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### Quantification and confirmation of priority organic micropollutants in water by LC-tandem mass spectrometry

Elena Pitarch<sup>a</sup>; José M. Marin<sup>a</sup>; Francisco Lopez<sup>a</sup>; Elbert Hogendoorn<sup>b</sup>; Felix Hernández<sup>a</sup>

<sup>a</sup> Research Institute for Pesticides and Water, University Jaume I, caslón, Spain <sup>b</sup> Laboratory for Analytical Chemistry, National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

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## Quantification and confirmation of priority organic micropollutants in water by LC-tandem mass spectrometry

ELENA PITARCH<sup>†</sup>, JOSÉ M. MARIN<sup>†</sup>, FRANCISCO LOPEZ<sup>†</sup>,  
ELBERT HOGENDOORN<sup>‡</sup> and FELIX HERNÁNDEZ<sup>\*†</sup>

<sup>†</sup>Research Institute for Pesticides and Water, University Jaume I, Castellón, Spain

<sup>‡</sup>Laboratory for Analytical Chemistry, National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

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Liquid chromatography coupled to tandem mass spectrometry with a triple quadrupole analyser was used to determine selected (medium) polar organic pollutants—*isoproturon*, *diuron* and *pentachlorophenol*, as the herbicides *simazine*, *atrazine*, *terbuthilazine*, *alachlor*, and *metolachlor*—in treated water from urban solid-waste leachates. Two millilitres of water was preconcentrated by on-line trace enrichment (solid-phase extraction liquid chromatography) which allowed rapid analysis, but still with a satisfactory sensitivity, as the limits of quantification were  $0.05 \mu\text{g L}^{-1}$ , while the limits of detection were in the range of  $0.001\text{--}0.01 \mu\text{g L}^{-1}$ . Confirmation of the identity of compounds was ensured by the use of two tandem mass spectrometry transitions. Moreover, a study of matrix effects was thoroughly investigated by applying the developed procedure to different ground and surface waters. A simple dilution of the water sample with high-performance-liquid-chromatography-grade water was sufficient to minimize and/or remove this undesirable effect in all water samples tested, this approach being feasible due to the excellent sensitivity of the method.

**Keywords:** Organic pollutants; Water analysis; Municipal solid waste leachates; LC-MS; Matrix effects; Tandem mass spectrometry

### 1. Introduction

Nowadays, many organic contaminants can be present in environmental water, normally at the  $\mu\text{g L}^{-1}$  level or below [1, 2]. One of the routes for the contaminants to enter into the aquatic environment is from municipal solid waste landfill leachates. These leachates frequently contain a variety of hazardous chemicals which may cause severe biological effects in the aquatic environment, as many of the identified compounds are highly toxic or even carcinogenic [2–5]. Therefore, efficient treatment of landfill leachates is required, and monitoring of organic pollutants is compulsory to assure the water quality after treatment.

\*Corresponding author. Fax: +34-964-387368. Email: hernandf@exp.uji.es

Gas chromatography coupled to mass spectrometry (GC-MS) has been the major adopted analytical technique to perform multiresidue monitoring of semi-volatile compounds [6, 7]. Nowadays, enrichment via non-selective solid-phase extraction (SPE) using relatively low sample volumes followed by GC-MS, or even better, GC coupled to tandem mass spectrometry (MS/MS), is the preferred approach for GC-amenable organic micropollutants. The high separation efficiency and the suitability of GC-MS for identification/confirmation of compounds is also widely accepted [8].

For more polar, less or non-GC-amenable contaminants, liquid chromatography coupled to mass spectrometry (LC-MS) with the appropriate choice of atmospheric pressure ionization interfaces (API) is increasing in environmental trace-level analysis, drastically changing the analytical methods used to detect polar pollutants in water [9, 10]. However, there is growing awareness and experimental evidence that matrix present in the samples may affect the ionization of the target analytes and may result in erroneous LC-MS quantification. Interesting approaches to compensate or to remove matrix effects in environmental samples have been reviewed recently [9]. Several authors have reported comprehensive reviews discussing the perspectives of the LC developments and their impact on current and future applications in pesticide trace analysis [11] or dealing with the complementarity of LC- and GC-based techniques for the trace-level determination of pesticides and their transformation products in water [8].

In order to improve sensitivity as well as selectivity in LC-MS-based methods, a trace enrichment step is commonly applied in the processing of water samples. On-line SPE is frequently chosen for this purpose, as it is a simple way of preconcentration and also of removing some interferences present in the matrix with very little sample manipulation. The combination of on-line SPE with tandem mass spectrometric detection (SPE-LC-MS/MS) has proven to be a powerful approach for the direct, sensitive, and selective multiresidue analysis for both medium polar and polar compounds [12–19] and has been successfully applied for this purpose at our laboratory [12, 17–19].

The multiresidue determination of 55 organic contaminants in treated water has been carried out in our laboratory by the complementary use of GC-MS and LC-MS. Provided that the determination of low-polarity compounds by GC-MS has been largely studied in the bibliography, the work presented in this article is focused only on the development of SPE-LC-MS/MS methodology for the determination of eight polar and medium-polar contaminants in water, selected among the pollutants monitored, while the rest of the analytes have been determined by a conventional GC-MS procedure.

## 2. Experimental

### 2.1 Reagents and chemicals

Standards were purchased from Dr Ehrenstorfer (Augsburg, Germany). Individual stock solutions (generally around  $500 \mu\text{g mL}^{-1}$ ) were prepared by dissolving standards in acetone and stored in a freezer at  $-20^\circ\text{C}$ . For LC analysis, solutions were diluted in methanol or high-performance-liquid-chromatography (HPLC)-grade water.

Acetone (pesticide-residue analysis), acetonitrile, and methanol (HPLC grade) were purchased from Scharlab (Barcelona). HPLC-grade water was obtained by purifying

demineralized water in a Nanopure II system (Barnstead Newton, MA). Ammonium acetate (Scharlab) was of reagent-grade.

## 2.2 Samples

Treated water samples were collected between May 2003 and November 2004, from urban solid-waste leachates that were treated in RECIPLASA, a municipal treatment plant sited in Onda (Castellón, Spain). The general waste landfill leachate treatment consisted of a reverse-osmosis process.

Groundwater and surface-water samples used to check matrix effects were collected at different sites from the Comunidad Valenciana between April and November 2003.

## 2.3 LC-MS instrumentation

The HPLC system interfaced to the mass spectrometer was based on a 233XL autosampler with a loop of 2000  $\mu\text{L}$  (Gilson, Villiers-le-Bel, France) and two pumps: an Agilent 1100 (Agilent, Waldbron, Germany) binary pump as P-1 and a Waters Alliance 2690 (Waters, Mildford, MA) quaternary pump as P-2. The system has been described in more detail in our previous work [12]. The SPE preconcentration was performed using a cartridge  $\text{C}_{18}$ ,  $10 \times 2$  mm,  $5 \mu\text{m}$  (Teknokroma, Barcelona) used as C-1. For the LC separation, a Kromasil  $\text{C}_{18}$  column  $125 \times 2$  mm,  $5 \mu\text{m}$  (Scharlab, Barcelona) was used as C-2. The mobile phases were water and acetonitrile in P-1, and a mixture of methanol–water (5 mM ammonium acetate in both solvents) in P-2. The linear gradient used in P-2 was as follows: 0 min, 30%; 1 min, 30%; 12 min, 90%; 13 min, 90%; 14 min, 30%; 20 min, 30% at a flow rate of  $0.3 \text{ mL min}^{-1}$ .

A Quattro LC (triple quadrupole) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. The drying gas and nebulizing gas was nitrogen generated from pressurized air in an NG-7 nitrogen generator (Aquila, Etten-Leur, The Netherlands). The nebulizer gas flow was set to approximately  $80 \text{ L h}^{-1}$  and the desolvation gas flow to  $800\text{--}900 \text{ L h}^{-1}$ . Infusion experiments were performed using a Model 11 single syringe pump (Harvard, Holliston, MA), directly connected to the interface.

For operation in MS/MS mode, the collision gas was 99.995% argon (Carbueros Metalicos, Valencia, Spain) with a pressure of  $1 \times 10^{-3}$  mbar in the collision cell. Capillary voltages of 3 and 3.5 kV were used in the negative and positive ionization mode, respectively. The interface temperature was set to  $350^\circ\text{C}$ , and the source temperature to  $120^\circ\text{C}$ . Dwell times of  $0.1 \text{ s scan}^{-1}$  were chosen.

## 2.4 SPE-LC-MS/MS procedure

SPE  $\text{C}_{18}$  cartridges were sequentially conditioned with acetonitrile for 3 min, followed by 3 min with water using P-1 (flow rate of  $1 \text{ mL min}^{-1}$ ). The water sample (2 mL) was then preconcentrated on-line in the cartridge using water as mobile phase in P-1 ( $1 \text{ mL min}^{-1}$ ). Then, it was washed with 3 mL of HPLC water. After washing, the analytes were backflushed and transferred to the analytical column (C-2), using a P-2

Table 1. Mass spectrometry optimized parameters for the LC-MS/MS determination of selected herbicides and pentachlorophenol.

Compounds	Transition used <sup>a</sup>	Precursor ion ( <i>m/z</i> )	Product ion ( <i>m/z</i> )	Collision energy (eV)	Cone voltage (V)	<i>Q/q</i> ratio	Number of IPs [23]	LOD (ng L <sup>-1</sup> )																																																																																																			
Simazine	<i>Q</i>	202	132	20	30	1.5	4	6																																																																																																			
	<i>q</i>	202	124	20	30				Atrazine	<i>Q</i>	216	174	15	35	2.2	4	2	<i>q</i>	216	96	15	35	Isoproturon	<i>Q</i>	207	72	15	25	3.7	4	1	<i>q</i>	207	165	15	25	Diuron	<i>Q</i>	233	72	18	25	1.5	5	2	<i>q</i>	235	72	18	25	Terbutylazine	<i>Q</i>	230	174	15	30	3.6	5	1	<i>q</i>	232	176	15	30	Pentachlorophenol <sup>b</sup>	<i>Q</i>	265	265	15	45	1.9	3	10	<i>q</i> <sub>1</sub>	267	267	15	45	<i>q</i> <sub>2</sub>	263	263	15	45	Alachlor	<i>Q</i>	270	238	10	10	0.9	5	10	<i>q</i>	238	162	18	25	Metolachlor	<i>Q</i>	284	252	15	25	1.8	4	3	<i>q</i>
Atrazine	<i>Q</i>	216	174	15	35	2.2	4	2																																																																																																			
	<i>q</i>	216	96	15	35				Isoproturon	<i>Q</i>	207	72	15	25	3.7	4	1	<i>q</i>	207	165	15	25	Diuron	<i>Q</i>	233	72	18	25	1.5	5	2	<i>q</i>	235	72	18	25	Terbutylazine	<i>Q</i>	230	174	15	30	3.6	5	1	<i>q</i>	232	176	15	30	Pentachlorophenol <sup>b</sup>	<i>Q</i>	265	265	15	45	1.9	3	10	<i>q</i> <sub>1</sub>	267	267	15	45		<i>q</i> <sub>2</sub>	263	263	15	45				Alachlor	<i>Q</i>	270	238	10	10	0.9	5	10	<i>q</i>	238	162	18	25	Metolachlor	<i>Q</i>	284	252	15	25	1.8	4	3	<i>q</i>	284	176	25	25						
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<sup>a</sup>*Q*: quantification; *q*: confirmation.

<sup>b</sup>All analytes were measured in ESI positive mode, with the exception of pentachlorophenol, which was measured in ESI negative mode.

pump, to perform the chromatographic separation. Standards used for quantification were also preconcentrated on-line using the same SPE-LC procedure as for samples.

The determination was carried out by MS/MS under optimized conditions that are shown in table 1. A solvent delay of 8 min was included in the MS/MS programme to avoid contamination of the source.

### 3. Results and discussion

#### 3.1 General considerations

Around 50 organic pollutants in treated water samples from municipal solid-waste leachates were determined. Target analytes included were: (1) non-polar compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides; and (2) a number of more polar and medium-polar compounds, e.g. triazine herbicides, some organophosphorus pesticides, phenylurea herbicides, alachlor, or pentachlorophenol. Several of these compounds are relevant in the field of water policy of the European Union, and in fact are included in Annex X of the Directive 2000/60/EC [20].

Although the majority of analytes selected were determined by GC-MS, due to their low polarity and sufficient volatility, our aim was not to investigate the GC-MS methodology but simply to apply conventional (solvent extraction) procedures based on the literature [21]. Thus, our research was focused on the development of LC-MS/MS methodology for several compounds. LC-MS/MS method was first developed only for the determination of the polar, less-amenable GC compounds, pentachlorophenol,

diuron and isotroturon. In order to investigate the possibility of using LC-MS instead of GC-MS, the LC-MS/MS method was further optimized to also include several medium-polar GC amenable compounds, finally selecting eight analytes that were used as model compounds for a detailed study. Changing GC-MS by LC-MS/MS for the determination of medium-polar compounds gave us an opportunity to simplify sample pretreatment, as then GC-MS would be applied only to non-polar compounds, while the rest of the analytes could be determined by LC-MS/MS after a simple on-line trace enrichment with (almost) no sample manipulation.

### 3.2 LC-MS/MS procedure for treated water analysis

**3.2.1 LC-MS/MS optimization.** The full-scan mass and the MS/MS spectra of the compounds determined by SPE-LC-MS/MS were obtained from infusion of  $2.5 \mu\text{g mL}^{-1}$  of 50:50 methanol-water individual standard solutions at a flow rate of  $10 \mu\text{L min}^{-1}$ .

The mass spectrometry parameters selected and the precursor and product ions are shown in table 1. The two most intense transitions were normally selected for each compound: one for quantification and the other for confirmation. For a reliable confirmation, the intensity ratio between both transitions was calculated, and a deviation of  $\pm 20\%$  was accepted to consider a finding as positive. Pentachlorophenol presented a MS/MS spectrum without abundant fragments. Thus, three precursor ions were selected according to its chlorine pattern, at  $m/z$  263, 265, and 267. With an appropriate low collision energy (15 eV), these precursor ions were also measured as product ions trying to break possible interferences preserving the analyte molecule [12].

On-line trace enrichment (SPE-LC) was carried out using a  $\text{C}_{18}$  preconcentration cartridge and selecting 3 mL of HPLC water as the washing volume. As regards optimization of the elution and chromatographic separation of the analytes, different gradients of methanol:water and acetonitrile:water (5 mM ammonium acetate in both solvents) were checked. Methanol:water was finally selected because it provided a good peak shape for all the analytes, especially for pentachlorophenol and alachlor.

Under the experimental conditions selected (see section 2), the total chromatographic run from sample injection to the last peak elution was 17 min. This time included the first 8 min of solvent delay where the column eluate was sent to waste to avoid the contamination of the ionization source. The total analysis time per sample subjected to the overall analytical procedure, i.e. including on-line trace enrichment and LC-MS/MS analysis, was around 18 min, as the cartridge conditioning and SPE process for a sample overlapped (partly) with the chromatographic analysis of the previous sample.

Linearity was evaluated by means of calibration curves prepared by analysing standard solutions by triplicate in the same way as for samples, i.e. after SPE-LC-MS/MS. The concentration range studied was 10–1000  $\text{ng L}^{-1}$  (seven concentration levels), and the correlation coefficients were better than 0.99 for all compounds. Limits of detection were estimated from the chromatograms of the most diluted standards analysed and ranged between 1 and 10  $\text{ng L}^{-1}$  (table 1).

**3.2.2 Validation study.** Validation of the developed SPE-LC-MS/MS method was carried out in blank treated water spiked at two concentration levels (50 and 500  $\text{ng L}^{-1}$ ).

Table 2. Repeatability and reproducibility of the SPE-LC-MS/MS procedure in treated water spiked at two concentration levels: mean recoveries and relative standard deviation (in parentheses).

	0.05 $\mu\text{g L}^{-1}$		0.5 $\mu\text{g L}^{-1}$	
	Repeatability ( $n=5$ )	Reproducibility ( $n=9$ ) <sup>a</sup>	Repeatability ( $n=5$ )	Reproducibility ( $n=9$ ) <sup>a</sup>
Simazine	70 (16)	84 (18)	74 (5)	77 (11)
Atrazine	56 (16)	69 (17)	83 (8)	80 (12)
Isoproturon	95 (11)	96 (9)	90 (7)	90 (6)
Diuron	88 (20)	104 (16)	84 (15)	87 (7)
Terbutylazine	76 (12)	77 (11)	87 (9)	90 (15)
Pentachlorophenol	90 (13)	89 (19)	108 (10)	100 (14)
Alachlor	88 (20)	103 (4)	87 (16)	93 (9)
Metolachlor	88 (12)	96 (13)	83 (16)	92 (9)

<sup>a</sup>Data corresponding to the analysis of spiked treated water sample in 3 days,  $n=3$  each day.

The results (table 2) were satisfactory with recoveries of 70–110%, except for atrazine (56%) at the lowest level assayed. Precision (repeatability) was in general better than 15 and 20% for the highest and the lowest concentration level tested, respectively. Intermediate precision (precision between days) was also studied, performing analyses at three different days ( $n=3$ , each day) with blank treated water spiked at both concentration levels. As can be seen in table 2, the relative standard deviations (RSD) were better than 20% in all cases, and the average recoveries were satisfactory (most of them in the range of 70–100%) demonstrating the robustness of the method. The limit of quantification (LOQ) objective, defined as the lowest concentration level for which the method was validated, with satisfactory recoveries (70–110%) and precision (<20%), was 0.05  $\mu\text{g L}^{-1}$  for all compounds. The limits of detection (LOD), calculated as the concentration giving a peak of three times the signal-to-noise ratio in the chromatograms obtained at the LOQ level, were in the range of 1–10  $\text{ng L}^{-1}$ .

As the results show, a number of medium-polar and even low-polar analytes traditionally analysed by GC-MS can also be satisfactorily determined by LC-MS/MS, although the main applications of LC-MS/MS in water analysis are found for polar/ionic compounds. According to our experience, several pesticides typically determined by GC-MS, such as chlorpyrifos, dimethoate, methidathion, diazinon, etc., can also be successfully determined by LC-MS/MS with less sample manipulation [12, 17].

**3.2.3 Confirmation of analyte identity.** As regards the identification and confirmation of compound identity, the suitability of GC-MS and the availability of large libraries for searching and meeting defined criteria when using electron impact ionization are well known [8]. However, the benefits of spectral libraries in LC-API-MS are still a matter of debate. Due to the strong influence of instrumental as well as operational parameters on collision-induced fragmentation processes in API-MS, this approach is far less straightforward than GC-MS. The monitoring of two transitions ( $Q$ : quantification;  $q$ : confirmation) in LC-MS/MS procedures based on SRM (selected reaction monitoring) mode used to be sufficient for a safe positive finding [22–24] together with a  $Q/q$  ratio fitting accordingly (deviations  $<\pm 20\%$ ) with that of the standard reference. Using triple-quadrupole instruments, this typically results in

Table 3. Compounds detected in the analysis of treated and raw leachate water samples by SPE-LC-MS/MS.

	Treated water ( $n=29$ )		Raw leachate water ( $n=2$ )	
	Positive detections	Number of samples above LOQ (concentration range, $\mu\text{g L}^{-1}$ )	Positive detections	Number of samples above LOQ (concentration, $\mu\text{g L}^{-1}$ )
Diuron	14	4 (0.062–0.37)	1	1 (2.2)
Pentachlorophenol	3	1 (0.072)	0	–
Simazine	8	1 (0.066)	2	1 (5.8)
Terbutylazine	2	–	2	1 (0.37)

earning 4 identification points (IPs): 1 IP corresponding to the precursor ion and 1.5 for each product ion. In our work, the number of IPs ranged between 3 and 5, depending on the MS/MS transitions acquired (see table 1). The number of IPs for all analytes is acceptable for a satisfactory confirmation, although the specificity of the transition should also be considered, as we have discussed recently [24].

**3.2.4 Application to real samples.** The analytical methodology described was applied to the analysis of 29 treated water samples from a municipal leachate treatment plant, and also to two raw leachate samples. Raw samples were diluted 50 times with HPLC-grade water before being analysed. In every set of analyses, two blank treated waters spiked at 0.05 and 0.5  $\mu\text{g L}^{-1}$  were included as quality-control samples.

Table 3 shows the positive findings after the application of SPE-LC-MS/MS procedure. Four organic contaminants (diuron, pentachlorophenol, simazine, and terbutylazine) were detected, in most cases below the LOQ objective (0.05  $\mu\text{g L}^{-1}$ ). In spite of the low concentrations found, the detections could be confirmed as the intensity ratios ( $Q/q$ ) were  $\pm 20\%$  of those of reference standards.

In summary, among the 29 treated waters analysed, diuron and simazine were the most frequent pollutants. Pentachlorophenol was also found in three samples, and terbutylazine was detected in two samples. All the concentration levels were below 0.1  $\mu\text{g L}^{-1}$ , with the only exception of one sample that contained 0.37  $\mu\text{g L}^{-1}$  of diuron, a herbicide widely used in the study area.

With regards to the raw water samples analysed, one of them showed relatively low concentrations of contaminants, while the other had the highest concentrations found for diuron, simazine and terbutylazine. It seemed that after treatment of the raw leachate, the concentrations of organic pollutants were drastically reduced, as expected.

As an example, figure 1 shows selected chromatograms corresponding to the analyses of three positive samples, where diuron, pentachlorophenol, and simazine were detected. The excellent sensitivity of the procedure applied can be easily deduced from this figure, as all these compounds were found at concentrations below the LOQ objective, but still with satisfactory chromatographic peaks. Although the method was not fully validated at concentrations lower than 0.05  $\mu\text{g L}^{-1}$ , it seems evident that most of the analytes could be quantified below this value. From the  $Q/q$  ratios, together with the agreement in retention time of reference standards, the confident confirmation of the identity was ensured.



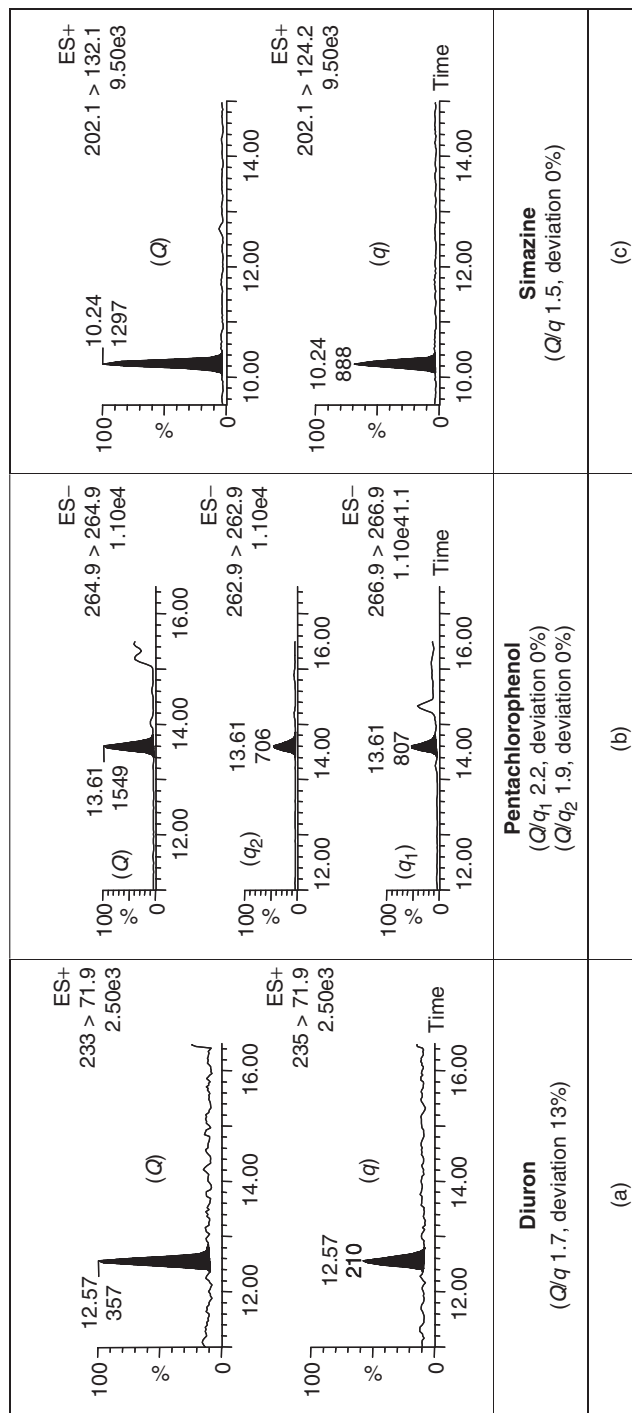


Figure 1. SPE-LC-(ESI)-MS chromatograms corresponding to: (a) treated water containing diuron at estimated concentration of 5 ng L<sup>-1</sup>, (b) treated water containing pentachlorophenol at estimated concentration of 30 ng L<sup>-1</sup> and (c) treated water containing simazine at estimated concentration of 30 ng L<sup>-1</sup>. For every compound, the MS/MS transitions used for quantification (Q) and confirmation (q) are shown. In brackets, the experimental Q/q intensity ratios and their deviations are shown.

### 3.3 Matrix effect study

The SPE-LC-MS/MS procedure developed was additionally applied for the analysis of other types of water, ground and surface waters collected in the Comunidad Valenciana area, in order to investigate the matrix effects, which might result in erroneous quantification due to enhancement or signal suppression in the ESI interface.

Matrix effects were evaluated by determining the experimental recoveries in a variety of water samples spiked at  $100 \text{ ng L}^{-1}$  ( $n=2$ ) after applying the SPE-LC-MS/MS method. Recoveries were obtained by comparison with a  $100 \text{ ng L}^{-1}$  standard analysed by the overall SPE-LC procedure. Eleven different water samples were selected to perform this study: one treated water (sample A), five surface waters (samples B–F) and five groundwaters (samples G–K).

As table 4 shows, six samples (A, B, C, D, E, and G) did not present appreciable matrix effects on any of the selected compounds, as the recovery values were 70–110%. Among the rest of the samples, three groundwaters (H, I, and K) exhibited a slight signal enhancement for several analytes, whereas a strong signal suppression occurred in two waters (surface F and ground J). This fact demonstrated the different ionization behaviour of the analytes depending on the matrix composition and could lead to a lack of robustness of the LC-MS/MS developed, as the quantification results would be dependent on the type of water analysed.

Samples presenting an alteration in the analyte MS response were diluted four times with HPLC-grade water and then re-analysed by SPE-LC-MS/MS. This simple dilution was found to be sufficient for minimizing or removing matrix effects, as the recoveries obtained for the five samples re-analysed were satisfactory (70–110%) for all the analytes. After sample dilution, both the interferences and the analytes are concentrated in the SPE cartridge, maintaining the same ratio as before. However, matrix effects are minimized, as the absolute amount of interferences decreases, and consequently an improvement of recoveries is observed. Obviously, the application of a fourfold dilution approach affects the LOD values but still maintains a satisfactory sensitivity.

In relation to pentachlorophenol, the only compound measured in negative mode, the matrix effect study was performed only in treated and surface waters, i.e. the first samples studied. Later, the equipment showed inconsistent behaviour when working in negative mode and for this reason, data for groundwater are not shown in this article.

The use of internal standards (surrogates) (IS) is the best way to compensate for matrix effects. However, this is troublesome in a multiresidue LC-MS analysis, as one should select a number of labelled analytes similar to that of the target compounds investigated, since the matrix effect is compound-dependent. This fact has been emphasized in the recent bibliography, where difficulties in finding adequate internal standards in LC-MS/MS based methods have been mentioned [25–27]. Ideally, the isotopically labelled analyte should be used to ensure adequate correction of matrix effects, although structural analogues are sometimes used [16]. However, the latter is unsatisfactory in some cases [25, 28], thus making problematic the use of structural analogues as IS in LC-MS methods applied to samples where one can expect notable variations in matrix composition. As an alternative to using internal standards, and accordingly to our data, a previous fourfold dilution of the sample seems to be a simple and satisfactory approach by which to remove matrix effects in water analysis, as a compromise between sensitivity and minimization of matrix effects.

Table 4. Mean recoveries ( $n = 2$ ) after applying the SPE-LC-MS/MS procedure to different types of water spiked at  $0.1 \mu\text{g L}^{-1}$ ; water samples analysed directly, without any dilution ( $\times 1$ ), or diluted four times with HPLC water ( $\times 4$ ).

	Treated				Surface								Ground			
	Water A $\times 1$	Water B $\times 1$	Water C $\times 1$	Water D $\times 1$	Water E $\times 1$	Water F $\times 1$	Water G $\times 1$	Water H $\times 1$	Water I $\times 1$	Water J $\times 1$	Water K $\times 1$	Water L $\times 4$	Water M $\times 4$	Water N $\times 4$	Water O $\times 4$	
Simazine	98	99	87	93	75	22	73	94	111	82	110	107	48	94	108	103
Atrazine	88	96	98	87	78	45	81	92	120	96	120	99	53	65	124	100
Isoproturon	97	94	95	90	84	62	97	91	110	100	110	95	58	84	113	101
Diuron	76	106	91	68	87	62	97	83	108	106	123	109	55	85	134	104
Terbutylazine	97	102	104	87	89	64	92	98	113	113	116	109	64	88	132	107
Pentachlorophenol	98	86	95	124	79	54	95	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
Alachlor	99	106	107	95	107	66	86	112	127	98	112	113	88	73	149	102
Metolachlor	103	113	105	94	108	64	78	111	125	108	110	114	88	88	148	108

<sup>a</sup>No consistent data obtained.

#### 4. Conclusions

Monitoring organic pollutants of wide polarity ranges in water requires the combined use of GC-MS (for the determination of non-polar (semi)volatile analytes) and LC-MS (for more polar analytes) methods. In this article, an automated on-line SPE-LC-MS/MS method has been developed for the determination of several (medium) polar analytes, meaning a short total analysis time, with minimum sample treatment and consumption of organic extracting solvents. Besides its excellent sensitivity, the procedure allows a confident confirmation of compounds detected by acquiring at least two MS/MS transitions and calculating the corresponding intensity ratio.

The application of conventional solvent extraction GC-MS methodology, together with the LC-MS/MS method developed, to treated water from urban solid-waste leachates has allowed the monitoring of 55 organic priority pollutants. The herbicides diuron and simazine have been the most frequently detected in treated water, although at concentrations below  $0.1 \mu\text{g L}^{-1}$ , while raw leachate water exceeded  $2 \mu\text{g L}^{-1}$ .

A study of matrix effects has been performed by applying the SPE-LC-MS/MS procedure to different type of waters (ground, surface, and treated water). A fourfold dilution of samples with HPLC-grade water before injection into the LC-MS equipment has been found to be a simple, rapid, and efficient approach by which to minimize signal suppression or enhancement, in all the water samples tested.

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