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Evaluation of surface- and ground-water pollution due to herbicides in agricultural areas of Zamora and Salamanca (Spain)

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Abstract

The pollution of agricultural land due to herbicides was assessed in the Guareña and Almar river basins, situated in the provinces of Zamora and Salamanca (Spain). A set of fifteen herbicides, including triazines, ureas, amides and others, was selected owing to their frequency of use, the amounts used, their toxicity and their persistence in the environment. Solid-phase extraction with polymeric cartridges, followed by HPLC with diode-array detection, were used to monitor the herbicides. This technique was chosen owing to the wide range of functionality and polarity of the analytes under study. The detection limits obtained were in the 0.004–0.025 μg/l range (λ=220 nm). Surface and ground waters, taken from different locations in the basins, were analyzed over a 6-month period. The presence of six out of the fifteen herbicides monitored — chlortoluron, atrazine, terbutryn, alachlor, diflufenican and fluazifop-butyl — was detected in several samples at levels ranging from the detection limit to 1.2 μg/l. The relationship of these herbicides to the agricultural activities of the zone is discussed.

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

The pollution of continental waters is due to many different factors, including industrial and urban wastes, livestock and crop raising activities, etc. In large areas of Spain, the pollution due to fertilizers and pesticides, used to increase agricultural production, merits special attention. The use of pesticides involves the risk of their retention in crops and soils, from which in turn — due to washing and leaching processes — these substances pass to surface and ground waters [1,2]. This uptake of pesticides into water courses, together with their transport by wind and their propagation through biological chains, means that both they and their degradation products must be monitored, not only in the areas where they are applied but also in more or less proximal areas.

The pollution of surface and ground waters by pesticides is governed by the physicochemical characteristics of the compounds, by the properties on the medium in which they are applied and by other external factors, such as the local rainfall and wind regimens or the topology of the area. Among

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the most important physicochemical properties of pesticides are their solubility in water, their capacity to be retained by the organic part of the soil (characterized by the K_{co} coefficient, which is closely related to the octanol–water partition coefficient K_{ow}) and their degradation rate, which is related to their molecular structures and which determines their persistence in soils [1].

The assessment of pesticide residues in surface and ground water has been conducted in several zones in Europe and in the US [3–8] and also in Spain [9–12], but to date no studies have been carried out in the area of Salamanca and Zamora, the focus of this study. The aim of the present work was to evaluate for the first time the pollution of agricultural land due to herbicides in the Guareña and Almar river basins, located in the above provinces.

To conduct the study, a set of fifteen herbicides was selected on the basis of the data provided by the authorities and local farmers concerning their frequency of use and the amounts used. These were: alachlor, atrazine, chloridazon, chlorsulfuron, chlortoluron, diflufenican, diuron, fluazifop-butyl, isoproturon, lenacil, linuron, metamitron, metribuzin, terbutryn and triasulfuron.

A method using HPLC was developed to monitor these herbicides owing to the polarity and thermal instability of several of them, which hinders their determination by gas chromatography. Diode-array detection was used, in order to ensure the selectivity of the method, together with solid-phase extraction, widely accepted in environmental analysis [13–18] as an alternative to conventional liquid–liquid extraction [19,20]. With this technique it is possible to achieve adequate sensitivity that allows the maximum concentrations set by European directives for drinking water to be detected; i.e., 0.5 μg/l for the sum of all pesticides and 0.1 μg/l for each individual compound [21]. The performances of two types of sorbents — C_{18} and polymeric Oasis HLB — were compared and finally the polymeric cartridges were selected.

The analytical methodology was applied to the monitoring of the fifteen selected herbicides in 41 environmental waters, including both surface and ground samples. Six of the herbicides sought were detected and their relationship with agricultural activity is discussed below.

2. Experimental

2.1. Description of the area

The study zone corresponds to the provinces of Salamanca and Zamora, located in Central-Western Spain (Fig. 1). The zone encompasses the basin of the River Guareña (approximate surface area, 1080 km^2), which flows directly into the Duero River, and the basin of the River Almar (approximate surface area, 590 km^2), an effluent of the River Tormes. The flow-rates of these rivers vary considerably since their courses do not have any dams or weirs. In summer, large parts of the basins are dried up; in the lower part of the River Guareña (province of Zamora), a flow-rate of some hundreds of litres/s is maintained while this is <1000 l/s at the end of the River Almar.

The main crops in the area are cereals (69%), followed by sunflower (15%). The remaining 16% is divided up between sugar beet (5%), grapes and corn (3% each) and others (potato, chick-pea, lentil, etc). On the basis of the data provided by the Territorial Service of Agriculture and Livestock Raising of the Junta of Castilla-León (Spain), fifteen herbicides from among those most used in the area were selected. These were: alachlor, atrazine, chloridazon, chlorsulfuron, chlortoluron, diflufenican, diuron, fluazifop-butyl, isoproturon, lenacil, linuron, metamitron, metribuzin, terbutryn and triasulfuron.

2.2. Sampling

Two samplings of surface waters were made, one between June and September 1998 and the other between October and December of the same year. The locations at which samples were taken (nine in each sampling) are shown in Fig. 1. Additionally, twenty-three samples of ground waters were taken, also shown in Fig. 1, in the above sampling sessions (fifteen in the first sampling and eight in the second one). Of these, nineteen were from wells (between four and twelve metres in depth), two from springs and two from small lakes.

Samples were collected in 1-l glass bottles. They were brought to the laboratory the same day of sampling and were stored at 4°C in the dark until solid-phase extraction, which was carried out in four

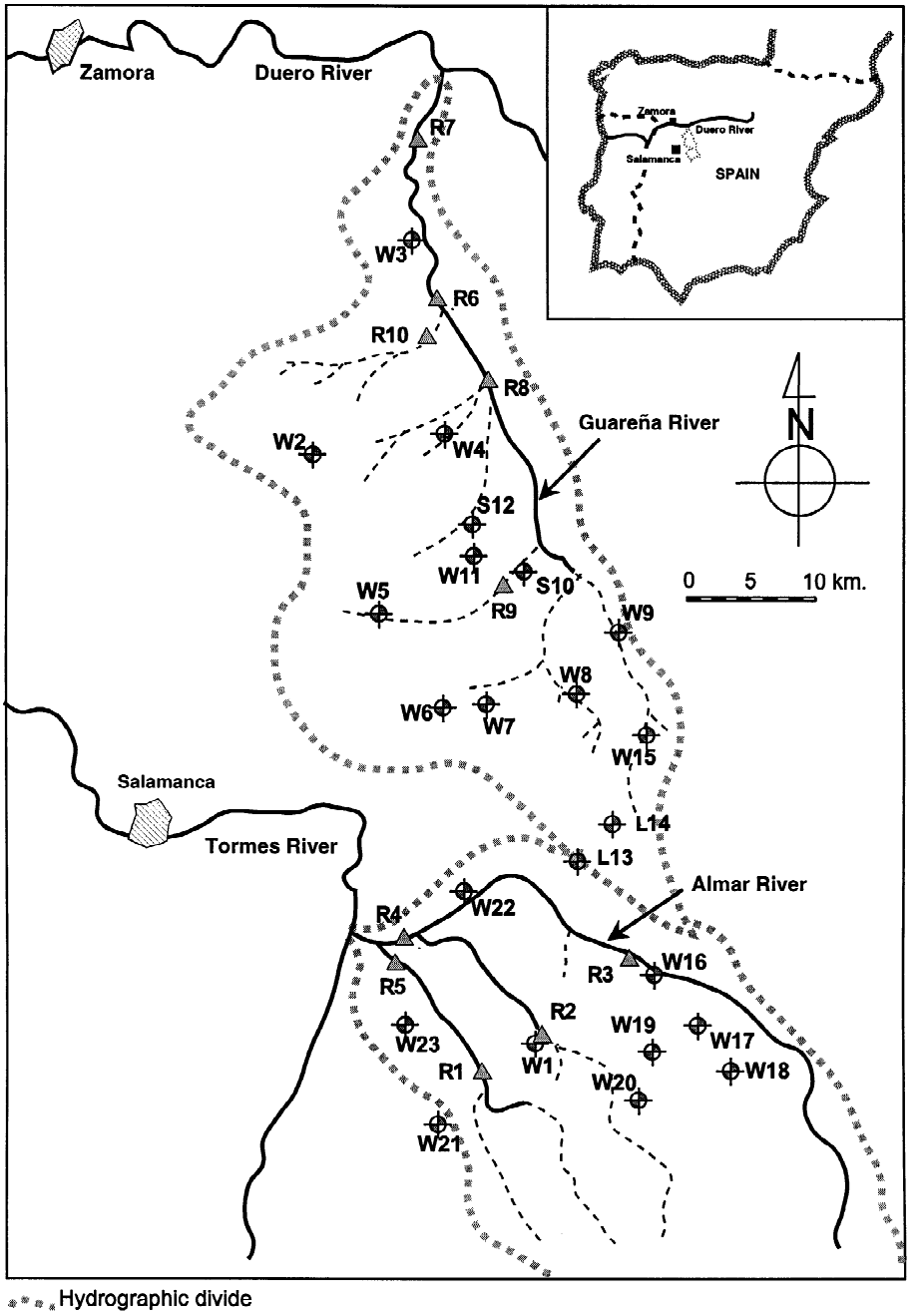

Fig. 1. Map of the studied zone (located in the provinces of Salamanca and Zamora) and sampling points. R, river; W, well; L, small lake; S, spring.

days or less after sampling. All samples were filtered through 0.45-μm pore-size nylon membrane filters (Millipore, Bedford, MA, USA).

2.3. Apparatus and chromatographic conditions

HPLC was performed on a HP 1100 Series

chromatograph from Hewlett Packard (Waldbronn, Germany), equipped with two pumps, a membrane degasser, an autosampler and a diode-array detector. The system was controlled by a HP CHEMSTATION, which also performed data collection from the diode array detection (DAD) system and quantitative measurements. The analytical column used was a 250× 4.0 mm I.D. Spherisorb S5 ODS2 packed with 5 μm particles (Waters, Mildford, MA, USA). The diode array detector was set at 210, 220, 230 and 245 nm. The spectra were recorded in the 190–400 nm range.

The mobile phase consisted of an acetonitrile (solvent A)–0.005 *M* phosphate buffer at pH 7.2 (solvent B) linear gradient, from 5 to 90% of solvent A in 60 min. Flow rate was 1 ml/min and the volume injected was 100 μl. The analytical column was thermostatted at 25°C.

Preconcentration of water samples was performed with Oasis HLB polymeric cartridges and C_{18} Sep-Pak-Plus bonded-phase silica cartridges (both from Waters, Milford, MA, USA). Samples were pumped through them by a Gilson Minipuls 2 HP 4 peristaltic pump at a maximum flow-rate of 8.0 ml/min.

2.4. Reagents and standards

The herbicides alachlor, atrazine, chloridazon, chlorsulfuron, chlortoluron, diflufenican, diuron, fluazifop-butyl, isoproturon, lenacil, linuron, metamitron, metribuzin, terbutryn and triasulfuron were purchased from Riedel-de Haën (Seelze-Hannover, Germany). Methanol, acetonitrile and ethyl acetate were of HPLC grade. Ultra-high quality water was obtained with a Elgastat UHQ water purification system. All other chemicals were of analytical grade.

Stock standard solutions of the herbicides (492–580 mg/l) were prepared by weighing and dissolving them in methanol. Another stock solution containing the fifteen herbicides was prepared from these in methanol. These solutions were stored at 4°C in the dark and were used for the preparation of dilute working standard solutions.

2.5. Environmental water sample preparation

Water samples (500 ml) were pumped through Oasis HLB polymeric cartridges, after conditioning them with 5 ml methanol, 5 ml ethyl acetate, 5 ml methanol and finally 5 ml ultrapure water.

After adsorption of the herbicides, the cartridges were dried for 15 min under vacuum and desorption was carried out with 10 ml ethyl acetate. This solvent was evaporated to dryness on a rotary evaporator (Büchi, Flawil, Switzerland) the residue was redissolved in 0.5 ml methanol–water (40:60, v/v) for HPLC injection.

2.6. Identification and quantification

Analyte identification was accomplished on the basis of the retention times of the analytes and by comparison between the UV spectrum of the reference compound in the library and the UV spectrum of the detected peak in the sample. A match equal or higher than 990 was fixed to confirm identification between both spectra for all the herbicides determined. Quantification was performed by external calibration. Sample analyses were run in duplicate and, in most, relative standard deviations of less than 10% were achieved.

3. Results and discussion

3.1. Characteristics of the method

In order to find suitable conditions for the separation of the target herbicides, a linear gradient solution (see Section 2.3.) was chosen. This afforded good resolution in a reasonable time (Fig. 2). Also, solid-phase extraction was used in order to achieve suitable sensitivity: this permitted detection limits of around 0.01 μg/l.

Two types of sorbents were studied — C_{18} and polymeric Oasis HLB — and different solvents were assayed for herbicide elution. Since the analytes had very different polarities (see Table 1) it was decided to perform a broad study to determine the optimum elution conditions. The recovery values obtained, expressed as percentages, are shown in Table 2. In each case, 500 ml of water spiked with the herbicides at a concentration close to 10 μg/l were passed through the cartridge, eluting the herbicides with either a single solvent or mixtures of solvents.

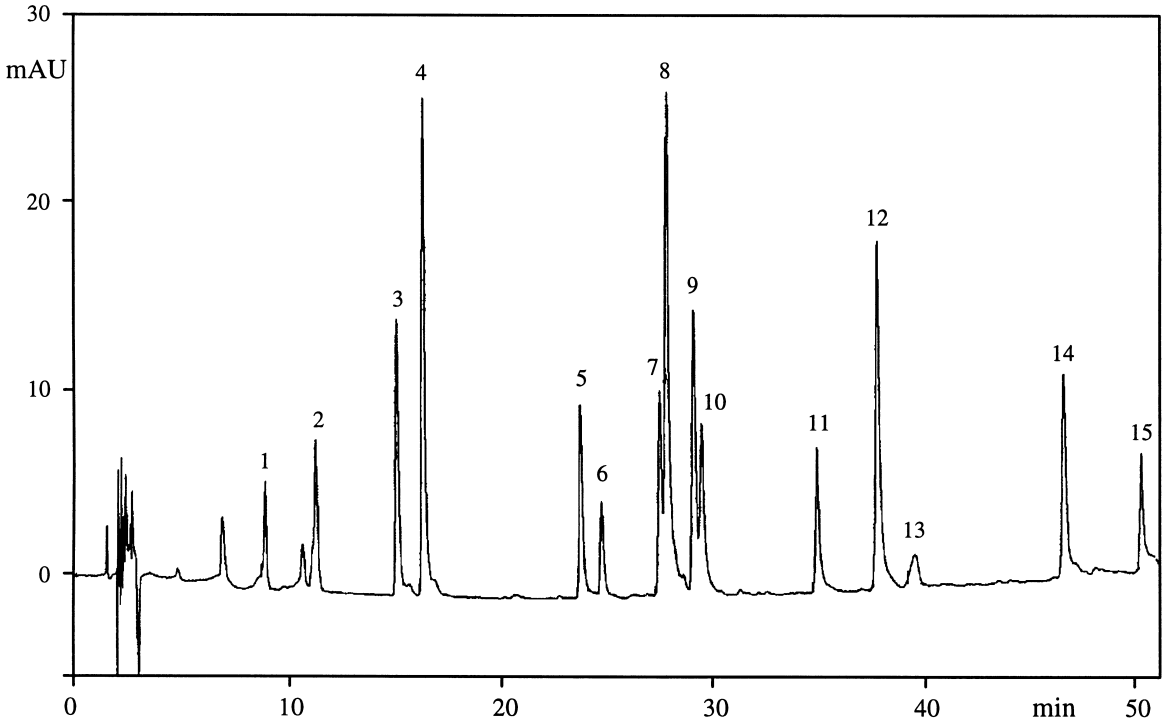

Fig. 2. Chromatogram of a standard solution of the fifteen herbicides tested at concentrations close to 0.5 mg/l. Mobile phase: acetonitrile–0.005 *M* phosphate buffer (pH 7.2). Gradient, from 5% to 90% of acetonitrile in 60 min. UV detection at λ=230 nm. Peaks: 1=chlorsulfuron; 2=triasulfuron; 3=metamitron; 4=chloridazon; 5=metribuzin; 6=lenacil; 7=chlortoluron; 8=atrazine; 9=isoproturon; 10=diuron; 11=linuron; 12=terbutryn; 13=alachlor; 14=diflufenican; 15=fluazifop-butyl.

In each case, the cartridge was conditioned with the solvent or mixture used for the elution.

In the case of methanol, the recoveries obtained with the C_{18} sorbent were lower than 70% for the herbicides with an octanol–water partition coefficient (log *P*) greater than 2.5. When acetonitrile was used, recoveries were higher than 70% for both types of sorbent, with the exception of diflufenican and fluazifop-butyl (log *P* 4.5). In the latter case, higher recoveries were obtained using mixtures of both solvents, although they were still only in the 33–58% range. The best results were obtained using ethyl acetate, with which most of the herbicides were recovered at about 100%, while the less polar compounds — diflufenican and fluazifop-butyl — were recovered at percentages of around 70%. In the light of this, ethyl acetate was chosen as the eluent. As sorbent the polymeric Oasis HLB was chosen because the cartridge drying phase, carried out prior to the elution of the herbicides, was less critical.

Calibration graphs were obtained by preconcentrating 500-ml volumes. Linear relationships were found between peak areas or heights and herbicide concentration in the 0.25–5 μg/l range of each herbicide. The detection limits, calculated as the ratio between twice the noise and the calibration slope, are given in Table 3 together with data from the calibration fittings (for peak heights) and relative standard deviations obtained from five replicate analyses at a concentration level of about 0.5 μg/l (0.49–0.67) of each herbicide.

3.2. Analysis of herbicides in river waters

The results obtained in the two samplings are summarized in Table 4, which shows the concentration ranges for the six herbicides detected as well as the number of samples in which they were detected. Table 5 shows the distribution of these samples in three concentration categories: detection

Table 1
Physicochemical properties of the herbicides studied shown in order of elution[a]

Herbicide	Chemical class	K_{ow} (log P)	Water solubility (mg/l)	Half-life (days)
Chlorsulfuron	Urea	−0.99	587 (pH 5) (25°C) 3180 (pH 7) (25°C)	Soil, 28–42 Aqueous solution, 28–56
Triasulfuron	Urea	1.1	32 (pH 5) (25°C) 815 (pH 7) (25°C)	Soil, 19 days, depending on the type of soil, pH, temperature and humidity
Metamitron	Triazinone	0.83	1700 (20°C)	–
Chloridazon	Pyridazinone	1.19	340 (20°C)	Water (pH 7), 6
Metribuzin	Triazinone	1.6	1050 (20°C)	Soil, 14–25
Lenacil	Uracil	2.31	6 (25°C)	Soil, 82–150
Chlortoluron	Urea	2.5	74 (25°C)	Soil, 30–40 Water, >200
Atrazine	Triazine	2.5	33 (22°C)	Field conditions, 16–77 (mean 41) Natural waters, 10–105 (mean 55) Ground waters, 105–200
Isoproturon	Urea	2.5	65 (22°C)	Soil, 6–28
Diuron	Urea	2.85	36.4 (25°C)	Soil, 90–180
Linuron	Urea	3.00	63.8 (20°C)	Soil, 38–67 Field conditions, 60–150
Terbutryn	Triazine	3.65	22 (22°C)	Soil, 14–50
Alachlor	Amide	3.09	242 (25°C)	Soil, 1–30 Surface waters, 28
Diflufenican	Amide	4.9	<0.05 (25°C)	105–210
Fluazifop-butyl	Phenoxy acid	4.5	1 (pH 6.5)	Soil, <7

[a] Data taken from reference [22].

Table 2
Recoveries obtained after solid-phase extraction with C_{18} and Oasis HLB cartridges of 500 ml of water spiked with 10 μg/l of each herbicide[a]

Herbicide	Eluent 1		Eluent 2		Eluent 3		Eluent 4		Eluent 5	
	C_{18}	Oasis	C_{18}	Oasis	C_{18}	Oasis	C_{18}	Oasis	C_{18}	Oasis
Chlorsulfuron	59	70	61	71	73	86	67	91	90	100
Triasulfuron	87	86	85	91	100	100	76	109	100	110
Metamitron	66	84	66	85	67	105	84	100	84	87
Chloridazon	86	90	76	100	85	100	89	110	97	97
Metribuzin	57	72	99	93	104	103	90	108	100	100
Lenacil	66	100	98	93	107	102	94	110	100	100
Chlortoluron	52	70	98	94	105	104	96	110	100	101
Atrazine	44	61	88	91	102	102	93	109	98	99
Isoproturon	61	75	94	92	106	105	96	110	100	99
Diuron	39	60	94	92	104	98	91	109	100	103
Linuron	11	23	83	89	84	97	91	94	89	100
Terbutryn	12	25	82	86	82	96	87	88	85	99
Alachlor	12	23	78	85	72	91	83	69	74	89
Diflufenican	–	–	40	44	58	40	57	55	81	72
Fluazifop-butyl	–	–	28	38	53	33	46	48	71	69

[a] Data represent means of three replicates; the relative standard deviations of the recoveries ranged between ±5 and 12%. Eluent 1: 10 ml methanol; eluent 2: 10 ml acetonitrile; eluent 3: 5 ml methanol followed by 5 ml acetonitrile; eluent 4: 5 ml ethyl acetate followed by 5 ml methanol–acetonitrile (50:50, v/v); eluent 5: ethyl acetate.

Table 3
Analytical characteristics of the method ($\lambda = 220$ nm)

Herbicide	Intercept	Slope	r^2	R.S.D (%)	DL[a] (μg/l)
Chlorsulfuron	(−0.3±0.6)	(14.3±1)	0.990	7.6	0.016
Triasulfuron[b]	(0.9±2)	(18.3±0.8)	0.995	14.8	0.005
Metamitron	(0.2±0.8)	(30.8±0.3)	0.999	12.4	0.008
Chloridazon	(0.7±1)	(52.9±0.6)	0.999	5.8	0.004
Metribuzin	(−1.0±0.5)	(22.8±0.4)	0.999	12.5	0.010
Lenacil	(−0.1±0.5)	(17.1±0.2)	0.999	6.7	0.013
Chlortoluron	(0.1±1)	(35.6±0.6)	0.999	8.0	0.006
Atrazine	(−0.8±2)	(56.7±0.8)	0.999	6.8	0.004
Isoproturon	(0.4±0.7)	(18.6±0.2)	0.999	3.8	0.012
Diuron	(0.3±1)	(33.1±0.6)	0.999	7.5	0.007
Linuron[b]	(0.5±0.5)	(17.2±0.2)	0.999	8.8	0.013
Terbutryn	(−0.8±0.6)	(40.7±0.7)	0.999	7.9	0.006
Alachlor	(0.2±0.3)	(9.4±0.2)	0.999	7.6	0.024
Diflufenican	(0.3±1)	(19.0±0.5)	0.998	10.6	0.012
Fluazifop-butyl	(0.6±0.6)	(9.3±0.2)	0.998	11.1	0.025

[a] DL: detection limit (twice the noise).
[b] Analytical characteristics of the method at $\lambda = 230$ nm for linuron and $\lambda = 245$ nm for triasulfuron due to interferences of the baseline at $\lambda = 220$ nm.

Table 4
Results obtained for the analysis of herbicides in river waters[a]

Herbicide	First sampling		Second sampling	
	Conc. range (μg/l)	No. of polluted samples	Conc. range (μg/l)	No. of polluted samples
Chlortoluron	DL–0.08	6	0.07–0.71	7
Atrazine	–	0	0.14	1
Terbutryn	0.17–0.42	3	0.16	1
Alachlor	0.09–016	3	–	0
Diflufenican	DL–0.08	7	DL	1
Fluazifop-butyl	DL–0.20	5	–	0

[a] Number of samples analysed was eighteen (nine in each sampling); DL: detection limit.

Table 5
Distribution of polluted samples according to their herbicide concentration[a]

Herbicide	River samples			Ground samples		
	A	B	C	A	B	C
Chlortoluron	2	5	6	1	1	3
Atrazine	0	0	1	0	1	1
Terbutryn	0	0	4	0	0	0
Alachlor	0	1	2	6	0	2
Diflufenican	6	2	0	6	1	0
Fluazifop-butyl	3	0	2	2	0	1

[a] A, detection limit; B, between the detection limit and 0.1 μg/l; C, >0.1 μg/l.

limit, higher than the detection limit but <0.1 μg/l and ⩾0.1 μg/l. Fig. 3a shows the chromatogram of a river water sample together with confirmation of the detected atrazine according to its UV spectrum.

Chlortoluron was the herbicide detected with the highest frequency and in the highest amounts; up to 0.71 μg/l. Its use as a pre-sowing herbicide in cereals — the most abundant crop in the zone studied (69% of the cultivated surface) — would account for its high frequency of appearance, also favoured by its relatively high polarity and water solubility (Table 1). The contents of chlortoluron in the two samplings were compared using a *t*-test for paired data. The level of significance was deter-

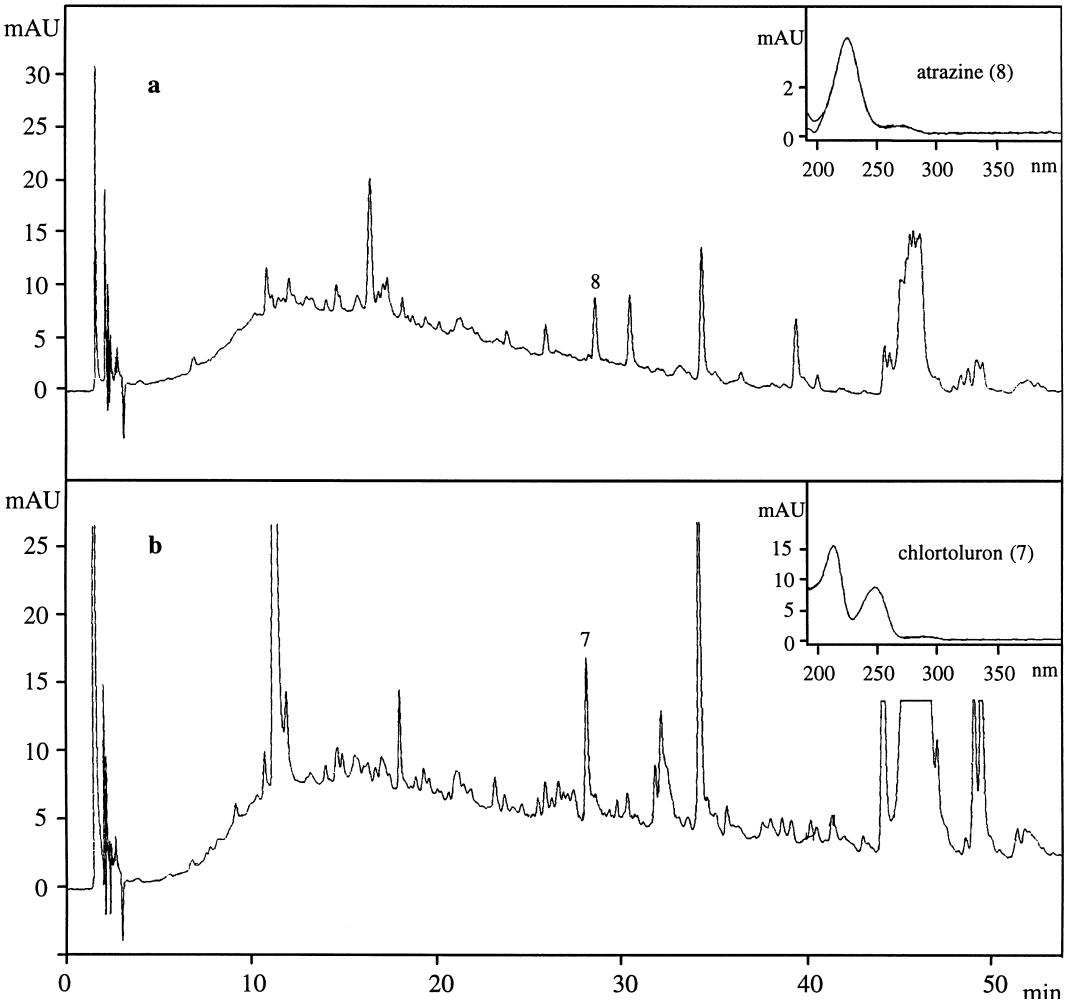

Fig. 3. Chromatograms obtained after solid-phase extraction with Oasis HLB cartridges of (a) 500 ml of a river water sample and (b) 500 ml of an underground water sample. Experimental conditions as in Fig. 2. In the insert, confirmation of (a) atrazine and (b) chlortoluron, according to their UV spectra.

mined, obtaining a value <0.05 (chosen as minimum level of significance), which shows that there were significant differences between them. This is related to the sowing of cereals, which is carried out in October.

The rest of the herbicides detected (with the exception of atrazine, which was only found in one sample from the second sampling session) appeared with the greatest frequency and in the highest amounts in the first sampling. Alachlor and fluazifop-butyl were not found in any case in the second sampling, probably due to the types of crop that the zone is used for: alachlor for corn, beet and potato and fluazifop-butyl for lentil and chick-pea, all of them sown between April and June. The concentration values obtained for diflufenican, used for cereals, never surpassed a level of 0.1 μg/l in any of the samples, possibly owing to the low solubility of this herbicide (Table 1).

3.3. Analysis of herbicides in ground waters

Table 6 summarizes the contents of herbicides found in ground water samples and also shows the number of polluted samples. The concentration distribution of the latter is shown in Table 5, classified

Table 6
Results obtained for the analysis of herbicides in ground waters[a]

Herbicide	First sampling		Second sampling	
	Conc. range (μg/l)	No. of polluted samples	Conc. range (μg/l)	No. of polluted samples
Chlortoluron	DL–1.2	4	0.02	1
Atrazine	0.02	1	0.22	1
Alachlor	DL–0.21	8	–	0
Diflufenican	DL–0.06	4	DL	3
Fluazifop-butyl	DL–0.18	3	–	0

[a] Number of samples analysed was 23 (15 in the first sampling and 8 in the second one); DL: detection limit.

in the same three categories as the river water samples. Fig. 3b shows the chromatogram of a well water sample, together with confirmation of the detected chlortoluron according to its UV spectrum.

The herbicides encountered in the greatest number of samples were alachlor and diflufenican. Despite its low solubility, diflufenican was found in ground waters, probably owing to its long half-life (105–210 days). In any case, its concentration (as in surface waters) never surpassed 0.1 μg/l. Alachlor and fluazifop-butyl were only found in the first sampling, as corresponds to the type of crop for which they are used. Table 5 shows that the number of surface and ground waters containing alachlor at concentrations higher than 0.1 μg/l is the same, probably because this herbicide is highly soluble in water.

Chlortoluron appeared less often in ground waters than in surface waters (22 versus 72%, respectively). It was also present at much lower concentrations, with the exception of the two small lakes that were sampled, in which concentrations of 0.6 and 1.2 μg/l were found (the highest value found in the whole study). This suggests a very particular problem of pollution. Regarding the triazines, terbutryn was not detected in any of the ground water samples, unlike atrazine (two samples), perhaps due to the greater polarity and water solubility of the latter.

In general, both in these and in the river water samples the herbicides chlortoluron, diflufenican and fluazifop-butyl were distributed in a fairly uniform way throughout the zone studied, as are the crops for which they are used. Alachlor was only found in the River Guareña zone, most points at which it was detected being close to the source of the river, corresponding to zones in which corn, beet and potatoes are cultivated. The triazines, atrazine and terbutryn, by contrast, appeared in very localized zones, the former mainly on the lower stretches of the river Guareña.

4. Conclusions

A LC–DAD method, after solid-phase extraction that uses polymeric cartridges is proposed, and has allowed the monitoring of fifteen herbicides of different types — ureas, triazines, amides and others — that are widely used in the provinces of Salamanca and Zamora (Spain). The detection limits obtained were in the 0.004–0.025 μg/l range.

The pollution due to the agricultural use of these herbicides in the zone was assessed over a period of 6 months, with six of them being found in river waters: chlortoluron, atrazine, terbutryn, alachlor, diflufenican and fluazifop-butyl. With the exception of terbutryn, all were also detected in ground waters. Concentration levels ranged from <0.01 to 1.2 μg/l. The highest values were found for chlortoluron, used in cereals, which are the most abundant crops in the region. Significantly higher levels of this same compound were also found in river water samples during the period from October to December, after cereal sowing. Of the six herbicides detected, all of them except diflufenican surpassed a concentration of 0.1 μg/l at some points. The change in the pollution level as a function of time is currently under study.

Acknowledgements

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