Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1067 (2005) 225–233
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of chloroacetanilides, triazines and phenylureas and some of their metabolites in soils by pressurised liquid extraction, GC–MS/MS, LC–MS and LC–MS/MS

T. Dagnac[a,*], S. Bristeau[a], R. Jeannot[a], C. Mouvet[b], N. Baran[b]

[a] *BRGM, Service "Metrology, Monitoring and Analysis", BP 6009, 45060 Orléans Cédex 2, France*
[b] *BRGM, Service "Water", BP 6009, 45060 Orléans Cédex 2, France*

Available online 8 December 2004

Abstract

Pressurised liquid extraction (PLE) technique was used for the simultaneous extraction of phenylureas, triazines and chloroacetanilides and some of their metabolites from soils. Extractions were performed by mixing 15 g of dried soil with 30 mL of acetone under 100 atm at 50 °C, during 3 min and with three PLE cycles. Prior to the analysis of naturally contaminated soils, each of the five representative soil matrices used as blanks (of different depths) was spiked in triplicate with standards of each parent and degradation compound at about 10, 30 and 120 μg/kg. For each experiment, isoproturon-D6 and atrazine-D5 were used as surrogates. Analysis of phenylureas and metabolites of triazines and phenylureas was carried out by reversed phase liquid chromatography/mass spectrometry (LC–MS) and LC–MS/MS in the positive mode. Gas chromatography (GC)/ion trap mass spectrometry was used in the MS/MS mode for the parent triazines and chloroacetanilides. The average extraction recoveries were above 85%, except for didesmethyl-isoproturon, and quantification limits were between 0.5 and 5 μg/kg. The optimised multi-residue method was applied to soils and solids below the root zone, sampled from agricultural plots of a small French hydrogeological basin.

Keywords: Herbicides; Soils; Pressurised liquid extraction; GC–MS/MS; LC–MS/MS

1. Introduction

Herbicides are extensively used in the world for over 40 years, with 45% of the total market value in 1993 [1]. Among the top ten herbicides atrazine is used worldwide, but there are also differences between the US and Europe regarding the top 10 lists. Phenylurea herbicides are on this list in Europe whereas in US they are not used at all. More than 80% of the herbicide use is concentrated in three agricultural areas: North America, Western Europe and East Asia. 22% of the total herbicides are also used for non-agricultural purposes, such as many triazines and phenylureas in Europe [1]. The use of atrazine is now strictly controlled in some countries (Denmark) and completely banned in others (e.g., Germany, Italy, Austria, Sweden and Norway). In France, atrazine was restricted to agriculture uses in February 1997, with dose limitations of 1000 g ha^{-1}. Despite this restriction, atrazine continues to be detected in groundwater. Consequently, authorities in some regions have decided to ban atrazine completely and have set up substitution programs. Sales of atrazine are forbidden since June 30, 2003 in France.

Chloroacetanilides (e.g. alachlor, metolachlor and acetochlor) are an important class of herbicides used to control grass weeds in various crops. Acetochlor, a herbicide used for maize, has been on the US market since 1994, following approval by the US Environmental Protection Agency. This approval will be renewed only if the total quantity of other herbicides used on this crop, including atrazine, decreases.

* Corresponding author. Tel.: +33 238643742; fax: +33 238643711.
E-mail address: t.dagnac@brgm.fr (T. Dagnac).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.11.058

Acetochlor was approved in France in 2000 and is now used in substitution programs.

Extraction of herbicides and of their main metabolites from solid matrices is frequently done by Soxhlet extraction, which requires large volumes of solvent and is a time-consuming process. Therefore, alternative techniques have been developed and applied in the past 10 years, such as supercritical fluid extraction (SFE) [2], subcritical water extraction (SWE), microwave-assisted extraction (MAE) and pressurised liquid extraction (PLE) [3]. Camel evaluated potential and pitfalls of SFE, MAE and PLE from a general point of view [4]. PLE uses organic solvents that remain in the liquid state under pressure and relatively high temperatures, to sequentially extract organic pollutants from solid matrices.

There are few applications of PLE to the simultaneous extraction of phenylureas, triazines and chloroacetanilides in soil [3,5–8], PLE being used until now mostly for PAH and PCB extractions. Guzella and Pozzoni performed one of the first successful studies on herbicides with PLE, by comparing it with Soxhlet procedures for triazine and chloroacetanilide extraction from agricultural soils [7]. Recoveries were 47–99% and the detection limits (LODs) were about 0.5 μg/kg. Another PLE method was developed to extract metribuzin and three metabolites (deaminometribuzin, deaminodiketometribuzin and diketometribuzin) with methanol/water (75/25) at 60 °C. Recoveries were about 75% with LODs of 1 μg/kg, except for diketometribuzin with only 50% recovery and LOD higher than 10 μg/kg [5]. Zhu et al. showed that water was the most effective modifier of PLE for quantitative recoveries (93–103%) of alachlor, metribuzin and hexazinone in four Hawaiian clayey soils [6].

Gas chromatography coupled with mass spectrometry (GC–MS) is a very powerful tool to identify and quantify a broad variety of thermally stable herbicides in complex environmental matrices, as shown by the numerous literature published in recent years for water [9–15] and soil [16-18]. Tandem mass spectrometry (MS/MS), which offers high sensitivity and selectivity, enables herbicide analysis at trace levels even if interfering compounds, with possibly the same parent mass, are co-eluted [19–21]. GC–MS/MS, usually with an ion trap system, is the method of choice for identification and quantitation purposes [5,22–29].

In liquid chromatography–mass spectrometry (LC–MS), the major instrumental improvement arose from the implementation of robust atmospheric ionisation interfaces such as electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI). ESI is more suited to polar and ionic compounds whereas APCI is used for moderately non-polar compounds. In the last five years, there has been an increase of the scientific publications dealing with LC–MS for the determination of herbicides in soil [30–32] and water [12,22,33–38]. Reversed-phase LC is the technique most widely used. Triazines, phenylureas and their main metabolites are analysed by using an APCI-MS configuration, often without any buffer or acid in the mobile phase, consisting of gradient of methanol/acetonitrile/water.

This paper addresses a new multi-residue method based on PLE of herbicides from soils followed by GC–MS/MS, LC–MS and/or LC–MS/MS. The method was applied to soils and solids below the root zone, sampled from agricultural plots of a small French hydrogeological basin, monitored as part of the PEGASE project [39]. Although our main purpose was the determination of acetochlor in the soil column, we also investigated the extraction of some triazines and phenylureas and their main metabolites.

2. Experimental section

2.1. Chemicals

Acetochlor (92%), alachlor (98.5%), metolachlor (98%), dimetachlor (10 mg/L in cyclohexane), atrazine (99%), atrazine-D5 (99.7%), terbutylazine-D5 (98%; 100 mg/L in acetone), desethyl-atrazine (DEA) (97.5%), desisopropyl-atrazine (DIA) (98%), isoproturon (99.5%), monodesmethyl-isoproturon (MIPU) (99.5%), didesmethyl-isoproturon (DIPU) (99.5%), chlortoluron (99.5%), linuron (99%), diuron (99%) and isoproturon D6 (99%, 100 mg/L in acetone), were all purchased from CIL Cluzeau (Sainte Foy La Grande, France).

Ethyl acetate for pesticide analysis (Carlo Erba, Val de Ré, France) and 2,2,4-trimethylpentane (VWR, Fontenay-sous-Bois, France) were used in GC/MS/MS. Acetonitrile for HPLC (J.T. Baker, Illkirch, France), methanol for HPLC (J.T. Baker) and water for HPLC (J.T. Baker) were used as constituents of the mobile phases in LC–MS.

2.2. Equipment

2.2.1. GC–MS/MS

GC–MS/MS analyses were performed using a Thermoquest (Les Ulis, France) system consisting of a Trace GC 2000 gas chromatograph equipped with a PTV split–splitless temperature injector, an AS 2000 autosampler and a POLARIS Q ion trap mass spectrometer (Thermofinnigan, Les Ulis, France). For data processing, Excalibur software from Thermofinnigan was used. The injector was equipped with a 12 cm × 2 mm i.d. Silcoseeve liner (Thermofinnigan). 2 μL of sample were injected onto the PTV injector in the constant flow mode set at 1 mL/min and with an injection speed of 1 μL/s. The split flow was set at 50 mL/min. The temperature of the injector was initially set at 55 °C, then increased to 260 °C at a rate of 10 °C/s where it was maintained for 12 min. The PTV split/splitless valve was operated in the splitless mode until the temperature of 260 °C was achieved. Once the temperature stabilised, it was maintained for 1.5 min, then changed to the split mode.

Compounds were separated on a 30 m × 0.25 mm i.d. column, coated with 0.25 μm of 95% dimethyl–5% phenyl

polysiloxane phase (BPX-5; SGE, Courtaboeuf, France). The temperature of the column was initially set at 55 °C for 1 min, then increased at a rate of 15 °C/min to 120 °C. Once at 120 °C, the rate was increased to 3 °C/min until it reached its final temperature of 220 °C, which was maintained for 3 min. Helium was used as the carrier gas at a constant flow of 1 mL/min. The transfer line was set at 280 °C with the external ion source at 280 °C.

2.2.2. LC–MS

A Varian 9100 autosampler and a Varian 9012 HPLC pump (Les Ulis, France) composed the chromatographic system. LC/MS analysis were performed by using a SSQ 7000 Thermo-Finnigan instrument equipped with an atmospheric pressure chemical ionisation source, APCI. The analytes were detected in the positive ion mode as their protonated molecular ions $(M + H)^+$, with CID offset (15 V) in the API source. The reversed phase column chosen for all experiments was an Omnispher C-18 150 mm × 3 mm i.d. and 3 μm particle size (Varian-Chrompack, Les Ulis, France). A gradient of mobile phases constituted of acetonitrile and water at 0.4 mL/min was used in order to separate phenylureas and triazines by injecting 20 μL of sample. Acetonitrile initially set to 85% was decreased to 40% and water initially set to 15% was increased to 100% in 32 min.

2.2.3. LC–MS/MS

A Thermo Finnigan autosampler (ASE 2000) and a Thermofinnigan HPLC pump (Surveyor MS) composed the chromatographic system. LC–MS/MS analysis were performed by using a DECA XP + Thermo-Finnigan ion trap instrument equipped with an atmospheric pressure chemical ionisation source or an electro spray ionisation source. The analytes were first detected in the positive ion mode as their protonated molecular ions $(M + H)^+$ (or sodium induct)$^+$ and the appropriate precursor ion was chosen to be isolated and fragmented in the MS/MS mode.

The reversed phase column chosen for all experiments was the same as for LC–MS analyses previously described. However, the operating conditions were modified and a gradient of mobile phases constituted of methanol and water at 0.4 mL/min was used in order to separate phenylureas and triazines by injecting 20 μL of sample. Methanol initially set to 85% was decreased to 40% and water initially set to 15% was increased to 100% in 32 min.

2.2.4. General conditions

In GC–MS/MS, the concentrations were calculated using the calibration curves established for each compound in internal standardisation mode with terbutylazine-D5 and dimetachlor as internal standards.

In LC–MS, external calibrations were used but matrix effects were assessed by using the method of standard additions on extracts of "blank" soil samples.

2.3. Soil sampling

The study took place in a small hydrogeological basin of some 3 km^2. It lies within the Paris Basin (70 km west of Paris). Soil cores were collected (at a maximum depth of 1 m) from two different soils before the herbicide was applied and six times over a 1-year monitoring period after the acetochlor application. This sampling scheme followed guidelines implemented in the frame of the PEGASE European project [39]. The cores were sent to the laboratory and cut, after the outer layer had been removed, into segments corresponding to depth intervals of 0–5, 5–10, 10–20, 20–30 cm, etc. Each sample was dried at 40 °C for 3 days then ground to 2 mm [40].

2.4. Characterisation of the soils studied

The two soils studied are a deep silty soil (PA, luvisol—FAO classification) and a shallower, more pebbly, more calcareous soil (PB, calcisol—FAO classification) that is also slightly more clayey in the surface layers (Table 1). Five soil matrices (in bold in Table 1) chosen as "blank" were sampled before acetochlor was applied. These soils were selected to cover the range of values of the parameters analysed to characterise the soil physico-chemical properties.

2.5. Extraction procedure

PLE was optimised to perform the extraction of chloroacetanilides, phenylureas, triazines and some of their metabolites from the soils and solids sampled as previously described (see Section 2.3). Extractions were carried out by mixing 15 g of dried soil with 30 mL of acetone under 101,300 kPa at temperature lower than 80 °C. Acetone, methanol or water/methanol mixtures are usually used as extracting solvent

Table 1
Grain size distribution and characterisation of the soils studied

Soil reference	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Total calcareous (%)	Organic matter (%)	CEC (meq./100 g)	Organic carbon (%)
PA-1	0–30	15.3	64.7	18.4	0	1.51	10.4	0.878
PA-2	30–60	20.5	64.7	14.1	0	0.74	10.9	0.43
PA-3	60–90	25.8	61.7	12	0	0.55	13.1	0.32
PA-4	90–110	30.0	54.6	14.9	0	0.52	15.0	0.302
PA-5	110–130	6.13	5.5	18.9	69.0	0.47	2.83	0.273
PB-1	0–25	22.7	19.6	10.8	3.69	2.81	17.4	1.63
PB-2	25–50	22.8	18.2	10.4	7.03	2.27	15.4	1.32

in PLE. Acetone was best suited to the extraction of the three herbicide families and reduced the sampling preparation time after PLE.

Each of the five representative soil matrices used as blanks was spiked in triplicate with standards of each parent and degradation compound at three concentrations levels (about 10, 30 and 90 μg/kg). For each experiment, isoproturon-D6 and atrazine-D5 were used as surrogates for the three pesticide families of concern. Two hundred to 500 μL of the spiking standard mixture (in methanol) were added to about 7 g of soil and the cell vessels were filled with the remaining 8 g of soil and then homogenised with Fontainebleau sand. The soil sample and the spiking mixture were left in contact for one hour before starting the PLE procedure. The operating conditions will be given in the part related to the PLE optimisation. After PLE, acetone extracts were evaporated at 40 °C to 1 mL and divided up between two sub-extracts of 500 μL. These extracts were then evaporated to dryness (under nitrogen flow) and reconstituted in methanol and ethyl acetate (or 2,2,4-trimethylpentane), the former being analysed by LC–MS and the latter by GC–MS/MS.

3. Results and discussion

3.1. Optimization of the PLE

A Doehlert design was applied in a "blank" Luvisol and a "blank" Calcisol (PA-1, 0–30 cm and PB-1, 0–25 cm), in order to assess the influence of the exposure time (1, 3 or 5 min) and the PLE temperature (40–80 °C) on the herbicide extraction yields. Preliminary experiments showed that high recoveries could be achieved with only three PLE cycles.

Polynomial models can be fitted from the matrix of experimental data to describe the variation of the herbicide recoveries. They showed that the optimum location always corresponded to an extraction time included between 2 and 3 min. Fig. 1 contains examples of modelling curves for the herbicide recoveries in a "blank" Calcisol, as a function of the temperature, setting the extraction time at 3 min. Recoveries increase with the temperature for triazines and acetochlor, with maxima values between 60 and 70 °C. In contrast, phenylurea recoveries decrease with the temperature increase, with a dramatic effect for isoproturon. Therefore, performing PLE at 50 °C for 3 min (with three cycles), provided extraction yields above 85% for all compounds of interest.

3.2. Mass spectrometry

The precursor ions were selected among the most intense characteristic ions of the MS spectrum, giving rise to the most efficient MS/MS transitions in the ion trap. Whenever possible, two or three product ions were monitored in full scan mode for unambiguous identification of the analytes (Tables 2–4).

Fig. 2 show typical GC–MS/MS chromatograms for the herbicide analysis in extract samples from a luvisol collected between 5 and 10 cm, 26 days after acetochlor application. The reconstructed ion MS/MS chromatograms at *m*/*z* 146, 200 and 172 clearly confirm the presence of acetochlor, atrazine and DEA in these soil samples.

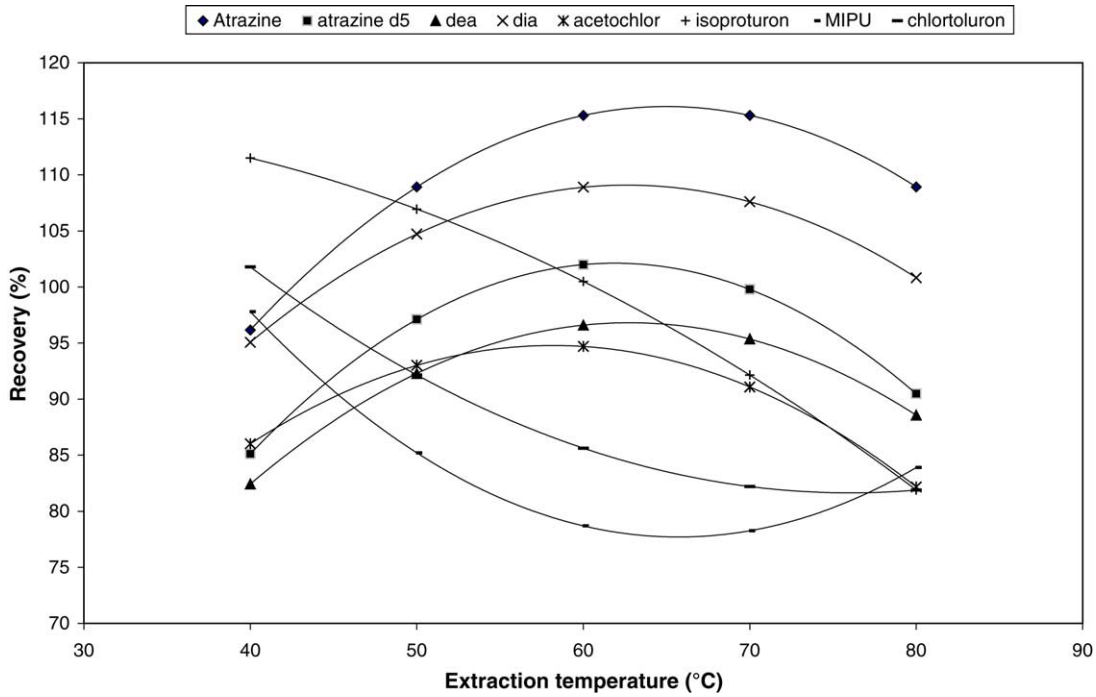

Fig. 1. Models fitted by a Doehlert design for herbicide recoveries after PLE in a Luvisol sample collected between 0 and 30 cm of depth.

Table 2
GC-MS/MS parameters for the quantification of triazines and chloroacetanilides

Compounds	Precursor ions (*m/z*)[a]	Product ions (*m/z*)	Retention time (min)
DIA	*145* + 158 + 173	68 + 110	20.5
DEA	*172*	79 + 105 + 130	20.8
Atrazine	*200* + 215	94 + 122 + 132	23.8
Acetochlor	*146* + 162 + 174	131	27.6
Alachlor	160 + *188*	160	28
Metolachlor	162 + *238*	162	29.2
Surrogate			
Atrazine-D5	*205* + 220	105 + 127 + 137	23.7
Internal standards			
Dimetachlor	*134* + 148 + 197	79 + 105	27.4
Terbuthylazine-D5	178 + *219*	137 + 141 + 178	24.4

[a] In italics, precursor ion chosen for the MS/MS transitions in full scan mode. *q*, 0.3, CID, 1 V, 2 μscan and maximum ion time: 20 ms.

Table 3
APCI-MS/MS optimised parameters for the herbicide analysis

Compound	Ionisation mode	Retention time (min)	Molecular mass (g/mol)	Precursor ions (*m/z*)[a]	Product ions (*m/z*)	Normalised collision energy (%)	Activation *q*
Atrazine D5	+	16.7	220.5	*221*	179 + 221	33	0.35
Atrazine	+	16.8	215.5	*216*	174 + 216	34	0.35
DIA	+	7.4	173.5	*174*	132 + 146 + 174	35	0.40
DEA	+	10.8	187.5	*188*	146 + 188	32	0.35
Acetochlor	+	21.3	269.5	*224* + 256 + 270	148 + 206 + 224	26	0.25
Metolachlor	+	21.3	283.5	252 + *284*	252 + 284	23	0.25
Alachlor	+	21.3	269.5	162 + *238* + 270	162 + 220 + 238	29	0.30
DIPU	+	16.3	179	136 + *179*	136 + 179	25	0.32
MIPU	+	17.2	193	136 + *193*	136 + 151 + 193	30	0.35
Isoproturon	+	17.5	207	136 + *207*	72 + 165 + 207	30	0.25
Chlortoluron	+	16.9	212.5	142 + *213*	72 + 213	26	0.26
Diuron	+	18.0	233	162 + *233*	72 + 215 + 233	26	0.26
Linuron	+	19.4	249	162 + *249*	160 + 182 + 249	27	0.25

[a] In italics, precursor ion chosen for the MS/MS transitions in full scan mode; 2 μscan and maximum ion time: 400 ms to isolate the selected precursor ions.

With the aim of extending the application field of the method, alachlor, metolachlor, linuron and diuron were added to the list of the herbicides to be determined by LC–MS/MS. They were not submitted to the previous PLE experiments. LC–MS/MS analyses for chloroacetanilides show that the acetochlor and alachlor are coeluted in our chromatographic conditions. Both chloroacetanilides having the same precursor ions in ESI mode, tandem mass spectrometry is mandatory to isolate each compound. APCI mechanism does not involve the same molecular ion as

Table 4
ESI-MS/MS optimised parameters for the herbicide analysis

Compound	Ionisation mode	Retention time (min))	Molecular mass (g/mol)	Precursor ions (*m/z*)[a]	Product ions (*m/z*)	Normalised Collision energy (%)	Activation *q*
Atrazine D5	+	16.7	220.5	*221* + 223	179 + 221	32	0.30
Atrazine	+	16.8	215.5	*216*	174 + 216	33	0.30
DIA	+	7.4	173.5	*174*	132 + 146 + 174	34	0.30
DEA	+	10.8	187.5	*188*	146 + 188	32	0.30
Acetochlor	+	21.0	269.5	256 + *270* + 292	224	30	0.25
Metolachlor	+	21.3	283.5	*284* + 306	252 + 284	25	0.25
Alachlor	+	20.9	269.5	*270* + 292	238	25	0.25
DIPU	+	16.3	179	*179* + 201 + 379	137 + 179	25	0.25
MIPU	+	17.2	193	*193* + 215 + 407	136 + 151 + 193	30	0.35
Isoproturon	+	17.5	207	*207* + 229 + 435	165 + 207	31	0.30
Chlortoluron	+	16.8	212.5	*213* + 235 + 447	72 + 213	28	0.27
Diuron	+	18.0	233	*233*	72 + 233	28	0.25
Linuron	+	19.4	249	*249*	160 + 182 + 249	27	0.30

[a] In italics, precursor ion chosen for the MS/MS transitions in full scan mode; 2 μscan and maximum ion time: 400 ms to isolate the selected precursor ions.

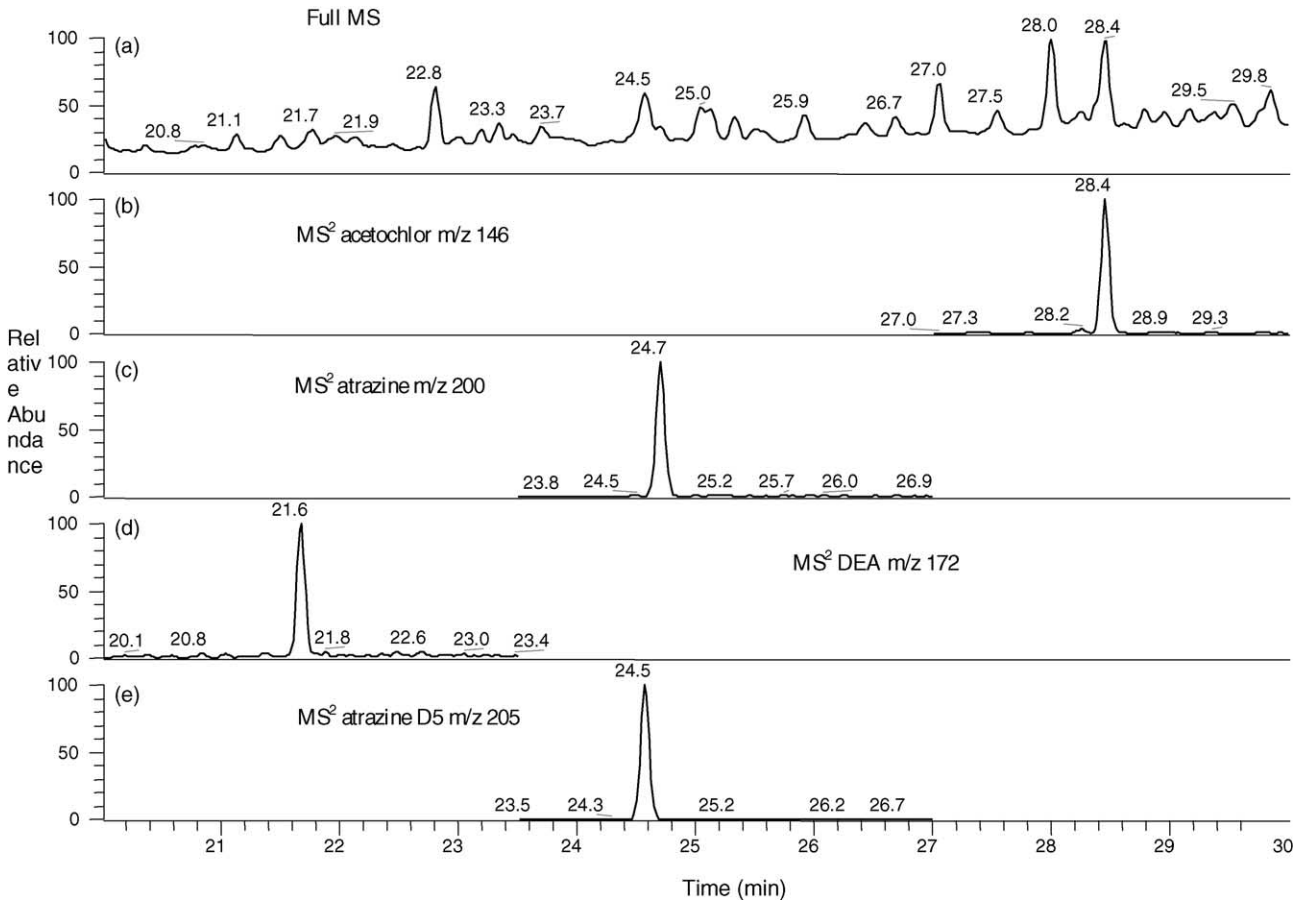

Fig. 2. (a) Full scan MS chromatogram for a GC–MS/MS analysis of an extract sample from a luvisol collected between 5 and 10 cm, 27 days after acetochlor application. (b) Reconstructed ion chromatogram for acetochlor at *m/z* 146 → 131. (c) Reconstructed ion chromatogram for atrazine at *m/z* 200 → 94 + 122 + 132. (d) Reconstructed ion chromatogram for desethyl-atrazine at *m/z* 172 → 79 + 105 + 130. (e) Reconstructed ion chromatogram for the surrogate, atrazine-D5 at *m/z* 205 → 105 + 127 + 137.

precursor, since acetochlor precursor ion is formed after loss of the methoxyethyl group, whereas alachlor precursor ion is produced after loss of the methoxymethyl group (Table 3).

ESI mechanism gives rise to sodium inducts (*m/z*, M + 23) for chloroacetanilides and some phenylureas, except for diuron, linuron and triazines (Table 4). Furthermore, phenylureas also produce bimolecular sodium inducts (*m/z*, M + M + 23). The ions corresponding to these inducts cannot be quantitatively isolated into the ion trap and give low MS/MS responses. In APCI mode, sodium inducts are not produced for any herbicide of interest.

3.3. Quantitative results

The combined influence of the LC conditions on the herbicide response and the ion suppression by matrix effect into the API interface, make the quantification procedure quite tricky. Therefore, all quantitations in LC–MS were performed by using standard addition methods (in-matrix calibrations) on each of the five "blank" soil samples.

3.3.1. Herbicide recoveries

The limited availability of certified reference materials for herbicides in soils is detrimental to the development of robust extraction methods. In many works, soils are therefore spiked with known quantities of herbicides and recoveries are calculated to check the applicability of the extraction method.

The five "blank" soil matrices were then spiked in triplicates with standard solutions of phenylureas, chloroacetanilides and triazines, at three concentration levels ranging from 10 to 120 μg/kg, likely to be found in agricultural contaminated soils. Nominal phenylurea and triazine concentrations were measured before spiking experiments, to correct the recovery values. Figs. 3 and 4 contain charts related to the herbicide recoveries at 30 μg/kg. The whole set of results show that average recoveries for phenylureas are between 60 and 120% at the lowest spiking level. They range from 100 to 120% at the medium and high spiking levels, with relative standard deviations lower than 15%. Triazine and chloroacetanilide average recoveries are never below 85%, regardless of the spiking concentration level. None systematic matrix effect on the triazine and chloroacetanilide recoveries could

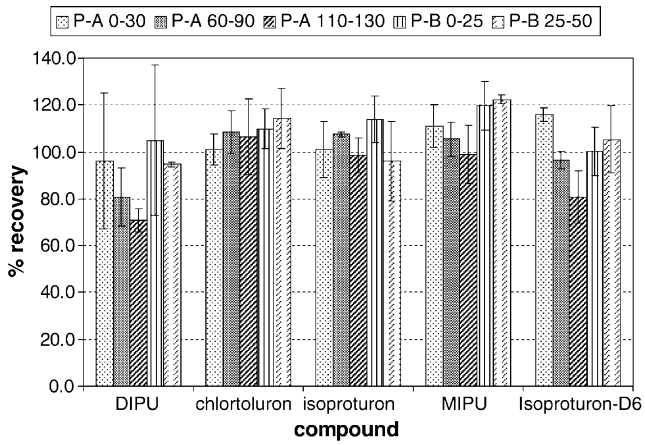

Fig. 3. PLE extraction recoveries (mean ± standard deviation, $n = 3$) for phenylureas after reconstitution in methanol, after spiking five soil matrices at 30 μg/kg.

be observed among the five soil matrices studied. In contrast, phenylurea recoveries are systematically lower in the deeper solid (high calcareous content, see Table 1) from parcel PA sampled between 110 and 130 cm. Actually, recoveries could not be measured at the lower spiking level (close to 10 μg/kg) in PA 110–130 cm for phenylureas. This highlighted a likely influence of the carbonate contents on the PLE efficiency.

The recoveries of the surrogates atrazine-D5 and isoproturon D6 are systematically above 90%, as shown in Figs. 1 and 2, except for isoproturon D6 in PA 110–130 cm (70%).

Fig. 5 shows the herbicide recoveries (30 μg/kg) after extract reconstitution in 2,2,4-trimethylpentane. These recoveries are very low for atrazine metabolites and hardly reach 80% for acetochlor and atrazine. This solvent has then been discarded for the forthcoming experiments.

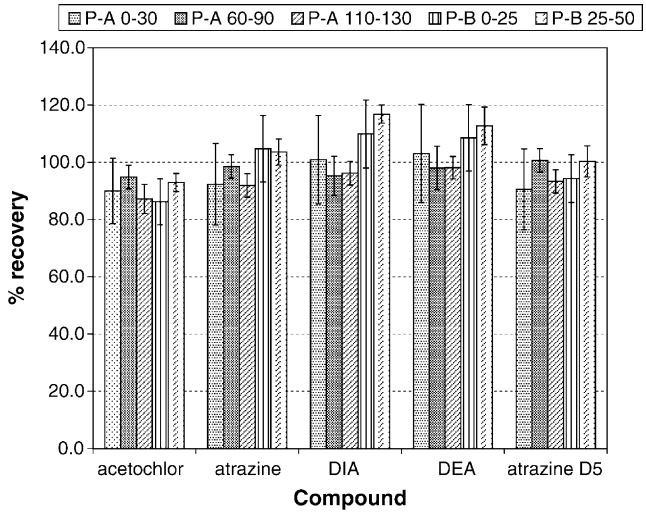

Fig. 4. PLE extraction recoveries (mean ± standard deviation, $n = 3$) for triazines and chloracetanilides after reconstitution in ethylacetate, after spiking five soil matrices at 30 μg/kg.

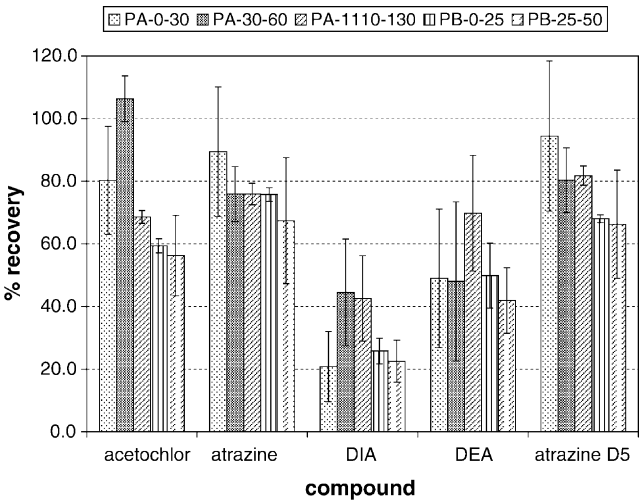

Fig. 5. PLE extraction recoveries (mean ± standard deviation, $n = 3$) for triazines and chloracetanilides after reconstitution in 2,2,4-trimethylpentane, after spiking five soil matrices at 30 μg/kg.

3.3.2. *Evaluation of method performance*

The limits of quantification (LOQ) and detection have been assessed for the five soil matrices after performing the extraction on 15 g of soil. In order to be quantified, a chromatographic peak area must exhibit a signal to noise ratio, at least of 9. Table 5 contains the limits of quantification for GC–MS/MS, LC–MS and LC–MS/MS measurements. For triazines and chloroacetanilides, performance are much better in GC–MS/MS than in LC–APCI/MS, with LOQs between 1 and 3 μg/kg. Acetochlor LOQ is significantly improved using GC–MS/MS or LC–MS/MS, this herbicide being very poorly detected in LC–APCI/MS (with the single quadrupole system). LOQs are around 3 μg/kg for phenylureas in LC–MS, except for DIPU with a LOQ close to 20 μg/kg.

All performances are improved with tandem LC–MS/MS, as pointed out for the determination of pesticides in water [28,29]. As regards phenylureas, the comparison of the two API sources shows that LOQs are lower by using APCI and even 10 times enhanced for linuron. In contrast, LOQs are

Table 5
Limits of quantification (μg/kg) for herbicide determination by GC–MS/MS and LC–MS(/MS)

Herbicide	GC–MS/MS	LC–APCI/MS	LC–ESI/MS/MS	LC–APCI/MS/MS
Atrazine	1.9	5.4	0.15	0.3
DIA	1.6	22	4.5	11
DEA	2.5	13	0.7	1.2
Metolachlor	0.3	6.3	0.3	0.3
Acetochlor	0.9	22	0.7	1.5
Alachlor	2.2		1.5	1.5
DIPU		22	6	1.5
MIPU		11	0.7	0.7
Isoproturon		4.8	0.7	3
Chlortoluron		10	7.5	3
Linuron			7.5	0.7
Diuron			4.5	4.5

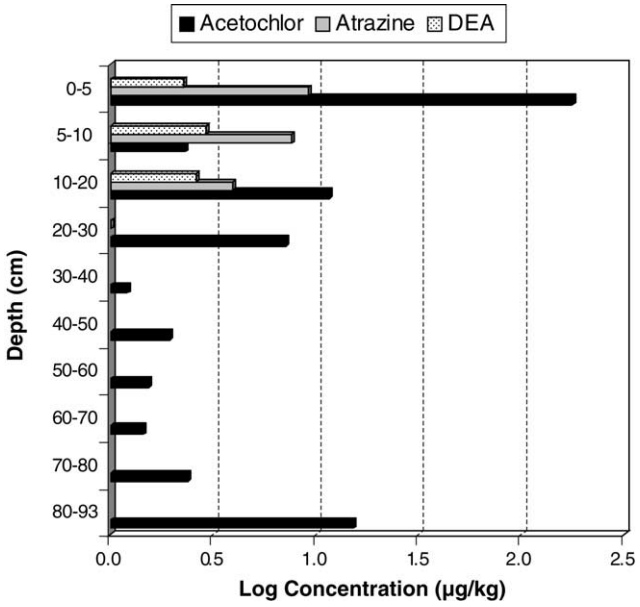

Fig. 6. Concentration profiles in a luvisol for acetochlor and triazines, 12 days after acetochlor application (2001) and 6 years after the last atrazine application.

slightly higher for triazines and chloroacetanilides with APCI than with ESI.

3.3.3. Application to soils treated with acetochlor

The overall methodology optimised on spiked soils was applied to soil samples collected from agricultural parcels. These samples were extracted using PLE and all herbicides of interest were quantified by GC–MS/MS and LC–APCI/MS. The need of using standard addition method for phenylureas in LC–MS implied that each soil extract had to be quantified by means of the "blank" soil better matching the contaminated soil, in terms of physico-chemical characteristics and depth.

Fig. 6 contains examples of profiles of acetochlor and triazine concentrations as a function of depth, in cores of a luvisol 26 days after acetochlor application. Since the chloroacetanilide concentration is close to 300 μg/kg between 0 and 5 cm, log scale was chosen to give a better overview of the deepest soil layers. Acetochlor was quantified around 15 μg/kg at the deepest level, close to the concentration observed between 10 and 20 cm and proof that this molecule was quickly leached. This behaviour could not be observed in recent surveys [41,42], probably because of much higher LOQ (close to 40 μg/kg). Besides, our previous studies showed that acetochlor was quickly degraded in oxanilic and sulfonic acid metabolites which were detected down to 50 cm of depth at several μg/kg, regardless of the soil type [30,40,43].

This monitoring also highlighted that atrazine and one of its main metabolites (DEA) can be quantified at concentrations included between 2 and 5 μg/kg down to the depth of 30 cm, even though atrazine has not been recently applied to these fields.

4. Conclusions

PLE was optimised to perform the simultaneous extraction of three herbicide families in soils (0–5 cm) and solids sampled below the root zone (down to 1 m). Our main target was the accurate extraction of acetochlor, but the determination of triazines and phenylureas and of their metabolites was also studied. Extraction recoveries were 80–120% in five soil matrices when applying PLE at 50 °C and for 3 min (three cycles).

Chloroacetanilide and triazine herbicides were analysed by either GC–MS/MS or LC–MS; phenylureas could only be analysed by LC–MS. Performance of both methods allowed the accurate monitoring of two contrasted agricultural soils, with the quantification of triazines down to 20 cm and acetochlor down to 1 m. The excellent LOQs provided new relevant information on the risk of acetochlor leaching in the soil column below the first layer.

In the case of phenylureas, this study could be extended with the benefit of the LC–MS/MS performance (down to several μg/kg), to obtain additional data on their transport and fate in soils. Nevertheless, the need of standard addition methods should be stressed to ensure the accuracy of the concentrations determined in extracts from naturally contaminated soils.

Acknowledgement

The work conducted here was partly financed through the PEGASE project, contract EVK1-CT1999-00028, financed by the EU through its fifth PCRDT.

References

[1] D. Barceló, M.C. Hennion, Introduction, in: Trace Determination of Pesticides and Their Degradation Products in Water, Elsevier, Amsterdam, NL, 1997.
[2] V. Camel, Analusis 26 (1998) M99.
[3] J.R. Dean, L.J. Fitzpatrick, Pesticides defined by matrix, in: Environmental Analysis, Handbook of Analytical Separations, vol. 3, Elsevier, Amsterdam, NL, 2001, pp. 123–173.
[4] V. Camel, Analyst 126 (2001) 1182.
[5] T. Henriksen, B. Svensmark, R.K. Juhler, J. Chromatogr. A 957 (2002) 79.
[6] Y. Zhu, K. Yanagihara, F. Guo, Q.X. Li, J. Agric. Food Chem. 48 (2000) 4097.
[7] L. Guzella, F. Pozzoni, Int. J. Environ. Anal. Chem. 74 (1999) 123.
[8] J.R. Dean, G. Xiong, Trends Anal. Chem. 19 (2000) 553.
[9] S.A. Heberle, D.S. Aga, R.H. Hany, S.R. Müller, Anal. Chem. 72 (2000) 840.
[10] J. Quintana, I. Martí, F. Ventura, J. Chromatogr. A 938 (2001) 3.
[11] W.T. Ma, K.K. Fu, Z. Cai, G.B. Jiang, Chemosphere 52 (2003) 1627.
[12] L.R. Zimmerman, R.J. Schneider, E.M. Thurman, J. Agric. Food Chem. 50 (2002) 1045.
[13] F. Hernandez, J. Beltran, F.J. Lopez, J.V. Gaspar, Anal. Chem. 72 (2000) 2313.
[14] R. Carabias-Martinez, C. Garcia-Hermida, E. Rodriguez-Gonzalo, F. Soriano-Bravo, E. Hernandez-Mendez, J. Chromatogr. A 1002 (2003) 1.

[15] D.A. Lambropoulou, V.A. Sakkas, D.G. Hela, T.A. Albanis, J. Chromatogr. A 963 (2002) 107.
[16] P. Carlo, G. Zambonin, F. Palmisano, J. Chromatogr. A 874 (2000) 247.
[17] S. Gang, L.H. Kee, J. Chromatogr. A 985 (2003) 167.
[18] V. Zisis, P.-M. Euphemia, J. Agric. Food Chem. 50 (2002) 5026.
[19] Z. Cai, D. Wang, W.T. Ma, Anal. Chim. Acta 503 (2004) 263.
[20] C. Gonçalves, M.F. Alpendurada, J. Chromatogr. A 1026 (2004) 239.
[21] J. González-Rodríguez, A. Garrido-Frenich, F.J. Arrebola, J.L. Martínez-Vidal, Rapid Commun. Mass Spectrom. 16 (2002) 1216.
[22] J.A. Shoemaker, J. Assoc. Off. Anal. Chem. Int. 85 (2002) 1331.
[23] J.D. Vargo, Anal. Chem. 70 (1998) 2699.
[24] A. Lagana, A. Bacaloni, I. De Leva, A. Faberi, G. Fago, A. Marino, Anal. Chim. Acta 462 (2002) 187.
[25] F. Hernández, J.V. Sancho, O. Pozo, A. Lara, E. Pitarch, J. Chromatogr. A 939 (2001) 1.
[26] R. Jeannot, H. Sabik, E. Sauvard, E. Génin, J. Chromatogr. A 818 (2000) 51.
[27] R.B. Geerdink, A. Kooistra-Sijpersma, J. Tiesnitsch, P.G.M. Kienhuis, U.A.T. Brinkman, J. Chromatogr. A 863 (1999) 147.
[28] R.B. Geerdink, W.M.A. Niessen, U.A.T. Brinkman, J. Chromatogr. A 970 (2002) 65.
[29] A.C. Hogenboom, W.M.A. Niessen, U.A.T. Brinkman, J. Sep. Sci. 24 (2001) 331.
[30] T. Dagnac, R. Jeannot, C. Mouvet, N. Baran, J. Chromatogr. A 957 (2002) 69.
[31] H. Berrada, G. Font, J.C. Moltó, Crit. Rev. Anal. Chem. 33 (2003) 19.
[32] M. Möder, P. Popp, R. Eisert, J. Pawliszyn, Anal. Bioanal. Chem. 363 (1999) 680.
[33] I. Ferrer, E.M. Thurman, D. Barceló, Anal. Chem. 69 (1997) 4547.
[34] K.A. Hostetler, E.M. Thurman, Sci. Total Environ. 248 (2000) 147.
[35] T. Dagnac, R. Jeannot, C. Mouvet, N. Baran, Determination of chloroacetanilide metabolites in waters and soils by LC/ESI–MS, in: Proceedings of the Second MGPR International Symposium of Pesticides in Food and the Environment, Valencia, Spain, 9–12 May 2001, p. 103.
[36] W.M. Draper, J. Agric. Food Chem. 49 (2001) 2746.
[37] M.F. Nogueira, T. Sandra, P. Sandra, Anal. Chim. Acta 505 (2004) 209.
[38] A. Di Corcia, C. Crescenzi, E. Guerriero, R. Samperi, Environ. Sci. Technol. 31 (1997) 1658.
[39] PEGASE PROJECT, Pesticides in European Groundwaters: detailed study of representative Aquifers and Simulation of possible Evolution scenarios, in: I.G. Dubus, C. Mouvet (Eds), Final report of the European project EVK1-CT1990-00028, BRGM/RP-52897-FR, 2004.
[40] N. Baran, C. Mouvet, T. Dagnac, R. Jeannot, J. Environ. Qual. 33 (2004) 241.
[41] L.N. Konda, Z. Pásztor, J. Agric. Food Chem. 49 (2001) 3859.
[42] Q. Ma, A. Rahman, P.T. Holland, T.K. James, D.E. McNaughton, J. Environ. Qual. 33 (2004) 930.
[43] N. Baran, C. Mouvet, X. Morvan. Fate of acetochlor and two of its major metabolites in a luvisol over two years with differing weather conditions, in: Proceedings of the XII Symposium on Pestic. Chem., ISBN 88-7830-359-3, Piacenza, Italy, 4–6 June 2003, pp. 89–98.