 205, 121	[12]			279, 150	[34,38,72]
		223 (5.5), 205 (4.4)	[13,25,29,76]			279 (18.0)	[29,75]
		223, 104	[74]			167	[26]
		223	[10,73]			149, 71, 57	[12]
		205	[75]			149	[73]
		150	[72]			307	[73]
DiBP	149 (100)	147, 73	[30]			149 (100)	307 (6.4)
			[26,33]			DUP	149 (100)
		223, 205, 167	[12]			DMIP	163
		223 (7.4), 205 (1.9)	[77]			DMP-d4	167
		223, 57	[34]			DEP-d4	153
		223	[73]	DiPrP-d4	153		
DPeP	149	57, 41	[30]			209, 227	[13,25]
			[33]	DnBP-d4	153 (100)	227 (6.3)	[7,26,34,73]
BMPP	149	237, 219, 167	[12]				
		237	[73]	DnHxP-d4	153		
DAIP	149	251, 167, 121	[12]			171 (31), 283 (14)	[13]
DnHxP	149 (100)	189	[10,73]	DBzP-d4	153	171 (41)	[7,33]
		251 (11), 233 (3.3)	[7]				[26,34]
		251, 104, 76	[12]	BBzP-d	153		
DcHxP	149 (100)	251, 43	[34]			210	[13]
			[26]				
		269, 167, 83	[12]	DnOP-d4	153 (100)	283 (17)	[29,73]
		249 (17), 167 (32)	[7,73]				
		167 (32), 249 (5.5)	[77]				
		167	[10,26]				

References: see indication in Table 1.

**Table 3:** Ions for selected ion monitoring (SIM) or MRM transitions of PAEs by LC/MS in positive and negative modes.

Analyte	Quantifier ion Q1	Qualifier ion Q3	Reference
<b>Positive mode</b>			
DMP	195	163, 133	[78]
DEP	149	177, 223	[43]
	223	149, 177	[78]
BMEP	283	207, 59	
BEEP	311	221, 149	
DnPrP	251	149, 191	
DiPrP	251	149, 191	
DnBP	279	149, 205	
	149		[80]
DiBP	279	149, 205	[78]
DnPeP	307	219, 149	
DiPeP	307	219, 149	
BMPP	335	167, 251	
DAIP	247	189, 149	
BBEP	367	101, 249	
DnHxP	335	149, 233	
DcHP	331	167, 249	
DEHP	149	167, 391	[43,80]
	391	167, 279	[78]
	413.8	414.8	[79]
DPhP	319	225, 77	[78]
BBzP	313	149, 205	
DiHpP	363	149, 233	
DnOP	391	261, 149	
DiNP	419	275, 149	
DiDcP	447	149, 289	
<b>Negative mode</b>			
DEHP	277		[73]

References: see indication in Table 1.

**Table 4:** Ions for SIM of the corresponding silyl derivatives of phthalic esters by GC/MS-EI (Kim et al., 2007).

Analyte	Quantifier ion (abundance)	Qualifier ion (abundance)
DBP-SE	131 (100)	103 (23), 145 (72)
DHP-SE	159 (100)	103 (42), 115 (5.0)
DCHP-SE	157 (97)	129 (100), 172 (23)
DEHP-SE	187 (80)	103 (100), 202 (0.1)
DBP-d4	295 (17)	147 (100), 310 (2.0)
DEHP-d4	153 (100)	227 (6.3)

**Figure 1:** Hydrolysis reaction and the derivatization of PAEs by silylation (Kim et al., 2007).

