Volume 17
Number 44
28 November 2025
Pages 8839–9052

Analytical Methods

rsc.li/methods

ISSN 1759-9679

ROYAL SOCIETY
OF **CHEMISTRY**

PAPER
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Cite this: *Anal. Methods*, 2025, **17**, 8877

Demonstrating the application of a liquid chromatography-mass spectrometry method for the determination of phthalate diesters in complex solid and liquid environmental samples

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Received 24th June 2025
Accepted 25th September 2025

DOI: 10.1039/d5ay01057h

rsc.li/methods

Phthalate diesters are ubiquitous contaminants of concern, yet their reliable determination in complex environmental matrices remains analytically challenging due to low environmental concentrations, matrix interferences, and widespread background contamination. Here, we present a robust LC-MS/MS workflow for the simultaneous quantification of eleven low- and high-molecular weight phthalates across four contrasting matrices: surface water, landfill leachate, soils, and municipal solid wastes. Sample preparation was streamlined using ultrasonication or filtration followed by solid-phase extraction (SPE), providing recoveries of 70–98% without the need for derivatisation. The method delivered sub-ng L^{-1} detection limits (as low as 0.2 ng L^{-1}) and high reproducibility (RSD <5%), while integrated contamination-control strategies, including delay columns and phthalate-free materials, enabled reliable trace analysis. Systematic evaluation of matrix effects confirmed robustness across diverse environmental samples. This method combines sensitivity, selectivity, and broad applicability, offering a practical platform for routine environmental monitoring of phthalates at trace levels.

Introduction

Phthalate esters (PAEs) are a class of synthetic organic compounds widely used as plasticizers to enhance the flexibility, durability, and workability of polymers, particularly polyvinyl chloride (PVC).[1] Due to their lack of covalent bonding to polymer matrices, PAEs can leach into the environment throughout the product life cycle, leading to their ubiquitous presence in various environmental compartments.[2,3] These compounds have been detected in surface waters, soils, sediments, landfill leachates, and municipal wastes,[4–7] as well as in consumer products such as food packaging, medical devices, and cosmetics.[8–11] Concerns over the health impacts of phthalates have grown significantly, as several PAEs are known or suspected endocrine disruptors capable of affecting hormonal balance and reproductive development. Evidence from animal studies suggests that phthalates can interfere with hormone production, particularly testosterone, leading to developmental issues in male offspring.[12] Recent studies highlight the widespread health impacts of phthalate exposure. Consistent associations have been found between phthalates and decreased sperm quality, ADHD symptoms in children, and altered neurodevelopment.[13] There is moderate to robust evidence linking phthalates to reduced anogenital distance in boys, low birthweight, endometriosis, and various cancers.[14] Phthalates can adversely affect the endocrine system, pregnancy outcomes, and child development,[15] and have also been increasingly implicated in cardiac risk.[16] Research also indicates phthalate-related alterations in placental morphology, hormone production, and vascularization, which may lead to complications like preterm birth and intrauterine growth restriction.[17] Despite regulations in some countries, more widespread measures are needed to reduce public exposure to phthalates. Regulatory actions have been taken to limit or ban certain phthalates such as benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP), di-*n*-octyl phthalate (DnOP), and diisodecyl phthalate (DiDP) due to their demonstrated toxicity.[18–20] However, replacement plasticizers introduced to comply with these regulations—often higher molecular weight phthalates—have not been as extensively studied and may pose similar risks.[2,20] The continued commercial use of both legacy and substitute phthalates underscores the need for comprehensive environmental monitoring tools that can simultaneously detect a broad range of PAEs.

Environmental monitoring of phthalates is analytically challenging due to their wide range of physicochemical properties, low environmental concentrations, and high risk of background contamination introduced *via* laboratory consumables and ambient sources.[5,21,22] Moreover, the partitioning

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behaviour of phthalates is influenced by molecular weight, with low molecular weight PAEs more often found in aqueous environments and high molecular weight PAEs tending to sorb to solids and sediments.[23,24] Given these matrix-specific behaviours and contamination risks, analytical workflows must be carefully designed to ensure reliable quantification across diverse environmental samples.[25,26]

Liquid–liquid extraction (LLE) has historically been employed in phthalate analysis for its simplicity, but it requires large volumes of phthalate-free solvents and is prone to contamination through additional glassware and processing steps.[21,22] More recently, solid-phase extraction (SPE) combined with liquid chromatography – mass spectrometry (LC-MS) has emerged as a preferred approach, offering improved sensitivity, selectivity, and adaptability to different sample matrices.[11,27,28] LC-MS methods also eliminate the need for derivatization – required in gas chromatography-based approaches – making them especially suitable for polar or thermally labile phthalates.[5,29]

Despite these advances, existing LC-MS/MS methods are typically restricted to either aqueous samples or limited analyte panels, and few simultaneously capture both low and high molecular weight phthalates in diverse matrices. To our knowledge, this is the first study to demonstrate a validated workflow for the simultaneous quantification of eleven phthalate diesters, including both legacy compounds and emerging replacements such as DiNP, DiDP, and DiPP, across liquid (surface water, landfill leachate) and solid (soil, municipal waste) matrices. Importantly, this work also introduces robust contamination-resilient features, such as instrument modifications, delay column integration, and systematic use of procedural blanks, which directly address the pervasive challenge of background phthalates in LC-MS/MS analysis. This study addresses that gap by presenting a robust LC-MS/MS method, coupled with matrix-specific SPE and ultrasonication protocols, for the sensitive and reliable quantification of eleven phthalate diesters in surface water, soil, landfill leachate, and municipal waste samples. The method incorporates comprehensive contamination control strategies and internal standard calibration to ensure high analytical confidence across complex and variable sample types.

Results and discussion

Quality control

The sourcing of solvents was carefully controlled, with Thermo Fisher Optima™ LC-MS grade solvents selected after preliminary trials revealed that alternative solvents, including those recommended in EPA Method 3535 A (*e.g.*, dichloromethane and acetone), introduced unacceptable levels of phthalate contamination. Optima™ solvents consistently yielded the lowest background levels, which was critical for accurate quantification given the ubiquity of phthalates and their susceptibility to trace contamination. However, phthalate contamination was still present in the analytical blanks, and it was hypothesised that the tubing and instrumental fittings were contributing to the phthalate background levels. A delay column was introduced, allowing any contaminant phthalates to elute at an alternate retention time. It was found that injector and column carry over was a major source of phthalate contamination in the analytical blank as the delay column removes instrumental contamination, a comparable finding to that of[30] for analysis of phthalates in wine, although the LOD/LOQ were three orders of magnitude higher than those in this study. A multi-wash system was used to reduce carry over from the needle and three analytical blanks were run between samples to ensure carry over from the column was removed. No peaks above LOD were detected in analytical blanks throughout all sample analysis. For each sample batch extracted by SPE, three procedural blanks were run to determine the amount of phthalate that was coming from background lab contamination. All procedural blanks were then subtracted from the sample to get the true environmental concentration. DBP, DiBP and DMP were found at the highest concentrations in the procedural blanks of all samples. All phthalates were detected within the blanks over the course of analysis, although the newer replacement phthalates like DiPP, DPP and DHP were often not detected. The vast majority of LC-MS methods[31–34] for phthalate detection do not incorporate a delay or hold-back column, which calls into question the issue of instrumental contamination.[35]

Fig. 1 shows an overlay illustrating the analyte peaks in relation to the analytical blank and the procedural blank. The sample in question was surface water from the WWTP discharge site, the analytical blank 100% ACN and the procedural blank was spiked ultra-pure water extracted in the same sample batch as the surface water in question.

Analytical validation

The linearity of the phthalate determination method evaluated using solvent-based calibration standards prepared in acetonitrile/methanol (50 : 50 v/v). Calibration curves were constructed in the in the concentration range 0.001 and 10 μg

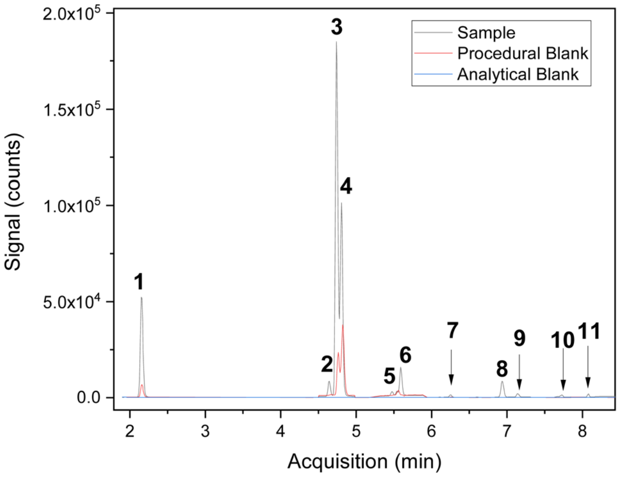


Fig. 1 Comparison of surface water sample, procedural blank and analytical blank showing peaks (1) DMP, (2) BBP, (3) DiBP, (4) DBP, (5) DiPP, (6) DHP, 8 (DEHP), 9 (DnOP), 10 (DiNP), and (11) DiDP.

Table 1 Analytical validation results for phthalate separation

Peak identifier	Compound	R^2 ($n = 3$)	RSD (%)	LOD (ng L^{-1})	LOQ (ng L^{-1})
1	DMP (see Fig. 2)	0.9989	0.15	0.5	2
2	BBP	0.9883	0.39	1	5
3	DiBP	0.9910	0.68	2	10
4	DnBP	0.9927	0.28	0.2	1
5	DiPP	0.9845	0.79	5	50
6	DPP	0.9786	1.80	5	10
7	DHP	0.9870	0.48	0.1	5
8	DEHP	0.9851	1.72	1	5
9	DnOP	0.9797	1.50	1	5
10	DiNP	0.9924	0.31	2	5
11	DiDP	0.9828	1.04	10	50

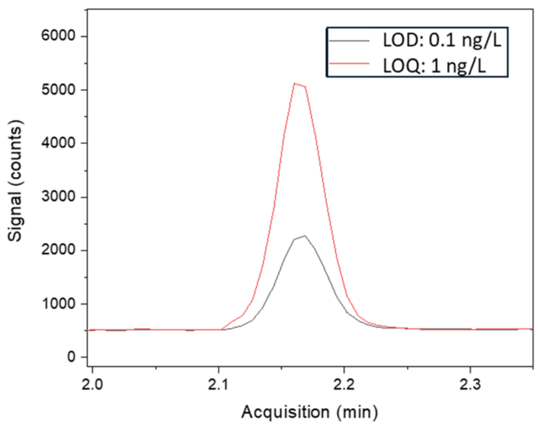


Fig. 2 *Example LOD/LOQ determination for DMP.

L^{-1} for each analyte and analysed in triplicate. Excellent linearity was observed, with coefficients of determination (R^2) greater than 0.98 across all target compounds (Table 1). Limits of detection (LOD) and limits of quantification (LOQ) of each phthalate were calculated as three times the signal to noise ratio and ten times the signal to noise ratio, respectively, based on these solvent standards (example, Fig. 2). This approach is consistent with international best practice for LC-MS/MS method validation and provides an accurate measure of instrument sensitivity.

To account for the complexity of the environmental matrices analysed in this study (surface water, landfill leachate, soil, and municipal wastes), additional matrix-specific validation was performed. Repeatability was assessed through replicate extractions and injections, with relative standard deviations (RSDs) below 5% across calibration runs, confirming intra-day precision. Inter-day performance was verified through repeated calibration curves at the start and end of each analytical batch, and reproducibility between batches was consistently within 5% RSD. Recovery studies were performed across all matrix types using representative phthalates (DMP, DEHP, DiDP) at three spike levels, with results ranging from 70–98% (Table 2). Matrix suppression and enhancement were quantified by comparing spiked matrix extracts with solvent standards, and suppression was observed consistently across all matrices, with the strongest effects in compostable waste (Table 3). These effects were effectively corrected using isotopically labelled internal standards. Short-term stability was monitored by injecting calibration and QC standards at intervals during each batch, which showed consistent peak areas (<5% RSD). Long-term stability and freeze–thaw cycles were not assessed in this study and represent a limitation for future work.

Table 2 Percentage recoveries for Soxhlet and ultra-sonication extraction trials for phthalates in soil and for solid matrices using selected ultra-sonication method

Extraction	DMP	DEHP	DiDP
Soxhlet	65.24 (±5.37)	56.47 (±7.63)	32.11 (±6.89)
Ultra-sonication matrix	78.06 (±3.75)	88.83 (±3.29)	89.76 (±2.42)
Soil	78.06 (±3.75)	88.83 (±3.29)	89.76 (±2.42)
Waste-recyclable	89.92 (±2.75)	95.25 (±3.33)	97.70 (±1.82)
Waste-general	87.43 (±3.28)	88.25 (±3.09)	92.76 (±2.08)
Waste-food	86.74 (±4.10)	90.48 (±3.12)	94.16 (±2.62)

Pre-extraction steps for solid samples

For the extraction of solid samples, an additional extraction prior to SPE must be carried out. Phthalate analysis has mainly used soxhlet and ultrasonic extraction for these purposes and both were investigated for this project. The QuEChERS method[36,37] is increasingly popular for solid matrix extraction but as this uses a high volume of plastics and additional reagents that are not phthalate free it was not investigated due to the probability of introducing high background contamination. SPE extraction was used for all aqueous samples, and solid samples used SPE coupled with ultra-sonication pre-extraction. Table 2 shows the recoveries achieved for the extraction methods and ultrasonication performance on each sample type.

The matrix effects for all matrices were examined. Spiked and blank samples were compared for triplicate samples. For the case of surface water, soil, and wastewater samples three different sites were compared and averaged. Wastes and leachate came from one site so triplicates were analysed from the same site. The recovery of the target analyte was calculated, and the matrix effect expressed as percentage change.[38,39]

Agilent MassHunter software was used to quantitate the phthalate concentrations in sample. The ratio of phthalate to

Table 3 Matrix effects on a sample matrix as a percentage of ion suppression

	Recyclable waste	General waste	Food waste	Leachate	Soil	Surface water
DMP	4.09 (±0.10)	1.94 (±0.06)	18.81 (±0.56)	8.28 (±0.22)	6.17 (±0.21)	0.33 (±0.01)
BBP	4.76 (±0.11)	9.52 (±0.30)	9.52 (±0.29)	7.93 (±0.21)	3.57 (±0.12)	3.57 (±0.10)
DiBP	6.90 (±0.17)	12.88 (±0.40)	9.06 (±0.27)	9.61 (±0.26)	2.34 (±0.08)	6.51 (±0.09)
DBP	0.19 (±0.01)	5.99 (±0.19)	16.29 (±0.49)	7.49 (±0.20)	10.11 (±0.27)	1.40 (±0.04)
DiPP	2.15 (±0.05)	8.87 (±0.27)	7.53 (±0.23)	6.18 (±0.17)	1.21 (±0.02)	4.84 (±0.14)
DPP	7.81 (±0.19)	12.50 (±0.39)	5.21 (±0.16)	8.51 (±0.23)	7.03 (±0.24)	8.59 (±0.25)
DHP	9.26 (±0.22)	14.81 (±0.46)	5.56 (±0.17)	9.88 (±0.27)	2.78 (±0.09)	6.94 (±0.20)
DEHP	1.34 (±0.03)	12.60 (±0.40)	4.99 (±0.15)	6.31 (±0.15)	2.83 (±0.10)	5.17 (±0.16)
DnOP	0.49 (±0.01)	18.57 (±0.56)	6.10 (±0.18)	8.39 (±0.23)	8.87 (±0.30)	0.69 (±0.02)
DiNP	2.99 (±0.07)	11.59 (±0.36)	4.65 (±0.14)	6.41 (±0.16)	8.51 (±0.29)	7.29 (±0.21)
DiDP	1.34 (±0.03)	7.53 (±0.23)	3.04 (±0.09)	3.97 (±0.11)	5.90 (±0.20)	4.82 (±0.13)

Internal Standard (IS) is above 100% for some phthalates due to high concentration in the procedural blank which was subtracted from the sample concentration. All matrices showed a negative percentage change in phthalate analyte detection and therefore demonstrating ion suppression for all matrices. The strongest effects were noted for compostable food wastes (Table 3). Matrix effects, expressed as percentage ion suppression or enhancement, were evaluated by comparing spiked matrix extracts with solvent standards, and ranged from minimal suppression in surface waters to more pronounced effects in solid waste samples. Internal standards were used to correct for these effects, and procedural blanks were systematically included to account for laboratory and instrumental contamination.

Once the matrix was extracted through soxhlet/ultrasonication the same SPE method was applied to the extract, with modifications for sample volume loads. Spiked and un-spiked samples were compared to determine percentage recoveries that include any losses through both pre-extraction step and SPE. Three phthalates were selected for the spike, DMP, DEHP and DiDP, representing peak 1, 2 and 3 respectively. These were chosen as they covered the lowest, mid-range and highest log K_{ow}. Soxhlet was found to have a much lower percentage recovery, used solvents of increased eco-toxicity and is a highly water intensive method. The ultra-sonication method therefore offered increased efficiency and is a greener method and was used for analysis of all solid samples. As shown in Table 3, all matrices demonstrated ion suppression, ranging from negligible (<1%) in surface waters to more pronounced suppression (>15%) in compostable waste. Internal standardisation compensated for these effects, ensuring accurate quantification across sample types.

Raw sample analysis

This work demonstrates the application of the LC-MS determination of target phthalate compounds on samples arising from household waste (compostable, recyclable and general), soil, landfill leachate and surface water. All samples were analysed through MRM mode but raw data was also examined through MS2 scan and SIM modes. MS2 scans ranged from 50–500 m/z, and demonstrated the extent of sample clean-up. SIM modes were run for the parent ions, while additional monitoring using the characteristic ion of 149 m/z for phthalic anhydride (which is common to all analytes), was also implemented. This was investigated as a possible method to screen for all phthalates, including ones not included in this study. However, SIM was not sufficient for this high throughput method, and 149 m/z did not capture all peaks in the LMW zone, so they are excluded from this study.

The results showed that at low concentrations, contamination peaks were at an intensity 2× fold higher than the low concentration standard injected (1 μg L^{-1}). All contamination peaks elute prior to 1.5 min. The results illustrate how critical the pre-column is for routine phthalate analysis, particularly with high-volume throughput on a shared instrument. Even with solvents running clean, the instrument itself can contribute high background levels of phthalates. Agilent MassHunter software was used to quantitate the phthalate concentrations in the samples. The ratio of phthalate to Internal Standard (IS) is above 100% for some phthalates due to high concentration in the procedural blank which was subtracted from the sample concentration.

Table 4 shows a summary of the analytical determinations with a comparison of the phthalate occurrence in different household wastes. Surface water samples was the cleanest matrix and therefore only required filtration through 0.45 μm nylon filters prior to pre-concentration by a factor of 100. This was the only matrix to not have a detection frequency of 100% while all other phthalates were detected in all samples tested. Surface water contained the most precise sample results and had very low levels of phthalates in the analytical blank. This is thought to be due to the significantly decreased analysis time reducing contact of sample with air.

The data obtained on the variety of matrices illustrate the ubiquitous occurrence of a range of diester phthalate compounds in our environment.[40–43] As shown in Table 4, recyclable wastes in all cases contain the greatest quantity of phthalates. This poses a question in relation to the circular contamination through this route as many of these materials will find other applications if recycled. Soil and surface waters are matrices that are a sink for all these compounds and in fact, these may contribute to their transport and mobility.

To contextualise the performance of this study, selected published methods for phthalate diester determination are summarised in Table 5. Compared with these approaches, the

Table 4 Summary of phthalate data from a variety of environmental samples analyte ($n = 3$, ±2SD)

Sample type	DMP	BBP	DiBP	DBP	DiPP	DPP	DHP	DEHP	DnOP	DiNP	DiDP
Surface water (ng L^{-1})	117.35 (±1.20)	64.23 (±1.97)	252.75 (±2.89)	428.27 (±13.76)	12.82 (±0.30)	49.67 (±3.30)	10.84 (±0.80)	83.35 (±1.79)	3.86 (±0.05)	2.67 (±0.09)	49.83 (±2.21)
Soil (μg g^{-1})	1.596 (±0.145)	1.055 (±0.152)	3.501 (±0.325)	5.006 (±0.558)	0.245 (±0.019)	1.595 (±0.166)	0.668 (±0.051)	0.553 (±0.076)	0.095 (±0.008)	0.271 (±0.042)	0.143 (±0.030)
Food waste (μg g^{-1})	0.62 (±0.06)	2.09 (±0.14)	6.05 (±0.68)	1.00 (±0.10)	0.15 (±0.02)	1.55 (±0.16)	0.62 (±0.06)	0.30 (±0.02)	0.03 (±0.002)	0.25 (±0.02)	2.08 (±0.06)
General waste (μg g^{-1})	10.42 (±0.42)	8.59 (±0.24)	30.59 (±1.24)	11.80 (±1.38)	1.74 (±0.08)	10.23 (±0.08)	5.30 (±0.38)	0.93 (±0.02)	0.09 (±0.01)	1.52 (±0.04)	17.71 (±1.78)
Recyclable waste (μg g^{-1})	26.96 (±0.76)	29.16 (±1.04)	136.36 (±6.66)	81.36 (±1.90)	5.30 (±0.34)	32.59 (±2.04)	12.19 (±0.30)	4.24 (±0.22)	0.25 (±0.01)	14.74 (±0.42)	40.31 (±1.42)
Leachate (μg L^{-1})											
Average lagoon	2.42 (±0.18)	0.01 (±0.001)	6.36 (±0.12)	2.37 (±0.16)	0.02 (±0.002)	0.05 (±0.004)	0.00 (±0.000)	0.15 (±0.01)	5.43 (±0.18)	5.59 (±0.13)	15.16 (±0.25)
Average sump	1.86 (±0.16)	0.01 (±0.001)	3.05 (±0.22)	1.17 (±0.08)	0.01 (±0.001)	0.01 (±0.001)	0.01 (±0.000)	0.08 (±0.002)	3.75 (±0.36)	3.19 (±0.24)	10.91 (±0.18)

present LC-MS/MS workflow achieves markedly lower detection limits (down to 0.2 ng L^{-1}), *versus* typical LOQs of 13–425 ng L^{-1} for water matrices[44] or 0.59–10.08 ng g^{-1} for soils,[32] while maintaining strong recoveries (70–98%) and reproducibility (RSD <5%). Importantly, the method integrates strict contamination control measures (delay column, phthalate-free materials, procedural blanks) rarely reported in the literature, an aspect highlighted by[30] for wine analysis but not widely applied to environmental matrices. Furthermore, in contrast to approaches tailored for single sample types (*e.g.*, DLLME for bottled waters,[45] ASE for soils,[32] or LC-GC-MS for landfill leachate[46]), the present method is validated simultaneously across four diverse environmental matrices (surface waters, landfill leachates, soils, and municipal solid waste). This breadth of applicability, coupled with low detection limits and excellent precision, demonstrates the novelty and practical utility of the method for routine environmental monitoring of both low- and high-molecular weight phthalates.

The results shown illustrate a robust demonstration of the analytical method through rigorous quality control, matrix management and replicate sample analyses. While calibration was performed in solvent standards, the method has been validated across multiple matrix types. The combination of solvent-based linearity, spiked recoveries, matrix effect assessment, and contamination controls demonstrates that the reported LODs and LOQs are both realistic and applicable for routine monitoring of diverse environmental samples.

Compared to existing LC-MS/MS methods for phthalate diester analysis, this study offers several novel contributions. Most published methods are constrained to either aqueous samples or limited phthalate panels, often excluding newer or higher molecular weight phthalates due to challenges in solubility, ionisation, or chromatographic separation. This method uniquely achieves simultaneous quantification of both legacy and emerging diesters, including DiDP, DiNP, and DiPP, without derivatization or compromise in sensitivity. Furthermore, while many studies employ generic SPE protocols or rely on commercial pre-packed cartridges without matrix-specific validation, this work optimises both SPE and ultrasonication parameters across distinct environmental matrices, allowing more accurate and reproducible extraction from highly variable solid waste and leachate samples. A key innovation is the integration of a delay column and instrument modifications to systematically displace background phthalates originating from the LC system itself, an issue often acknowledged in literature but rarely engineered against. Moreover, the use of time-staggered quality control strategies, including triplicate low-level standard injections and real-time RSD thresholds, adds a level of precision control not commonly implemented in routine methods. While the method requires careful maintenance of low-background instrumentation and high-purity solvents, its ability to reliably quantify phthalates across chemically and physically diverse samples fills a critical gap in current environmental monitoring capabilities.

Methods

Reagents and standards

All phthalate standards were purchased from Accu standard (New Haven, Connecticut, USA) as liquids. The list of target analytes is shown in Table 6. The standards were diluted in 50 : 50 (v/v) methanol:acetonitrile to obtain the concentrations required for the calibration standards. LC-MS grade methanol, dichloromethane (DCM) and acetonitrile were purchased from Thermo-Fischer (Waltham, Massachusetts, U.S.). Ultrapure water was sourced from a reverse osmosis system with 18.2 MΩ purity. Minimal standard preparation steps were taken, and all processes were carried out in a timely manner to avoid excess exposure to laboratory air. All glassware used was rinsed three times with LC-MS grade methanol after overnight bake-out at 200 °C. Although some literature suggests that mobile phase additives yield sharp peaks in LC-MS analysis, no buffer could be sourced that contained low enough levels of phthalates to incorporate into the method.

Sample collection

All samples were collected using phthalate-free, shatter-proof glass bottles to minimize contamination. Bottles were pre-

Table 5 Comparison of selected published methods for phthalate diester determination with the present study

Method & reference	Analytes	Matrices	Sample prep.	Detection (LOD/LOQ)	Precision/recovery	Practical notes
44	14 PAEs (+DEHA)	Treated wastewater, runoff, pond	NADES-DLLME; calibration	LOQs 0.013–0.425 μg L^{-1}	Rec. 70–127%; RSD <14%	Green, rapid; real-water validation
47	Several PAEs	Tap & bottled water	SBSE-LD + GC-MS	LODs 3–40 ng L^{-1}; linear 25–2000 ng L^{-1}	RSD <14.8%	Sensitive; good contamination control
45	Multiple PAEs	Bottled water	DLLME + GC-MS	LODs 5–220 ng L^{-1}; linear 0.05–150 μg L^{-1}	RSD 1.3–5.2%	Fast; very precise recovery
30	PAEs incl. DINP/DIDP	Wine	Dilute-and-shoot with hold-back column	QLs 1.6–9.8 μg L^{-1}; 7.5–26.6 μg L^{-1}	Not specified	Novel contamination suppression *via* hold-back column
32	14 PAEs + monoesters	Soils	ASE + in-line cleanup	MDLs 0.59–10.08 ng g^{-1} (d.w.)	Rec. 69–131%; RSD <15%	Robust; isotope dilution
46	Common PAEs	Leachate, wastewater	On-line LC-GC-MS (TOTAD)	LODs 0.1–1.4 μg L^{-1}	RSD ≤12%	Tailored for complex matrices
48	10 PAEs & alternatives	Food, air	TurboFlow online cleanup + LC-MS/MS	mLODs 0.001–2.08 ng g^{-1} (ww), 0.001–0.93 ng m^{-3} (air)	RSD <20%	High-throughput; automated
49	6 PAEs	Water	Magnetic COF-SPE + LC-MS/MS	LODs 0.14–22 ng L^{-1}; LOQs 0.46–73 ng L^{-1}	RSD intra 3.5–8.7%; inter 5.1–13.5%	Reusable SPE media; efficient
50	Several PAEs	River water, SPM, sediments	SPE/UAE + cleanup	LODs 0.14–2.7 μg kg^{-1} (d.w.)	RSD <7%	Environmental occurrence mapping
This study (2025)	11 PAEs (LMW–HMW incl. DiNP, DiDP, DiPP)	Water, leachate, soil, waste	Ultrasonication/ filtration + SPE	LODs down to 0.2 ng L^{-1}; LOQ <1 ng L^{-1}	Rec. 70–98%; RSD <5%	Derivatization-free; broad matrix, rigorous contamination control

Table 6 Characteristics of phthalates under investigation

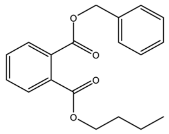
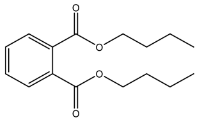
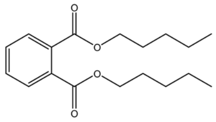
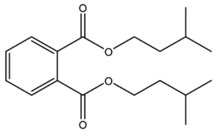
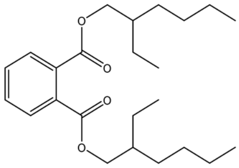
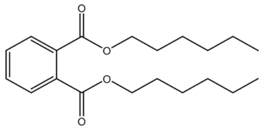
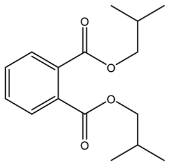
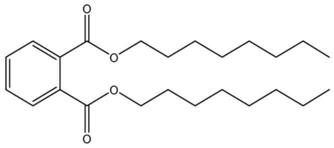
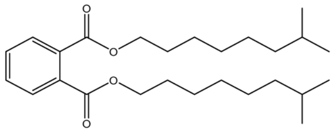
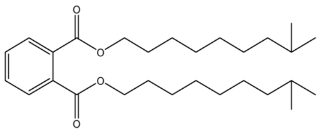
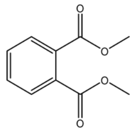
Compound	CAS	Structure	Mw (g per mole)	Log K_{ow}
Benzylbutyl phthalate (BBP)	85-68-7		312.36	4.65
Dibutyl phthalate (DBP)	84-74-2		278.34	4.16
Dipentyl phthalate (DNPP)	131-18-0		306.4	4.99
Diisopentyl phthalate (DIPP)	605-50-5		306.4	4.82
Diethylhexyl phthalate (DEHP)	117-81-7		390.56	7.5
Dihexyl phthalate (DHP)	84-75-3		334.46	6.8
Diisobutyl phthalate (DIBP)	84-69-5		278.35	4.12
Di-*n*-octyl phthalate (DNOP)	117-84-0		390.56	7.5
Diisononyl phthalate (DINP)	28 553-12-0		418.62	8.16
Diisodecyl phthalate (DIDP)	26 761-40-0		446.66	8.99
Dimethyl phthalate (DMP)	131-11-3		194.19	1.6

Table 7 Description of samples, sub-types, and extraction methods used

Sample type	Sample description	Number of samples	Extraction
Household waste	Large subsample from waste treatment site classed as food/organic, general, and recycling	3 Representative samples taken from each subsample type. One sampling date. ($n = 9$)	Ultrasonication, SPE
Landfill leachate	Lined landfill leachate from closed landfill site	3 Representative samples at lagoon and sump. 1 sampling date. ($n = 6$)	Filtration, SPE
Surface water	River samples (upstream, WWTP receiving waters and suburban downstream) seawater (river discharge point)	One representative sample taken at each site. 4 sampling dates ($n = 16$, extracted in triplicate)	Filtration, SPE
Soil	Farm organic (plastic cover, open field), farm traditional (tillage, pasture), urban parkland (lakeside, roadside, centre), urban business (roadside, centre, roadside)	Samples taken in triplicate from each subsite (*e.g.* farm traditional, tillage), 1 sampling date ($n = 10$, extracted in triplicate)	Ultrasonication, SPE

cleaned by triple rinsing with Optima LC-MS grade methanol and further rinsed on-site with the sample matrix prior to collection. Solid samples (*e.g.*, soil, sludge, and waste fractions) were stored in pre-cleaned glass containers that had been baked at ≥200 °C and rinsed with LC-MS grade solvents to eliminate residual phthalates. Upon arrival at the laboratory, all samples were acidified to pH 2 using HCl and stored at −20 °C in cooler boxes or freezers until extraction. Sample handling was conducted under contamination-controlled conditions using phthalate-free equipment. Table 7 shows the range of samples collected for analysis for the presence of phthalates, and the extraction method used. Fig. 3 illustrates the chain of events involved from sampling to final analysis.

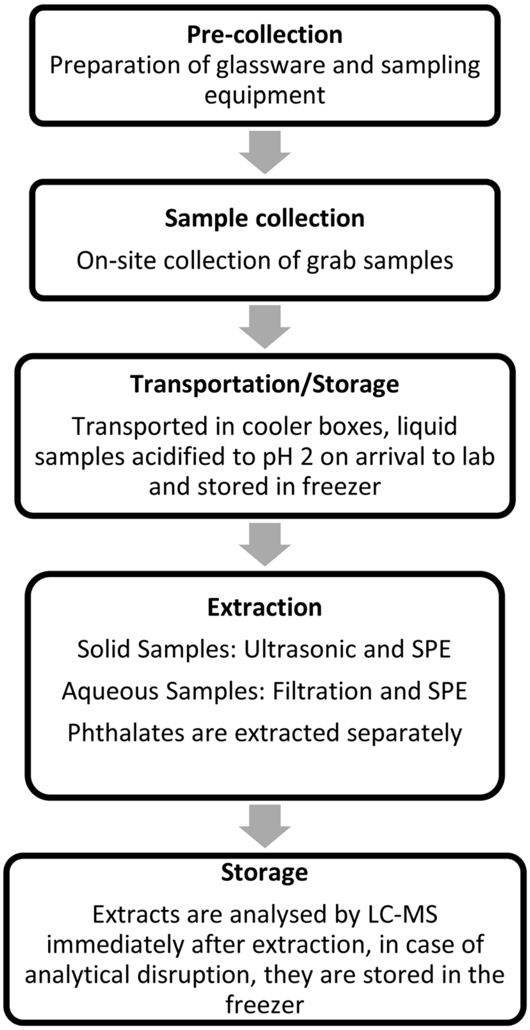


Fig. 3 Process flow diagram for sample collection, management, extraction and storage.

Sample preparation

All samples were extracted using Solid Phase Extraction (SPE). Solid samples required an extra clean up step prior to SPE due to the complexities of those matrices. Both soxhlet and ultrasonication were trialled for the pre-extraction step for solid matrices.

Solid phase extraction (SPE)

Samples were initially filtered with 0.8 μm glass fibre filters followed by 0.45 μm nylon filters to remove suspended solids.[51] Internal standards (dibutylphthalate-3,4,5,6-d4, and bis(2-ethylhexyl)phthalate-3,4,5,6-d, 50 μL, 1 μg L^{-1}) were then added prior to extraction. The filtered samples were solid-phase extracted using reverse phase cartridges. A validated method exists for the extraction of phthalate, EPA method 3535 A (U.S. EPA. 2007. "Method 3535 A (SW-846): Solid-Phase Extraction (SPE)," Revision 1. Washington, DC.), however, the EPA method uses dichloromethane and acetone which we were unable to source without significant phthalate contamination in the procedural blanks. Therefore, a modification of this method using ACN alone was investigated, and the percentage recoveries were sufficient, when using the same solvent to sample volume ratios and conditioning steps. Strata-X cartridges were conditioned with methanol (LC-MS grade, 2 mL) followed by acetonitrile (LC-MS grade, 2 mL) and water (Milli-Q, 4 mL). Samples (100 mL, spiked with dibutylphthalate-3,4,5,6-d4, and bis(2-ethylhexyl)phthalate-3,4,5,6-d, 0.5 μg L^{-1}) were loaded under low vacuum, then washed with water (Milli-Q, 1 mL).

Cartridges were dried under vacuum for 10 min and samples were eluted using acetonitrile (LC-MS grade, 4 mL). The extract was dried under nitrogen, then adjusted to a total volume of 1 mL with acetonitrile. Strata-X cartridges purchased from Phenomenex. Cartridges were conditioned with methanol (LC-MS grade, 2 mL) followed by acetonitrile (LC-MS grade, 2 mL) and water (Milli-Q, 4 mL). Samples (100 mL) were loaded under low vacuum, then washed with water (Milli-Q, 1 mL). Cartridges were dried under vacuum for 10 minutes and samples were eluted using acetonitrile (LC-MS grade, 4 mL). The extract was dried under nitrogen, then adjusted to a total volume of 1 mL with acetonitrile. Amber glass vials with Teflon-lined caps or foil seals were used for extract storage to prevent photodegradation and minimize leaching. The percentage recovery for this method ranged from 70 to 98%.

Solid sample extraction using ultrasonication

For solid matrices, acetonitrile (LC-MS grade, 100 g) was added to dried samples (30 g, spiked with dibutylphthalate-3,4,5,6-d4, and bis(2-ethylhexyl)phthalate-3,4,5,6-d, 5 μg L^{-1}). This was placed in an ultrasonicator, 1/2-inch below the surface of the solvent, but above the sediment layer. The sample was the extracted ultrasonically for 3 min, with output control knob set at 10, the mode set to pulse, and the percent-duty cycle knob set at 50%. The extract was decanted and filtered through Whatman No. 41 filter paper. This process was repeated twice with two additional 100 mL aliquots of clean solvent. On the final ultrasonic extraction, the entire sample was filtered through a Buchner funnel under low vacuum and the solvent extract was collected. This extract was then pre-concentrated by a factor of 10, using the same SPE method with modified load volume.

The soxhlet method used a conventional soxhlet apparatus setup. Solid sample (15 g, dried and homogenised) was placed in the thimble and DCM (150 mL, LC-MS grade) in the round bottomed flask. The water bath was equilibrated to 65 °C and the sample was extracted under reflux for 18 h.

Engineering controls to address contamination

The sample analysis was performed by LC-MS the details of which are summarised in Table 8. The LC-MS instrument (Agilent 6470 Triple Quad LC-MS) was retro fitted with stainless steel tubing and pump heads. The degasser was bypassed to prevent build-up of phthalates in the mobile phase. A delay column was installed after the mixer to push interfering phthalates from mobile phase and system into a different retention time window and a dynamic multi-reaction method (DMRM) was developed, removing any of these interferences from the analysis window. A multi-wash system was used. A stronger solvent than the mobile phase was injected between runs to ensure no carry-over from the column (IPA : ACN 50 : 50).

Table 8 Mass spectrometer source and chromatographic conditions

Parameter	Value
Mass spectrometer system	G6470A
Ionization mode	Positive
Gas temperature	350
Gas flow	10 L min^{-1}
Nebulizer	35 psi
Capillary	4000 V
Sheath gas temperature	400
Sheath gas flow	12 L min^{-1}
Nozzle voltage	2000 V
Delay column	Eclipse plus C18, 3.5 μm, 4.6 × 50 mm
Analytical column	Poroshell 120 EC-C18, 2.7 μm, 2.1 × 150 mm
Injection volume	2 μL
Column temperature	50 °C
Mobile phase	(A) Water (B) Methanol : ACN (50 : 50)
Gradient	0 min 60% B, 2 min 80% B, 5 min 100% B
Run time	9 min
Post time	2 min

Mass spectrometry conditions

Full scans of all target analytes were run to assess precursor and possible product ions. The precursor ions were selected from the molecular weight of the empirical formula, +H, as the phthalate diesters favoured positive ionization. The Agilent Optimizer program was then used with these transitions to determine the optimal fragmentor voltages and collision energies for each compound. This could be done manually by running samples at varying fragmentor voltage and collision energy. The MS source was surface cleaned daily and deep cleaned weekly with a weekly flush of nebuliser.

To optimize MS signal the source parameters were carefully controlled. Agilent Source Optimizer runs a variety of temperatures, flows, voltages and pressures to analyse which settings increase analyte detection. The parameters chosen gave the best average signal for all phthalates. Triplicate injections of reference standard (1 μg L^{-1}, ACN : MeOH) over the course of 0, 2, 4, 6, 8 h were shown to be precise, with under 5% RSD from the first sets of injections. To ensure that any variation was noted in the method, a calibration run was conducted at the start and end of an analytical batch, if there was a deviation of greater than 5% RSD the instrument was checked and samples re-run. The linearity and sensitivity of response was determined through repeated calibration curve runs. These combined features – the breadth of validated matrices, the inclusion of both legacy and emerging phthalates within a single workflow, and the comprehensive contamination controls – constitute the novelty of this method compared with previously reported LC-MS/MS approaches.

Conclusions

This study presents a novel LC-MS/MS method that advances beyond existing approaches by (i) enabling simultaneous quantification of eleven phthalate diesters spanning low to high molecular weight compounds, (ii) validating extraction and detection across an unusually wide range of complex solid and liquid environmental matrices, and (iii) introducing robust contamination-resilient features that directly address the ubiquitous presence of phthalates in laboratory workflows. The method integrates tailored sample preparation strategies -ultrasonication for solids and SPE for both solids and liquids – with rigorous contamination control measures including instrument retrofitting, delay column installation, and procedural blanks. This is, to the authors' knowledge, the first time an analytical workflow has been developed and validated for the simultaneous quantification of both low and high molecular weight phthalates in complex environmental samples such as municipal waste, landfill leachate, soil, and surface water, while effectively addressing the pervasive issue of background phthalate contamination. The method achieves high recoveries (70–98%), low detection limits ($\leq$0.2 ng L^{-1}), and excellent linearity ($R^2 > 0.98$), without the need for derivatization. Internal standardisation and matrix-specific quality controls ensure analytical robustness even in samples prone to ion suppression and interference. Although stability and inter-operator reproducibility were not included in the present work, the method was validated for linearity, recovery, repeatability, and matrix effects across diverse sample types, demonstrating strong performance under realistic analytical conditions. This approach enables comprehensive environmental monitoring of both legacy and emerging phthalate contaminants, supporting regulatory compliance and risk assessment frameworks. The methodology developed here offers a valuable platform for routine analysis of phthalates and can be readily adapted for broader micropollutant surveillance.

Author contributions

All authors contributed to the writing. F. R.: method development, data analysis, interpretation, C. A.: sample preparation, method development, data analysis, interpretation, J. L.:, method development, data analysis, interpretation.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including LC-MS/MS data are available at the DCU institutional research repository at https://doras.dcu.ie/26150/.

Acknowledgements

This work was undertaken with funding from the Irish EPA Project 2015-HW-MS-3: Potential Sources and Environmental Fates of Certain Phthalates. The authors are grateful for the support of the SFI and HEA funded Nano-Bio Research Facility at DCU for technical support and access to equipment.

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