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Trace analysis of sulfonylurea herbicides in water samples by solid-phase extraction and liquid chromatography-tandem mass spectrometry

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ABSTRACT

A sensitive method for the simultaneous determination of 30 sulfonylurea herbicides in tap and leaching waters has been developed. Liquid chromatography tandem-mass spectrometry (LC-MS^2) in electrospray ionization positive mode was used for the separation, identification and quantification of these compounds. The procedure involves a preconcentration step based on solid-phase extraction with a silica-based bonded C_{18} cartridge (Sep-Pak Plus) and a *N*-vinyl-pyrrolidone polymer cartridge (Oasis HLB). The best results were obtained with Oasis HLB using methanol as elution solvent. Average recoveries of 30 analytes from water samples were in the range of 79–115% with a relative standard deviation of $<6.1\%$. The limits of quantification (LOQs) obtained in tap and leaching water samples were in the range of 0.1–5.9 and 0.4–5.8 ng L^{-1}, respectively. The proposed method was used to determine sulfonylurea herbicide levels in leaching water samples taken from three lysimeters located in an experimental greenhouse.

1. Introduction

Groundwater contamination by pesticides is receiving increasing attention in European countries because groundwater represents about 98% of the available fresh water of our planet. Thus, maximum admissible concentration of pesticides and related products established by the European Union (EU) for drinking water is 0.1 μg L^{-1} for individual pesticides and 0.5 μg L^{-1} for total concentrations of all pesticides [1].

Sulfonylurea herbicides, discovered in the mid-1970s are used at low application rates for the control of most broad-leaved weeds and annual grasses in numerous crops. The first commercially available sulfonylurea, sulfometuron methyl, was introduced in 1982 by the Dupont Corporation. They act by inhibition of acetolactate synthase, also known as acetohydroxyacid synthase, the first enzyme in branched-chain amino acid (valine, leucine, and isoleucine) biosynthesis in plants [2]. These compounds are weak acids, highly phytotoxic, and essentially non-volatile and they are subject to pH-dependent hydrolysis of the sulfonylurea linkage. Depending on the pH, sulfonylurea herbicides which are susceptible to contraction of the sulfonylurea linkage degrade in water 10 to 1000 times faster than the others [3]. In addition, due to their high solubility in water, moderate to high mobility and slow degradation [4–6], they are being detected in surface and groundwater [7]. According to the Groundwater Ubiquity Score (GUS) index developed by Gustafson [8], most of them are pesticides likely to leach [9]. For these reasons, the determination of sulfonylurea herbicides at low concentrations in water samples is of prime importance.

These herbicides have been previously analyzed in water samples with a variety of techniques, including capillary electrophoresis with UV-diode array detection [10], immunoassay [11], gas chromatography with mass spectrometry detection using diazomethane or pentafluorobenzyl bromide derivatization [12–14] and liquid chromatography (LC) with UV-diode array detection [15–19]. Solid-phase extraction-liquid chromatography-mass spectrometry detection has been the most frequent technique used for analyzing sulfonylurea herbicides [19–25]. The aim of this works was to develop a simple method for the determination of 30 sulfonylurea herbicides, commonly used in many areas, by solid-phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS^2) in various kinds of water. Their chemical structures and common names are listed in Table 1. In addition, the results concerning recovery rates obtained by using different SPE cartridges and sonication extraction method described by Fenoll et al. will be reported here [20].

2. Experimental

2.1. Chemicals and solutions

All solvents were residue analysis grade and were purchased from Scharlau (Barcelona, Spain).

Pesticide standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany) with purity ranging from 94 to 100%. Stocks

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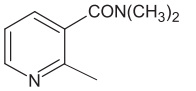
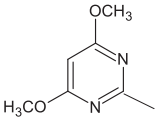
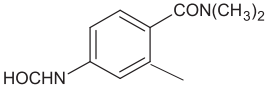
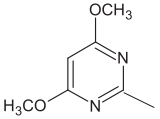
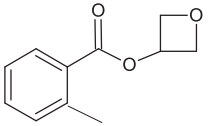
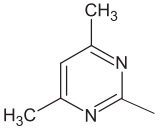
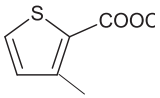
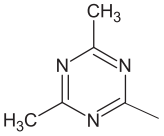
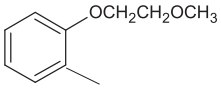
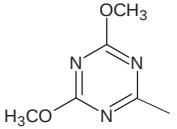
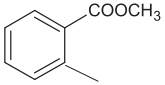
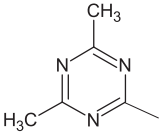
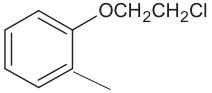
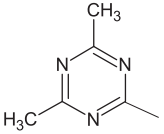
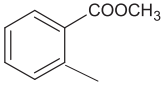
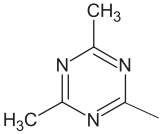
Table 1
Chemical structures and analytical conditions of the studied sulfonylurea herbicides.

Herbicide	**X**-SO_2NHCONH-**Z**		M_w	t_R(min)	Quantitation MRM_1	$Fragmentor_1$ (V)	E. $Collision_1$ (V)	Confirmation MRM_2	$Fragmentor_2$ (V)	E. $Collision_2$ (V)
	X	**Z**								
Nicosulfuron			410.4	14.22	411.0→182.0	110	20	411.0→213.0	110	20
Foramsulfuron			452.5	14.37	453.0→182.0	110	20	453.0→255.0	110	20
Oxasulfurom			406.4	15.06	407.0→150.0	110	20	407.0→210.0	110	20
Thifensulfuron-methyl			387.4	15.17	388.0→167.0	110	10	388.0→141.0	110	10
Cinosulfuron			413.4	15.51	414.0→183.0	110	10	414.0→157.0	110	20
Metsulfuron-methyl			381.4	15.52	382.0→167.0	110	10	382.0→141.0	110	20
Triasulfuron			401.8	15.91	402.0→141.0	110	20	402.0→167.0	140	10
Sulfometuron-methyl			364.4	15.93	365.0→150.0	110	20	365.0→107.0	130	40

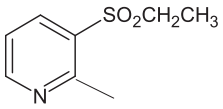
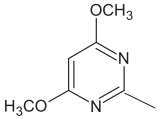
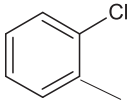
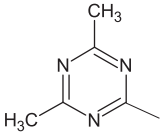
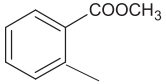
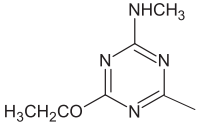
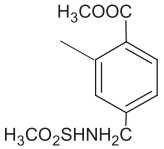
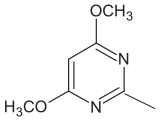
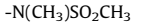
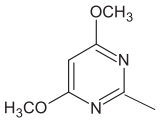
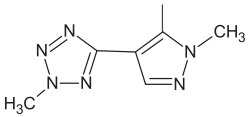
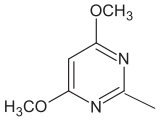
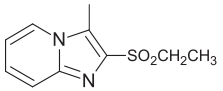
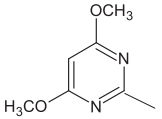
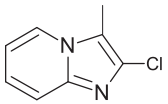
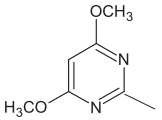
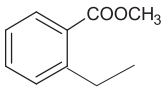
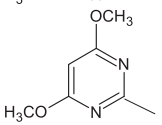
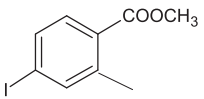
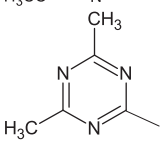
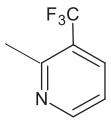
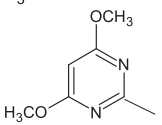
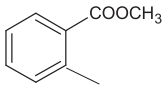
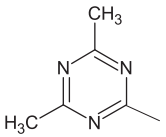
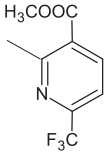
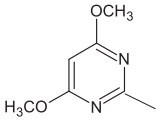
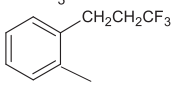
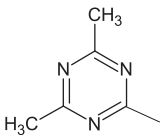
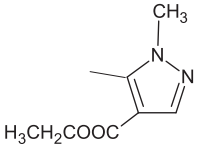
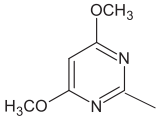
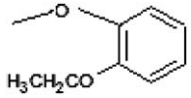
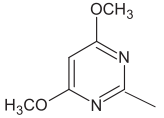
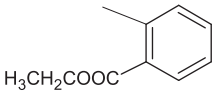
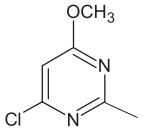
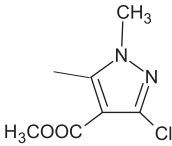
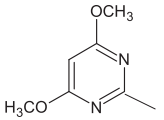
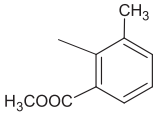
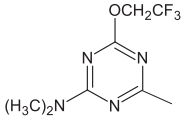
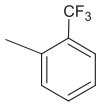
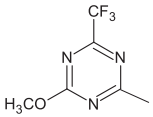
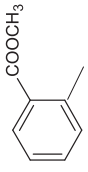
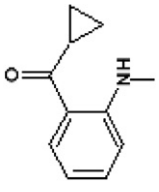
Rimsulfuron			431.4	15.98	432.0→182.0	130	20	432.0→325.0	140	10
Chlorsulfuron			357.8	16.04	358.0→141.0	110	20	358.0→167.0	110	20
Ethametsulfuron-methyl			410.4	16.19	411.0→196.0	110	10	411.0→168.0	110	30
Mesosulfuron-methyl			503.5	16.32	504.0→182.0	110	20	504.0→162.0	130	40
Amidosulfuron			369.4	16.54	370.0→261.0	70	10	370.0→218.0	110	20
Azimsulfuron			424.4	16.61	425.0→182.0	70	10	425.0→156.0	110	30
Sulfosulfuron			470.5	16.98	471.0→211.0	110	10	471.0→261.0	110	10
Imazosulfuron			412.8	17.52	413.0→156.0	110	20	413.0→258.0	110	20
Bensulfuron-methyl			410.4	17.63	411.0→149.0	110	20	411.0→182.0	110	20
Iodosulfuron-methyl-sodium			529.2	17.88	508.0→167.0	110	20	508.0→141.0	110	20
Flazasulfuron			407.4	17.91	408.0→182.0	130	20	408.0→227.0	140	20

Table 1 (*continued*)

Herbicide	**X**-SO_2NHCONH-**Z**		M_w	t_R(min)	Quantitation MRM_1	$Fragmentor_1$ (V)	$E.\ Collision_1$ (V)	Confirmation MRM_2	$Fragmentor_2$ (V)	$E.\ Collision_2$ (V)
	X	**Z**								
Tribenuron-methyl			395.4	17.92	396.0→155.0	110	10	396.0→181.0	110	20
Flupysulfuron-methyl			487.3	18.97	488.0→178.0	130	20	488.0→333.0	130	20
Prosulfuron			419.4	19.02	420.0→141.0	130	20	420.0→167.0	130	20
Pyrazosulfuron-ethyl			414.3	19.21	415.0→182.0	110	20	415.0→139.0	130	40
Ethoxysulfuron			398.4	19.68	399.0→261.0	110	10	399.0→218.0	110	20
Chlorimuron-ethyl			414.8	19.69	415.0→186.0	110	20	415.0→121.0	110	40
Halosulfuron-methyl			434.8	19.86	436.0→183.0	110	20	436.0→139.0	110	40
Triflusulfuron-methyl			492.4	20.24	493.0→264.0	130	20	493.0→238.0	140	20
Tritosulfuron			445.3	20.28	446.0→195.0	130	20	446.0→221.0	130	20

Primisulfuron-methyl		468.3	20.64	469.0→254.0	130	20	469.0→199.0	130	20	30
Cyclosulfamuron		421.4	20.69	422.0→261.0	70	10	422.0→218.0	110	30	30

solutions (1000 μg mL^{-1}) of each pesticide standard were prepared by dissolving 0.025 g of the pesticide in 25 mL of acetonitrile. Fluometuron was used as internal standard. A pesticide intermediate standard solution (10 μg mL^{-1}) was prepared by transferring 1 mL from each pesticide solution to a 100 mL volumetric flask and diluting to volume with acetonitrile to obtain a concentration of 10 μg mL^{-1}. Several standard solutions, with concentrations of 5–200 μg L^{-1}, were injected to obtain the linearity of detector response.

2.2. SPE procedure

Preconcentration of the sulfonylurea herbicides from water samples (0.5 L) was accomplished by solid-phase extraction with two different types of sorbents: *N*-vinyl-pyrrolidone polymeric cartridges (Oasis HLB 200 mg, 6 mL, Waters) and silica-based bonded C_{18} cartridges (Sep-Pak Plus 500 mg, 6 mL, Waters).

The SPE cartridges were first conditioned with 5 mL of acetonitrile or 5 mL of methanol, followed by 5 mL of deionised water. Extraction of water samples was carried out at 8 mL min^{-1} flow rate. After the samples were loaded onto the cartridges, they were washed with 10 mL deionised water and dried for 15 min under a vacuum. The analytes retained were eluted with 5 mL of acetonitrile or 5 mL of methanol. The solution was filtered through a 0.45 μm filter and analyzed by LC-MS^2 under conditions described above.

Water samples were passed through 2 mm sieve. The main physico-chemical characteristics of the water were as follows: Water A (tap water): pH=8.22, EC=0.93 dS m^{-1}, TOC=1.42 mg L^{-1}, NO_3=6.4 mg L^{-1}, and NO_2^- < LOD. Water B (leaching water): pH=8.41, EC=4.32 dS m^{-1}, TOC=130 mg L^{-1}, NO_3^- = 547 mg L^{-1}, and NO_2^- =0.12 mg L^{-1}.

2.3. Method validation

The parameters considered for validation of the method developed were linearity, calibration curves, matrix effects, detection limit, quantification limit, repeatability and recovery. Finally, in order to prove the effectiveness of the validated method and its suitability for routine analysis, it was applied to real samples.

2.4. LC-MS^2 conditions

The high performance liquid chromatography HPLC-MS^2 analyses were performed on a Agilent Series 1100 liquid chromatograph (Agilent Technologies, Santa Clara, CA, USA) with a vacuum degasser, autosampler and a binary pump, interfaced to a G6410A triple quadrupole mass spectrometer from Agilent equipped with an ESI interface operating in positive ion mode. 5 μL was injected and the pesticides were chromatographically separated using a reversed phase C8 analytical column of 150 mm × 4.6 mm and 5 μm particle size (Zorbax Eclipse XDB-C8) was maintained at 25 °C. The flow-rate used was 0.6 mL min^{-1}. Mobile phases A and B were acetonitrile and 0.1% formic acid, respectively. The analytes were separated with the following gradient program: 0–5 min, 10% A constant; 5–10 min, 10–50% A; 10–20 min, 50–70% A; and 20–25 min, 70–100% A. 8 min post-run time was used after each analysis. The MS parameters were capillary voltage, 4000 V; nebulizer pressure, 40 psi; drying gas, 9 L min^{-1}; and drying gas temperature, 350 °C. Nitrogen was served as the nebulizer and collision gas. Mass spectra were recorded across the range 50–1000 m/z.

Two time windows with ±1 min overlapping range around the borders were constructed. The star times of the first and second segments were 0 and 18.4 min, respectively. Fig. 1 shows the total ion chromatogram of 30 sulfonylurea herbicides (all of them at 50 ng mL^{-1} concentrations). Under the described chromatography

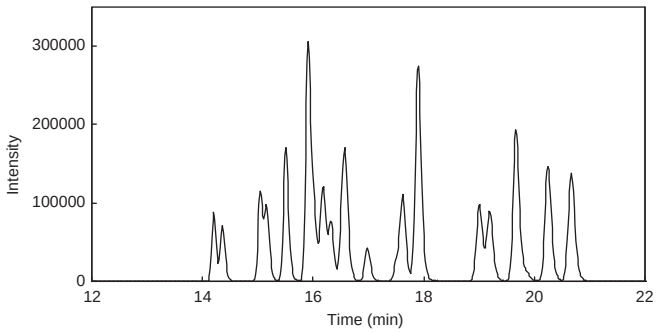


Fig. 1. LC-MS^2 total ion chromatograms in selected reaction monitoring (SRM) mode obtained of 30 sulfonylurea herbicides at the 50 ng mL^{-1} concentration level.

conditions, the herbicides eluted from 14 to 21 min. Agilent Mass Hunter Data Acquisition; Qualitative Analysis and Quantitative Analysis software were used for method development and data acquisition.

3. Results and discussion

3.1. Liquid chromatography-tandem mass spectrometry analysis

The LC-MS^2 system was used for analysis of water samples. A preliminary study of the optimal SRM transitions for every compound was carried out by injecting individual analytes at a concentration level of 10 μg mL^{-1}, with the objective of obtaining the protonated molecule and selecting those transitions with higher molecular in order to avoid the disruptive effects of the matrix, as far as possible. Various fragmentor voltages and collision energies were applied to the compounds under study. The most intense transitions were chosen for merging and creating the method. Table 1 lists the pesticides along with their retention times and their optimized SRM transitions with a dwell time of 20 ms.

The identification procedure for sulfonylurea herbicide residues in water was carried out using the retention time and two transitions. The most intense transition was used as quantifier and the other one as qualifier peak for the confirmatory analysis. The ratio between these transitions was also used for confirmatory purposes. Five herbicides presented common precursor ion: nicosulfuron-ethametsulfuron-methyl-bensulfuron-methyl (m/z=411) and pyrazosulfuron-ethyl-chlorimuron-ethyl (m/z=415); and one pair of herbicides has one transition in common: nicosulfuron-bensulfuron-methyl (411→182). However, these compounds can be identified by using the retention times (Fig. 2). The values of the SRM ratios for all the transition pairs selected are between 5% and 100%; only 10% of the compounds presented a SRM ratio lower than 10%, allowing a correct identification and quantification in the concentration range studied. More than 90% of the compounds presented SRM variability lower than 20% in concentration ranged studied. This criterion is in compliance with the DG SANCO/2007/3131 of the European Quality Control Guidelines, based on ion-ratio statistics for the transitions monitored.

3.2. Solid-phase extraction optimization

Prior to LC-MS^2 determination, solid-phase extraction (SPE) was used in order to achieve a more sensitive method for the analysis of sulfonylurea herbicides. Extraction efficiencies were compared on a Sep-Pak Plus C_{18}-bonded silica and an Oasis HLB *N*-vinyl-pyrrolidone polymeric phase. Our aim was to evaluate the feasibility of these sorbents in retaining these compounds

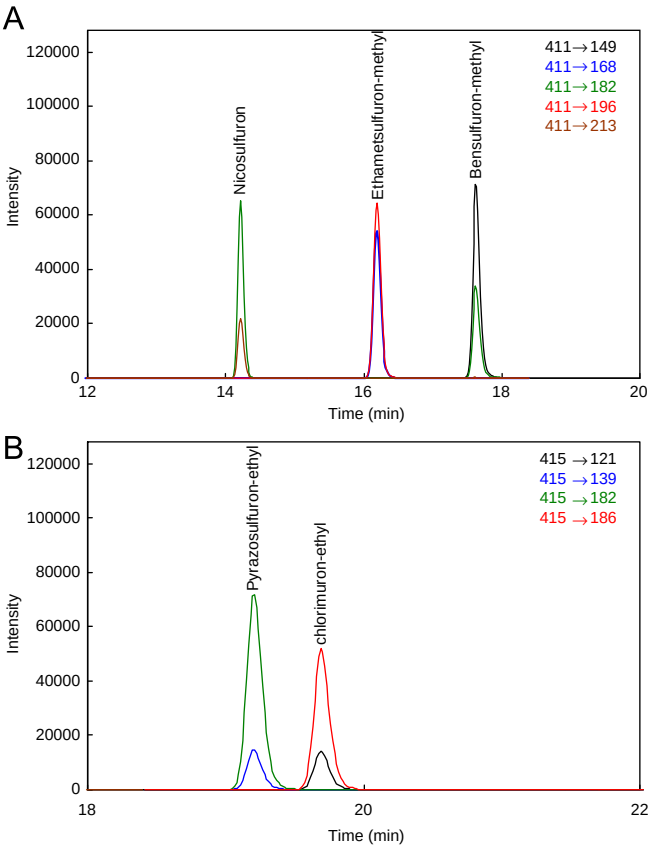


Fig. 2. Examples for common transitions.

from an aqueous solution. To accomplish this, samples of tap water were spiked with the sulfonylurea herbicides at 0.1 and 1.0 μg L^{-1}. For eluting these compounds acetonitrile was used. Fig. 3 shows the recovery values obtained with the two cartridges, using acetonitrile as eluent. More than 85% of the herbicides under study presented recoveries between 70 and 105% when the Oasis HLB cartridges were used. In this sorbent, low recoveries were detected for ethametsulfuron-methyl, flazasulfuron and ciclosulfamuron. For these three herbicides good recoveries were obtained when sonication extraction method described by Fenoll et al. [20] was used. However, this method is less sensible and presents matrix effect for the more polar analytes. In the case of the Sep-Pak Plus C_{18} cartridges, a very deficient recovery of most of the analytes was observed. As for the sulfonylureas, Oasis HLB was chosen for obtaining higher recoveries. On the other hand, acetonitrile and methanol were tested to elute these herbicides. It may be seen that the behavior of acetonitrile and methanol using Oasis HLB cartridges was similar, except in the case of nicosulfuron, rimsulfuron, ethametsulfuron-methyl, flazasulfuron and ciclosulfamuron, whose recoveries only reached 75% when eluted with methanol. Methanol was chosen because it permitted recoveries between 78 and 114% for all the herbicides studied (Fig. 4).

3.3. Linearity, matrix effects, limit of detection and limit of quantification

The seven-point-calibration curves in solvent and on both waters (tap and leaching) were constructed by plotting peak area *vs.* concentrations and compared at 5, 10, 20, 50, 75, 100 and 200 μg L^{-1}. This comparison gave information not only about linearity and sensitivity but also about matrix effects (ion suppression or enhancement). The correlation coefficients derived from linear regressions were in all cases higher than 0.997, with

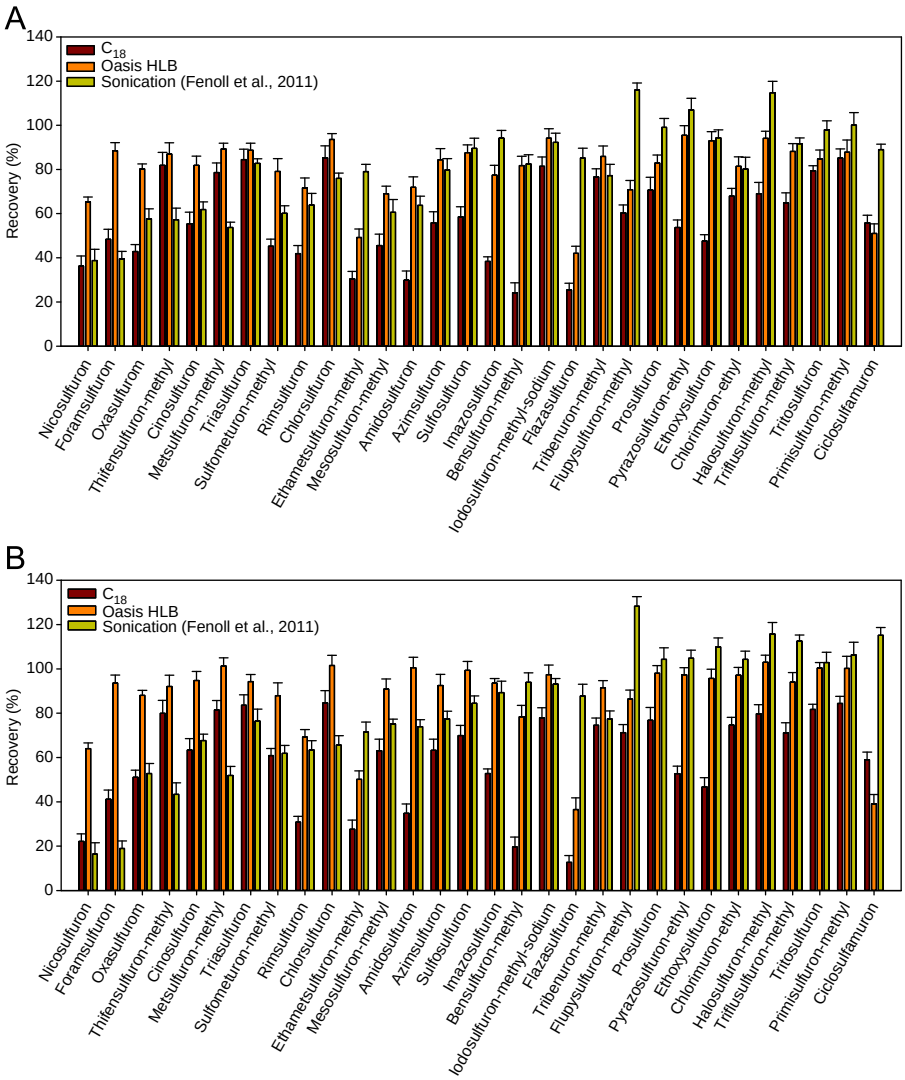


Fig. 3. Levels of sulfonylurea herbicides recovered from tap water, using solid-phase extraction (C_{18} and Oasis HLB cartridges) and sonication extraction method [20]. Eluent: 5 mL of acetonitrile. Samples spiked with 0.1 μg L^{-1} (A) and 1.0 μg L^{-1} (B).

significant correlation between concentration and area for all herbicides (Table 2).

Matrix effects in LC–MS^2 with electrospray ionization source are very important for the determination of pesticides in different matrices. The response of the analytes can be reduced or enhanced, compared to solvent-based standards. This is due to the fact that coeluting species presented in the matrix can interfere in the ionization of the target compounds. To evaluate these possible effects, the slopes obtained in the calibration with matrix-matched standards were compared with those obtained with solvent-based standards, calculating matrix/solvent slope ratios (S_m/S_s) for each sulfonylurea herbicide (Table 2). On both waters, the sulfonylurea herbicides presented very low signal suppression or enhancement (−20% to +20%). More than 80% of the compound were below or equal to 10% signal suppression or enhancement. The two types of water matrices had similar values with a slightly lower percentage. Because the matrix effect was not observed, matrix-matched standard calibration was not necessary to determine these compounds in the studied matrices.

LODs and LOQs were evaluated by injecting standard solution into blank-matrix at the different concentration levels. The limits of detection (LOD) and limit of quantification (LOQ) of the proposed method were estimated as the value where the signal-to-noise (*S/N*) ratio of 3 and 10, respectively. LOQs obtained for the individual sulfonylurea herbicides in tap and leaching waters are shown in Table 2. The LOQs obtained for all herbicides ranged from 0.1 to 5.9 ng L^{-1} for tap water and 0.4 to 5.8 ng L^{-1} for leaching water. These comply with the maximum admissible concentration of pesticides and related products for drinking water established by the European Union (EU). For most of the pesticides, the quantification limits were not affected, or were only slightly affected, by the studied matrices.

Overall, the LOQs obtained in the present study were similar or even lower than those obtained by other authors that analyzed these pesticides in water by using SPE-HPLC-DAD [19], sonication-HPLC-MS^2 [20], SPE-HPLC-MS [21] or SPE-HPLC-MS^2 [23].

3.4. Repeatability and recovery

The repeatability of our chromatographic method was determined by performing the analysis of tap and leaching waters spiked at 50 and 100 ng L^{-1} of pesticide, injected five times, to evaluate the intra-day (within one day) and inter-day (between days) RSDs of the signal intensities. For determining inter-day precision, samples were stored at −20 °C. Intra-day and inter-day RSDs were below 8 and 11%, respectively. This complies with the

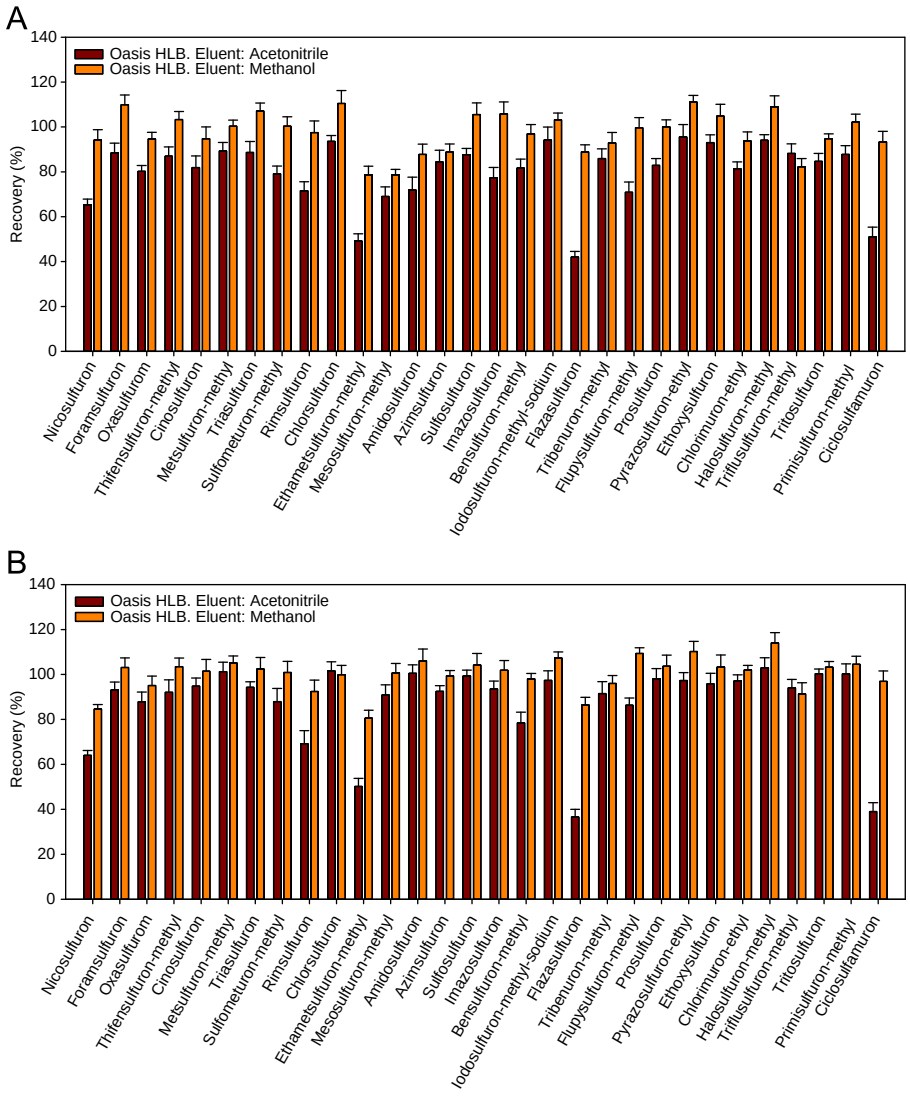


Fig. 4. Levels of sulfonylurea herbicides recovered from tap water, using solid-phase extraction (Oasis HLB cartridges). Eluent: 5 mL of methanol or acetonitrile. Samples spiked with 0.1 μg L^{-1} (A) and 1.0 μg L^{-1} (B).

RSD accepted by the DG SANCO/2007/3131 of the European Quality Control Guidelines.

For the recovery study, spiked samples were prepared from each of the two waters (tap and leaching) and examined at 100 and 200 ng L^{-1} spiking levels. The data evaluation was carried out by comparing the peak areas of the spiked samples to those obtained by solvent calibration. The distribution of the recoveries is shown in Fig. 5. The recoveries obtained for all sulfonylurea herbicides ranged from 79.6 to 114.8% for tap water and 83.2 to 114.4 for leaching water. These recoveries were in the acceptance range of the DG SANCO/2007/3131 of the European Quality Control Guidelines 70–120% in all cases. The relative standard deviation (RSD) was $<6.1\%$ in the most unfavorable case.

3.5. Real samples

Real samples were taken from 3 lysimeters (3.5 m × 4 m × 1 m) from an experimental greenhouse located in Campo de Cartagena, Murcia (SE Spain). A clay loam soil (pH 8.7 and OM = 0.22%) was used and spiked with commercial product at the doses recommended by the manufacturers: triasulfuron [LOGRAN 20 20% WG (Syngenta)] and chlorsulfuron [GLEAN 75% w/v WG (DuPont)]. In each lysimeter, different treatments were carried out with a sprayer (Matabi) with an adjustable nozzle size of 1 mm. The soil was irrigated every 2 days by three dripperlines (45 min per day and 50 mL min^{-1} per emitter). About 100 L was collected from each lysimeter. The preparation procedure was the same as the one mentioned above. Chorsulfuron (GUS = 5.38) and triasulfuron (GUS = 3.81) residues were found in these samples in the linear range of the analytical method (Table 3). In order to justify the extractability of the compounds using the described method, the leaching waters were also analyzed by HPLC according to the methods described previously by Fenoll et al. [20]. Similar results were obtained by both methods (Table 3).

4. Conclusions

In this study, the determination of 30 sulfonylurea herbicides in water was evaluated using solid-phase extraction-liquid chromatography tandem-mass spectrometry (SPE-LC-MS^2). The linearity, matrix effect, limits of detection, limits of quantification, repeatability and recovery were studied in tap and leaching waters. The described method is very sensitive and selective, and matrix effect was not observed. Another advantage of the method is that it allows simultaneous extraction of these

Table 2
Linearity, matrix effects and limits of quantification (LOQ, ng L^{-1}).

Herbicide	Solvent		Water A (tap water)		Water B (leaching water)		Slope matrix/slope solvent		Matrix effect (%)[a]		LOQ	
	Slope	R	Slope	R	Slope	R	Water B	Water B	Water A	Water B	Water A	Water B
Nicosulfuron	3258.0	0.9997	2645.5	0.9987	2783.3	0.9992	0.812	0.854	18.8	14.6	1.9	2.3
Foramsulfuron	3182.4	0.9996	3223.1	0.9998	3072.5	0.9997	1.013	0.965	−1.3	3.5	1.6	2.1
Oxasulfurom	5371.8	1.0000	5119.0	0.9998	5037.4	0.9999	0.953	0.938	4.7	6.2	1.0	0.8
Thifensulfuron-methyl	3559.5	0.9997	3681.1	0.9999	3779.6	0.9998	1.034	1.062	−3.4	−6.2	1.4	1.7
Cinosulfuron	2761.4	1.0000	2853.2	0.9998	2745.5	0.9999	1.033	0.994	−3.3	0.6	1.8	2.4
Metsulfuron-methyl	4421.1	1.0000	4709.6	0.9998	4212.9	0.9999	1.065	0.953	−6.5	4.7	1.1	0.9
Triasulfuron	2158.4	0.9991	2177.0	0.9998	2100.4	0.9994	1.009	0.973	−0.9	2.7	2.3	3.1
Sulfometuron-methyl	10849.8	0.9999	10965.4	0.9998	10632.1	0.9998	1.011	0.980	−1.1	2.0	0.1	0.4
Rimsulfuron	951.0	0.9973	859.3	0.9998	869.3	0.9985	0.904	0.914	9.6	8.6	5.8	5.5
Chlorsulfuron	2813.7	0.9999	2733.8	0.9999	2598.0	0.9999	0.972	0.923	2.8	7.7	1.8	2.5
Ethametsulfuron-methyl	4624.1	0.9996	3713.8	0.9993	3820.8	0.9995	0.803	0.826	19.7	17.4	1.3	1.7
Mesosulfuron-methyl	4082.5	0.9992	4109.0	0.9996	4003.2	0.9994	1.006	0.981	−0.6	1.9	1.2	1.0
Amidosulfuron	2898.3	0.9976	3203.2	0.9996	2775.7	0.9986	1.105	0.958	−10.5	4.2	1.6	2.3
Azimsulfuron	2832.3	0.9982	2883.6	0.9995	2798.6	0.9988	1.018	0.988	−1.8	1.2	1.7	2.3
Sulfosulfuron	2381.1	0.9999	2490.7	0.9979	2299.6	0.9989	1.046	0.966	−4.6	3.4	2.0	2.8
Imazosulfuron	1315.7	1.0000	1332.9	0.9995	1284.6	0.9998	1.013	0.976	−1.3	2.4	3.8	5.1
Bensulfuron-methyl	4664.1	0.9998	4587.1	0.9998	4521.3	0.9998	0.984	0.969	1.6	3.1	1.1	0.9
Iodosulfuron-methyl-sodium	3732.9	1.0000	4059.1	0.9996	3702.1	0.9998	1.087	0.992	−8.7	0.8	1.2	1.8
Flazasulfuron	6910.4	0.9999	5900.1	0.9999	5996.9	0.9999	0.854	0.868	14.6	13.2	0.8	0.7
Tribenuron-methyl	6152.8	0.9997	5945.2	1.0000	5798.6	0.9998	0.966	0.942	3.4	5.8	0.5	0.8
Flupysulfuron-methyl	1272.3	0.9989	1422.8	0.9991	1129.0	0.9990	1.118	0.887	−11.8	11.3	3.5	5.8
Prosulfuron	4955.5	1.0000	5191.8	1.0000	4878.8	1.0000	1.048	0.985	−4.8	1.5	1.0	1.3
Pyrazosulfuron-ethyl	6054.9	0.9991	6630.1	0.9999	5987.2	0.9995	1.095	0.989	−9.5	1.1	0.5	1.1
Ethoxysulfuron	5966.4	0.9998	6137.6	0.9999	5988.6	0.9999	1.029	1.004	−2.9	−0.4	1.1	0.8
Chlorimuron-ethyl	3909.1	0.9999	4069.8	0.9999	3876.3	0.9999	1.041	0.992	−4.1	0.8	1.2	1.7
Halosulfuron-methyl	755.5	0.9999	850.2	0.9987	732.1	0.9993	1.125	0.969	−12.5	3.1	5.9	4.8
Triflusulfuron-methyl	8666.5	1.0000	8108.9	1.0000	8023.1	1.0000	0.936	0.926	6.4	7.4	0.2	0.5
Tritosulfuron	1435.8	0.9996	1510.3	0.9999	1385.6	0.9998	1.052	0.965	−5.2	3.5	3.3	4.7
Primisulfuron-methyl	2453.2	1.0000	2578.8	1.0000	2312.3	1.0000	1.051	0.943	−5.1	5.7	1.9	2.8
Ciclosulfamuron	3953.0	0.9998	3889.4	0.9984	3709.3	0.9991	0.984	0.938	1.6	6.2	1.3	1.8

[a] Matrix effect (%)=(1−(slope matrix/slope solvent)) × 100.

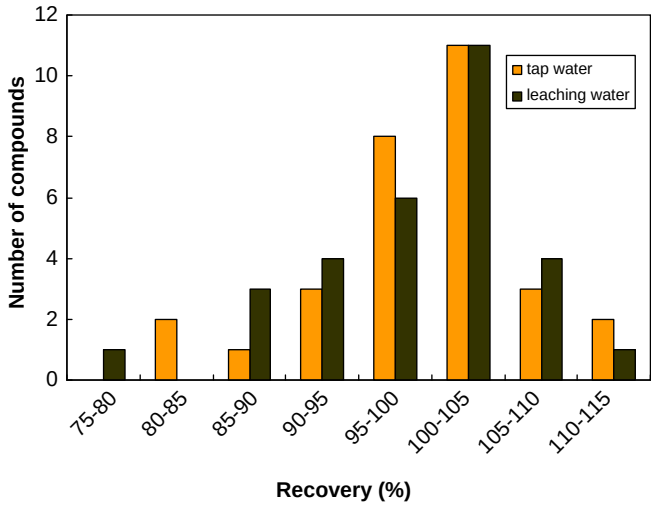


Fig. 5. Data distribution of recoveries.

Table 3
Sulfonylurea residues (μg L^{-1}) found in real water samples.

Sample	Proposed method[a]		Reference method[ab]	
	Triasulfuron	Chlorsulfuron	Triasulfuron	Chlorsulfuron
Water 1		15.3 ± 0.2		16.1 ± 0.3
Water 2	22.6 ± 0.3		21.0 ± 0.4	
Water 3	26.4 ± 0.3	19.5 ± 0.3	23.9 ± 0.3	18.1 ± 0.3

[a] Mean of four determinations ± RSD.
[b] Residue values obtained by a reference method described by Fenoll et al. [20].

compounds from water without modified pH of the sample. In addition, this method allowed the determination of the herbicides considered at concentration below 0.1 μg L^{-1}, the limit established by European legislation for individual pesticides in drinking water. Linearity, repeatability and recovery were found to be within the range of acceptance. Finally, analysis of real samples showed the validity of method used, which allowed the determination and identification of pesticides present in the samples.

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