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### Long-Term Monitoring of Pesticides and Polar Transformation Products in Ground Water Using Automated Online Trace-Enrichment and Liquid Chromatography with Diode Array Detection

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# LONG-TERM MONITORING OF PESTICIDES AND POLAR TRANSFORMATION PRODUCTS IN GROUND WATER USING AUTOMATED ON-LINE TRACE-ENRICHMENT AND LIQUID CHROMATOGRAPHY WITH DIODE ARRAY DETECTION

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An automated system using on-line trace-enrichment, separation by liquid chromatography with a gradient elution and diode array detection is described for monitoring pesticides in ground water. Two systems were used for covering the wide range of polarities of the targeted pesticides: the first one consisted of a PLRP-S precolumn and a C<sub>18</sub> analytical column for moderately polar to non polar compounds and the second one, specially designed for the determination of polar pesticides and degradation products, consisted of a precolumn and analytical column both packed with porous graphitic carbon. The detection limits that can be reached by the two systems are in the low 0.1 µg/l for the ground water samples of interest with the handling of 100–150 ml of water. An application is presented with the first objective of monitoring the quality of a ground water reservoir which comes from a small basin where the amount and nature of pesticides applied are known and where atrazine has been banned for the last five years and replaced by terbutylazine. The second objective was to have a better knowledge of the behaviour and persistence of pesticides from the results of a long-term survey of 18 months. Obviously, the water solubility is an important parameter for the leachability of pesticides. Although banned on this site for the last five years, atrazine and deethylatrazine are found at constant concentrations, 0.5 and 0.7 µg/l respectively all the year round. The on-line system with the PGC precolumn and analytical column allowed to confirm the deethylatrazine concentration as well as the very low concentration (< 0.05 µg/l) of both hydroxyatrazine and deisopropylatrazine. Although applied in replacement of atrazine, neither terbutylazine nor its major dealkylated metabolite were detected until now. Other more soluble compounds such as isoproturon or metamitron are detected during the period following their application.

**KEY WORDS:** Pesticides, on-line solid-phase extraction, liquid chromatography, multiresidue analysis, ground water.

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## INTRODUCTION

Trace of pesticides and some of their degradation products are regularly detected in ground and surface water, and consequently, with environmental protection on the agenda of many countries, monitoring programs for pesticides and degradation products are currently being set up<sup>1-5</sup>. Therefore, there has been a growing interest in using more powerful analytical methods which can be automated and can allow multiresidue analysis of pesticides at a trace-level.

The study reported in this paper was carried out with two objectives. First, the need for monitoring pesticides in ground water exists for preserving its quality as drinking water sources. Second, long-term monitoring in agricultural areas is expecting to contain information on the real behaviour of pesticides in comparison with laboratory experiments. The monitoring program was greatly facilitated because the amount and the nature of the pesticides applied in the area were known. More than 90 different pesticides are annually applied for plant protection on the basin. A set of 21 pesticides and degradation products was selected owing to their usage, amount, toxicity and leachability properties. Since this mixture contained compounds with a wide range of functionality, polarity and solubility, liquid chromatography was selected due to its high suitability for multiresidue analysis<sup>6-9</sup>. Solid-phase extraction was selected for the trace-enrichment step which was coupled on-line to the LC separation with UV diode array detection. On-line techniques offer a fast, modern and reliable approach with the possibility of using an automated device with no risk of loss or contamination since there is no sample manipulation between the sample percolation and the analysis.

In this work, we first report on the evaluation of an automated on-line device for the sample pretreatment used in combination with an automated LC-DAD system. The conventional systems utilize a precolumn packed with the apolar copolymer PLRP-S for the preconcentration and an analytical C<sub>18</sub> column for the separation<sup>10-15</sup>. This system was evaluated for the monitoring of moderately polar and non-polar analytes and its reliability for quantification and identification of compounds was studied as a function of the sample volume and of the polarity of pesticides. Since the system cannot accurately quantify polar compounds or metabolites such as deisopropylatrazine at the low 0.1 µg/l level, another system coupling a precolumn and an analytical column both packed with a porous graphitic carbon-based sorbent was then evaluated as a complement for confirmation of the presence of the more polar analytes. The different parameters have been optimized. Several ground water samples taken at different locations in the basin were analysed every two weeks during a 18-month period and the results of the monitoring are discussed in relationship with the targeted pesticides and amounts applied as well as their leaching properties.

## EXPERIMENTAL

### *Apparatus*

A model 9010 liquid chromatograph equipped with a 9065 Polychrom diode array detector (Varian, Palo Alto, CA, USA) was used for direct injections and precolumn elution. Trace enrichment was performed on disposable cartridges using the Prospekt (Spark Holland, Emmen The Netherlands). Quantitative measurements were provided by using the software of the Polychrom using the whole on-line procedure with spiked LC-grade water samples.

### *Stationary phases*

A C<sub>18</sub> analytical column, TSK ODS80-TM (250 mm × 4.6 mm I.D., 5 μm particle size) from Varian and a column packed with Hypercarb porous graphitic carbon (100 mm × 4.6 mm I.D., 5 μm particle size) from Shandon HPLC (Runcorn, UK) were used.

Samples were preconcentrated on precolumns specially made for the Prospekt apparatus, 10 × 2 mm I.D) prepacked with styrene-divinylbenzene copolymer PLRP-S (Polymer Laboratories, Church Stretton, UK) and with porous graphitic carbon PGC from Shandon. Samples were analysed without any filtration.

### *Chemicals*

HPLC-grade acetonitrile was obtained from Baker France (Noisy-le-Grand, France). LC-grade water was prepared by purifying demineralized water in a milli-Q filtration system (Millipore, Bedford, MA, USA). Pesticides and degradation products were supplied by Cluzeau (Sainte-Foy-la-Grande, France). Stock solutions of pesticides were prepared by weighing and dissolving them in methanol. The standard solutions were stored at 4°C and were used for the preparation of diluted standard solutions and for spiking the water samples. Final spiked water samples did not contain more than 0.5% of methanol.

### *HPLC conditions*

The separation of 21 pesticides was performed using the C<sub>18</sub> column with a gradient of acetonitrile and a 5.10<sup>-3</sup> M phosphate buffer at pH 7.2 at a flow-rate of 1 ml per min. The gradient was 15% of acetonitrile from 0 to 10 min, 50% at 33 min, 50% at 40 min and 70% at 48 min. Using the Hypercarb column, the separation of DEA and DIA was also performed with the above mixture of mobile phase but with a different gradient, from 15% to 35% of acetonitrile from 0 to 35 min.

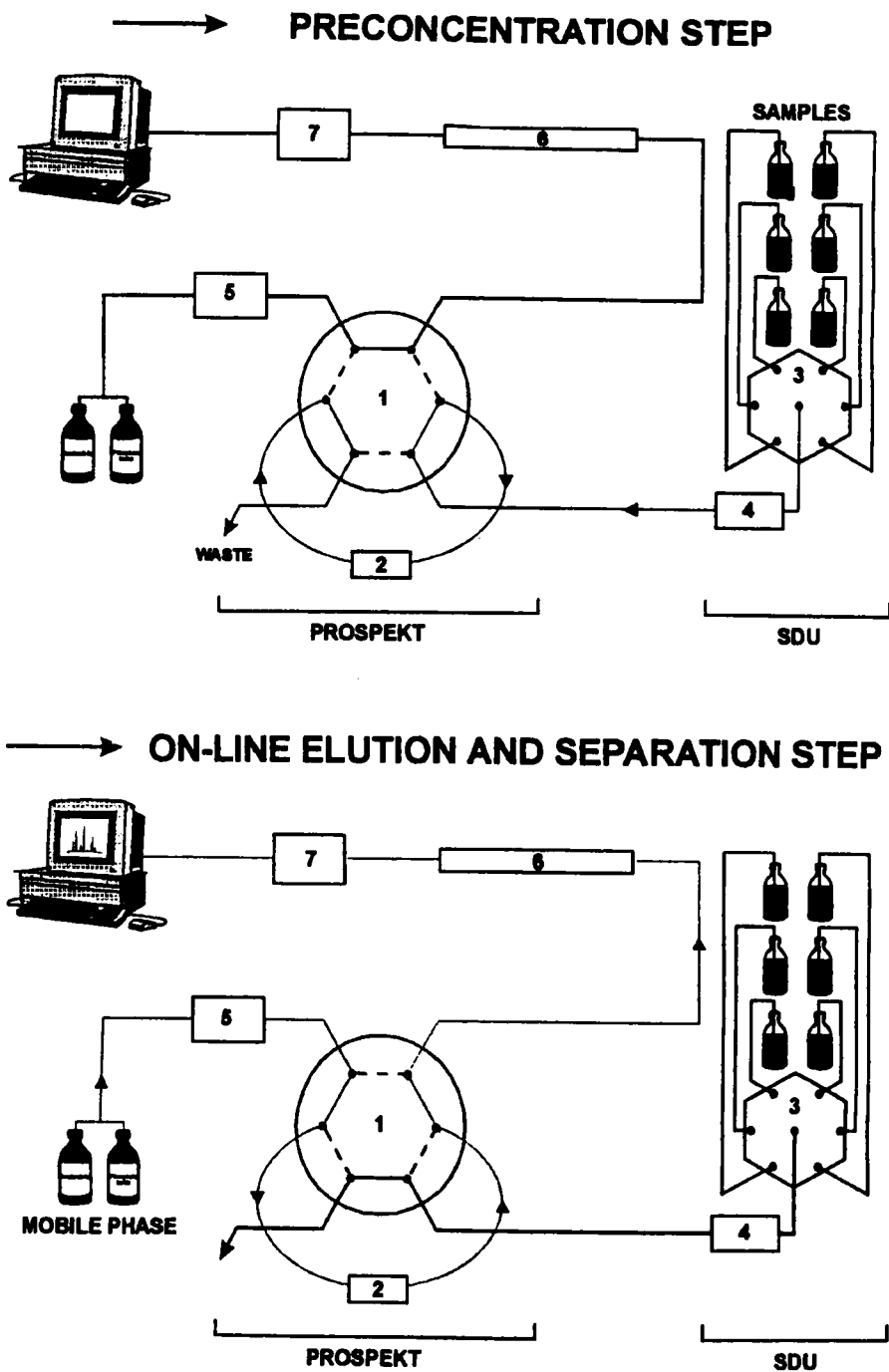
### *On-line SPE-HPLC procedure*

The Prospekt was programmed so that the preconcentration of a sample could be performed during the LC analysis time of the previous sample. The solid-phase extraction sequence contained a conditioning step with 5 ml of acetonitrile, 5 ml of methanol and 5 ml of LC-grade water. Then the aqueous sample (150 ml or 100 ml) was adjusted to pH 7 if required and was applied at a flow rate of 2 or 3 ml/min. A pH value of 7 was required for the preconcentration of hydroxyatrazine (pK<sub>a</sub> around 5). Then, the precolumn was washed with 3 ml of LC-grade water before automatic exchange for on-line desorption via the Prospekt device. The setup of the on-line system is represented in Figure 1.

## RESULTS AND DISCUSSION

### *Selection of the pesticides and degradation products*

The drinking water of Paris City, which is managed by the SAGEP, originates partly from surface water following treatment in plants and partly from ground water. The



**Figure 1** Scheme of the on-line system representing (a) the preconcentration step, the Solvent Delivery Unit allowing the automated conditioning of cartridges and sample application and (b) the on-line elution and separation step by automatic exchange of the cartridge via the Prospekt system.

(1) LC switching valve, (2) precolumn, (3) SDU valve, (4) preconcentration pump, (5) LC pump, (6) analytical column, (7) diode array detector.

ground water represents an average of 40% of the city consumption and comes from different springs which are located as far as 150 km from Paris and are transported to reservoirs in Paris via aqueducts which were constructed in the last century. Some springs are located in large forest areas where no contamination is detected but also in agricultural drainage basins where contamination by pesticides really exists. In a small drainage basin (around 1500 ha), atrazine has been detected for several years. With the cooperation of farmers atrazine has been banned since 1990 and replaced by other herbicides, especially terbutylazine. Furthermore, the pesticides and amounts applied these last years are known, which was a great help for the selection of products in the monitoring program. Various crops such as wheat, barley, corn, beet, peas are grown and for example, more than 90 products were applied in 1993. Diuron was added to the list because it is applied on roads and railways tracks. Only the pesticides and amounts applied in private gardens are not known. It was impossible to monitor all these pesticides and a set of 21 compounds was selected owing to their usage and leachability through soil both of which are related to their hydrolysis half-time and their soil adsorption coefficient. Atrazine and its dealkylated and hydroxylated transformation products were included since they are still detected. These compounds and their main physico-chemical and environmental properties are reported in Table 1. As it can be observed, the pesticides and their transformation products have a wide range of physico-chemical properties as shown by solubility and water-octanol partition coefficient values. A different environmental behaviour can also be predicted depending on the half-time values ( $DT_{50}$ ) in which 50% of the parent compound has disappeared from soil or from water by transformation and on the sorption coefficient in soil,  $K_{oc}$ , normalized to carbon organic content of the soil. A wide range of values are found, showing that these values depend greatly on the experimental conditions: laboratory or field experiments, nature of the soil samples, moisture, etc...

#### *On-line chromatographic analysis using a PLRP-S precolumn and a $C_{18}$ analytical column*

A serious limitation to the on-line SPE-LC system is the use of small precolumns which contain therefore a small amount of sorbent. The breakthrough volume, which corresponds to the maximum sample volume which can be percolated through the precolumn with a theoretical recovery of 100%, depends on the polarity of the analytes and on the nature and amount of sorbent in the precolumn<sup>8,19</sup>. It is a critical parameter because if this volume is too small, the extracted amount is not large enough to allow trace-level analysis. Usually, a precolumn packed with an apolar copolymer is selected because the retention of the compounds is 20 to 40 times higher than that obtained on classical  $C_{18}$  precolumns as shown in Table 2. A  $C_{18}$  precolumn cannot be used when moderately polar compounds are to be determined at a trace-level because of early breakthrough. Figure 2a represent the chromatogram obtained at 220 nm when directly injecting 50 ng of each analyte of the mixture into the  $C_{18}$  analytical column whereas Figure 2b represents the on-line preconcentration of 150 ml of drinking water spiked with 0.1  $\mu\text{g/L}$  of each analyte. Recoveries are lower than 100% for peaks 1–5, as expected from the results of Table 2. Peaks 4 and 10 corresponding respectively to deethylatrazine (DEA) and atrazine are higher due to the presence of these two compounds in the non-spiked drinking water sample at concentrations around 0.1  $\mu\text{g/l}$ .

On-line systems are best suited for eliminating sources of errors due to sample manipulation. Reproducible results were obtained even when breakthrough of analytes occurs<sup>11,14,20</sup>. It was shown that quantitative results were similar using calibration

**Table 1** Various characteristics of the targeted pesticides and degradation products. Solubility according to ref. 16,17; octanol-water partition coefficient,  $\log P_{ow}$ , according to ref. 16–18. Hydrolysis  $DT_{50}$  in water,  $DT_{50}$  in soil and  $K_{om}$  (sorption coefficient divided by fraction of organic matter in soil), range of selected values and mean, according to ref. 16,17.

No	Compounds	Group	Solubility (mg/l)	$\log P_{ow}$	$DT_{50}$ (water) (days)	$DT_{50}$ in soil (days)		$K_{om}$ in soil (dm <sup>3</sup> /kg)	
						range	mean	range	mean
1	Deisopropylatrazine	Triazine	670	1.2	no data	no data	no data	no data	
2	Metamitron	Triazinone	1820	0.8	no data	20–40	30	49–151	100 (VSM)
3	Hydroxyatrazine	Triazine	6	1.4	no data		164	no data	
4	Deethylatrazine	Triazine	3200	1.6	no data		45		18 (SM)
5	Chloridazon	Diazine	400	2.2	72–144	15–46	31	37–91	64 (SM)
6	Aldicarb	Carbamate	6000	1.1–1.6	77–>300	1.3–2.5	2.4	2.2–7.2	4.7 (M)
7	Simazine	Triazine	3.5–5	2.3	>28–96	31–85	58	11–107	59 (SM)
8	Deethylterbutylazine	Triazine			no data	no data		no data	
9	Carbofuran	Carbamate	350–700	1.6	21 (mean)	18–90	50	25–63	22 (SM)
10	Atrazine	Triazine	30	2.7	86	38–62	58	28–112	70 (SM)
11	Isoproturon	Phenylurea	60–70	2.25	no data	24–44	35	28–58	46 (SM)
12	Diuron	Phenylurea	42	2.6–2.8	no data	79–108	94	146–318	232 (VSM)
13	Propazine	Triazine	8.6	2.9–3.0	83	102–157	132	29–87	58 (VSM)
14	Terbutylazine	Triazine	8.5	3.0–3.1	>200	30–114	85	306–1350	(VSM)
15	Linuron	Phenylurea,	75–81	2.7	>30	47–236	131	165–301	231 (VSM)
16	Terbutolone	triazole	32	3.7	>22	355–841	652	540–705	613 (VSM)
17	Alachlor	chloroacetamide	240	2.8	>30	14–29	22	117–190	117 (VSM)
18	Metolachlor	chloroacetamide	530	3.1–3.3	>200	59–144	101	62–144	103 (VSM)
19	Fenoxaprop	Phenoxy	0.7–0.9	no data	2.4–700	0.6–0.7	(RD)	4.3–12	8.7 (MM)
20	Pendimethalin	Toluidine	0.3	5.2	>28	129–207	171	66–1227	111 (VSM)
21	Trifluralin	Trifluoromethyl	0.05	4	0.1–0.2	186–255	221	2899–5204	3775 (VSM)

Degradability (D for degradable); R: readily, F: fairly, S: slightly and VS: very slightly  
Mobility (M for mobile); M: moderately, S: slightly, VS: very slightly.

**Table 2** Comparison of breakthrough volumes (in ml) obtained on a 1 cm × 0.2 cm i.d. precolumn packed with C<sub>18</sub> silica (a) or with PLRP-S (b).

<i>Compound</i>	<i>C<sub>18</sub></i>	<i>PLRP-S</i>
Oxamyl	4 ± 1	30 ± 5
DIA	2 ± 1	25 ± 10
Metamitron	3 ± 1	75 ± 10
DEA	3 ± 1	85 ± 15
Chloridazon	2 ± 1	90 ± 20
Carbendazim	4 ± 1	180 ± 20
Aldicarb	6 ± 1	250 ± 30
Simazine	23 ± 5	> 350
Carbofuran	32 ± 8	> 350
Atrazine	80 ± 2	> 350
Isoproturon	80 ± 20	> 350
Terbutylazine	130 ± 30	> 350

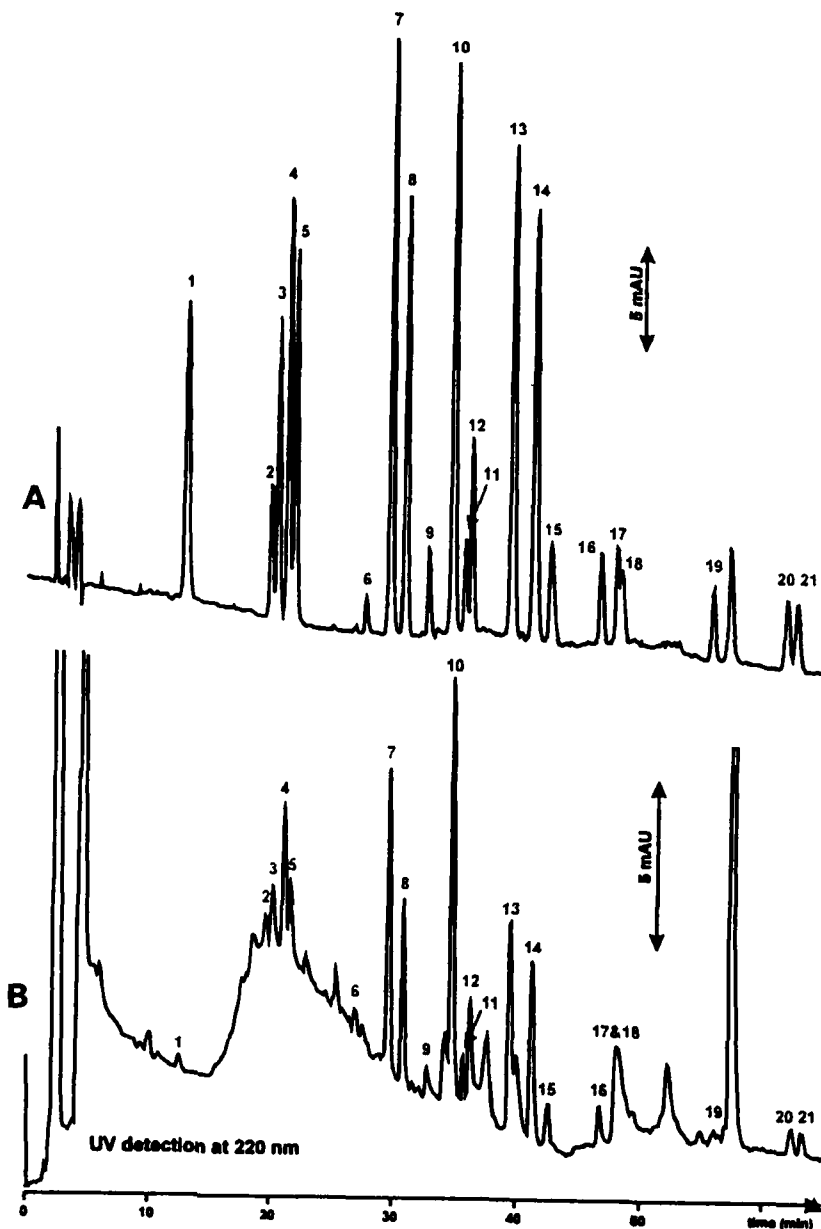
constructed from real spiked samples with the same experimental conditions (sample volume, nature of the precolumn, gradient applied), or using standard addition, or using the MCA (multicomponent analysis) software included in the software of the DAD provided that data have been introduced via the whole on-line system from spiked samples and not from direct injections<sup>11</sup>. Lacorte *et al*<sup>21</sup> have also validated the reliability of data given by the on-line system using a Prospekt device through interlaboratory calibrations.

The on-line system using a PLRP-S precolumn and a C<sub>18</sub> analytical column was applied to the analysis of 150-ml aliquots of ground water samples and a typical chromatogram obtained at three different wavelengths is represented in Figures 3 a-c. The compounds are identified first by their retention times and secondly by the correspondence between the UV spectrum of the reference compound in the library and the UV spectrum of the detected peak in the sample which occurs at the same retention time. As shown for some of the compounds, the match between the UV spectra of the unknown and reference peaks is excellent and it was possible to identify and quantify deethylatrazine, atrazine, isoproturon and metamitron without further need of confirmation. Owing to its characteristic UV property, metamitron can be detected at a very low level even if breakthrough has occurred; a very low attenuation range (10 times lower than at 220 or 244 nm) could be used (Figure 3c) because the chromatogram at 306 nm was free from interfering compounds. Thanks to the DAD software, it was also possible to unambiguously affirm that compounds with retention times similar to those of pesticides in the reference chromatogram were not the targeted pesticides.

#### *On-line chromatographic analysis using a PGC precolumn and a PGC analytical column*

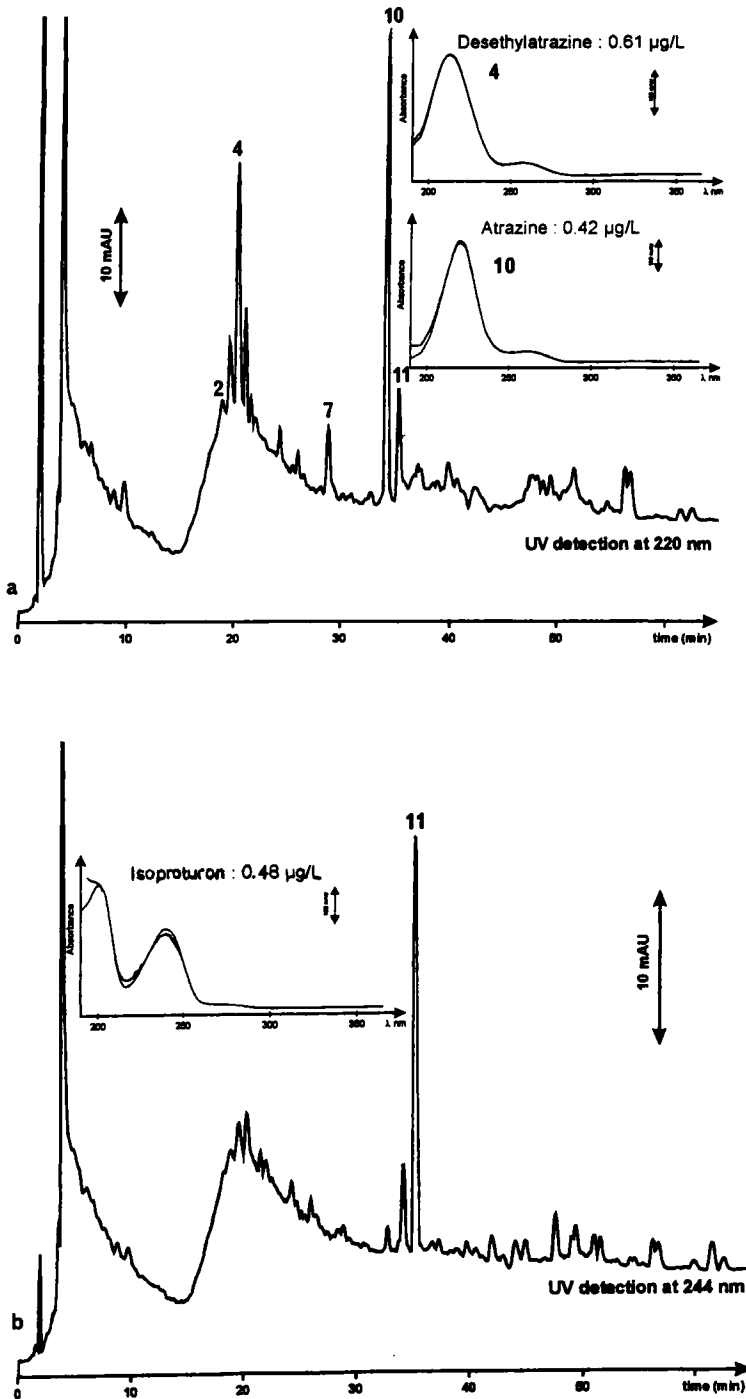
In the sample analysed in Figure 3, the concentrations of DEA and atrazine are respectively 0.61 ± 0.06 µg/l and 0.42 ± 0.05 µg/l. Simazine (peak 7) was also determined at a concentration of 0.05 ± 0.01 µg/l. No traces of hydroxyatrazine or of the other dealkylated metabolite DIA were detected. However, the recovery of DIA is low on the PLRP-S precolumn due to its breakthrough and, as can be observed in the





**Figure 2** (A) Direct injection of 10 µl of a standard mixture at 5 mg/l and (B) On-line analysis of 150 ml of a drinking water sample spiked with 0.1 µg/l of each 21 pesticides using the Prospekt system.

Precolumn: 1 cm × 0.2 cm i.d. packed with PLRP-S from Polymer Laboratories; C<sub>18</sub> analytical column ODS-80TM, 25 cm × 0.46 cm i.d., water acetonitrile gradient: 15% acetonitrile from 0 to 10 min, 50% at 33 min, 50% at 40 min, 70% at 70 min; UV DAD detection, chromatogram at 220 nm, peak number: (1) Deisopropylatrazine, (2) metamitron, (3) hydroxyatrazine, (4) deethylatrazine, (5) chloridazon, (6) aldicarb, (7) simazine, (8) deethylterbutylazine, (9) carbofuran, (10) atrazine, (11) isoproturon, (12) diuron, (13) propazine, (14) terbutylazine, (15) linuron, (16) terbuconazole, (17) alachlor, (18) metolachlor, (19) fenoxaprop-p-ethyl, (20) pendimethalin, (21) trifluralin.



**Figure 3** On-line analysis of 150 ml of a ground water sample (Glatigny spring, April 1994). Chromatogram represented (a) at 220 nm with identification of DEA and atrazine, (b) at 244 nm with identification of isoproturon and (c) at 306 nm with identification of metamitron. Same experimental conditions as in Figure 2.

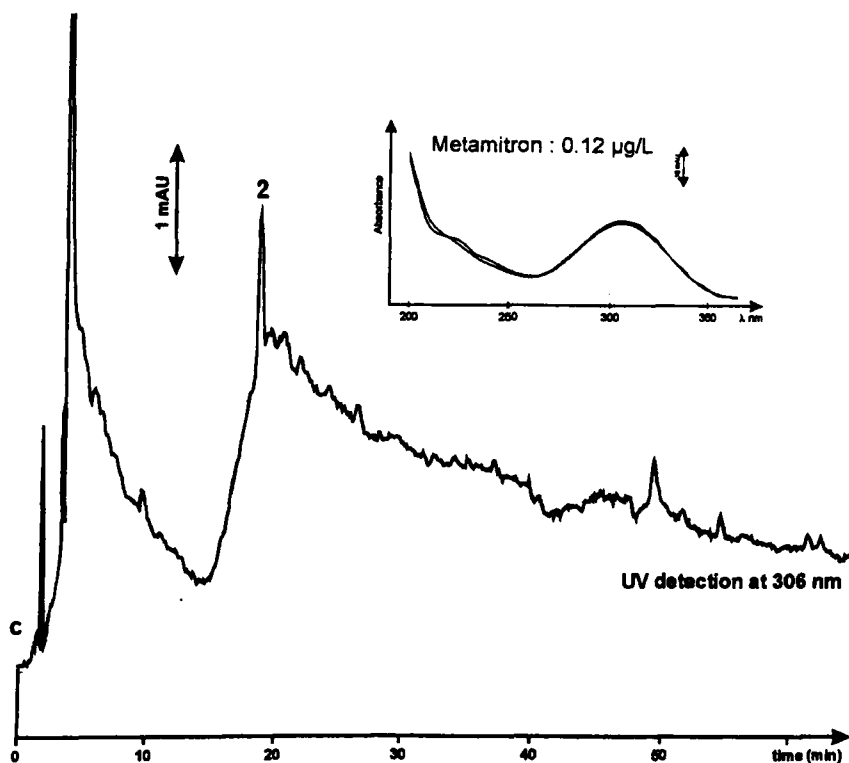


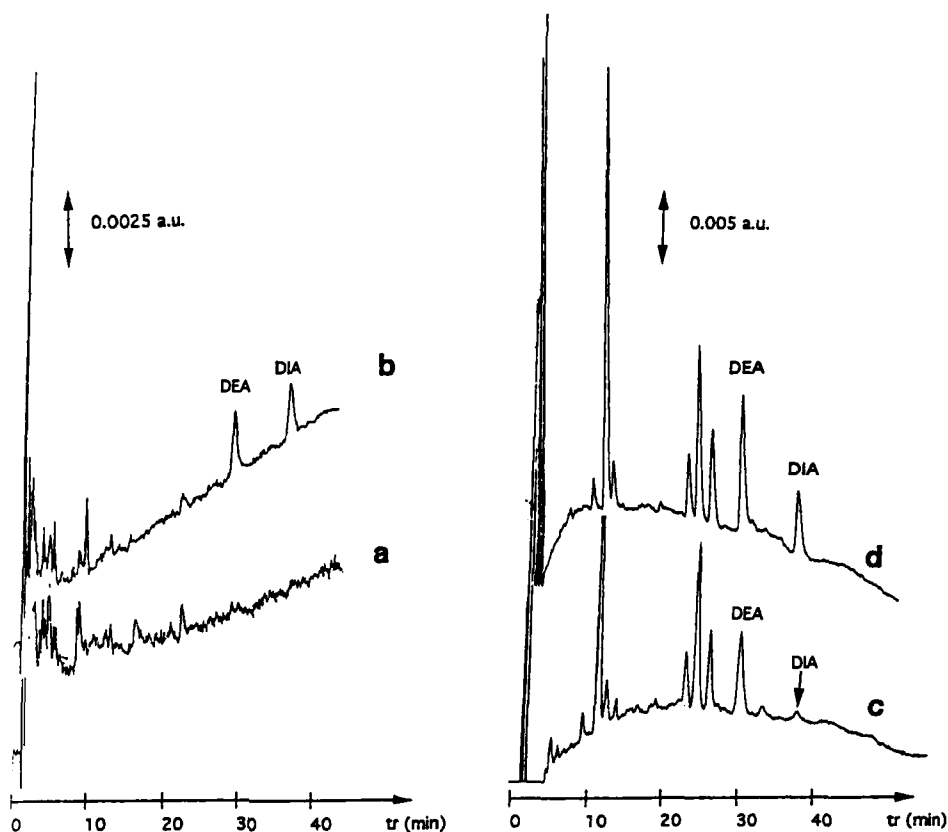
Figure 3 (Continued).

chromatogram represented in Figure 2b, the detection limit is 0.1  $\mu\text{g/l}$  and no accurate quantification can be obtained at this level. In contrast to metamitron which has a characteristic UV spectrum and can be detected at 306 nm, the detection of DIA at 210–220 nm is hindered by the presence of many interfering compounds. Owing to the high concentration of atrazine detected previously, it seemed important to have methods able to accurately quantify the dealkylated and hydroxylated transformation products.

Extensive works have been made by our group to study the potential of carbon-based sorbents as a preconcentration sorbent<sup>22–24</sup>. Porous graphitic carbon (Hypercarb) has a highly ordered and homogeneous structure made of large bands of delocalized electrons so that the retention mechanism is not based only on hydrophobic interactions as that observed with  $\text{C}_{18}$  silica or apolar copolymers. Electronic interactions are very important, so that very polar and water-soluble compounds can be highly retained in an aqueous mobile phase<sup>25</sup>. It was shown that the very polar degradation products of atrazine such as deethyldeisopropylatrazine, ammeline (2,4-diamino-6-hydroxy-1,3,5-triazine), ammelide (2-amino-4,6-dihydroxy-1,3,5-atrazine) and cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine) could be strongly retained by PGC whereas they were not retained by  $\text{C}_{18}$  silica and slightly retained by PLRP-S<sup>26</sup>. Moreover, the retention order can be different since atrazine is eluted before simazine, as well as DEA is eluted before DIA.

The on-line system coupling a precolumn of PGC and a  $\text{C}_{18}$  analytical column was investigated, but such a coupling was impossible because of the too large difference in

retention of polar analytes in the PGC precolumn and in the  $C_{18}$  analytical column. It was therefore necessary to use a system with both a PGC precolumn and a PGC analytical column<sup>27,28</sup>. The breakthrough volumes were measured on a  $8 \times 2$  mm I.D. PGC precolumn and were found higher than 100 ml. Figures 4a,b represent the chromatograms corresponding to 100 ml of LC-grade water non-spiked and spiked with  $0.2 \mu\text{g/l}$  and Figures 4c, d represent the chromatograms corresponding the 100 ml of a ground water sample non-spiked (Figure 4c) and spiked with  $0.5 \mu\text{g/l}$  of each compound. It is impossible to have on the same chromatogram the metabolites and the parent molecule since atrazine is strongly retained even when eluted with pure methanol. The match (not represented) between the UV spectra of the reference and unknown peaks was excellent. The concentration of DIA was  $0.05 \pm 0.01 \mu\text{g/l}$  whereas that of DEA was  $0.6 \pm 0.1 \mu\text{g/l}$ .



**Figure 4** On-line pre-concentration using the on-line coupling PGC-precursor/PGC-analytical column. (a) 100 ml of non-spiked LC-grade water, (b) 100 ml of LC-grade water spiked with  $0.2 \mu\text{g/l}$  of DEA and DIA, (c) 100 ml of non-spiked ground water (Pigeons spring, March 95), (d) 100 ml of the same ground water spiked with  $0.5 \mu\text{g/l}$  of DEA and DIA, Mobile phase: acetonitrile gradient with a  $5.10^{-3}$  M phosphate buffer at pH 7, 15% of acetonitrile at 0 min to 35% at 40 min; UV detection at 220 nm.

### Results of the monitoring

On the list of Table 1, the highest amounts (more than 300 kg of active substances on the basin) were applied in 1993 for isoproturon and metamitron. More than 100 kg of terbutylazine, metolachlor, pendimethalin and trifluralin were also applied whereas the average amount of the other ones ranged between 50 and 100 kg. Simazine, atrazine and propazine were not applied by the farmers, but the origin can be private house usage, although the basin is rather located in a rural area.

Several springs were monitored in the same basin. As similar results have been obtained, we report here the results of the monitoring of one spring (Glatigny spring). Figures 5 and 6 represent the concentrations of atrazine, DEA, metamitron and isoproturon detected during the 18-month monitoring. The average concentration of atrazine is 0.48  $\mu\text{g/l}$  whereas that of DEA is higher and equal to 0.60  $\mu\text{g/l}$ . The concentration profile of simazine was also constant during the period but at an average low level of  $0.07 \pm 0.02$   $\mu\text{g/l}$  (minimum of 0.04 and maximum of 0.11) was observed. Hydroxyatrazine was detected at concentrations ranging between 0.09 and 0.13  $\mu\text{g/l}$  in January and February 95 and DIA concentrations were always in the range 0.03–0.06  $\mu\text{g/l}$ . Traces of terbutylazine ( $< 0.04$   $\mu\text{g/l}$ ) were detected in June and July 95 in the Glatigny water only. Results of this monitoring cannot be easily explained. Atrazine has been monitored on the site for these last 5 years and the results are in agreement with the previous observations, i.e. a constant amount of atrazine without any trend to decrease as was expected after the banning of atrazine in 1990–91. Degradation products were not monitored before, so that no comparison can be made.

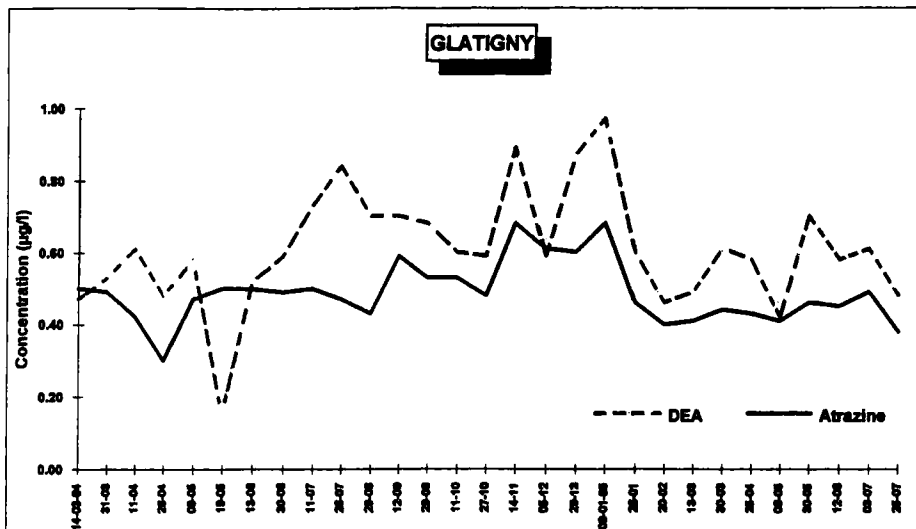


Figure 5 Variation of atrazine (—) and deethylatrazine (- -) concentrations in spring waters from Glatigny.

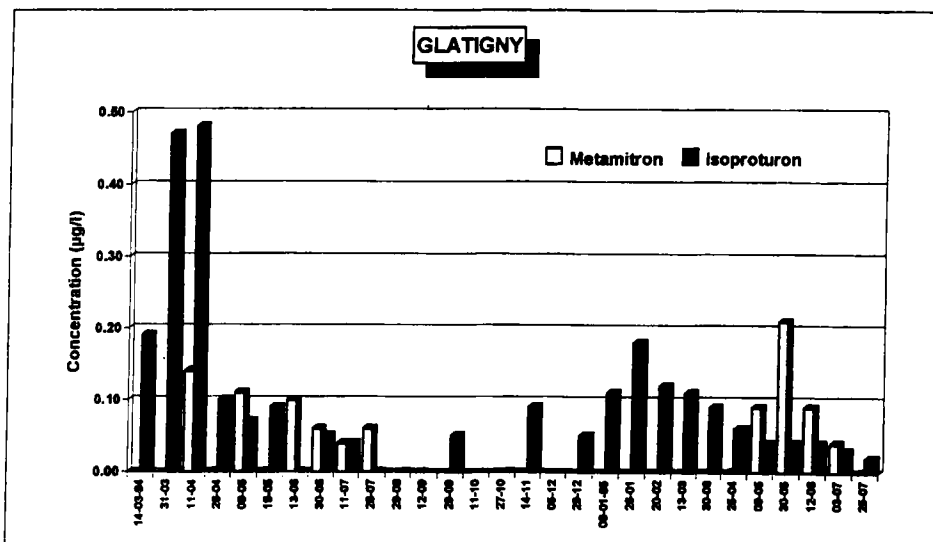


Figure 6 Variation of concentration of metamitron and isoproturon in spring water from Glatigny.

#### *Occurrence of herbicides in relation with their leachability properties and application in agriculture on the basin*

Pesticides can occur in ground water as consequences of a direct pollution with surface water runoffs, infiltration of polluted water from lakes and rivers and leaching of surface-applied pesticides through mass flow or preferential soil macropores. The leaching of pesticides through soils depends on many factors related to both the pesticide properties and to the soil nature and moisture. Usually, leaching has been shown to occur when the water solubility of a pesticide is higher than 30 mg/l, its adsorptivity ( $K_{oc}$  or  $K_{om}$ ) is lower than 300–600 dm<sup>3</sup>/kg, its soil half-life higher than 15–20 days, its hydrolysis water half-life higher than 25 weeks<sup>1,3,29–31</sup>. When comparing the applied pesticides and their characteristics reported in Table 1, it is not surprising to detect metamitron which is very soluble, and isoproturon, which are classified as probable leachers by the EU<sup>1</sup>. As shown in Figure 6, these compounds are detected in periods after their application. This is particularly relevant for isoproturon, since its application period is usually in December-January, but it was applied later on in the winter 94 owing to strong rains. In the survey, the occurrence of isoproturon was delayed in 1994 as compared to 1995. Metolachlor has been classified as a probable leacher but was not detected in the springs. However, this compound is more difficult to detect at trace-levels owing to its poor UV absorption property and did not receive much attention in the survey. Carbofuran was monitored with more attention but was not detected.

The other compounds which were applied in moderate amount, such as terbutylazine, pendimethalin and trifluralin were never detected. This can be easily explained by their very low solubility, their very slight degradability and slow mobility. It is impossible to predict if these compounds which are moving very slowly will leach one day in the ground water.

*Persistence of triazines and transformation products*

Although no more used for agricultural purpose, DEA and atrazine have been always detected during this survey. Moreover, average concentrations are rather high, around 1–1.2 µg/l, and constant all the year around. Non-agricultural usage could not lead to so high amounts of atrazine and DEA, but one can question about the correct knowledge of the hydrology of the basin. However, the constant amounts seem to indicate that occurrence of DEA and atrazine are not related to the period of application of atrazine in agricultural usage. If an eventual pollution has occurred coming from runoff water, this should have induced a disturbance in the atrazine-DEA ratio.

The occurrence of atrazine and its dealkylated products has been extensively studied by the group of Thurman in surface waters and soils in the Midwestern United States<sup>32–36</sup>. They have demonstrated that the ratio of deethylatrazine to atrazine (DAR) could be used to record the first major runoff of herbicides from non-points source corn fields to surface waters. As in many laboratory studies, it was measured that dealkylated products, DEA and DIA accounted for only 6% and 3% respectively of the degradation of atrazine, when runoff occurs just after atrazine application on soil, the transport of DEA is less than 10% of the parent compound in surface waters and this is in agreement with a DAR value less or around 0.1. However, long-term survey of surface water indicated that the DAR value is not constant but increases to values approximately 0.4–0.6 during and after the harvest season and remains constant in the late season and in winter. In river Po, DAR values above 1 have been found in winter 1991<sup>37</sup>. One explanation is that there are movements of ground water to surface in the late season which is accompanied with a selective removal of DEA from the soil since from estimated Koc values, there is a ten more capacity sorption of atrazine than either DEA or DIA by soil organic matter (see also values reported in Table 1). Considering the different types of flow paths for water, over the surface, leaching and lateral flow through the shallow soil, there is a preferential movement of DEA in each case, owing to its lower Koc value and higher water solubility. From these observations, the DAR value increased and during the late season, and DEA (plus DIA) can become a significant metabolite in surface water. Therefore, DAR values can be indicator of surface and ground water interactions.

The DAR values were calculated from the mean concentrations of Figure 5 and were found in the range 1.23–1.35 for all the sites. Thurman *et al.* have measured the amount of atrazine and metabolites in soil pore water and in soil cores in the unsaturated zone at depths of 15, 30 and 45 cm and during 200 days after atrazine application on an experimental field<sup>36</sup>. Just after the application, the compounds were detected at 15 cm in proportions which were in agreement with the laboratory experiments (atrazine >> DEA > DIA). After 200 days, the profile was different and both atrazine and DEA were detected, but in similar concentration at 30 cm and, at a depth of 45 cm, the concentration of DEA was higher than that of the parent molecule. After 200 days, atrazine and metabolites were only detected in the 30-cm lysimeter and concentration of DEA was much higher than that of atrazine and DIA was at low trace-level. In agricultural soils, the dealkylation process mainly occurs only in the surface layers of the soils. When migration has reached the subsurface layer, no longer degradation occurs.

The high amounts of DEA in the ground water relative to atrazine primarily result of two processes. First atrazine has a higher soil adsorption so that adsorption and bound residue of atrazine increased year after year during the application of atrazine whereas DEA which has less soil sorption and which is more soluble leached at a higher velocity. The constant amount of both atrazine and DEA suggests that these compounds have been bound several years ago, when the rates of application were much greater than

nowadays, has been accumulated in subsoil and are migrating slowly at different velocities. This chromatographic effect explains the constant and different concentrations in atrazine and DEA, the higher concentration of DEA and the desorption process which occurs all around year. More study are needed to try to date the atrazine that is leaching now and to be able to predict when there will be a decrease in concentration. Analysis of soil should give more information and will also be considered in further studies. However, in order to avoid any entry of eventual contamination, coring is not allowed in the protected area of the ground water reservoir.

Hydroxyatrazine was detected only at trace level. But, although it represents up to 40% of the degradation measured in laboratory condition, its behaviour in soil is very different from that of the dealkylated metabolites, since it can be partially protonated in soil due to its pka value around 5. Its adsorption to soils is greater than that of atrazine, and therefore, it should not leach in ground water.

We can predict that terbutylazine which is less soluble, less mobile, and more hydrophobic than atrazine, which leach more slowly, since its degradation in soil and water should be similar to atrazine. The same processes should occur for the leaching of the major dealkylated metabolite, deethylterbutylazine. Four years after terbutylazine application, it was not detected, nor the parent compound (only in one spring at very low level).

## CONCLUSION

Monitoring of ground water is necessary to understand the process that governs the leachability of the herbicides. At comparable hydrophobicity constant, various solubilities are measured and significantly Koc values are obtained. It is often said that the solubility effect is included in the log  $P_{ow}$  value and/or in the Koc values. Values reported in Table I show that there is a large range of measured Koc values for one compound whereas the uncertainty on the solubility does not exist. No doubt that solubility is an easy and rapid parameter to first consider for leachability prediction

The problem encountered with the high concentration of atrazine and deethylatrazine requires more attention and extension to other ground water, since some soil can be large reservoir for these compounds for many years. A better understanding is also necessary to find out replacement products.

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