

## MEASUREMENT OF ATRAZINE RESIDUES IN SOIL AND GROUNDWATER

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### SUMMARY

A study was conducted to determine whether contamination of groundwater was likely to result from legitimate agricultural use of atrazine. Two wells were drilled in an untreated area of a maize field where atrazine was to be used for weed control. Groundwater samples were collected on a monthly basis starting before application. Stratified soil samples to 1 m depth were also taken from the field on several selected occasions and analysed for atrazine residues. Atrazine was detected in the soil to a depth of 70 cm 2 months after application and also found in the groundwater in very low concentrations 2 - 5 months after application. The reasons why these events are not considered a threat to the environment are discussed.

**Keywords:** herbicide residues, atrazine, groundwater, soil residues, leaching.

### INTRODUCTION

Contamination of groundwater has become a global issue since pesticides, including atrazine, were first found in groundwater samples from Iowa (USA) in 1975. In some of the midwestern states, surveys suggest that up to 30% and 60% of public and private wells respectively may contain pesticide residues (Hallberg 1989). In Western Europe, atrazine is the most commonly found pesticide in shallow groundwater (Leistra and Boesten 1989).

There are several reasons and much debate as to why atrazine is the most frequently found herbicide in groundwater. Among the most obvious and accepted reasons are its heavy usage and its long residual activity. Atrazine is used for weed control in maize, sorghum, fruit crops and industrial situations. It is the most extensively used residual herbicide in the world with 90,000 tonnes consumed in 1980 (Barceló 1991). Its soil half life has been variously reported in the range from 8 to 70 days. Factors which could influence the movement of atrazine into groundwater in a particular situation include soil type, organic matter content, pH and area hydrogeology (Hance 1988).

Many models have been developed in an endeavour to predict or explain the behaviour of pesticides in the environment, in particular their potential for contamination of groundwater. Some, eg. DRASTIC, are based mostly on the hydrogeology of the region with some contribution from loosely grouped pesticide characteristics such as degradation class and mobility class (Close 1991). Others are more closely related to particular soil/herbicide properties such as the partition coefficient between soil organic carbon and water ( $K_{oc}$ ), and soil half-life (Gustafson 1989; Barceló 1991). One thing these models have in common is their ability to identify atrazine as a prime candidate for groundwater contamination in certain situations.

Despite the extensive documentation of atrazine contamination of groundwater, including numerous studies on its behaviour in the soil and predictive modelling, many cases have failed to identify the true source of the contamination. While some can be directly attributed to legitimate agricultural use, many others are suspected to come from point sources such as inappropriate dumping, back siphoning in wells and high use rates in industrial weed control (Hallberg 1989).

*Proc. 47th N.Z. Plant Protection Conf. 1994: 401-405*

Of the two documented cases of atrazine contamination of groundwater in New Zealand, one is loosely associated with atrazine use in an adjacent field (Close 1991) while the other is most likely from a point source (Smith 1993). The study reported here was conducted to establish whether or not atrazine was reaching the groundwater from a major agricultural use situation.

## MATERIALS AND METHODS

### Site selection and sampling

Using some of the hydrogeological factors from the DRASTIC index, a susceptible site (shallow water table, sandy soil, flat terrain) where atrazine was to be used for weed control in maize for the first time was selected for this study. The site was on a Horotiu sandy loam soil and some of the soil properties are presented in Table 1. Maize was planted on the site on 19.10.91 and atrazine (Gesaprim) at 1.5 kg/ha was applied on 20.10.91. Two wells, 90 mm diameter, were drilled with a Gillings trailer mounted rig. They were about 100 m apart and sited on the 1 m wide untreated strip between the maize and an ephemeral drain running through the middle of a 4 ha maize field. The wells were lined with 75 mm slotted PVC pipe and sealed around the top with bentonite clay. Water samples were collected at monthly intervals, commencing 3 months before application, with a stainless steel dipper that had a one-way valve at the bottom. From 0.5 - 2 litres was collected at each sampling and stored in amber glass bottles at 4°C until analysis. Stratified soil samples were collected at selected time intervals (Table 2) with a modified motorised post-hole borer that had a 50 mm diameter split tube inside the auger. Three soil cores were collected from the treated area adjacent to the wells at each sampling and after stratification the corresponding layers were bulked together and stored at -18°C until analysis.

**TABLE 1: Some soil characteristics of the trial site.**

Soil depth (cm)	pH	Organic C (%)	Soil property Sand (%)	Silt (%)	Clay (%)
0-10	5.8	3.0	44	22	34
10-20	5.8	4.1	39	22	40
20-30	5.8	1.9	47	32	21
30-50	6.3	0.3	46	27	27
50-70	6.3	0.3	45	30	23
70-100	6.3	0.2	49	27	25

### Analysis of samples

Solid-phase extraction (SPE) similar to Balinova (1993) was used for the water samples. Briefly, duplicate 100 ml subsamples were aspirated through Extract-Clean C18 columns (Alltech, 0.5 g sorbent) and the adsorbed material eluted with methanol. The eluent was collected, evaporated under nitrogen and redissolved in 1 ml methanol/water (10:90) for high-performance liquid chromatographic (HPLC) analysis.

Soil samples were extracted after the method of Huang and Pignatello (1990). Briefly, duplicate soil samples (50 g dry matter) were shaken for 3 h with 100 ml methanol/water (70:30) at 50°C and then allowed to settle for 18 h at the same temperature before 10 ml of the supernatant solution were collected and diluted with 90 ml water. This solution was then treated in the same way as the water samples except the final residues were first redissolved in 0.25 ml of methanol to which 0.75 ml of water was added and then filtered in preparation for HPLC analysis.

HPLC analysis was performed on a Shimadzu LC-6A gradient system with a Zorbax ODS (4.6 mm ID x 15 cm) reversed-phase column. The mobile phase was methanol/water (52:48 v/v) at 1 ml/min giving a retention time for atrazine of 9.5 min. Injection size was either 50 µl or 100 µl for the water samples and from 20 µl to 100 µl for the soil samples. Detection was by UV detector at 245 nm or 220 nm. Multiple wavelength acquisition was also employed on selected samples to confirm the identity

of the atrazine peak. When using 100 µl injections and 220 nm detection setting, these conditions gave detection limits for water of 0.05 µg/litre and for soil of down to 2 µg/kg.

### RESULTS AND DISCUSSION

In the top soil layer (0 - 10 cm) the concentration of atrazine found 1 and 2 months after application accounted for just under half of the applied atrazine (Table 2). After this date the concentration declined (due to degradation and leaching), to reach about 4% of that applied 11 months after application. These results are comparable to previous bioassay studies on the same soil type with a similar (low) organic matter status (Rahman *et al.* 1976). The results from the next two depths are more surprising in that the concentration of atrazine remained relatively constant throughout the year. In the 10 - 20 cm layer the concentration fluctuated between 35 and 50 µg/kg (2% of applied) and in the 20 - 30 cm layer between 5.2 and 9.7 µg/kg (0.4% of applied). This indicates that either the atrazine was being replenished from above at a rate equal to its degradation or that once atrazine was introduced to these soil depths it was relatively stable and neither moved further nor degraded very rapidly. In practice there may have been a combination of these two factors. This idea is supported by the fact that atrazine was found at deeper depths on only one occasion (2 months after application) when it was found at low concentrations in the 30 - 50 cm and 50 - 70 cm layers but not in the 70 - 100 cm layer. It appears that initially, within the first 2 months of application, there was a rapid downward movement of atrazine through the soil profile. The rainfall for this period (Table 2) was about average for the first month but was well below average for the second month. So it is likely that much of the movement occurred in the first month. This is also supported by the fact that the concentration of atrazine in the 10 - 20 cm and 20 - 30 cm layers had reached a steady state within 1 month. After the second month no atrazine was found below 30 cm despite some periods of heavy rainfall. By this time the atrazine was probably more tightly bound in the soil and thus less prone to leaching.

**TABLE 2: Soil residues of atrazine and rainfall data for the 12 month period following herbicide application on 20.10.91. Residues are the average of two analyses from three bulked soil samples.**

Sampling date	Atrazine soil residues (µg/kg)						Rainfall <sup>1</sup> (mm)
	Sampling depth (cm)						
	0-10	10-20	20-30	30-50	50-70	70-100	
20.11.91	879 <sup>2</sup>	45	6.0	n.d. <sup>3</sup>	n.d.	n.d.	114
17.12.91	826	41	9.3	3.9	3.1	n.d.	32
16.1.92	472	35	6.6	n.d.	n.d.	n.d.	92
25.3.92	308	50	9.7	n.d.	n.d.	n.d.	162
23.6.92	148	35	6.0	n.d.	n.d.	n.d.	232
22.9.92	72	44	5.2	n.d.	n.d.	n.d.	387

<sup>1</sup> Rainfall is the total accumulated for the periods between samplings. The first period commenced on the application date.

<sup>2</sup> Using a soil bulk density of 0.7 kg/litre, the theoretical concentration of atrazine in the top 10 cm is 2140 µg/kg immediately after application of 1.5 kg/ha.

<sup>3</sup> n.d. = not detected with detection limit of 2 µg/kg.

The soil properties (Table 1) indicate that while the soil is sandy, it has a reasonably high organic matter content down to 20 cm. These two properties would tend to work against each other in terms of leaching of atrazine. Hance (1988) has shown that while atrazine is more mobile in a sandy soil it also has a moderately high  $K_{oc}$  which means that it is more likely to be bound in the soil organic matter. Also, atrazine is less prone to leaching in acidic soils compared to neutral soils (Wagenet *et al.* 1985). Thus the

sandy texture of the site indicates that leaching of atrazine into the groundwater could occur to some extent.

Atrazine was first detected in both wells 2 months after application, at concentrations of 0.26 µg/litre and 0.08 µg/litre (Table 3). This coincided with the time when residues were found in the deeper soil layers and was probably a part of the same event. Subsequently atrazine residues were repeatedly found in similar concentrations until the wells went dry in March and April. No atrazine was detected in the wells when the water table rose again in winter. This is indicative of a rapid, one-off movement of atrazine through the soil profile to the groundwater, but that after this event there was no further leaching of atrazine.

**TABLE 3: Atrazine contamination found in the groundwater and monthly rainfall data. Analysis results are the average of two subsamples.**

Sampling date	Atrazine concentration (µg/litre)		Monthly rainfall (mm)
	Well A <sup>1</sup>	Well B <sup>2</sup>	
16.7.91	n.d. <sup>3</sup>	n.d.	68
16.8.91	n.d.	n.d.	212
19.9.91	n.d.	n.d.	100
16.10.91	n.d.	n.d.	119
19.11.91	n.d.	n.d.	114
20.12.91	0.26	0.08	32
31.1.92	0.17	0.09	106
19.2.92	0.19	0.09	68
25.3.92	dry	0.06	50
23.4.92	dry	dry	60
3.6.92	dry	n.d.	101
3.7.92	n.d.	n.d.	78
18.8.92	n.d.	n.d.	277
24.9.92	n.d.	n.d.	122

<sup>1</sup> Depth of water-table in Well A fluctuated between 1.0 m and 1.8 m (the depth of the well).

<sup>2</sup> Depth of water-table in Well B fluctuated between 1.3 m and 2.2 m (the depth of the well).

<sup>3</sup> n.d. = not detected at detection limit of 0.05 µg/litre.

Although this study showed that atrazine was leached into the groundwater after legitimate agricultural use, this must be considered to be a minor event for several reasons. Firstly, the site was chosen as being particularly susceptible to leaching, particularly in terms of the shallowness of the water-table. Secondly, the amount of atrazine detected was very small. Although the EC has set a limit of 0.1 µg/litre for a single herbicide, this limit is not based on scientific evidence of risk but rather on the limit of detection at the time it was set (Hance 1988). A more scientific limit is that set by the World Health Organisation at 2 µg/litre (Hance 1988). The amount found in this study is well within that limit. Thirdly, the contamination was found only over a period of 4 months suggesting that it was degraded in the environment well within the growing season. Further study would be required to firmly establish the extent and duration of any contamination into the wider groundwater environment and under different use situations.

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