



Quality assessment of environmental water by a simple and fast non-ionic hydrophobic natural deep eutectic solvent-based extraction procedure combined with liquid chromatography tandem mass spectrometry for the determination of plastic migrants

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Abstract

A non-ionic hydrophobic natural deep eutectic solvent (HNADES) based on thymol and menthol was proposed for the liquid-liquid microextraction of fourteen phthalates and one adipate from environmental water samples. Separation, identification, and quantification were achieved by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry. The main factors affecting the extraction efficiency were thoroughly studied. Sample pH of 8 and 100 μL of thymol:menthol at molar ratio 2:1 were selected as the best conditions, while ionic strength and type of dispersant solvent were not relevant for the extraction of the target compounds. The whole methodology was validated for treated wastewater, runoff, and pond water matrices, using di-*n*-butyl phthalate-3,4,5,6- d_4 and dihexyl phthalate-3,4,5,6- d_4 as surrogates. Recovery ranged from 70 to 127% with relative standard deviation values lower than 14%. Limits of quantification of the method were in the range 0.042–0.425 $\mu\text{g/L}$ for treated wastewater, 0.015–0.386 $\mu\text{g/L}$ for runoff, and 0.013–0.376 $\mu\text{g/L}$ for pond water. The methodology was applied for the analysis of real treated wastewater, runoff, and pond water samples from different places of Tenerife and Gran Canaria (Canary Islands) finding the presence of diethyl phthalate, diallyl phthalate, dipropyl phthalate, benzylbutyl phthalate, di-*n*-butyl phthalate, bis-(2-*n*-butoxyethyl) phthalate, di-*n*-pentyl phthalate, dicyclohexyl phthalate, and bis-(2-ethylhexyl) phthalate at concentrations between 105.2 and 3414 ng/L.

Keywords Phthalic acid esters · Green solvent · Liquid-liquid microextraction · Water samples · Ultra-high-performance liquid chromatography · Mass spectrometry

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Abbreviations

[BMIM][PF ₆]	1-Butyl-3-methylimidazolium hexafluorophosphate
[OMIM][PF ₆]	1-Octyl-3-methylimidazolium hexafluorophosphate
[TBDP][BF ₄]	Tributyl dodecyl phosphonium tetrafluoroborate
AA	Air-assisted
ACN	Acetonitrile
BBP	Benzyl butyl phthalate
BPA	Bisphenol A
ChCl	Choline chloride
DAD	Diode-array detector
DAP	Diallyl phthalate
DBEP	Bis-(2- <i>n</i> -butoxyethyl) phthalate
DBP	Di- <i>n</i> -butyl phthalate

DBP-d ₄	Di- <i>n</i> -butyl phthalate-3,4,5,6-d ₄
DCHP	Dicyclohexyl phthalate
DEEP	Bis-(2-ethoxyethyl) phthalate
DEHA	Bis-(2-ethylhexyl) adipate
DEHP	Bis-(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DES	Deep eutectic solvent
DHP-d ₄	Dihexyl phthalate-3,4,5,6-d ₄
DINP	Diisononyl phthalate
DLLME	Dispersive liquid-liquid microextraction
DMEP	Bis-(2-methoxyethyl) phthalate
DMP	Dimethyl phthalate
DNOP	Di- <i>n</i> -octyl phthalate
DNPP	Di- <i>n</i> -pentyl phthalate
DPP	Dipropyl phthalate
FID	Flame ionisation detector
GC	Gas chromatography
HDES	Hydrophobic deep eutectic solvent
HF	Hollow fibre
HNADES	Hydrophobic natural deep eutectic solvent
HPLC	High-performance liquid chromatography
IL	Ionic liquid
LC	Liquid chromatography
LLME	Liquid-liquid microextraction
LOQ	Limit of quantification
ME	Matrix effect
MIP	Molecularly imprinted polymer
MOF	Metal-organic framework
MRM	Multiple reaction monitoring
MS/MS	Tandem mass spectrometry
MS	Mass spectrometry
MWA	Microwave-assisted
PAE	Phthalic acid ester
RSD	Relative standard deviation
SFOD	Solidified floating organic droplet
TC	Temperature-controlled
UHPLC	Ultra-high-performance liquid chromatography
US EPA	United States Environmental Protection Agency
UV	Ultraviolet detector
VWD	Variable wavelength detector
WHO	World Health Organization

Introduction

The development of the plastic industry and the many benefits that plastic materials bring to the welfare of society have made them practically irreplaceable products. Its versatility, and unique properties, cost, and easy production have made plastic one of the most widely used materials nowadays. However, beyond the environmental pollution associated with the tons

of plastics that are worldwide generated and not recycled, the additives that are added to plastic to obtain the desired properties also constitute an important concern in this sense, due to their known persistence. Their presence in the environment represents a real risk for living organisms and, in particular, for the health of human beings. Among the different families of additives, including flame retardants, antioxidants, and stabilisers, among others, phthalic acid esters (PAEs) are compounds widely used from the early twentieth century as plasticisers in the manufacture of plastic products. Since then, their use has spread to such an extent that the presence of these compounds in the environment is universal [1, 2].

Concentration of phthalates in the environment can vary from few nanograms per liter to hundreds of milligrams per liter which constitutes a clear over-exposition of the general population to these hazardous substances [2]. For this reason, several international organisations have established different regulations, lists, and guidelines, in which some PAEs with demonstrated endocrine disrupting activity have been included. Among them, the European Union have published regulations and guidelines referring to the Registration, Evaluation, Authorisation and Restriction of Chemicals in order to ensure environmental and human health protection [3] and quality standard of water policy [4], in which bis-(2-ethylhexyl) phthalate (DEHP), bis-(2-methoxyethyl) phthalate (DMEP), benzyl butyl phthalate (BBP), di-*n*-butyl phthalate (DBP), di-*n*-pentyl phthalate (DNPP), and dicyclohexyl phthalate (DCHP) are classified as toxic substances for reproduction. The United States Environmental Protection Agency (US EPA) pointed out BBP, DBP, DCHP, and DEHP as high-priority substances [5], while dimethyl phthalate (DMP), diethyl phthalate (DEP), BBP, DBP, DEHP, and di-*n*-octyl phthalate (DNOP) were included in the 126 Priority Pollutants List [6], and BBP, DBP, DNPP, DEHP, DNOP, and diisononyl phthalate (DINP) in the US EPA Phthalates Action Plan due to their toxicity and environmental and human potential risk [7]. In addition, the same organisation [8] and the World Health Organization (WHO) [9] reported a regulation and a guideline about drinking water, in which reference values for bis-(2-ethylhexyl) adipate (DEHA) in the first case and DEHP in both cases were established. In this sense, it is intended that there are controls and restrictions for all those substances categorised as priority pollutants, among which are DEHP and DEHA that constitute an important environmental threat, in terms of toxicity to aquatic life and bioaccumulation in ecosystems, as well as damage to human health.

Several procedures have been applied for the extraction of PAEs from environmental matrices. In this regard, conventional techniques such as liquid-liquid extraction, solid-liquid extraction, solid-phase extraction, and Soxhlet and alternative methodologies as liquid-phase microextraction in its

different approaches, solid-phase microextraction, dispersive solid-phase extraction and its magnetic version, stir-bar sorptive extraction, supercritical fluid extraction, and pressurised solvent extraction, among others, combined with gas (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) have been the most commonly used [2]. Among them, liquid-liquid microextraction (LLME) procedures show the main advantages of dispersive liquid-liquid microextraction, such as simplicity, high preconcentration factors using extraction solvent volume in the order of microliter, rapidity, and low cost, but avoiding the use of disperser organic solvents [10]. Originally, toxic chlorinated solvents were used as extractants. However, with the advancement of material science, alternative solvents such as ionic liquids (ILs) and, more recently, deep eutectic solvents (DESs) have emerged. Particularly, DESs have arisen as the solvents of the twenty-first century, with properties similar to ILs, but with higher biocompatibility and biodegradability, easier preparation, lower cost, and wider availability of raw materials [11]. Different classifications of DESs have been proposed, based on their components (types I–V) or their origin (composed by primary and secondary metabolites or not). However, most of them present high hydrophilicity hindering their applicability in aqueous media. In this regard, hydrophobic DESs (HDESs) have been presented as excellent alternative to overcome this issue. This kind of DESs can also be classified in two different categories: ionic HDES and non-ionic HDES. In the first group, long-chain tetraalkyl quaternary ammonium salts and long-chain alcohols or fatty acids are commonly used as HDES components, while in the second one, terpenes (menthol, thymol, and camphor), fatty acids (octanoic, decanoic, dodecanoic acids), or combination of them are the most tested [12]. In the case of PAE analysis, in most cases, hydrophilic DESs are employed. Thus, the use of HDESs represents a very significant improvement in terms of aqueous sample compatibility and procedure simplicity which also turns into lower cost of analysis. In addition, the selection of natural HDESs (HNADESs), based on the natural occurrence of their components, involves the development of more sustainable and safe procedures, avoiding additional contamination on the environmental media.

In this work, thymol:menthol HNADES-based LLME prior to ultra-high-performance liquid chromatography (UHPLC)-tandem mass spectrometry (MS/MS) was evaluated for the first time for the analysis of 14 PAEs and DEHA in environmental samples, including treated wastewater, runoff water, and pond water. In this sense, water samples destined to agricultural activities have been analysed considering the presence of phthalates in them as a consequence of human activities and, therefore, their potential harm to humans through the transport of these compounds between natural source water, soil, and crop products. To the best of our knowledge, this is the first work in which a thymol-based

HNADES has been used for the extraction of PAEs and DEHA.

Experimental

Chemicals and materials

Analytical standards of DMEP (CAS 117-82-8), diallyl phthalate (DAP; CAS 131-17-9), dipropyl phthalate (DPP; CAS 131-16-8), DBP (CAS 84-74-2), DCHP (CAS 84-61-7), DEHP (CAS 117-81-7), DNOP (CAS 117-84-0), DINP (CAS 20548-62-3), and DBP-3,4,5,6-d₄ (DBP-d₄; CAS 93952-11-5) with purity higher than 97.0% (w/w) were supplied by Sigma-Aldrich Chemie (Madrid, Spain). DMP (CAS 131-11-3), bis-(2-ethoxyethyl) phthalate (DEEP; CAS 605-54-9), DEP (CAS 84-66-2), BBP (CAS 85-68-7), bis-(2-*n*-butoxyethyl) phthalate (DBEP; CAS 117-83-9), DNPP (CAS 131-18-0), DEHA (CAS 103-23-1), and dihexyl phthalate-3,4,5,6-d₄ (DHP-d₄; CAS 1015854-55-3) with a purity higher than 97.0% (w/w) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Stock solutions, previously prepared in acetonitrile (ACN) of LC-MS grade at 100 mg/L for DMEP and DBP-d₄; 500 mg/L for DEEP, DEP, DAP, DPP, BBP, DBP, DBEP, DNPP, DCHP, DEHA, and DNOP; and 1000 mg/L for DMP, DEHP, DINP, and DHP-d₄, were used for the preparation of daily working mixtures of PAEs and DEHA by dilution. All solutions were stored in the darkness at –18 °C.

All chemicals were of analytical reagent grade (except in those cases specifically indicated) and used as received. ACN and methanol of LC-MS grade and hydrochloric acid (25.0%, w/w) were from Merck (Darmstadt, Germany). (±)-Menthol (99.8% w/w), thymol (99.5%, w/w), sodium chloride (≥99.5%, w/w), and hydroxide (≥98.0%, w/w) were acquired from Sigma-Aldrich Chemie (Madrid, Spain). Deionised water was obtained from a Milli-Q system A10 (Millipore, MA, USA).

With the purpose of assuring the absence of phthalate contamination in the laboratory, a cleaning glass reagent (Godax Laboratories, MD, USA) was applied for volumetric glassware, while the rest of glassware was heated for 4 h at 550 °C. Moreover, plastic material free of PAEs was used, and laboratory blanks were daily analysed to evaluate the possible presence of plastic migrants.

Apparatus and software

Fourier-Transform Infrared (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC), and thermogravimetric analysis (TGA) were used to characterise the lab-made HNADESs and their individual components. FTIR spectra were obtained using a Cary 630 FTIR spectrometer (Agilent Technologies)

equipped with a diamond attenuated total reflectance module and a KBr beam splitter. Spectra were recorded in the range 600–4500 cm^{-1} , performing 256 scans of the background and samples with a resolution of 4 cm^{-1} . DSC curves were recorded in a Discovery DSC 25 equipment (TA Instruments) with a Refrigerated Cooling System 90. Measures were made under inert atmosphere (N_2) at a flow rate of 50 mL/min in a hermetic Tzero aluminium pan (TA Instruments). Heating cycles were made between -80 and 300 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ for the HNADESs while -80 to 80 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$ was used for thymol and menthol. TGAs were carried out in a simultaneous thermal analyser Discovery SDT 650 (TA Instruments) in the range 25 – 300 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$. A hermetic Tzero aluminium pan and a N_2 flow of 50 mL/min were used. All characterisation information and discussion can be found in the Supplementary Information (ESM; Characterisation of HNADESs Section and Figs. S1–S2).

Analyses of PAEs and DEHA were carried out in a Waters Acquity UPLC® H-Class, constituted of a sample manager with flow-through needle and a quaternary solvent from Waters Chromatography (Milford, MA, USA). The UHPLC system was coupled to an MS Xevo TQD (Waters Chromatography) using an electrospray ionisation interface in positive mode. Masslynx™ software from Waters Chromatography was used to control the pumps and sample manager, as well as MS parameters and the collection and process of spectrum data. Separation was carried out in an Acquity BEH C_{18} column (50 mm \times 2.1 mm, 1.7 μm) using a pre-column with the same stationary phase (5 mm \times 2.1 mm, 1.7 μm), both from Waters Chromatography. Column and pre-column temperatures were settled at 40 $^\circ\text{C}$.

The mobile phase was composed of ACN (solvent A) and water (solvent B), both containing 0.1% (v/v) of formic acid. Composition was established at 80/20 (v/v) A/B, at the beginning of the gradient. It was changed to 100% A (v/v) in one min, which was held during 1 min. Finally, the initial conditions were set up in 1 min and maintained during 2 min until system stabilisation. The flow rate was 0.3 mL/min and the injection volume was 5 μL at 10 $^\circ\text{C}$.

The MS analysis was performed in multiple reaction monitoring (MRM) mode using the retention time and two different transitions as identification points. Besides, maximum tolerance of $\pm 20\%$ for the relative intensity of the product and precursor ions was established [13]. Source conditions were applied as previously developed by Santana-Mayor et al. [14]. MRM transitions, cone voltages, and collision energies applied for each analyte are shown in Table S1 of the ESM.

Samples selection

Three different environmental water samples, treated wastewater, runoff water, and pond water, with pH values 8.40, 8.77, and 8.69 at 25 $^\circ\text{C}$, respectively, were selected as matrices

to perform the validation of the method. Treated wastewater was obtained from a wastewater treatment plant in Tenerife (Canary Islands, Spain), equipped with ultrafiltration membrane bioreactor for biological wastewater treatment. Rainwater runoff was collected in the North of Tenerife and pond water in a metallic pond from the same island. All samples were previously filtered through a Durapore® PVDF membrane filter with 0.45- μm pore size to remove solid particles.

Besides, 15 additional water samples were analysed to assess the occurrence of PAEs and DEHA in real samples. Five treated wastewaters were taken from treatment plants in Tenerife (pH values ranging 7.52–8.16 at 25 $^\circ\text{C}$); three rainwater runoff samples and one from an underground gallery runoff (pH between 7.72 and 7.98 at 25 $^\circ\text{C}$) were collected at different locations of Tenerife (Canary Islands, Spain); and six pond water samples (pH of 7.55–8.60 at 25 $^\circ\text{C}$) were collected from different ponds in Tenerife and Gran Canaria (Canary Islands, Spain).

Runoff and pond waters are used to irrigate agricultural crops and gardens, while treated wastewaters of reclaimed quality, after a process of ion removal to their high conductivity, could be used for the same purpose, especially in those places with water shortage issues [15]. In the Canary Islands, it is a common practice to store raining, underground, or even desalinated water in tanks to use them to irrigate different typical crops of the islands, such as banana plantations, avocado trees, and different tropical and sub-tropical fruits, or citrus fruits, among others [16, 17].

Synthesis of HNADESs

In this study, HDESs were prepared by mixing two natural secondary metabolites, thymol (as hydrogen bond donor) and menthol (as hydrogen bond acceptor), at molar ratios of 1:1, 1:2, and 2:1. For synthesis, the HDES components were placed in a glass vial and then stirred at 80 $^\circ\text{C}$ for 10 min until a homogeneous liquid is formed [18]. The solvents were cooled to room temperature and stored in a vacuum desiccator to avoid the absorption of moisture.

Liquid-liquid microextraction procedure

The pH of 10 mL of spiked or non-spiked aqueous sample was adjusted to 8, using NaOH 10 M or HCl conc., and transferred into a 15-mL glass centrifuge tube. Then, 100 μL of HDES thymol:menthol 2:1 was added to the sample and vortexed for 1 min. At this stage, a cloudy solution of microdroplets of HNADES was formed in the aqueous sample. Afterwards, it was centrifuged at 2465g for 10 min at 15 $^\circ\text{C}$ in a 5810 R centrifuge from Eppendorf (Hamburg, Germany) to achieve phase separation. Then, HNADES upper enriched-phase containing

target analytes was collected, transferred into an injection vial, and 20-fold diluted with ACN. Next, 5 μL was injected into the UHPLC-QqQ-MS/MS system. Due to the simplicity of the synthesis, as well as the low cost of raw materials and its good biocompatibility and biodegradability in aqueous systems [19–21], the extraction solvent was used only once to avoid possible carry-over problems, and the use of toxic solvents, involved in the cleaning procedure of HNADES.

Results and discussion

UHPLC-QqQ-MS/MS method

In this work, a group of 14 PAEs and one adipate were analysed using an Acquity BEH C_{18} column. Based on the previous experience in the separation of this kind of compounds, different gradients consisted of ACN/ H_2O (v/v) mixtures, both containing 0.1% (v/v) of formic acid, were evaluated. In this case, the use of an HDES limits its application in reverse phase LC due to the need of high amount of organic mobile phase at the beginning of the gradient, which hampers the chromatographic performance. This issue was resolved increasing the initial percentage of ACN up to 80% (v/v) and using the gradient described in the “Apparatus and software” section. Good separation was achieved with an analysis time below 3.5 min.

HNADES-LLME optimisation

This work constitutes the first one in which PAEs and DEHA have been extracted from environmental samples using an HNADESs. Thus, prior to the validation and application of the methodology, an optimisation of those factors influencing the extraction efficiency, such as HNADES molar ratio and volume, as well as sample pH was developed. All experiments were performed in duplicate using Milli-Q water to avoid the possible influence of co-extracted matrix components. Hence, 10 mL of Milli-Q water spiked with the target analytes at a concentration of 100 $\mu\text{g/L}$ of each compound was employed.

Other parameters such as ionic strength (NaCl 0–15%, w/v) and the use of a dispersant solvent (ACN and methanol) were also evaluated. However, the obtained results showed that there are no significant improvements in efficiency or reproducibility of the extraction procedure when those were modified. Therefore, ionic strength was not modified and dispersant was not used, which reduce the use of additional toxic organic solvents, increasing the green character of the methodology.

Selection of HNADES molar ratio

The molar ratio thymol to menthol will play an important role in HNADES stability and physicochemical properties and, therefore, in its extraction capacity favouring or limiting the solubility of the target analytes in the solvent [22]. Hence, the extraction efficiencies of three different molar ratios of thymol:menthol HNADESs (i.e., 1:1, 1:2, and 2:1) were evaluated while the rest of conditions remained identical (10 mL of Milli-Q water at pH 6 and 100 μL of thymol:menthol HNADES). As can be seen in Fig. 1, molar ratio of 2:1 provided the best results for most of analytes, whereas decreasing the ratio of thymol produces a general decrease in the recovery values. This fact could be explained because an increase in the amount of thymol increases the number of hydrogen bond donors and, therefore, a greater number of interactions with the oxygenated groups of PAEs and DEHA [23]. Likewise, π - π interactions between the aromatic rings of thymol and PAEs are favoured since its phenolic character could boost the solubility of PAEs, as aromatic compounds.

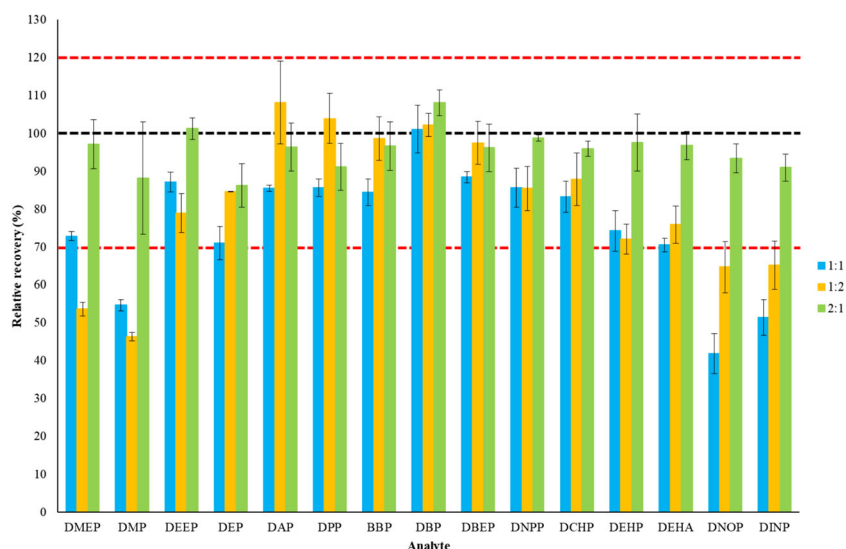
Selection of sample pH

The pH of sample solution can be a critical aspect in the transfer of organic compounds from the aqueous phase to the extraction organic phase [24]. Despite that PAEs and DEHA are not ionisable compounds (there is not pKa values established for these compounds), sample pH can influence the different interactions between analytes and HDES and, therefore, the extraction performance [25]. In this way, the effect of this parameter on the efficiency of the extraction was evaluated in the range 2–10, maintaining the rest of parameters unchanged: 10 mL of Milli-Q water and 100 μL of thymol:menthol 2:1, as extraction solvent. As can be seen in Fig. S3 (see ESM), no significant differences were found, except for DMP to which a decrease of the recovery was observed with pH increase. However, pH 8 was established as the most suitable value since it presented lower relative standard deviation (RSD) values with recovery values around 100%. In addition, it implied less modification of the initial conditions of sample and, therefore, a shorter preparation time.

Selection of HNADES volume

In LLME procedures, the volume of extraction solvent has a key role. The volume of extraction solvent delimits the amount of fine microdroplets formed, which is closely linked to the mass transfer of target analytes from the aqueous to the organic phase, and thus the extraction efficiency. Besides, it has an important effect on the preconcentration/dilution effect [10, 26]. Thus, the volume of HNADES was evaluated in the range 50–150 μL (every 25 μL). The results showed that

Fig. 1 Effect of thymol:menthol HNADES composition on the extraction efficiency of the target analytes after the application of the LLME procedure. Extraction conditions: 10 mL of spiked Milli-Q water at pH 6 and 100 μL of thymol:menthol. Injected concentration of target analytes and surrogates: 100 $\mu\text{g/L}$

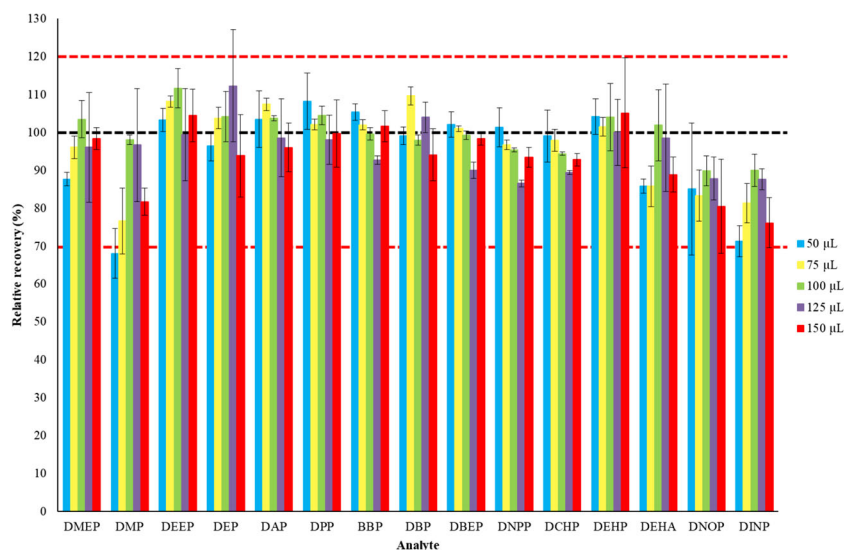


100 μL was found adequate to obtain an efficient extraction of the target analytes (see Fig. 2).

LLME-UHPLC-QqQ-MS/MS validation

The ubiquitous presence of phthalates in the laboratory environment as a consequence of the extended use of plastic materials, due to its low cost and versatility, is widely known. Even high-purity solvents, and separation and detection systems are important sources of contamination, giving rise to an important background signal that makes difficult the correct determination of these compounds [27]. Based on that, laboratory blanks of Milli-Q water were daily analysed to avoid obtaining biased results. Furthermore, blank samples were also analysed finding the presence of DEP, DBP, DEHP, and DEHA in all studied matrices. Consequently, to perform a fit for purpose validation, the peak areas of the analytes were subtracted when necessary.

Fig. 2 Effect of HNADES volume on the extraction efficiency of the target analytes after the application of the LLME procedure. Extraction conditions: 10 mL of spiked Milli-Q water at pH 8 and thymol:menthol 2:1. Injected concentration of target analytes and surrogates: 100 $\mu\text{g/L}$



Considering that this work constitutes the first application of a HNADES for the extraction of PAEs and DEHA from environmental samples, a thorough validation of the procedure, in terms of matrix effect (ME), linearity, extraction efficiency, reproducibility, and sensitivity, was carried out. DBP- d_4 was used as surrogate for DMEP, DMP, DEEP, DEP, DAP, DPP, BBP, DBP, DBEP, DNPP, and DCHP, while DHP- d_4 was applied for DEHP, DEHA, DNOP, and DINP, because of their similar behaviour to the compounds evaluated. With the aim of correcting the possible errors during the analytical procedure and improving the reproducibility of the method, surrogates were spiked at the beginning of the whole methodology [28].

Based on the influence of matrix components on the MS signal, by a suppression or enhancement effect [29], an ME study was performed at three concentration levels (low level: 2.5 $\mu\text{g/L}$, intermediate level: 125.0 $\mu\text{g/L}$, high level: 187.5 $\mu\text{g/L}$), using the Matuszewski method [30]. In this

way, five extractions were carried out by spiking each matrix at the indicated concentrations at the end of the extraction procedure. ME was calculated as the percentage of ratio areas between the spiked sample and a standard solvent at the same concentration level. As can be seen in Table S2 (see ESM), while DMEP, DMP, DPP, BBP, DBEP, and DEHP showed low or moderate signal suppression in one or more of matrices, low or moderate enhancement of the signal was observed for most of compounds, except for DEP and DAP in all types of samples and DEEP and DPP in runoff and pond which present high increase of the signal due to the possible competition between analytes and co-extracted matrix components during ionisation process [31–34].

Taking into account the widespread environmental presence of PAEs in the matrices evaluated and the results obtained from the ME study, matrix-matched calibration curves for each matrix were obtained by injecting seven different concentration levels ($n = 7$) in triplicate with the aim of studying the linearity of the developed methodology in the range of concentration of interest. As shown in Table S3 (see ESM), adequate R^2 values, higher than 0.9954, were obtained for all phthalates and DEHA and matrices.

To assess the extraction efficiency of the methodology, a recovery study was developed for all samples comparing the peak areas obtained when matrices were spiked at three levels of concentration at the beginning and at end of the procedure (low level: 2.5 $\mu\text{g/L}$, intermediate level: 125.0 $\mu\text{g/L}$, high level: 187.5 $\mu\text{g/L}$) by the extraction of five replicates at each level. As can be seen in Table 1, the obtained results showed a good efficiency and reproducibility of the extraction procedure, with relative recovery values in the range 74–118% for treated wastewater, 77–127% for runoff water, and 70–114% for pond water, and ruggedness with RSD values lower than 14% in all cases. Limits of quantification (LOQs) of the method, calculated as the lowest matrix-matched calibration concentration which provided a signal-to-noise ratio higher than 10 for the quantification transition and at least 3 for the confirmation transition, and taking into account the recovery of the method and the preconcentration/dilution factor, were also obtained. Values ranged between 0.042 and 0.425 $\mu\text{g/L}$ for treated wastewater, between 0.015 and 0.386 $\mu\text{g/L}$ for runoff water, and between 0.013 and 0.376 $\mu\text{g/L}$ for pond water (see Table 1), which demonstrate the good sensitivity achieved with the developed HNADES-based LLME-UHPLC-QqQ-MS/MS method.

Water quality assessment and occurrence of plastic migrants

Once the whole methodology was successfully validated, a group of 18 real samples were analysed using the developed LLME-UHPLC-QqQ-MS/MS method, with the aim of determining the concentration levels of the studied PAEs and

DEHA in environmental water samples from Tenerife and Gran Canaria: six treated wastewater samples (TWW1–TWW6), five runoff waters (RW1–RW5), and seven pond water samples (PW1–PW7). As shown in Table 2, seven of the studied PAEs were found in some of the analysed samples (DEP, DAP, DPP, BBP, DBP, DCHP, and DEHP). The presence of DEP, BBP, DBP, DCHP, and DEHP (see Fig. 3) is especially remarkable since the last four are included in the Appendix 6 of the Regulation No. 1907/2006 as toxic for reproduction (category 1B) [3]. In addition, DEP, BBP, DBP, and DEHP are also classified as toxic and Priority Pollutants under the Clean Water Act [6], as well as in the US EPA Phthalate Action Plan (BBP, DBP, and DNOP) due to their prevalence in the environment, widespread use, human exposure, and toxicity [7], and BBP, DBP, DCHP, and DEHP are designated as High-Priority Chemical Substances under the Toxic Substances Control Act [5], both of the US EPA.

Taking into account that in previously studies in which DESs were applied for the determination of PAEs in water samples only bottled and tap waters were analysed, the results obtained in this study were compared with others previously published, using other extraction procedures, in which similar matrices were evaluated. Regarding treated wastewater, a temporary dependence of the levels was found in these samples, which were taken in different time periods (November 2019, May 2020, June 2020, and July 2020). Considering the state of quarantine caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) pandemic, decreed in Spain in March 2020, and specifically in the Canary Islands, it seems that the concentrations found in the periods that included the quarantine time, the concentrations of PAEs dropped as a consequence of the decrease in human activity, such as tourism which represents the most important economic sector in the Canary Islands (TW2 and TW3). In the same way, the concentrations increase, reaching values close to 2700 ng/L for DBP as of mid-July 2020 (TWW5), which could be associated with an activity increase due to the return to work and leisure activities, as well as the opening of international means of transport.

The main mechanisms by which PAEs are eliminated using a membrane bioreactor in treated waters are adsorption and metabolic degradation processes, taking advantage of the retention of suspended solids and membrane (ultra)filtration to eliminate contaminants. However, depending on their molecular weight, they are easier to biodegrade or to absorb into suspended matter. Therefore, the procedure used in the purification plants could be crucial to reduce or eliminate PAEs from wastewater samples [35]. According to the last reports of the European Union, removals higher than 90% could be achieved in sewage treatment plants for BBP, DBP, and DEHP [36–38], although the bibliographic data shows different efficiency values depending on the treatment applied.

Table 1 Results of the recovery study of the LLME-UHPLC-QqQ-MS/MS method for the selected compounds in water matrices at three levels of concentration

Analyte	Type of sample	Relative recovery %			LOQ _{method} ^d (µg/L)
		Level 1 ^a (n=5) (RSD, %)	Level 2 ^b (n=5) (RSD, %)	Level 3 ^c (n=5) (RSD, %)	
DMEP	Treated wastewater	101 (10)	101 (10)	105 (8)	0.044
	Runoff water	100 (12)	101 (11)	105 (4)	0.017
	Pond water	98 (7)	101 (9)	87 (4)	0.034
DMP	Treated wastewater	88 (8)	92 (10)	92 (8)	0.203
	Runoff water	88 (10)	90 (11)	83 (3)	0.049
	Pond water	72 (7)	78 (8)	70 (3)	0.018
DEEP	Treated wastewater	113 (8)	108 (9)	110 (7)	0.042
	Runoff water	116 (7)	114 (8)	120 (3)	0.015
	Pond water	108 (8)	114 (9)	96 (4)	0.030
DEP	Treated wastewater	113 (12)	104 (9)	106 (6)	0.044
	Runoff water	77 (9)	112 (8)	105 (2)	0.045
	Pond water	79 (7)	96 (7)	84 (3)	0.074
DAP	Treated wastewater	106 (13)	108 (7)	107 (1)	0.042
	Runoff water	107 (6)	119 (4)	115 (3)	0.015
	Pond water	97 (6)	99 (4)	88 (3)	0.014
DPP	Treated wastewater	107 (7)	105 (4)	107 (2)	0.043
	Runoff water	107 (6)	119 (1)	112 (4)	0.016
	Pond water	98 (4)	98 (3)	88 (2)	0.014
BBP	Treated wastewater	107 (5)	98 (3)	107 (1)	0.086
	Runoff water	109 (3)	123 (1)	119 (3)	0.036
	Pond water	101 (2)	100 (3)	92 (3)	0.013
DBP	Treated wastewater	118 (12)	102 (5)	105 (2)	0.085
	Runoff water	100 (3)	125 (1)	108 (3)	0.040
	Pond water	77 (9)	93 (3)	88 (2)	0.376
DBEP	Treated wastewater	112 (5)	101 (3)	106 (1)	0.425
	Runoff water	116 (2)	125 (1)	125 (3)	0.072
	Pond water	105 (3)	104 (4)	99 (5)	0.126
DNPP	Treated wastewater	111 (4)	100 (10)	104 (3)	0.087
	Runoff water	109 (3)	127 (1)	126 (2)	0.036
	Pond water	104 (3)	100 (4)	95 (3)	0.033
DCHP	Treated wastewater	110 (7)	98 (4)	103 (2)	0.088
	Runoff water	100 (3)	124 (1)	123 (1)	0.038
	Pond water	108 (3)	101 (4)	95 (3)	0.032
DEHP	Treated wastewater	86 (6)	109 (8)	87 (7)	0.049
	Runoff water	117 (5)	95 (4)	87 (4)	0.075
	Pond water	73 (5)	80 (5)	85 (6)	0.074
DEHA	Treated wastewater	75 (6)	109 (10)	89 (11)	0.051
	Runoff water	110 (6)	99 (7)	97 (3)	0.073
	Pond water	74 (6)	75 (3)	82 (3)	0.076
DNOP	Treated wastewater	74 (14)	105 (7)	88 (8)	0.209
	Runoff water	94 (13)	91 (3)	98 (6)	0.041
	Pond water	104 (8)	87 (8)	84 (3)	0.064
DINP	Treated wastewater	86 (8)	73 (3)	84 (5)	0.204
	Runoff water	99 (13)	97 (6)	97 (5)	0.386
	Pond water	97 (8)	86 (10)	80 (3)	0.135

Concentration of the target analytes was ^a 2.5 µg/L; ^b 125.0 µg/L; ^c 187.5 µg/L. ^d Defined as the lowest matrix-matched calibration concentration which provides a signal-to-noise ratio higher than 10 for the quantification transition and at least 3 for the confirmation transition taking into account the preconcentration/dilution factors as well as the recovery values of the method

These facts may explain that the concentrations found in the treated wastewater samples analysed were not as high as might be expected in this type of sample. If the results obtained are compared with other previously developed studies in which effluent samples were analysed, it can be corroborated that the concentrations found are far below. In this regard, Gao et al. [39] found DEP, DBP, BBP, and DEHP, among other PAEs, at concentrations ranging between 1.11 and 25.4 µg/L, whereas the concentrations found in the samples analysed in

this work were much lower (0.120–3.414 µg/L). Another example is the work carried out by Clara et al. [40], in which DEP, DBP, BBP, and DEHP were found at concentrations in the range 0.083–6.6 µg/L. These values were very similar with those obtained by Gani et al. [41] in North India, who found DEP, DBP, BBP, and DEHP in 15 effluents at mean concentrations of 1.555 to 4.864 µg/L. Al-Saleh et al. [42] analysed 114 samples of five wastewater treatment plants in three major Saudi cities. DEP, DBP, BBP, and DEHP were

found at mean concentrations in the range 0.182–0.748 µg/L. The values obtained are in the same range to the ones found in this work, in contrast with the studies of Clara and Gani, in which higher concentrations of the analytes were found.

Regarding the pond waters, the samples stored in plastic ponds, despite even being from different Islands (PW2 and PW6), showed the same trend, in which all the analytes detected are at very similar levels of concentrations (116.1–358.0 ng/L), with the exception of DBP (1974.4 ng/L and 1035.8 ng/L, respectively). In contrast, those samples from open-cement ponds (PW3 and PW5) presented very different concentrations of PAEs. This may be because one of them (PW3) is supplied with rainwater, while the other (PW5) is supplied with water by a Gran Canaria dam transported through PVC pipes over approximately 12 km. It contained very high concentration levels of DEP and DBP. What does seem to stand out is that the first sample is the one with the highest concentration of DEHP (1083.0 ng/L), despite being stored on a pond made of cement. However, it can also be influenced to a greater extent by wind and rain and, therefore, by human activities and their waste. Likewise, it seems remarkable that the highest concentrations of DEP, not only in pond water but also in all the samples analysed, were found in a pond water sample from an open-cement pond (PW5), and a pond water sample from a polyester fibre glass tank (PW7) (1536.5 ng/L and 1539.6 ng/L,

respectively), both from the island of Gran Canaria. Another important aspect is the fact that DAP is presented in three pond water samples (PW2, PW5, and PW7). This could be related to one of the tanks which is made of plastic, the other is supplied through PVC pipes, and the last one is made of fibreglass-reinforced polyester.

If data obtained from pond water analysis are compared with previous one, DBP has been found in other works in a wide range of concentrations (0.226–112.4 µg/L) [14, 43–45]. DEP was found by He et al. [43] at 0.25 µg/L, while DPP and BBP were found by Santana-Mayor et al. [14] at concentrations of 35 ng/L and 16 ng/L, respectively. These values are lower than those obtained in the present study. Only the work carried out by Ye et al. [44] quantified DEHP at a concentration of 31.2 µg/L, which is a much higher value than the reference values and the indications of the different international organisations.

Regarding runoff water samples, only DBP, at concentrations between 105.2 and 1156.7 ng/L, and DEHP in the runoff water sample stored in a plastic tank (142.0 ng/L) were quantified. Likewise, DEP, BBP, and DCHP were found in some of them at concentrations below the LOQs of the method (45 ng/L, 36 ng/L, and 38 ng/L, respectively). These values agree with those previously obtained by Rodríguez-Ramos et al. [46], in which samples of agricultural soils from crop

Table 2 Results of the analysis of different environmental water samples using the developed LLME-UHPLC-QqQ-MS/MS method

Sample	Analyte concentration ± confidence interval (ng/L) ^a						
	DEP	DAP	DPP	BBP	DBP	DCHP	DEHP
TWW1	122.6±0.8	n.d.	n.d.	n.d.	619.9±0.4	n.d.	< LOQ
TWW2	< LOQ	n.d.	n.d.	n.d.	< LOQ	n.d.	< LOQ
TWW3	< LOQ	n.d.	n.d.	n.d.	< LOQ	n.d.	< LOQ
TWW4	130.1±0.8	n.d.	n.d.	< LOQ	674.9±0.4	< LOQ	< LOQ
TWW5	387.1±0.7	n.d.	n.d.	n.d.	2692.4±0.4	n.d.	< LOQ
TWW6	127.1±0.8	n.d.	n.d.	n.d.	< LOQ	< LOQ	3414±1
RW1	< LOQ	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ
RW2	< LOQ	n.d.	n.d.	n.d.	105.2±0.3	< LOQ	< LOQ
RW3	< LOQ	n.d.	n.d.	< LOQ	1156.7±0.3	< LOQ	< LOQ
RW4	< LOQ	n.d.	n.d.	n.d.	938.1±0.3	n.d.	< LOQ
RW5	< LOQ	n.d.	n.d.	< LOQ	304.6±0.3	< LOQ	142.0±0.7
PW1	< LOQ	n.d.	n.d.	< LOQ	811.7±0.3	207.4±0.4	229.6±0.6
PW2	263.9±0.7	152.6±0.3	143.0±0.5	116.1±0.4	1974.4±0.3	211.2±0.4	< LOQ
PW3	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	1083.0±0.6
PW4	177.6±0.8	n.d.	n.d.	n.d.	1227.7±0.3	211.3±0.4	< LOQ
PW5	1536.5±0.7	151.1±0.3	n.d.	< LOQ	1736.2±0.3	206.4±0.4	< LOQ
PW6	358.0±0.7	n.d.	n.d.	120.0±0.4	1035.8±0.3	215.4±0.4	< LOQ
PW7	1539.6±0.7	153.8±0.3	n.d.	111.0±0.4	660.6±0.3	213.9±0.4	< LOQ

n.d., not detected. TWW1–TWW6: treated wastewater samples. RW1, RW3–5: rainwater runoff samples; RW2: underground gallery runoff sample. PW1: metallic tank pond water sample; PW2 and PW6: plastic tank pond water samples; PW3 and PW5: open-cement tank pond water samples; PW4: close-cement tank pond water sample. ^a Results obtained as an average of three analyses for each sample

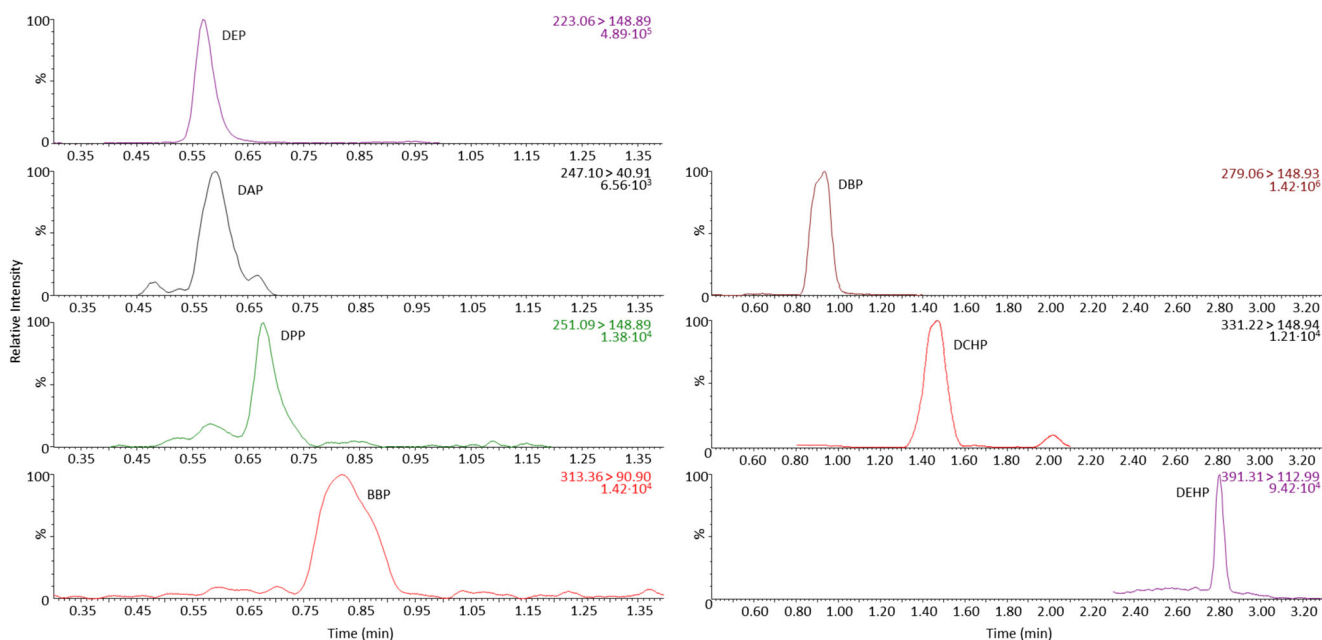


Fig. 3 UHPLC-QqQ-MS/MS chromatograms of PAEs found in a pond water sample stored in a plastic tank (PW2). Concentration of analytes: 263.9 ± 0.7 ng/L for DEP, 152.6 ± 0.3 ng/L for DAP, 143.0 ± 0.5 ng/L for

DPP, 116.1 ± 0.4 ng/L for BBP, 1974.4 ± 0.3 ng/L for DBP, 211.2 ± 0.4 ng/L for DCHP, and lower than 0.074 ng/L for DEHP

areas of Tenerife were analysed. In these samples, DEP and DCHP were found at concentrations below their LOQ of the method ($0.63 \mu\text{g}/\text{kg dw}$ and $0.14 \mu\text{g}/\text{kg dw}$, respectively), while BBP was quantified at $5 \mu\text{g}/\text{kg dw}$. DBP, for its part, was quantified between 9 and $52 \mu\text{g}/\text{kg dw}$. It is noteworthy that the underground gallery runoff water sample (RW2) presented lower concentration levels of PAEs, compared to a rainwater runoff (RW3) from the same area. This fact can be explained because the rock that makes up the structure of the gallery can filter the surface water, thus improving its quality. All these runoff water samples, except the one stored in a plastic tank, are found in areas with high agricultural activity. Therefore, the high concentration at which some PAEs, such as DBP, have been found (1156.7 ng/L for RW3 and 938.1 ng/L for RW4) is not surprising. In addition, RW5 is the only runoff water sample in which DEHP has been quantified (142.0 ng/L) which can be attributed to the material of the container in which the sample was preserved. Taking into account that no works have been found in which rainwater runoff has been analysed, and that the evaluated runoff waters were mostly urban, the results obtained for these samples have been compared with those works in which rainwater samples were analysed. Teil et al. [47] evaluated the atmospheric fate of PAEs in an urban area in Paris (France), Fernández-Amado et al. [48] in sub-urban area of A Coruña (Spain), and Polyakova et al. [49] in rainwater samples from the southwest of Moscow (Russia), finding the presence of DEP, BBP, DBP, and DEHP at concentration values between 0.081 and $189 \mu\text{g}/\text{L}$. In general terms, the concentrations at which PAEs were presented in these samples are much higher

than the ones found in this work (0.105 – $1.157 \mu\text{g}/\text{L}$). The difference in concentrations with respect to the analysed runoff water samples is very clear, except for DBP, with an occurrence range 0.029 – $7.600 \mu\text{g}/\text{L}$ compared to 0.105 – $1.157 \mu\text{g}/\text{L}$ in this study.

In general, the concentration values obtained for DEHP are well below the permissible limits established by the US EPA of $6.0 \mu\text{g}/\text{L}$ [8] and by the WHO of $8 \mu\text{g}/\text{L}$ [9] for drinking water. Likewise, in particular for wastewater samples, the quantified value is above the maximum annual average established by the European Union [4] on environmental quality standards in the field of water policy for priority substances ($1.3 \mu\text{g}/\text{L}$).

Comparison with other methods

The main aspects of the developed method performance were compared with those in which alternative solvents were employed for the extraction of plastic migrants from water matrices (Table 3). In this regard, the LOQ values obtained in the present work are much lower than those obtained in previous works in which the evaluation of PAEs and/or DEHA in water samples was carried out using DESs [50] or ILs [51–55]. Only the approaches developed by Mogaddam et al. [56] and Mirzajani et al. [57], in which polyethylene-packed injection solutions and mineral water were analysed, respectively, obtained LOQs in the same order. In the first case, $65 \mu\text{L}$ of menthol:decanoic acid 1:2 HNADES was applied in a microwave (MWA) and air-assisted (AA)-LLME of 5 mL of sample solution prior to GC-MS for the determination of three PAEs

Table 3 Comparison of the HNADES-LLME-UHPLC-QqQ-MS/MS method with others previously applied for the determination of plastic migrants from water samples

Analytes	Sample (amount)	Extraction method (time)	Analytical technique (run time)	Solvent (volume)	Linear range ($\mu\text{g/L}$)	Recovery (RSD %) ^b	LOQ ($\mu\text{g/L}$)	Reference
9 PAEs	Tap and mineral water (20 mL)	DLLME (16 min)	HPLC-UV (31 min)	L-Menthol:acetic acid (1:1 ^a ; 100 μL)	4–425	71–120 (20%)	3.6–22	[50]
4 PAEs	River, lake, and reservoir water (8 mL)	SFOD-LLME (2 h)	HPLC-VWD (22 min)	[TBDP][BF ₄] (60 μL)	5–500	73–95 (8%)	0.27–1.1 ^c	[51]
5 PAEs	Mineral and soda water (3 mL)	MWA-DLLME (6 min)	HPLC-UV/Visible (25 min)	[BMIM][PF ₆] (100 μL)	16.5–238	85–103 (6%)	2.37–6.46	[52]
3 PAEs	Tap, mineral, and river water (5 mL)	TC-DLLME (13 min)	HPLC-VWD (20 min)	[OMIM][PF ₆] (32 μL)	2–100	90–99 (8%)	0.68–1.36 ^c	[53]
2 PAEs	Melted snow, tap, lake, and sewage water (10 mL)	TC-LLME (50 min)	HPLC-DAD (25 min)	[OMIM][PF ₆] (40 μL)	1–100	86–103 (6%)	0.23–0.47 ^c	[54]
4 PAEs	Tap, lake, and treated wastewater (10 mL)	DLLME (10 min)	HPLC-UV (20 min)	[OMIM][PF ₆] (80 μL)	50–600	83–92 (5%)	10.6–28.5	[55]
4 PAEs and BPA	Medical injection solutions (5 mL)	SFOD-MWA-AA-LLME (-)	GC-MS (30 min)	Menthol:decanoic acid (1:2 ^a ; 65 μL)	0.047–200	79–94 (6%)	0.047–0.110	[56]
4 PAEs	Mineral water (10 mL)	HF-SPME (30 min)	GC-FID (20 min)	ChCl:glycerol (2:1, w/v; 100 μL)	0.01–1000	96–100 (4%)	0.028–0.12	[57]
14 PAEs and DEHA	Treated wastewater, runoff and pond water (10 mL)	LLME (11 min)	UHPLC-MS/MS (3.5 min)	MOF-DES/MIP Thymol:menthol (2:1 ^a ; 100 μL)	0.100–250	70–127 (14%)	0.013–0.425	This work

[BMIM][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [OMIM][PF₆], 1-octyl-3-methylimidazolium hexafluorophosphate; [TBDP][BF₄], tributyldecylphosphonium tetrafluoroborate; AA, air-assisted; BPA, bisphenol A; ChCl, choline chloride; DAD, diode-array detector; DEHA, bis-(2-ethylhexyl) adipate; DLLME, dispersive liquid-liquid microextraction; FID, flame ionisation detector; GC, gas chromatography; HF, hollow fibre; HPLC, high-performance liquid chromatography; LLME, liquid-liquid microextraction; LOQ, limit of quantification; MIP, molecularly imprinted polymer; MOF, metal-organic framework; MS/MS, tandem mass spectrometry; MWA, microwave-assisted; PAE, phthalic acid ester; SFOD, solidified floating organic droplet; TC, temperature-controlled; UHPLC, ultra-high-performance liquid chromatography; UV, ultraviolet detector; VWD, variable wavelength detector. ^a Molar ratio. ^b Maximum relative standard deviation (RSD %). ^c Limit of detection

(DEP, DBP, DEHP), DEHA, and bisphenol A (BPA). In the second case, a hollow fibre (HF) and a monolithic fibre based on metal-organic framework (MOF) (UMCM-1)-DES (choline chloride (ChCl):glycerol 2:1 (w/v))/molecularly imprinted polymers (MIPs), in which DES was used as substrate for MOFs, were employed for the extraction of four phthalates (DMP, DEP, DIBP, DBP), and determination by GC-flame-ionisation detector (FID). In addition, a reduced number of PAEs were evaluated in these previous studies highlighting not only the difficulty of coupling DES to chromatographic systems [21, 58] but also the limitations of the use of conventional detection systems such as diode-array detector (DAD), ultraviolet detector (UV), or FID with the characteristic chromatographic bands associated with DESs. Another important advantage of the developed method is the extraction time since only two works achieved a slightly lower extraction time but requiring additional assistance like microwave [52], cooling in an ice-bath [55], or as in the case of Zhang et al. [53], the control of temperature. In line with this, the analysis time employed is the shortest one, taking advantage of the combination of UHPLC with MS/MS which provides not only a selective and sensitive determination, but also a fast chromatographic performance.

Apart from that, an important aspect that need to be consider when novel and sustainable methodologies are proposed in the literature should be highlighted, especially for the evaluation of environmental samples due to the complexity of this kind of matrices. The use of adequate surrogates or instrumental internal standards that guarantee the reliability of the obtained data should be considered. In this sense, the use of isotopically deuterated compounds is preferred since the application of other PAEs, which although are not included into the target selected compounds, have been demonstrated to be in the evaluated samples [59–61] as occur in the works of Ortega-Zamora et al. [50] and Mogaddam et al. [56], which could pose serious doubts on the reliability of the obtained results. This practice is especially questionable when, in addition, the selected surrogates are also classified as toxic substances and priority pollutants with prevalence in the environment [3, 5–7].

This work constitutes a very simple method that does not entail any modification of the initial conditions of the samples, including pH or temperature, in contrast to others such as that of Ortega-Zamora et al. [50], Mogaddam et al. [56], or Mirzajani et al. [57]. Moreover, the high water stability of the thymol:menthol HNADES employed [18] in contrast to other DES previously applied for the evaluation of aqueous matrices has been demonstrated [50].

Finally, in economic terms, compared with other methodologies in which ILs or complex sorbents were prepared, the proposed extraction methodology highlights for its very inexpensive performance. With only 4.50€, 100 samples can be analysed (less than 5 euro cents per sample).

Conclusions

In this study, an analytical method based on a non-ionic HNADES (thymol:menthol) LLME procedure combined with UHPLC-QqQ-MS/MS for the evaluation of 14 PAEs and one adipate (DEHA) in water samples of environmental concern (treated wastewater, runoff water, and pond water) has been developed for the first time. The whole methodology was thoroughly validated in terms of matrix effect, linearity, extraction capacity, and sensitivity, with excellent results. Good linearity was obtained in all cases (R^2 higher than 0.9954), while recovery values were in the range 70–127% with RSDs lower than 14% in all studied matrices. LOQs of the method were found in the range 0.013–0.425 µg/L for all samples and analytes which demonstrated the good sensitivity of the procedure despite the need of diluting the final extract to assure the good performance of the UHPLC-QqQ-MS/MS analysis.

The combination of thymol:menthol as green extraction solvent together with UHPLC-MS/MS analysis allows the determination of organic contaminants of highly concern, such as PAEs or DEHA, at very low concentration levels in a single run. In this regard, an interesting and sustainable alternative extraction technique has been proposed and offers a smart, simple, fast, inexpensive, effective, and safe alternative. In addition, it allows the use of very low volumes of a biocompatible solvent to achieve excellent results in terms of extraction efficiency and sensitivity. Finally, the methodology was applied to the analysis of treated wastewater, runoff water, and pond water samples from Tenerife and Gran Canaria, finding the presence of DEP, DAP, DPP, BBP, DBP, DCHP, and DEHP in some on the evaluated matrices, in the range 105.2–3414 ng/L. The proposed method constitutes a good green approach that fulfils the main principles of Green Analytical Chemistry, for the analysis of highly concern compounds in aqueous environments.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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