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Determination of rice herbicides, their transformation products and clofibric acid using on-line solid-phase extraction followed by liquid chromatography with diode array and atmospheric pressure chemical ionization mass spectrometric detection

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Abstract

A simultaneous method for the trace determination of acidic, neutral herbicides and their transformation products in estuarine waters has been developed through an on-line solid-phase extraction method followed by liquid chromatography with diode array and mass spectrometric detection. An atmospheric pressure chemical ionization (APCI) interface was used in the negative ionization mode after optimization of the main APCI parameters. Limits of detection ranged from 0.1 to 0.02 ng/ml for 50 ml of acidified estuarine waters preconcentrated into polymeric precolumns and using time-scheduled selected ion monitoring mode. Two degradation products of the acidic herbicides (4-chloro-2-methylphenol and 2,4-dichlorophenol) did not show good signal response using APCI-MS at the concentration studied due to the higher fragmentor voltage needed for their determination. For molinate and the major degradation product of propanil, 3,4-dichloroaniline, positive ion mode was needed for APCI-MS detection. The proposed method was applied to the determination of herbicides in drainage waters from rice fields of the Delta del Ebro (Spain). During the 3-month monitoring of the herbicides, 8-hydroxybentazone and 4-chloro-2-methylphenoxyacetic acid were successively found in those samples. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Frequent contamination by herbicides in surface and ground waters occur due to their high use [1–3]. Acidic herbicides are an important class applied to control a variety of weeds in many crops. In general, these herbicides have a long residual activity in soils and also in water, remaining for several months due

to their low microbial activity [4,5]. Their relatively low vapor pressures and moderate water solubilities also make the monitoring in environmental water an issue of priority concern.

Liquid chromatography–mass spectrometry (LC–MS) techniques are widely applied to the water monitoring of polar pesticides due to the achieving of a high sensitivity allied to the inherent high selectivity of mass spectrometric detection [6]. Among the different LC–MS interfaces, the high flow pneumatically-assisted electrospray ionization (ESI) and atmospheric pressure chemical ionization

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(APCI) interfaces have become the most recently applied to determination of acidic herbicides and their degradation products in environmental waters [7–9]. In general, the acidic properties of the acidic herbicides demands a negative ionization (NI) mode for identification of such compounds. Chiron et al. [10] used LC–ESI–MS in the NI mode for the determination of bentazone and their degradation products at a 0.01 $\mu\text{g/l}$ level, but the need for postcolumn addition of a neutralization buffer could have contributed to the high relative standard deviation. Kjøppen and Spliid [11] found that ESI was more sensitive than APCI for the analysis of acidic herbicides in the NI mode, with method detection limits in the 0.001–0.01 $\mu\text{g/l}$ range in the selected ion monitoring (SIM) mode. However, bentazone presented a non-linear response which was attributed to its improper ability to form deprotonated molecular ions in the electrospray ionization process.

The analysis of acidic herbicides requires that the preconcentration and posterior chromatographic separation are made under acidic conditions, preferably at pH below the pK_a of the compound, to guarantee suitable ionization suppression, although Geerdink et al. have obtained satisfactory results at high pH for precolumn clean-up and subsequent elution [12]. Graphitized carbon black [7,13], C_{18} [10,14] and polymeric sorbents are currently used as solid-phase extraction (SPE) materials for enrichment of acidic herbicides, although polymeric materials are considered more useful since they permit a broader range of pH conditions.

The compounds selected in this work are herbicides commonly applied over rice fields. Some of them, such as propanil and molinate, lead the rice pesticide list [1] and are used in the first stages of rice cultivation to control the germinating of water grasses and broadleaf plants. Post-emergent acidic herbicides such as bentazone, 4-chloro-2-methylphenoxyacetic acid (MCPA) and mecoprop are also applied. Fig. 1 presents the structures of the compounds included in this study. The herbicide formulations in maize and rice crops are mixtures of phenoxyacetic acids, but also propanil and molinate are applied in high amounts. Thus, it is important to develop a dependable and sensitive method for the simultaneous determination of such compounds in sample waters. In this work, an analytical method is

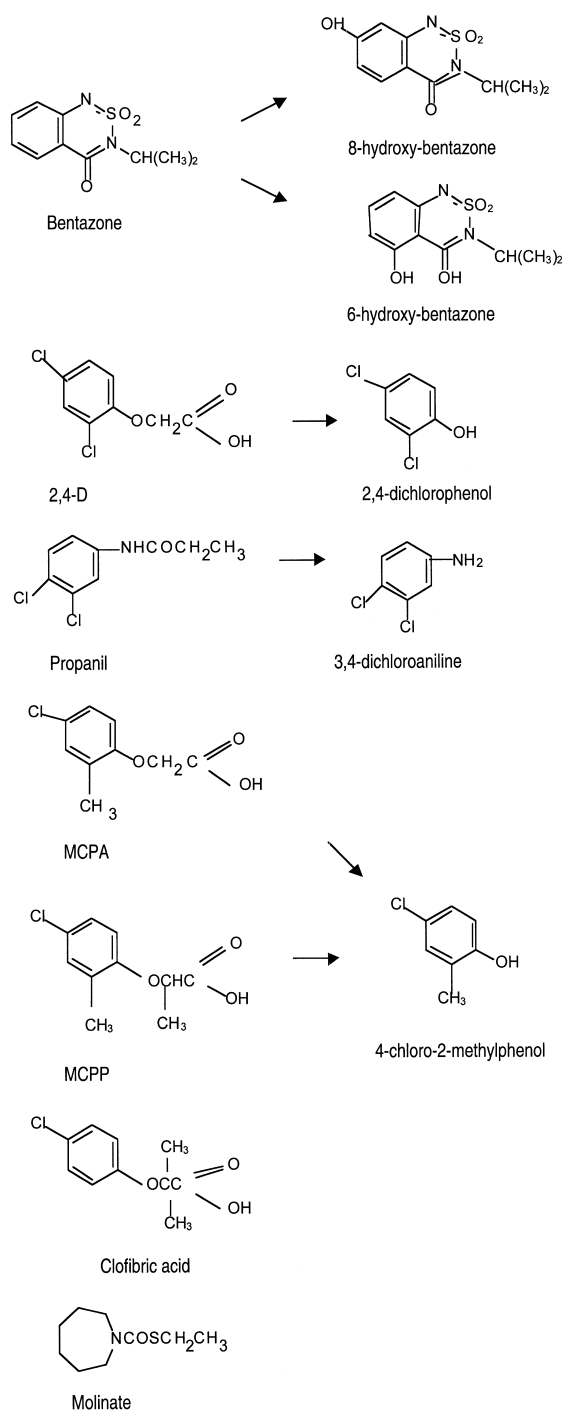


Fig. 1. Chemical structures of the studied compounds.

proposed for determining a range of neutral and acidic herbicides and also a structural isomer of the mecoprop herbicide, the clofibric acid, a pharmaceutical drug previously detected in Swiss lakes [15] (structures given in Fig. 1). The determination of acidic herbicides by LC is preferable, since the relative polarity and low vapor pressure of these compounds require derivatization processes such as pentafluorobenzoylation or esterification with hazardous reagents such as diazomethane or BF_3 [16,17]. The method now proposed associates the reproducibility of UV detection to the selectivity of MS detection. By using time-scheduled selected ion monitoring the sensitivity of the method is enhanced.

The main aims pursued in this work were: (i) to develop a sensitive method for simultaneous analysis of acid and neutral herbicides through on-line SPE–LC–diode array detection (DAD) and LC–APCI–MS and (ii) to monitor the presence of the herbicides and their degradation products in the Ebro Delta area during the months of major inputs of such herbicides.

2. Experimental

2.1. Chemicals

HPLC-grade water, acetonitrile, methanol, hydrochloric acid, ammonium formate and formic acid were purchased from Merck (Darmstadt, Germany). All the solvents were previously passed through 0.45- μm membrane filters (Millipore, Bedford, MA, USA). Standards of the pesticides and their degradation products were: bentazone, mecoprop (MCP), 4-chloro-2-methylphenol (ChemService, West Chester, PA, USA), 2,4-D (PolyScience, Niles, IL, USA), molinate, 3,4-dichloroaniline, 6-hydroxybentazone, 8-hydroxybentazone (Dr. Ehrenstorfer, Augsburg, Germany), propanil, MCPA (Riedel-de Haen, Seizle, Germany), 2,4-dichlorophenol (Merck). Clofibric acid was obtained from Aldrich (Deisenhofen, Germany). All the standards had a minimum purity of 99%. Stock and diluted solutions of the standards were prepared in methanol and were stable for several months when stored in a freezer at -20°C .

2.2. Chromatographic conditions

The chromatographic analyses were performed using a system from Hewlett-Packard, Model 1090 diode array UV–Vis detector coupled in series with the LC–APCI–MS HP 1100 mass-selective detector (Hewlett-Packard, Palo Alto, CA, USA). The automated on-line preconcentrations were made with an OSP-2 (Merck) connected to a L-6200A Intelligent Pump (Merck–Hitachi, Germany) for delivery of the conditioning solvents and the sample. Disposable precolumns of 10×2 mm I.D. were used, prepacked with PLRP-S (Polymer Labs., Church Stretton, UK). Precolumns were firstly conditioned with 5 ml of methanol and Milli-Q water, acidified to pH 2 with hydrochloric acid, and then water sample volumes of 5 to 50 ml were preconcentrated at a flow-rate of 2 ml/min.

The analytical column was a LiChrocart cartridge (250×4.6 mm I.D.), packed with a LiChrospher 60RP select B of 5 μm of particle size (Merck). Gradient elution was accomplished by using acetonitrile (solvent A) and a buffer solution of ammonium formate–5 mM formic acid at pH 3 (solvent B), from A–B (20:80) to A–B (35:65) in 10 min, then to A–B (45:55) in 20 min, A–B (90:10) in 10 min and back to initial conditions in 5 min, at a flow-rate of 0.9 ml/min. For quantification using DAD the wavelength was set at 220 nm (8-hydroxybentazone, 6-hydroxybentazone, bentazone, propanil and molinate), 230 nm (2,4-D, MCPA, 4-chloro-2-methylphenol, clofibric acid, 2,4-dichlorophenol and mecoprop) and 240 nm (3,4-dichloroaniline).

2.3. Mass spectrometric conditions

An APCI interface was used in the LC–MS system HP 1100, with the acquisitions performed in the negative ion mode. The APCI–MS conditions were optimized by direct injection of standard solutions (10 ng/ μl of each compound) into the mobile phase of A–B (40:60), at a flow-rate of 0.9 ml/min, without the analytical column connected. The selected parameters were as follows: drying nitrogen gas at 350°C and a flow-rate of 4 ml/min; nebulizer pressure at 60 p.s.i.g. (1 p.s.i.=6894.76 Pa); vaporizer temperature at 350°C ; capillary voltage at 4500 V and corona current at 25 μA . The chromatograms

Table 1
Selected ion monitored in time-scheduled at different fragmentor voltages

Time (min)	Fragmentor voltage (V)	Compounds (<i>m/z</i> fragment monitored)
10.0–20.5	70	8-Hydroxybentazone (255) 6-Hydroxybentazone (283, 255) Bentazone (239, 176) 2,4-D (219, 161) MCPA (199, 141)
20.6–26.5	70	Clofibric acid (213, 127) Mecoprop (213, 141)
26.6–30.0	100	Propanil (216, 160)

obtained for quantitation were recorded under time-scheduled SIM, with different fragmentor voltages according to the studied compound, such as shown in Table 1.

2.4. Sample preparation

Water samples were collected from drainage channels and from a lagoon, both receiving irrigation waters from the rice fields of the Delta del Ebro (Tarragona, Spain). The sampling points were selected due to herbicides and their metabolites having been previously detected [18], and samples were collected during the period of major herbicide inputs. Water samples (1 l) were collected in glass amber bottles, sampling at 20–50 cm below the surface. Conductivities and pH ranged from 1266 $\mu\text{S}/\text{cm}$ (drainage channels) to 13.66 mS/cm (lagoon) and from 7.6 to 8.5, respectively. Maximum variation of water temperature during the day was from 23 to 34°C. Just after collection, the water samples were passed through membrane filters and then acidified to pH 2 with 10 ml diluted hydrochloric acid.

3. Results and discussion

3.1. General remarks

Due to the notable variation in the polarity of the studied compounds ($\log K_{\text{ow}}$ ranging from 1.26, for mecoprop, up to 5.84, for bentazone), the stationary phase selected for the extraction of the analytes was the styrene–divinylbenzene copolymer PLRP-S. In

general, polymeric materials are more suitable than alkyl-bonded silica materials for extraction of polar and relatively polar compounds in acidic pH medium [19,20]. In the last few years, satisfactory results were also obtained by using chemically modified polymeric materials [21] and graphitized carbon black [7,13]. Table 2 shows that recoveries were higher than 76% using the polymeric material, with relative standard deviations (RSDs) below 10%.

Not all the selected compounds could be detected by both detectors. 2,4-Dichlorophenol, 4-chloro-2-methylphenol, 3,4-dichloroaniline and molinate had poor sensitivity using APCI-MS in the NI mode and were therefore quantified by DAD.

In order to suppress ionic moieties of the analytes and hence to assure a suitable retention into the

Table 2
Recoveries range and relative standard deviation (RSD) ($n=6$) of the compounds in 50 ml of spiked Delta del Ebro estuarine water (spiking level of 0.5 ng/ml for each compound)

Compound	Recoveries range (%)	RSD (%)
8-Hydroxybentazone	93.8–102.6	3.8
6-Hydroxybentazone	85.4–99.0	5.4
Bentazone	91.0–113.4	8.8
2,4-D	90.7–106.9	6.7
MCPA	85.8–104.1	7.4
Clofibric Acid	84.5–104.8	9.1
4-Chloro-2-methylphenol	88.9–111.0	9.1
2,4-Dichlorophenol	76.4–92.2	7.8
Mecoprop	95.3–99.1	1.5
3,4-Dichloroaniline	79.9–89.1	3.7
Propanil	85.2–105.1	8.2
Molinate	86.7–104.5	6.8

stationary phase, the determination of acidic herbicides at low concentrations requires the acidification of the sample and also the mobile phase used for desorption [10,11,14]. As the pK_a values of the studied acidic herbicides are between 2.64 and 3.78, the water sample and gradient of elution were acidified at pH 3. However, acidification of natural water samples is frequently a hindrance due to humic substances containing acidic and phenolic groups which can be co-extracted, consequently causing a broad peak at the beginning of the chromatogram. Clean-up and also elution procedure with addition of organic solvents or even performance at high pH have been demonstrated to be an alternative for the elimination of such interferences, but the pattern of the matrix sample should directly influence the analyte recoveries [12,22]. In the present study, all the procedures were carried out at acidic pH to guarantee better recoveries and reproducibility. The

humic substances, hump at the beginning of the chromatogram, did not affect the analysis of the compounds under investigation, since they appeared after 10 min (Fig. 2).

3.2. Selection of the APCI-MS conditions

APCI provides a soft ionization of the analyte molecule which yields little structural information. Additional spectral information can be gained by using high cone voltage, but additional fragmentations are obtained at the expense of the sensitivity and thus a compromise between unambiguous identification and sensitive quantification should be attained. The optimization of the APCI-MS parameters were made for three different class of herbicides (bentazone, MCPA and propanil), as shown in Fig. 1, and the results obtained were taken into consideration for all the studied compounds. Throughout the

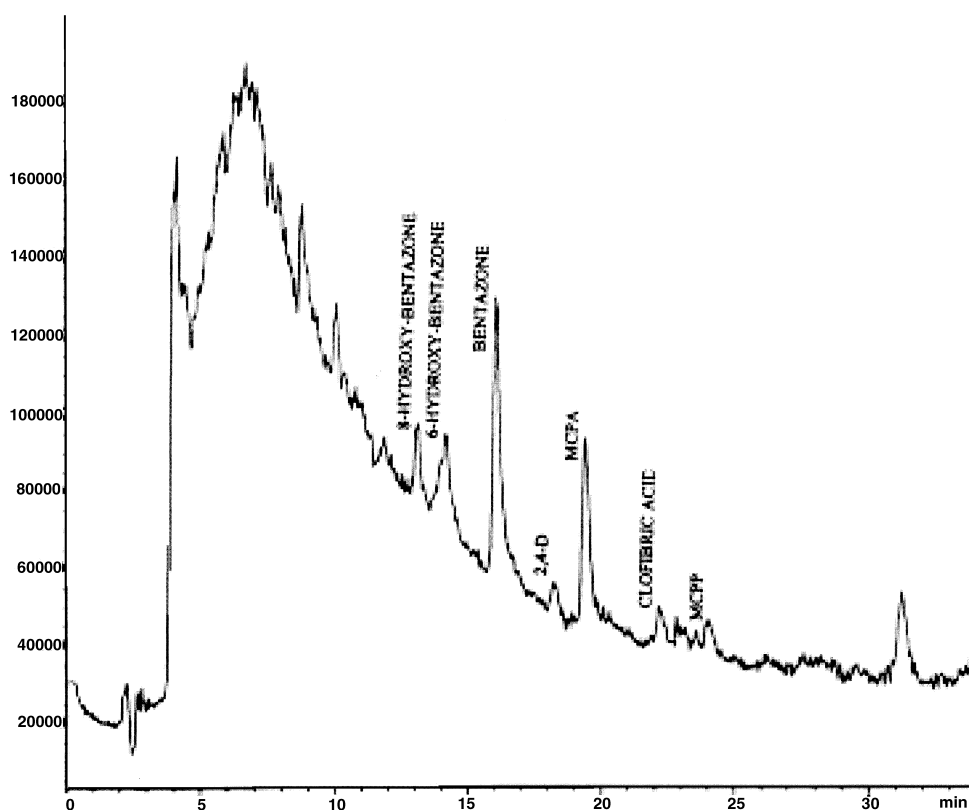


Fig. 2. Chromatogram obtained by on-line SPE-LC-APCI-MS, in the NI mode, for an estuarine water sample (0.1 ng/ml of each compound).

investigation, some parameters were fixed at values high enough to provide a rapid evaporation and desolvation of the sample: nebulizer pressure was set at 60 p.s.i.g., whereas drying gas temperature and flow-rate were set at 350°C and 4 ml/min, respectively. Fig. 3 shows the selected parameters for optimization, which are those most directly concerned to the ionization process, i.e., the corona current, capillary voltage and fragmentor voltage. A suitable vaporizer temperature prevents the formation of clusters of analyte and solvent molecule into the ion source region. The corona discharge established at the tip of the needle promotes the reactant ion formation that is also maintained by the high capillary voltage. For the compounds under investigation it was observed that high corona current and capillary voltage produced better sensitivity, and hence the values selected for these parameters were 25 μ A and 4500 V, respectively. For most of the studied

compounds, fragmentor voltages at 60 V provided good sensitivity and structural information. However, for propanil the minimum fragmentor voltage of 100 V was necessary to the formation of other ion fragment besides the deprotonized molecular ion $[M-H]^-$. Typical fragment ions are shown in Table 3. Despite that APCI-MS conditions had been changed in such way that all the studied herbicides and their metabolites should have a sensitive signal response, some of them did not present good sensitivity under the selected conditions. For 2,4-dichlorophenol, for example, Puig et al. [9] had obtained low limit of detection by using an on-line SPE-LC-APCI-MS, in the NI mode, and at fragmentor voltages lower than 60 V. Unfortunately, the need for a higher fragmentation voltage for most of the studied compounds made it impossible to obtain better sensitivity for 2,4-dichlorophenol. Low sensitivity was also observed for 4-chloro-2-

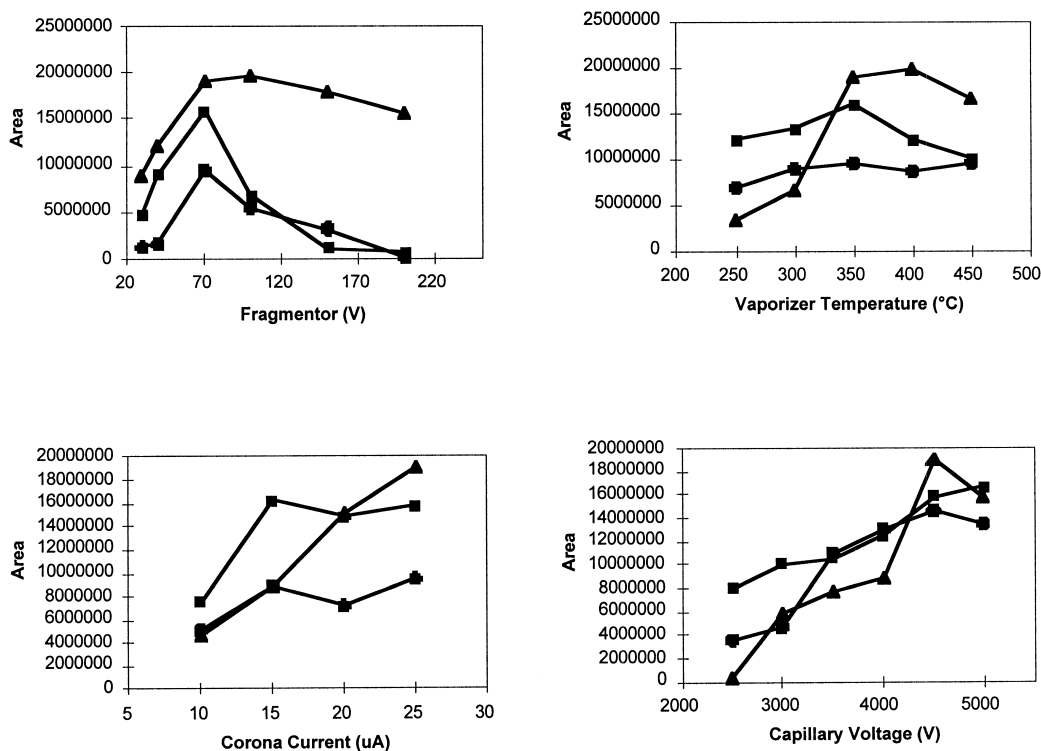


Fig. 3. Optimization of the main APCI-MS parameters for bentazone (●), MCPA (■) and propanil (▲) obtained for direct flow injection of 200 ng of each herbicide into a mobile phase of 40% of acetonitrile and 60% of ammonium formate–5 mM formic acid (pH 3), at a flow-rate of 0.9 ml/min. The signal response was set as the sum of fragments for each compound, fixing the other parameters: nebulizer pressure at 60 p.s.i.g., drying gas flow at 4 ml/min and drying gas temperature at 350°C.

Table 3
Typical fragment ions and their relative abundances by flow injection analysis–APCI-MS using the NI mode at different fragmentor voltages

Compound	Molecular mass	<i>m/z</i>	Fragment ion assignments	Fragmentor voltage	
				70 V	100 V
8-Hydroxybentazone	256	255	[M–H] [–]	100	
6-Hydroxybentazone	256	255	[M–H] [–]	3	100
		283	[M–H–OH+HCOO] [–]	100	
Bentazone	240	239	[M–H] [–]	100	100
		176	[M–SO ₂] [–]	3	4
2,4-D	220	219	[M–H] [–]	100	10
		161	[M–CH ₂ COOH] [–]	35	100
		127	[M–CH ₂ COOH+H–Cl] [–]		3
MCPA	200	199	[M–H] [–]	100	24
		166	[M–Cl+H] [–]	15	4
		155	[M–COOH] [–]		3
		141	[M–CH ₂ COOH] [–]		100
Clofibric acid	214	213	[M–H] [–]	100	17
		127	[M–C(CH ₃) ₂ COOH] [–]	18	100
Mecoprop	214	213	[M–H] [–]	100	16
		141	[M–CH(CH ₃)COOH] [–]	20	100
		138	[M–COOH–CH ₃ –CH ₃ –H] [–]		46
Propanil	217	216	[M–H] [–]		100
		160	[M–COCH ₂ CH ₃] [–]		10

methylphenol under the proposed conditions, probably due to the fact that ion spray ionization is more suitable for the analysis of methylphenols. These compounds have been found to be unsuitable for analysis by APCI [9]. For molinate and 3,4-dichloroaniline ionization in the positive ion mode was preferable [14,23]. Table 4 shows the calibration data obtained by LC–DAD and APCI-MS-SIM, the linearity ($R^2 > 0.98$) and LODs.

3.3. Monitoring study

The proposed method was used in the monitoring study carried out with drainage waters of rice fields of the Delta del Ebro during a typical period of herbicide applications, from June to August. The data obtained showed MCPA, bentazone and moreover 8-hydroxybentazone, were the only persistent compounds detected during the monitoring study (Fig. 4). Higher concentrations were observed in the

drainage channel which is concurrent with previous work carried out using same sampling points [14,18]. The lagoon water samples had lower observed concentrations possibly due to a dilution effect at that sampling point. The bentazone concentration decreased from 8.8 to 0.02 ng/ml while the degradation product, 8-hydroxybentazone, varied from 0.05 to 0.8 ng/ml (Fig. 5). 6-Hydroxybentazone was not detected during the monitoring period.

Although molinate and propanil were the most extensively applied herbicides over the rice fields (annual amounts of $70 \cdot 10^3$ kg and $50 \cdot 10^3$ kg of active ingredient, respectively), neither of these compounds nor the degradation product of propanil, 3,4-dichloroaniline, were detectable in the collected samples. It was surprising that such compounds had not been observed in the rice field drainage water. Just a week after the sampling in June, water samples from two rice fields of the Delta del Ebro previously treated with propanil were analyzed, and

Table 4

Calibration data and limits of detection (LODs) for the compounds using LC–DAD and LC–APCI-MS (SIM, NI mode) after preconcentration of 50 ml of paddy water, at spiking levels of 0.1, 0.5, 2, 4, 6 and 10 ng/ml

Compound	Calibration equation	R^2	LOD (ng/ml)
<i>LC–DAD</i>			
8-Hydroxybentazone	$y=254.1x+70.77$	0.998	0.04
6-Hydroxybentazone	$y=131.6x+56.06$	0.999	0.02
Bentazone	$y=302.5x+68.75$	0.998	0.05
2,4-D	$y=90.9x+51.68$	0.982	0.05
MCPA	$y=95.7x+6.34$	0.987	0.1
Clofibric acid	$y=105.8x+43.57$	0.981	0.05
4-Chloro-2-methylphenol	$y=128.2x+98.04$	0.996	0.1
2,4-Dichlorophenol	$y=139.1x+37.96$	0.979	0.1
Mecoprop	$y=203.1x+112.9$	0.984	0.04
3,4-Dichloroaniline	$y=157.6x+165.7$	0.988	0.05
Propanil	$y=174.0x+204.6$	0.997	0.06
Molinate	$y=79.8x+396.9$	0.994	0.05
<i>LC–APCI-MS</i>			
8-Hydroxybentazone	$y=(26.9x+2.2)10^5$	0.999	0.06
6-Hydroxybentazone	$y=(183.4x-8.4)10^4$	0.999	0.06
Bentazone	$y=(666.1x-1.51)10^4$	0.998	0.01
2,4-D	$y=(20.4x-4.69)10^5$	0.991	0.02
MCPA	$y=(25.7x-3.80)10^5$	0.995	0.02
Clofibric acid	$y=(31.6x-1.11)10^5$	0.998	0.09
Mecoprop	$y=(38.3x-2.16)10^5$	0.992	0.1
Propanil	$y=(81.6x-3.94)10^4$	0.990	0.1

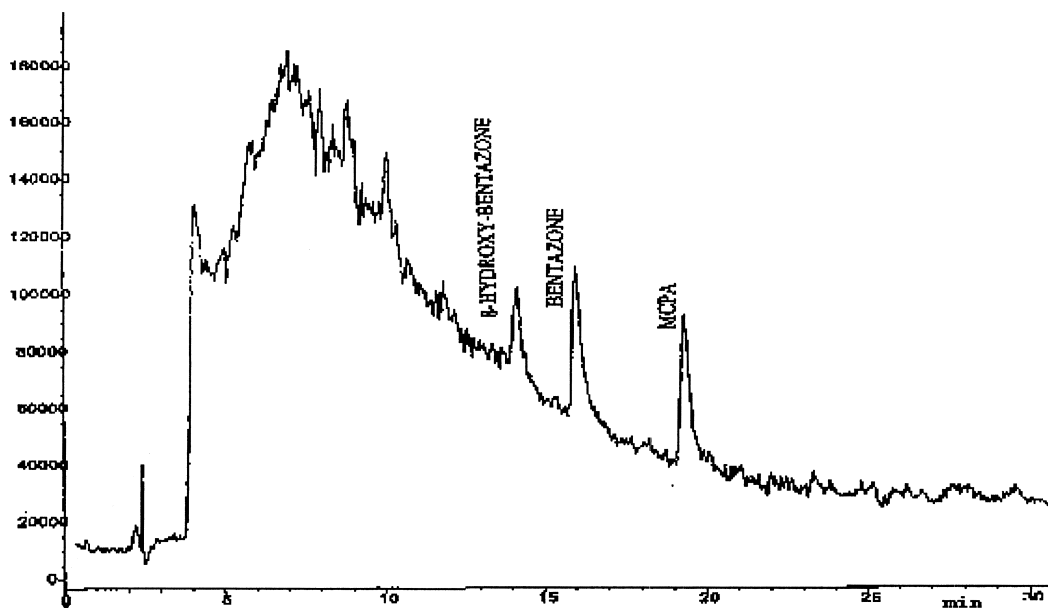


Fig. 4. Chromatogram obtained by on-line SPE–LC–APCI-MS monitoring of a drainage channel water sampled in June, in which bentazone, its major degradation product (8-hydroxybentazone) and MCPA were observed.

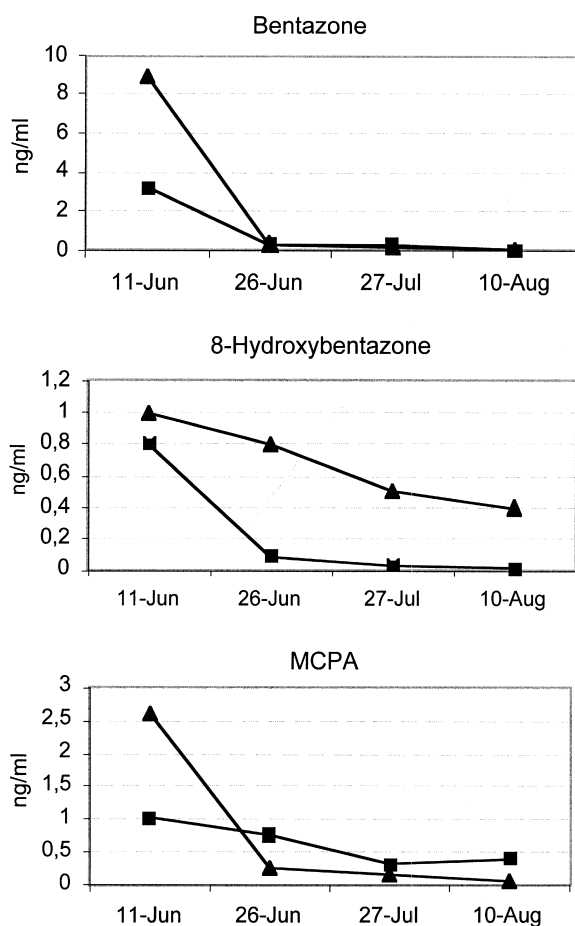


Fig. 5. Acidic herbicides and degradation products found in the drainage channels (▲) and lagoon (■) of the Delta del Ebro (Spain).

the residual concentrations obtained for propanil and 3,4-dichloroaniline ranged from 16.5 to 18.2 ng/ml and from 28.9 to 43.0 ng/ml, respectively. The fact that such compounds were not detected in the drainage waters was attributed to their rapid transformation into the rice fields. Propanil and 3,4-dichloroaniline must have suffered degradation by abiotic and biotic process in such a way that by the following week when the drainage channel and lagoon water were sampled no detectable concentrations of the herbicide and its degradation product were observed. Like propanil, molinate must have also degraded and the fact that available standards of

the degradation products were not accessible precluded their determination.

4. Conclusions

The proposed on-line SPE–LC–DAD–APCI–MS method permitted the analysis of the most applied herbicides in waters drained from rice fields. Acidic and neutral herbicides and their main degradation products were simultaneously analyzed. Analytical sensitivity was poor for some compounds under the established conditions, thus a further study should investigate lower fragmentor voltages or even the change for another interface in order to optimize the analytical method.

A monitoring study was carried out by using the method during the period of major input of the herbicides in the Delta del Ebro area. The study showed that only bentazone, its degradation product 8-hydroxybentazone and MCPA were persistent. Propanil and 3,4-dichloroaniline, which were found in the rice field water at relatively high concentrations, were not observed in the drainage channel and lagoon waters and this was attributed to the rapid degradation of the herbicide and its degradation product.

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