

## Persistence and Leaching of Atrazine in Corn Culture in the Experimental Site of La Côte Saint André (Isère, France)

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**Abstract.** The fate of atrazine in corn culture was studied under field conditions during the years 1991–1992. After a preemergence treatment (1000 g/ha atrazine used under a flowable formulation) occurring at the end of April, samples of soil-water and soil were collected periodically at different depths in the one-meter-thick upper layer of the soil, supporting the corn culture at the Experimental Farm of La Côte Saint André (Isère, France). Atrazine and its metabolites deethylatrazine and deisopropylatrazine, measured by GC analysis, were present throughout the year in soil samples and soil-water samples at every sampling date and at each depth. Atrazine concentration varied from 0.2 to 14.7 µg/L in soil-water samples. The total content of atrazine, deethylatrazine, and deisopropylatrazine dissolved in the soil water of the one-meter-thick upper soil layer varied throughout the year from 33 to 94 g/ha. Under our conditions of sampling, the total amount (atrazine and metabolites) leached annually was tentatively estimated as the product of the weekly concentration of the soil water at 80 cm depth by the total volume of water drained for the corresponding week. The total amount of atrazine plus metabolites obtained through this estimation procedure was close to 50 g/ha, representing approximately 5% of the treatment applied (0.6% when atrazine alone was taken into account). Due to the importance of the rapid macropore transport of water after a heavy rainfall in the fluvio-glacial type of soil studied here, there most probably was an important leaching of free atrazine on the occasion of abundant rains during the first month after treatment. The amount dissolved in soil-water seemed to be but remotely associated with the adsorbed content in soil since partition equilibrium conditions, as shown, for example, in experiments establishing Koc values, were probably only rarely obtained between soil and soil-water under field conditions. Atrazine, initially

exclusively located on the soil surface, appears progressively at all levels of the one-meter layer studied. One year after the spraying of 1 kg/ha atrazine, only 15% of the initial deposit was still present (in the form of atrazine, deethylatrazine, or deisopropylatrazine) in the one-meter-thick upper layer. The major part of the atrazine deposit (close to 80–85%) was dissipated essentially through metabolization, early leaching, and volatilization, while the role played by plant absorption and formation of non-extractable residues remained low. Just before a new crop season, the average amount of atrazine and metabolites in the one-meter layer was measured to be close to 400 g/ha (150, 125, and 125 for atrazine, deethylatrazine, and deisopropylatrazine, respectively).

Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) is one of the most widely used herbicides, especially for corn, sorghum, sugarcane, and pineapple cultures. Over 120,000 tons of this active ingredient (a.i.) are applied annually preplant, preemergence, or postemergence in nine upper Midwest states of the USA (Gianessi and Puffer 1990). In France, 5,000 tons are used annually, essentially for 3 million ha. of corn culture. Atrazine is highly selective for corn since the plant is able to metabolize this a.i. very intensively, through two ways at least: 1) a chemical exchange of a Cl with benzoxazinone, leading to the formation of OH-atrazine in roots (Shimabukuro 1967); and 2) the formation, in the aerial parts of the plant, of glutathion conjugates (Lamoureux *et al.* 1972).

Concurrently, atrazine is an efficient weed killer in corn culture, with the exception of some graminaceous weeds such as *Echinochloa crus-galli*, for which the addition of another preemergence a.i. such as alachlor is required (Salembier and Gomaud 1992). However, during the last three decades, several resistant preexisting varieties of weeds, unable to bind atrazine to their D<sub>1</sub> protein, have developed at an extraordinary pace in

corn areas all around the world, making necessary a postemergence control by a.i. such as pyridate or bentazone (Decoin 1992).

Two of the major consequences of the world-wide use of atrazine are 1) that analytical techniques allowing the titration of this product at trace levels in water and soils have become very common either through GC measurements with nitrogen-phosphorus detector or through Elisa tests (Bushway *et al.* 1988; Leavitt *et al.* 1991), and consequently, 2) that atrazine or some of its degradation products are often detected in soils, groundwater (Pionke and Glotfelty 1989), and foods, even in milk (Pylypin and Hankin 1991). A great number of studies are available with regard to soil and groundwater contaminations in several types of soils, climates, and agricultural practices (Tierney *et al.* 1993; Bester and Hühnerfuss 1993; Ourisson and Balu 1993; Yang 1992; Belluck *et al.* 1991; Qiao and Hummel 1992; Deleu *et al.* 1992). These studies raised several points with regard to atrazine contamination such as: the level of risk of atrazine exposure that is acceptable, and along those lines, the determination of the risk/benefit ratio of atrazine use, the possibilities of reducing atrazine contamination levels, and the legal implications and policy in atrazine contamination.

The present report studied the annual dissipation of atrazine under field conditions at the experimental farm of La Côte Saint André (Isère, France) between April 1991 and February 1993 and attempted to establish a mass balance for the amount of a.i. (1 kg/ha) sprayed yearly in corn culture. For this purpose, atrazine (A), deethylatrazine (DEA), and deisopropylatrazine (DIA) contents in soil and soil-water samples were measured periodically in the one-m-thick upper layer. Volatilization, absorption by plants, and groundwater contamination were estimated concurrently. The type of fluvio-glacial soil chosen for this study, very common in the southeast of France, is largely used for corn culture for which reducing groundwater contamination by herbicides is of great concern.

## Materials and Methods

The experimental field was a 2 ha. area located on the grounds of the Agricultural Experiment Station of La Côte Saint André about 60 km west of Grenoble (Isère, France). The soil was a typical fluvio-glacial alluvial deposit, widely represented in the southeast of France. It was an approximately one-m-thick shallow sandy loam, with a very high permeability, overlaying a layer of gravel and pebbles (10 to 15 m thick) which contained a water-table aquifer used intensively for irrigation and the supply of drinking-water. The total amounts of water resulting from both natural rainfall and irrigation were close to 1000 mm (980 mm in 1991 and 1095 mm in 1992). Since the area was nearly flat, runoff contribution to atrazine movement was low; however, the high permeability of the soil material (the value of saturated hydraulic conductivity ranked between 50 and 200 mm/h; for more details, see Kengni *et al.* 1994), combined with intensive cultivation techniques, induced a very high risk of groundwater pollution. In fact, for nearly 50% of the wells, the legal European Community value of 50 ppm of nitrate had been reached already, and there was a great concern about non-point source pollution by pesticides.

The tilled upper layer (0–30 cm) was characterized by the presence of pebbles for 30 to 40% and by a high organic matter content (2.5–2.8%), the latter amount being obtained through the addition of manure and maize culture residues. After a 2 mm sieving, the composition of the soil was 44% sand, 39% silt, and 17% clay. The average pH was 6.5–6.8.

The experimental area has been instrumentated intensively with 8 measuring sites, each of them equipped with a neutron probe for soil moisture measurements associated with tensiometers and with ceramic suction cups for soil water sampling (details are given in Kengni *et al.* 1994).

## Corn Culture and Herbicide Treatment

Two of the measuring sites remained without culture. The other six were planted with corn at the end of April (4-22-1991 and 4-23-1992). Maize plants were no longer physiologically active after the end of September. Atrazine + alachlor were sprayed preemergence on the whole field 2–3 days after sowing. Commercial formulations of the studied herbicides were used in this experiment: Atraphyt EL (Sipcam-Phyteurop) for atrazine, and Lasso (Monsanto) in the case of alachlor. Atrazine was applied at 1 kg/ha and alachlor at 2 kg/ha. All treatments were made with a tractor-mounted sprayer calibrated to give 400 L/ha water. The homogeneity of the spray mixture emitted from the nozzles was checked.

During dry periods of summer (July–August), additional irrigations were carried out, each time with an amount of water of about 35 mm (6 times in 1991 and 4 times in 1992). Corn was harvested in late October. At that date, the density of the culture was close to 80,000 plants/ha.

## Soil-Water Sampling

Every measurement site was equipped with six ceramic suction porous cups (DTS 2000 Nardeux Humisol, Tours, France) at three depths: two replicates at 30 cm depth, two at 50 cm, and two at 80 cm. Soil-water samples were extracted weekly after submitting each cup to a two-hour vacuum. The volume of extracted water was measured and samples were filtered *in situ* (Millex filters, SLHV 025LS, Millipore) and rapidly stored at  $-20^{\circ}\text{C}$  until used for analysis. The representativity of the soil-water sampling from the 8 sites was checked and the results published elsewhere (Tasli *et al.* in press)

## Collection of Soil Samples

Soil samples were collected monthly through a manual procedure between the soil surface and 40-cm depth. Once a year (February), samples were collected down to a 1-m depth. Each soil sample was constituted of sub-samples extracted separately from five representative places. After screening the pebbles to sizes above 8 mm, each sample (5 to 6 kg) was carefully mixed, stored in bags, and frozen at  $-20^{\circ}\text{C}$ . Moisture contents were determined just before freezing.

## Extraction Procedure for Soil Samples

Air-dried soil aliquots (20g) were extracted for 1 h with 100 ml of a methanol/water solvent (1/1) at pH 5. This procedure was repeated twice. Following the removal of methanol by vacuum rotoevaporation (at  $40^{\circ}\text{C}$ ), the aqueous soil extracts were stored at  $-20^{\circ}\text{C}$  until used for GC analysis.

## Sample Preconcentration and GC Analysis

The GC analyses were carried out by the Service Central d'Analyse (CNRS, Vernaison, France) on a Hewlett-Packard 5890 (series II)

instrument equipped with a nitrogen-phosphorus detector. The size of the capillary column, a DB 5 type from J. and W. Scientific with a phenylmethylpolysiloxane stationary phase, was 30 m × 2.25 mm. Temperature was programmed from 60 to 230°C (25°C/min between 60 and 100°C, 3°C/min between 100 and 230°C). Gas flows were 1 ml/min helium for the column, 3.2 ml/min hydrogen, and 110 ml/min air for the detector.

### Sample Stability

Ten reference samples of soil, soil-water, and soil extracts were periodically measured during the course of storage and showed no significant decrease in triazine content for several years.

### Calculations

The A + DEA + DIA content (C) of the water contained in each 10 cm-layer corresponded to the following formula:  $C = \text{water volume} \cdot \text{concentration}$ . The average water content represented  $22.5 \pm 1.2\%$  of the weight of wet soil in the upper layers.

The A, DEA, and DIA contents in 10-cm thick layers of soil (g/ha) were determined according to the ppb value obtained in 100 ml extracts (coming from 20 g dry soil) following the equation:  $\text{content (g/ha)} = 5 \cdot \text{ppb value}$  (the volume of a 10-cm thick layer per ha representing  $10^6$  L and approximately  $10^6$  kg of dried and sieved soil).

Leaching amounts were determined with the use of the following equation:  $\text{concentration in soil-water samples at 80 cm depth} \cdot \text{volumes of water drained}$  (drainage values were previously determined by Kengni *et al.* 1994).

## Results

### *Atrazine, DEA, and DIA Contents in Soil Water at Different Depths and Dates*

The results presented in Table 1 show that the quantitative changes of the products dissolved in the soil-water contained in 10 cm-thick layers at 30, 50, and 80 cm depths in 1991. The values show that atrazine, DEA, and DIA were present in water all over the season of culture. The atrazine concentration varied from 0.2 to 14.7 µg/L, the highest values being found, as expected, in the earliest period after treatment at the upper water sampling level (30 cm). The presence of the corn culture seems to induce no great difference in the soil-water concentration and distribution of atrazine and metabolites (comparison of the results obtained with or without corn culture, Table 1). If 33 mg/L is taken as the standard value for maximum concentration of atrazine in distilled water at 20°C (*The Pesticide Manual* 1987), the values of atrazine concentration found in water samples are from  $5.10^4$  to  $5.10^6$ -fold lower. The average annual values of atrazine, DEA, and DIA concentration in water do not change greatly from one depth to the other (Table 2): ratios of the average annual concentrations at 30 cm to 80 cm depth were only 2.10 for A, 1.85 for DEA, and 1.30 for DIA. The average annual water concentration of DEA was almost twice that of atrazine and underwent a similar decrease with the depth. The mean DIA concentration was close to 70% of that of DEA, but its distribution according to depth was more uniform (Table 2). The average value of A + DEA + DIA in

all the water samples obtained weekly during one year at 30, 50, and 80 cm was  $55 \pm 13$  g/ha ( $41 \pm 9$  g/ha over 1991 and  $72 \pm 21$  g/ha over 1992, expressed in atrazine equivalents). Figure 1 represents the quantitative annual changes of the total amount of A + DEA + DIA (atrazine equivalents) dissolved in the soil-water in the one-meter-upper layer. This figure shows that the total content dissolved varied from 33 to 94 g/ha. The values presented were the average of two independent measurements for which  $\sigma$  was calculated: the differences in A + DEA + DIA contents in soil-water throughout a year and from one year to the other were probably not significant. Figure 2 shows the annual changes in the atrazine dissolved at three depths (30, 50, and 80 cm), expressed in g/ha solubilized in the soil-water contained in a 10-cm-thick layer of soil. Atrazine was always present. In the first three months after treatment, free atrazine was at its highest concentration in the water of the superficial layer (1 to 2.1 g). Later, high amounts of unmetabolized atrazine appeared in the water at 50 cm and 80 cm of depth, mainly during the September-October period.

### *Estimation of Atrazine, DEA, and DIA Amounts Leaving the One-Meter Thick Soil Layer Through Leaching During the 1992 Season of Culture*

The study of soil-water transport within the bare soil sites had demonstrated that the total volume drained below 1-m depth represented 50% of the rainfall amounts between April and the end of September, and 90% between October and March (Kengni *et al.* 1994). In contrast, for measurement sites with corn culture, cumulative precipitation amounts received by the soil under both rainfall and irrigation during the dry July-August periods were not followed by any loss of water (Kengni *et al.* 1994). In a first attempt, it seemed acceptable to estimate the amounts of A + DEA + DIA leaching from the shallow one-meter-thick layer as the result of the volume of leached water multiplied by the concentrations of A, DEA, and DIA in the water extracted from the soil at 80 cm depth (Table 3). Under our field conditions, the total amount evaluated in this way can be estimated to be close to 50 g/ha (atrazine equivalents) which represent 5% of the applied treatment (0.6% for atrazine alone). The estimation carried out in Table 3 shows that the greatest amounts of compounds leached under the one-meter upper layer were represented by the metabolites DEA + DIA (41.5 g/ha atrazine equivalents), all over the year, with a leaching faster for DEA than for DIA. In order to evaluate the validity of our estimation system (volumes of leached water multiplied by concentrations measured weekly), two types of indicative experiments were carried out with the use of 1) soil columns under continuous water flux and in which non-formulated atrazine was added, and 2) small lysimeters treated with formulated atrazine, under limited artificial rains. In each case, the transfer of atrazine was shown to be very fast, with important concentration changes during the three hours following the beginning of the rain. From these results, it was suggested that weekly sampling of water underestimated the A + DEA + DIA transport through the soil, especially during the early rainfall periods. Samples of the shallow soil (0 to 30 cm) were therefore harvested on the experimental field two h after the beginning of a heavy rain (45 mm in three h) occurring two days after

**Table 1.** Quantitative changes in atrazine (A), deethylatrazine (DEA), and deisopropylatrazine (DIA) contents in soil water samples during the 1991 corn culture

Date	Days after treatmt	Depth (cm)	Soil water concentration ( $\mu\text{g/L}$ )			Estimated amounts in soil water present in a 10-cm-thick layer (g/ha)					Total in water of the 1 m layer (g/ha) <sup>d</sup>	
			A	DEA	DIA	A	DEA <sub>eq</sub> <sup>a</sup>	DIA <sub>eq</sub> <sup>b</sup>	$\Sigma\text{Met}_{\text{eq}}$ <sup>c</sup>	$\Sigma\text{Met}_{\text{eq}}$		
With corn culture	06-19	56	30	13.3	7.7	0.9	3.00	2.00	0.25	2.25	5.25	32
		50	5.4	3.1	1.9	1.22	0.80	0.53	1.33	2.55		
		80	2.1	2.9	2.0	0.47	0.75	0.56	1.31	1.78		
	07-04	71	30	—	—	—	—	—	—	—	—	40
		50	3	9.8	5.0	0.68	2.54	1.40	3.94	4.61		
		80	2.1	2.9	2.0	0.47	0.75	0.56	1.31	1.78		
	07-24	91	30	9.3	14.0	8.0	2.10	3.62	2.20	5.82	7.92	33
		50	2.2	2.6	2.7	0.50	0.67	0.75	1.42	1.92		
		80	2.5	3.3	2.3	0.56	0.85	0.64	1.49	2.05		
	09-04	133	30	1.2	3.8	1.8	0.27	0.98	0.50	1.48	1.75	65
		50	2.7	7.8	9.9	0.61	2.02	2.80	4.82	5.43		
		80	0.3	2.0	7.3	0.07	0.52	2.04	2.56	2.63		
10-04	163	30	4.6	13.0	10.1	1.04	3.40	2.82	6.22	7.24	34	
	50	13.3	14.0	1.1	3.00	3.60	0.31	3.91	6.91			
	80	0.2	14.3	5.7	0.05	3.70	1.59	5.29	5.34			
Without corn culture	06-19	56	30	14.7	8.7	0.8	3.30	2.25	0.22	2.47	5.77	41
		50	5.8	6.8	2.5	1.30	1.76	0.70	1.83	3.76		
		80	3.4	4.5	2.8	0.77	1.16	0.78	1.94	2.71		
	07-04	71	30	12.1	16.5	1.7	2.72	4.27	0.47	4.74	7.46	35
		50	2.9	5.9	1.2	0.65	1.53	0.33	1.86	2.51		
		80	0.8	1.3	0.3	0.18	0.34	0.08	0.42	0.60		
	07-24	91	30	4.4	5.9	2.9	0.99	1.53	0.81	2.34	3.33	34
		50	7.4	6.5	4.7	1.67	1.68	1.31	2.99	4.66		
		80	2.8	3.9	2.1	0.63	1.01	0.59	1.60	2.23		
	09-04	133	30	—	—	—	—	—	—	—	—	47
		50	2.9	3.0	2.6	0.65	0.78	0.73	1.51	2.16		
		80	8.6	6.7	6.9	1.94	1.73	1.93	3.66	5.60		
10-04	163	30	7.7	26.6	6.2	1.73	6.88	1.73	8.61	10.34	3	
	50	0.7	7.1	1.7	0.16	1.84	0.47	2.31	2.47			
	80	3.0	0.8	1.3	0.68	0.21	0.36	0.57	1.25			

<sup>a</sup>DEA<sub>eq</sub> = amount of deethylatrazine expressed in atrazine equivalent = amount of DEA  $\times$  1.15 (1.15 = molecular weight ratio A/DEA)

<sup>b</sup>DIA<sub>eq</sub> = amount of deisopropylatrazine expressed in atrazine equivalent = amount of DIA  $\times$  1.24 (1.24 = molecular weight ratio A/DIA)

<sup>c</sup> $\Sigma\text{Met}_{\text{eq}}$  = Total amount DEA<sub>eq</sub> + DIA<sub>eq</sub>

<sup>d</sup>Total in water = estimated total amount in the soil water contained in the one-meter upper layer

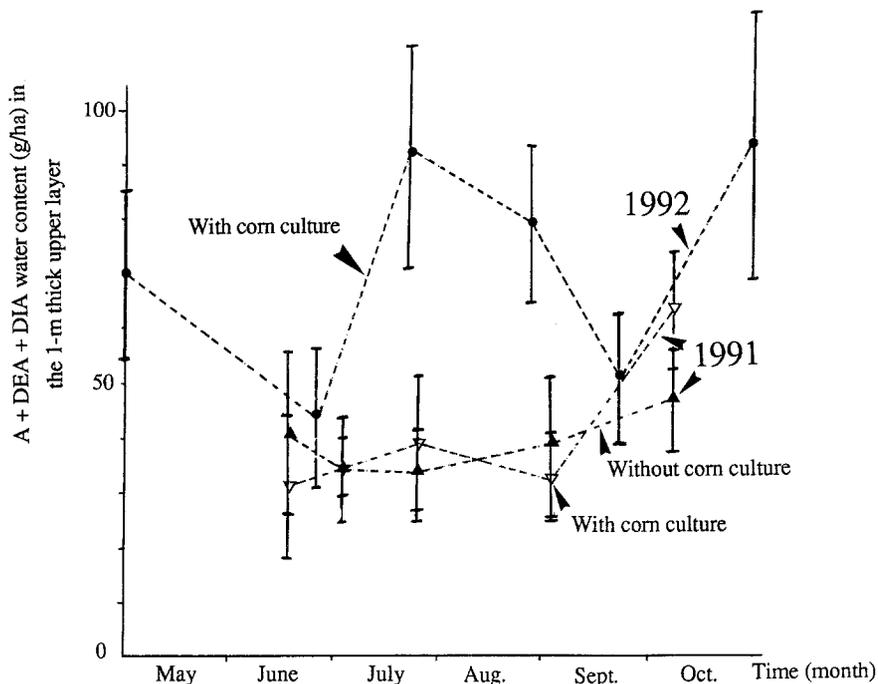
$$= \frac{\Sigma \text{Tot}_{\text{eq}} (30 \text{ cm}) + \Sigma \text{Tot}_{\text{eq}} (50 \text{ cm}) + \Sigma \text{Tot}_{\text{eq}} (80 \text{ cm})}{3} \times 10$$

**Table 2.** Average annual concentrations of A, DEA, and DIA in soil water collected at 30, 50, and 80 cm depths. Concentrations [C] are expressed in  $\mu\text{g/L}$  (1991 + 1992 values)

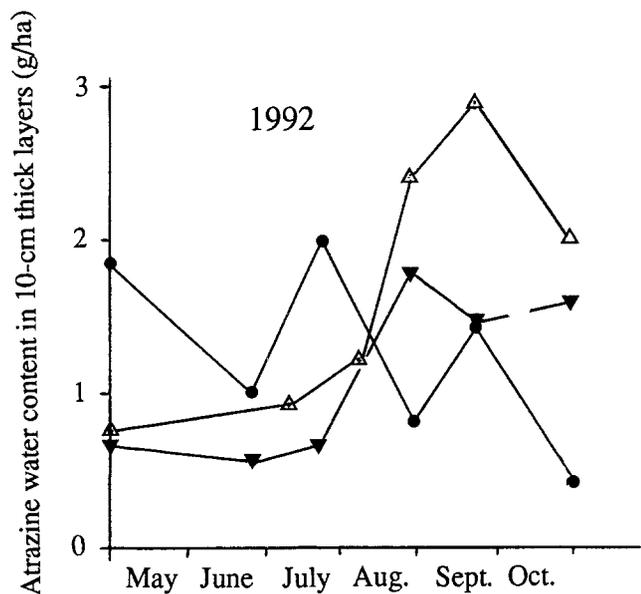
Depth (cm)	Number of samples	[C] Atrazine	[C] DEA	[C] DIA	[C] expressed in atrazine equivalent			
					DEA <sub>eq</sub> <sup>a</sup>	DIA <sub>eq</sub> <sup>a</sup>	$\Sigma_{\text{eq}}$ DEA + DIA	$\Sigma_{\text{eq}}$ A + DEA + DIA
30	14	7.20 $\pm$ 2.38	13.10 $\pm$ 3.66	6.77 $\pm$ 4.00	15.00	8.40	23.40	30.60
50	16	5.14 $\pm$ 2.72	8.14 $\pm$ 2.75	6.25 $\pm$ 3.35	9.36	7.75	17.10	22.25
80	16	3.48 $\pm$ 1.84	7.06 $\pm$ 3.15	5.07 $\pm$ 2.30	8.12	6.29	14.41	17.90
Mean	46	5.19 $\pm$ 1.12	9.27 $\pm$ 1.81	6.00 $\pm$ 1.69	10.66	7.44	18.10	23.30
30 + 50 + 80								

Confidence interval:  $\frac{t\sigma}{\sqrt{n}}$  (P < 0.05)

<sup>a</sup>DEA eq, DIA eq: expression in atrazine equivalents for DEA and DIA; the molecular weight ratios are 1.15 for A/DEA and 1.24 for A/DIA



**Fig. 1.** Annual changes in the amount of A + DEA + DIA dissolved in the soil water of the upper one-meter layer studied. Treatment days: April 22, 1991 and April 23, 1992. Bars  $\pm \sigma$



**Fig. 2.** Annual changes in the amount of atrazine content dissolved in the water of a 10-cm soil thick layer.  $\bullet$  25–35 cm depth,  $\Delta$  45–55 cm depth,  $\blacktriangledown$  75–85 cm depth

50% of the rainfall amounts during April, May, and June) during the first heavy rain occurring just after treatment.

*Atrazine, DEA, and DIA Soil Contents*

One kg/ha atrazine was applied each year at the end of April, corresponding to a theoretical concentration of 1 mg/kg of dry soil in the upper 10 cm-thick layer (the ratio between weight and volume of dry soil being close to 1 after tillage and a 10 cm-thick layer for one ha representing  $10^6$  litres). From that moment, the atrazine soil content decreased to an average concentration of 8  $\mu\text{g/kg}$  soil in the upper-thick 10-cm layer just after harvesting (Figure 3, results of November). Furthermore, atrazine, which was initially exclusively located on the soil surface, could be found, at this stage, at all levels in the soil layer (Figure 4, 5).

In February, the atrazine content in the upper 10-cm-thick layers had considerably decreased (4 to 5  $\mu\text{g/kg}$  representing 40 to 50 g/ha). In deeper 10-cm layers (under 40 cm), atrazine concentrations fell lower than 1  $\mu\text{g/kg}$  representing 10 g/ha (Figure 5). As a whole, for 1 kg/ha. amount of a.i. sprayed on the soil in the spring, the remaining amount in February was 215 g/ha, and was irregularly distributed at different depths. At the beginning of the following spring (1993), approximately 15% of the free atrazine added to the soil during the preceding year still remained in this layer, the largest part of the a.i. being located in the tilled layer (0–40 cm).

There was no simple relation between the annual distribution of atrazine and that of the two metabolites studied, DEA and DIA (Figure 4). Over winter, the average amount of DEA and DIA in the soil was nearly 310 g/ha, the total A + DEA + DIA representing 525 g/ha. At the beginning of the following crop season, the DEA + DIA content was measured to be close to 250 g/ha (125 g/ha for DEA and 125 g/ha for DIA).

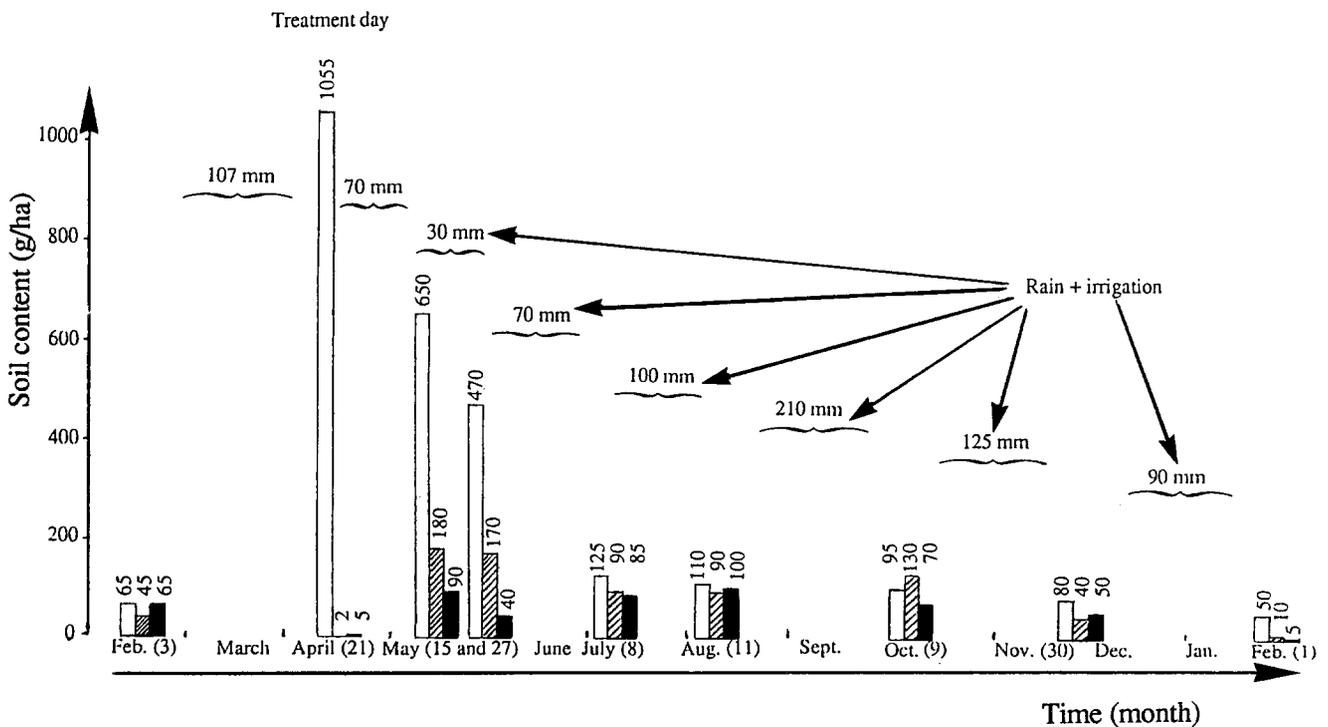
treatment. These samples were quickly centrifuged. The concentration of atrazine in the water supernatants was very high (reaching 1,500  $\mu\text{g/L}$ ), suggesting that the value of 50 g/ha for A + DEA + DIA annual leaching was greatly underestimated. An estimation based on this value of 1500  $\mu\text{g/L}$  (representing 75 times the upper concentrations found in the water sampled from the suction cups) yields a leached amount of atrazine of 350 g/ha (225  $\text{m}^3$  of water drained under 1-m depth with a 1,500  $\mu\text{g/L}$  atrazine concentration, drainage representing about

**Table 3.** Water input, drainage of water, and leached amounts of atrazine and metabolites during one year of agricultural practice

	1992								1993			TOTAL
	May	June	July	August	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March <sup>a</sup>	
Rain (mm) + Irrigations	92.9	118.3	133.4	149.3	81.2	159.2	98.2	64.2	28.7	9	9	944 mm
Drainage <sup>b</sup> (mm)	46.5	59	0	0	41	143	88.4	58	26	8	8	478 mm or 4780 m <sup>3</sup> /ha
Average atrazine concentration (ppb)	0.68	0.54	0.63	1.82	1.44	1.62	<-----1.62-----> estimation					
Leached Atrazine (g)	0.32	0.32	0	0	0.59	2.31						6.53 g/ha
DEA (ppb) concentration	3.08	0.78	3.54	3.7	1.84	5.28	<-----5.28----->					
Leached DEA (g)	1.43	0.46	0	0	0.75	7.55						20.14 g/ha
DEA eq. atraz. = DEA × 1.15	1.65	0.53	0	0	0.88	8.7						23.20 g/ha
DIA (ppb) concentration	1.03	1.40	3.9	2.7	0.53	4	<-----4----->					
Leached DIA (g)	0.48	0.83	0	0	0.22	5.72						14.80 g/ha
DIA eq. atraz. = DIA × 1.24	0.59	1.02	0	0	0.27	7.1						18.30 g/ha
TOTAL LEACHED AMOUNTS (A + DEA + DIA) = 48 g/ha/year												

<sup>a</sup>The column April 1993 was suppressed because no rain occurred during this month.

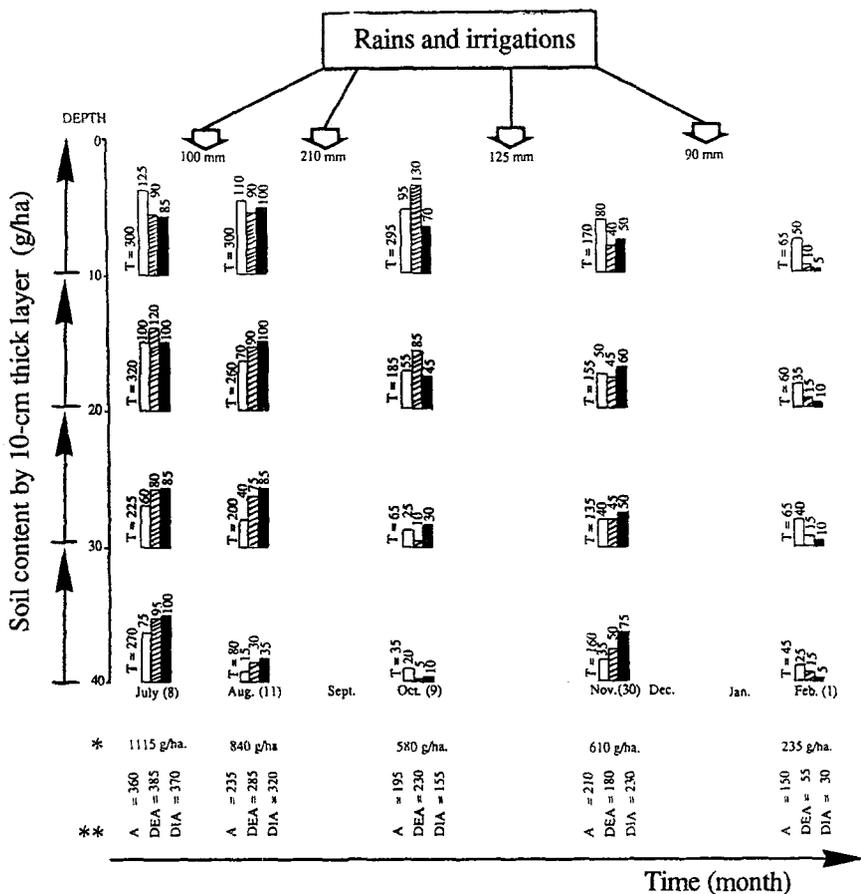
<sup>b</sup>Drainage under crop: during May, June, and September = 50% of total rain  
 during July, August = 0% of total rain and irrigations  
 between October and April = 90% of total rain



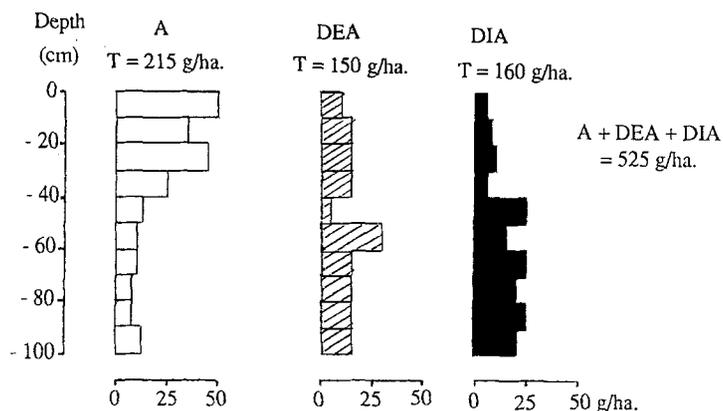
**Fig. 3.** Atrazine, deethylatrazine (DEA), and deisopropylatrazine (DIA) contents in the 10-cm upper layer of soil between February 1992 and February 1993. Blank = atrazine, hatching = DEA, black = DIA. Number on the top of rectangles refers to amounts (g/ha) of the considered product. Arrows indicate rain and irrigation amounts (mm) between two sampling dates

As a whole, one can see that 60–70% of the group of A + DEA + DIA partially disappeared from the soil layer (the remaining part being measured to be approximately 400 g/ha in the spring of 1993: 150 g/ha for A and 250 g/ha for

DEA + DIA). During late autumn, winter, and early spring, the dissipation process could be considered to be exclusively represented by leaching since the microbial activities were very low during this period of time. During the growing season,



**Fig. 4.** Atrazine (A), deethylatrazine (DEA), and deisopropylatrazine (DIA) distribution in 10-cm layers between the soil surface and 40 cm depth, between July 1992 and February 1993. Results are expressed in g/ha. T = total amount of triazines at one depth and at one date. Numbers under the arrows concern the amount of rain or rain + irrigation (mm) between two measures. Blank = atrazine, hatching = DEA, black = DIA. \*Total A + DEA + DIA (g/ha) in the upper 40 cm layer, \*\*A, DEA, or DIA content (g/ha) in the 40 cm layer



**Fig. 5.** Atrazine (A), deethylatrazine (DEA), and deethylatrazine (DIA) distribution in 10-cm layers of soil in the upper one-meter depth during winter (February 1993). Percentages express the proportion of each compound compared to A + DEA + DIA in the layers studied. T = total amounts of A or DEA or DIA in the one-meter layer of soil. Table at the bottom is a cumulative expression of results with soil depth

Depth (cm)	A		DEA		DIA		DEA + DIA		A+DEA+DIA g/ha.
	g/ha.	%	g/ha.	%	g/ha.	%	g/ha.	%	
0 - 40	150	64	55	23	30	13	85	36	235
40 - 100	65	22	95	33	130	45	225	78	290
0 - 100	215	41	150	29	160	30	310	69	525

dissipation was the cumulative result of 1) volatilization, 2) metabolism in soil, 3) leaching, 4) plant absorption and metabolism, and 5) incorporation in soil matrix under forms of inextractable residues. During the culture period, as DEA-

soil-content increased and decreased more rapidly than DIA-soil-content, it might be suggested that DEA was more readily produced than DIA from atrazine in the upper soil layer and that DEA was more easily dissipated than DIA either through

further metabolization or through leaching. During winter, the mean contents of either DEA or DIA in the upper one-meter-thick layer were quite similar (150–160 g/ha), whereas the remaining free atrazine reached 215 g/ha (Figure 5).

## Discussion

### *Relations between Soil and Water Concentrations*

In February 1993, the soil content of A + DEA + DIA was close to 525 g/ha in the soil layer (1 m). Just before sowing, at the end of April 1993, this content was estimated to be approximately 400 g/ha.

The A + DEA + DIA contents measured throughout the year, from samples of soil-water obtained weekly in the 1-m upper layer of soil, were between 33 and 94 g/ha. The amount dissolved in water seemed to be but remotely associated with the changes in the total content of the soil. The average value of the ratios between dissolved contents and total contents for 20 measurements distributed throughout the year was  $5.1 \pm 1.84\%$  ( $\sigma/\sqrt{n}$ ). For instance, this ratio calculated for the 30–40 cm soil layer and the water sampled at 30 cm was 2.5 in May, 10 in August, and 11% in October. In fact, these changes could be analyzed as related to kinetics of water transport inside this type of soil, after each rain. The thermodynamic equilibrium conditions yielding to the Koc values were probably never obtained in this layer. The preeminent factor explaining the xenobiotic distribution in this soil seems to be the presence of a dense net of macropores, which are known to play an important role in atrazine transfer (Baer *et al.* 1992; Graham *et al.* 1992; Edwards 1991).

Under our field conditions, these macropores represent approximately 7% of the soil volume (Kengni 1993) and are probably responsible for an annual pesticide leaching representing much more than 5% of the applied treatment (taking into account A + DEA + DIA) and 0.6% for atrazine alone. The suggestion that the 5% value was underestimated is certainly due to our weekly sampling. This was corroborated by measurements of atrazine transfer in soil columns and lysimeters. Under our field conditions, two roles could be played by the dense macroporous net: 1) in the case of a heavy rain, it could be responsible for the rapid leaching of high amounts of atrazine directly from the solid a.i. present on the soil surface during the first weeks following treatment; 2) in the case of rain, whatever the period and the intensity, water transported through the macroporous net could be mixed with one part of the water contained inside the microporous structure and could dilute atrazine and its metabolites, which had probably reached the normal partition equilibrium between microporous water and the solid soil structure.

The results obtained elsewhere show that losses on nearly flat land generally amount to only a few percent of the applied quantity: less than 2% in Georgia (Wauchope 1978), 0.15% for atrazine and its metabolites in drain water (Muir and Baker 1976), and 0.04% for a total atrazine loss (Southwick *et al.* 1990). In comparison with these results, the experimental field appears as a greatly leachable soil even if the underestimated value of 50 g/ha is considered. Moreover, it has to be emphasized that during the first month after treatment, a rapid and important additional leaching might occur during the most important rainfalls. Such a rapid leaching has also been described in microlysimeter studies by Demon *et al.* (1994).

### *Metabolization*

The only metabolites that have been taken into account in this study are deethylatrazine (DEA) and deisopropylatrazine (DIA). These compounds were detected in many cases (Adams and Thurman 1991; Schiavon *et al.* 1992; Karlaganis and Bradley 1992; Levanon 1993; Mandelbaum *et al.* 1993). In some cases, the mineralization of alkyl amino-side chains of atrazine seems to be due mainly to fungal activity (Levanon 1993). Hydroxyatrazine was the main metabolite in the case of bacterial mixed cultures (Mandelbaum *et al.* 1993). *N*-deethylation was shown to be 8 times faster than deisopropylation, and metabolization was greatly reduced under anaerobic conditions (Nair and Schoner 1992). Furthermore, the results seem to agree with those of Kruger *et al.* (1993) which showed 1) a lower persistence of DEA in sandy soils than in clay and 2) a decrease of metabolic activity with soil depth.

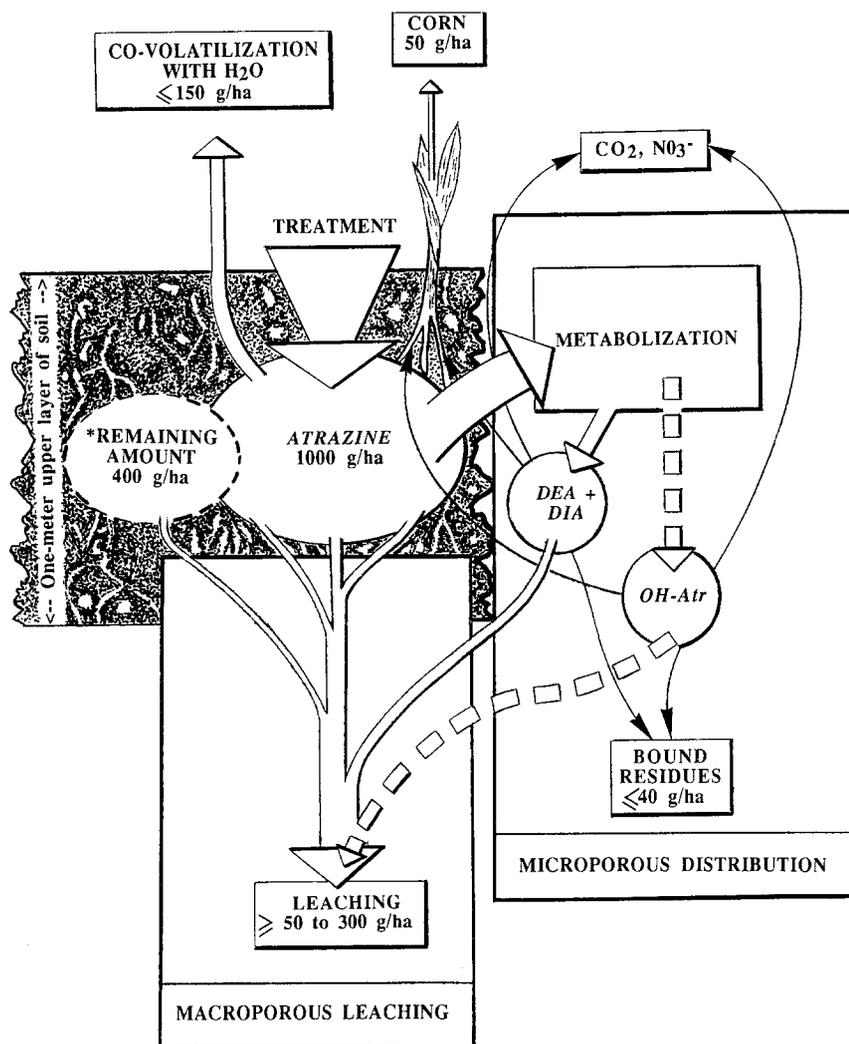
It would be interesting to extend this study to the analysis of didealkylatrazine, OH-atrazine, and hydroxylated derivatives (OH-DEA, OH-DIA, and OH-didealkylatrazine) which are most probably present, especially OH-atrazine, which was very persistent in some cases (Winkelmann and Klaine 1991; Demon *et al.* 1994).

### *Atrazine Mass Balance in the Agrosystem*

Several field and laboratory experiments under our conditions have shown that triazine loss through early volatilization was far from being negligible (Foster *et al.* in press), as was shown in other reports (Khan and Saidak 1981; Schneider *et al.* 1992; Von Neuruer and Womastek 1992).

In this field, the volatilization process was estimated to represent 15% of the amounts sprayed (Foster *et al.* in press). The amounts of products absorbed by weeds are negligible, as the weight of these weeds per ha. is also negligible in contrast with that of the corn culture, which represents more than 30 tons/ha of dry matter during the harvesting period (density: 80,000 plants/ha). The amounts of atrazine and derivatives absorbed by the corn culture are presently under study. A first estimation corresponds to a maximum of 50 g/ha. The main amount of atrazine is therefore submitted to soil metabolization during a rapid distribution process within the soil; this step corresponds to the disappearance of the herbicidal effect in the upper soil layer. Incorporation of OH-atrazine in the humic and fulvic acids during the formation of these substances from the plant organic matter seems a very active process which has not been studied here but for which very high rates were shown elsewhere (Schiavon *et al.* 1992; Winkelmann and Klaine 1991).

As a whole, the results can be summarized as shown in Figure 6. The different amounts eliminated, at the end of each year, reached the following approximative values: 150 g/ha through volatilization, 50 g/ha through absorption by plants, and between 50 and 300 g/ha through leaching of A, DEA, and DIA. One of the major characteristics of leaching in this type of soil is that it could lead to a very rapid movement of a great amount of atrazine towards groundwater, in the case of early rains dissolving the a.i. sprayed on the soil surface. This event might remain unobserved with a weekly sampling of soil-water with suction porous cups. Such a rapid and possibly powerful contamination of groundwater seems to be a risk specific to certain types of soils, which hence may be named "sensitive soils."



**Fig. 6.** Scheme summarizing the fate of atrazine in the one-meter-thick shallow layer of soil one year after treatment in a corn culture. \*Amount of A + DEA + DIA remaining from the previous cultures

The amount remaining in the upper layer of soil (0–1 m.) just before sowing was close to 400 g/ha. The total atrazine amount estimated in this way was therefore close to 650–900 g/ha/year. One kilogram is sprayed on the soil at the beginning of each corn culture, at the end of April. Taking into account the remainder of the preceding year, there was an unbalance of 500–750 g/ha in our evaluation. Two major points can explain this discrepancy:

a) The system of weekly sampling of soil water underestimated leaching. Atrazine transport through the upper layer of soil is a very rapid phenomenon, as shown with soil columns and also with lysimeters submitted to an artificial controlled rain. Therefore, spring rain is probably able to dissolve high amounts of atrazine from the formulated deposit and to leach this a.i. through a very rapid transfer in macropores without significant adsorption on the microstructures.

b) In the upper soil layer (from 0 to 30 cm depth), one part of atrazine is transformed into metabolites not taken into consideration in this study (OH-atrazine, OH-DEA, OH-DIA, didealkylatrazine, etc.). It was verified that, under controlled aerobic conditions (90% relative humidity, 25°C, aerated atmosphere), a very intense metabolization of  $^{14}\text{C}$ -labelled atrazine occurred in soil samples. After 45 days of experimentation, 40% of the radioactivity added to the soil was present as  $^{14}\text{CO}_2$

in a KOH trap. One-half of the triazine pool was found in the first methanol-water (1/1, pH 5) extract with the presence of A + DEA + DIA, the second half of the triazine derivatives being present in a second acidic extract (water-acetic acid, 4/1). The formation of hydroxylated derivatives is therefore probably a very active phenomenon in the soil studied. The labelled non-extractable bound residue was always very low (under 4% of the total amount added). Experiments for the accurate determination of the metabolization rate of A + DEA + DIA and of the rate of rapid transfer of A + DEA + DIA under heavy rain are presently being carried out.

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