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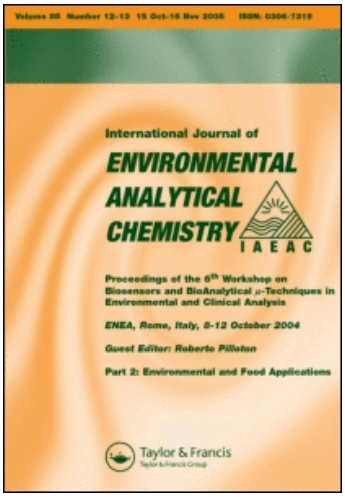

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VERTICAL MOBILITY OF SOIL CONTAMINANTS: PRELIMINARY RESULTS OF A SURVEY ON THE HERBICIDE ATRAZINE

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Atrazine is considered a potential contaminant of water bodies, where it has been repeatedly detected. Its use in Italy is almost limited to the Northern part of the country where corn monocultures are common. Northern Italy is characterized by the presence of an area with soil quite permeable and where ground waters are often present at not very deep levels. In this area well waters, which represent the main source of drinking water, have been frequently found contaminated by atrazine. A program has been started aimed at studying the role of soil nature and local factors in the process of groundwater contamination. Two atrazine application rates were used at two sites with loamy and loamy-sandy soils. Results clearly show a different mobility of atrazine in the two soil types. Since the two sites have similar organic carbon levels, the major proportion of clay to sand and the lower pH of loamy soil may explain the lower vertical mobility of atrazine in this soil. Work is in progress to study atrazine behaviour to a soil depth of 30 cm and the effect of repeated atrazine applications on ground water pollution.

INTRODUCTION

Atrazine is a worldwide herbicide introduced in 1957 and mainly used for weed control in corn.[1] On the basis of its physico-chemical characteristics and environmental properties, atrazine is considered to be a potential contaminant of groundwater.[2–4] Indeed, this herbicide has been found in water bodies of several countries.[5] In Italy, the extensive use of atrazine started in the 60's corresponding to the widespread application of corn monocultures, mainly present in the northern part of the country. In 1983, the Italian atrazine consumption[6] was of

2.6×10^3 tonnes (as technical product), most of which in some northern regions. Northern Italy is characterized by the presence of a Piedmont area where soils, due to their composition in gravel and sand, are particularly permeable, and groundwaters are often present at shallow levels. In these regions atrazine has been frequently detected in groundwaters, which represent the main source of drinking water.[7]

Several experimental and mathematical models have been applied to predict atrazine behaviour in soil.[8–11] Atrazine leaching has been also studied under different outdoor conditions.[12–15] In spite of this, as different local factors may play a determining role in the process of groundwater contamination, we believed it useful to study atrazine behaviour in two different types of soil representative of an area in the Lombardy Region where atrazine was detected in groundwaters used for human consumption.[7]

This paper reports preliminary results so far obtained in this study.

EXPERIMENTAL

Treatment of Soil

Atrazine was applied at two sites prepared for corn sowing at the rate of 800 and 2000 g a.i./ha. Afterwards, corn was sown and cultivated according to current agricultural practice, including rain irrigation.

Soil Sampling

Soil samples were taken from April to September 1987 on the vertical wall of an open trench dug out in the trial sites. Hollow punches with rectangular cross section (10×4 cm high) were inserted into the wall to take samples at different depths. A new trench was dug each time samples were to be taken. Moist soil samples weighed 500–700 grams. Samples were transferred to the laboratory in a refrigerated box (4 °C) and stored at −80 °C until the determinatons.

pH

pH was determined on a portion of air-dried and sieved samples after extraction in distilled water using a ratio of 1:2.5 (soil:water) for 30 minutes.

Dry Mass

After removing large stones and crushing, dry mass was determined by heating at 105 °C for 3 hours until constant weight.

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Organic Carbon Content

It was carried out by automatic HCN apparatus – Carlo Erba, Milano, in the soil that has been dried for Dry mass determination.

Texture of Soil Samples

It was determined according to published procedures.[16]

Atrazine Determination

Extraction: fifty grams of air-dried non-sieved soil samples were weighed in a 500 ml Erlenmayer flask and extracted with 3 × 100 ml n-hexane + acetone (80 + 20) by mechanical shaking for 30, 15, and 15 min, respectively. The organic solution was filtered through cotton wool and concentrated to dryness by rotary evaporator (40 °C; reduced pressure). The extract was dissolved in 5.00 ml ethyl acetate and analyzed by gas chromatography (GC) for a first determination. On the basis of the atrazine level found, a suitable portion of this raw solution was cleaned up by thin layer chromatography (TLC) and reanalyzed by GC.

Cleanup: a portion (0.5–1 ml) of the raw solution was deposited as a 1 cm band onto a silica gel plate (Merck, 10 cm × 5 cm × 0.25 mm layer thickness; activated at 105 °C for 1 hour) beside a band of 15 μg of atrazine standard. The plate was developed with petroleum ether 40–60° + ethyl acetate (70 + 30) in a saturated tank. Atrazine standard was located by viewing under 254 nm light and the zone of the sample lane with the same Rf of atrazine was marked and scraped. The collected silica gel was eluted wih 20 ml ethyl acetate, concentrated to a suitable volume by rotary evaporation and analyzed by GC.

The GC analysis was carried out under the following conditions: VARIAN 3700 gas chromatograph with a Thermoionic Specific Detector (TSD) selective for N-containing compounds. GC column: "wide-bore", fused silica column, 10 m × 0.53 mm, CPWAX 52 CB (Carbowax) (Chrompack 007648). Oven temperature programme: 80 °C for 2 min., then to 230 °C at 5 °C × min^{-1}, hold at 230 °C for 35 min. Injector: "flash", made of a glass insert (90 × 2 mm I.D.) packed (5 cm length) with Carbowax 20 M 5% on Gas Chrom Q 100–120 mesh. Temperatures: injector, 210 °C; detector, 250 °C. Carrier gas: Helium delivered through a flow controller at 15 ml × min^{-1}. Make up gas to the detector: Helium at 15 ml × min^{-1}. Hydrogen and air flow to the detector were according to manufacturer's directions.

Identification was via retention time comparison and cochromatography with standard atrazine. Quantitation was via peak height comparison.

RESULTS AND DISCUSSION

In Table 1 are reported the physico-chemical properties of the trial soils. As shown

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Table 1 Physico-chemical properties of the experimental soils

Soil A					
depth	*sand*[a]	*silt*[a]	*clay*[a]	*organic carbon*[a]	*pH*
0–5	35	27	38	1.3	6.5
5–10	41	26	34	1.3	6.6
10–15	37	26	38	1.4	6.8
15–20	39	25	37	1.4	6.8
20–25	35	27	39	1.3	6.7
25–30	35	25	41	1.4	6.8
Soil B					
depth	*sand*	*silt*	*clay*	*organic carbon*	*pH*
0–5	46	27	29	1.5	7.6
5–10	49	22	28	1.5	7.8
10–15	47	20	34	1.5	7.8
15–20	47	21	32	1.4	7.8
20–25	45	20	34	1.0	7.8
25–30	43	22	34	0.7	7.8

[a]percentage

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in this table, soil A and B may be classified essentially as loamy and loamy-sandy soil, respectively. Furthermore, soil A is slightly acidic, whereas soil B is slightly basic. Organic carbon content is similar in the two soils.

In Table 2 for soil A and in Table 3 for soil B, are reported the analytical data on the levels of atrazine found at different depths and at different times after application.

As can be seen from data in Table 2 for loamy soil (A), the atrazine concentration at Day 0 was, of course, determined only in the top layer (0–5 cm) and its values are consistent between the two application rates used. The atrazine levels in the top soil layer (0–5 cm) decreases with time so that it was no longer detected at Days 94 and 154 for 800 and 2000 g a.i./Ha application rate, respectively. Atrazine penetration into the soil is detectable at Day 21, showing measurable concentration in the deepest layer assayed (25–30 cm) at Day 50 for both application rates. An almost uniform distribution of values with depth was obtained earlier for the lower application rate (at Day 50 compared to Day 94). From data at Day 21 it can be seen that atrazine is almost confined in the 0–10 cm layer, but concentration values are lower than those at Day 0 (at least for the 2000 g a.i./Ha application rate). Effects other than percolation (degradation, volatilization, run off) may account for the missing atrazine.

For the loamy-sandy soil B (Table 3) the value of atrazine concentration at Day 0 in the top (0–5 cm) layer are not consistent between the two application rates and this fact is not easily explainable. In this top layer the decrease with time of atrazine concentration is such that atrazine was no longer detected at Day 135 for both treatments. Atrazine penetration into the loamy-sandy soil (B) at Day 29 has

Table 2 Atrazine concentration at different time and depth following application to loamy soil (A) in open field at 800 and 2000 g a.i./ha

Soil depth (cm)	*Application rate: 800 g a.i./ha*				
	Atrazine concentration (mg/Kg dry soil)				
	time (days)				
	0	*21*	*50*	*94*	*154*
0–5	0.59 ± 0.34[a]	0.50	0.07	n.d.	n.d.
5–10	n.s.	0.13	0.05	n.d.	n.d.
10–15	n.s.	0.02	0.03	n.d.	n.d.
15–20	n.s.	n.d.	0.02	n.d.	n.d.
20–25	n.s.	n.d.	0.03	n.d.	n.d.
25–30	n.s.	n.d.	0.01	n.d.	n.d.
Soil depth (cm)	*Application rate: 2000 g a.i./ha*				
	Atrazine concentration (mg/Kg dry soil)				
	time (days)				
	0	*21*	*50*	*94*	*154*
0–5	1.16 ± 0.20[a]	0.42	0.27	0.02	n.d.
5–10	n.s.	0.01	0.03	0.02	n.d.
10–15	n.s.	n.d.	0.02	0.01	n.d.
15–20	n.s.	n.d.	0.02	0.01	n.d.
20–25	n.s.	n.d.	0.02	0.01	n.d.
25–30	n.s.	n.d.	0.01	0.01	n.d.

[a]Mean of 5 replicates ± standard deviation
n.s. = Not sampled
n.d. = Not detected at the limit of the determination of 0.01 mg/Kg

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already reached the deepest layer assayed (25–30 cm) in contrast with findings obtained in the loamy soil (A). Vertical mobility of atrazine in the loamy-sandy soil (B) is greater than in the loamy soil, as expected. In the loamy-sandy soil (B) an almost uniform distribution of values which was attained at Day 75 for the lower application rate and a little later for the higher application rate.

As it is shown in Tables 2 and 3 a difference of concentration of atrazine between the two dosages used is evident only in the loamy soil (A).

The different mobility of atrazine in the two soil types may be explained with the different physico-chemical properties of soils (see Table 1). Since the organic carbon concentration is the same in the two soils, the higher proportion of clay to sand and the lower pH of loamy soil (A) may explain the lower vertical mobility of atrazine in this soil compared to the loamy-sandy soil (B).

As this study was conducted in the field, it should be borne in mind that factors such as inherent dishomogeneity of the soil both along the depth and among the different sampling sites may have influenced the "true typical" characteristics of the soils.

The experimental data are well fit by mathematical functions of the type:

Table 3 Atrazine concentration at different time and depth following application to loamy-sandy soil (B) in open field at 800 and 2000 g a.i./ha

Soil depth (cm)	*Application rate: 800 g a.i./ha*			
	Atrazine concentration (mg/Kg dry soil)			
	time (days)			
	0	*29*	*75*	*135*
0–5	0.94 ± 0.23[a]	0.24	0.03	n.d.
5–10	n.s.	0.22	0.03	n.d.
10–15	n.s.	0.08	0.03	n.d.
15–20	n.s.	0.07	0.02	n.d.
20–25	n.s.	0.04	0.02	n.d.
25–30	n.s.	0.05	0.02	n.d.
Soil depth (cm)	*Application rate: 2000 g a.i./ha*			
	Atrazine concentration (mg/Kg dry soil)			
	time (days)			
	0	*29*	*75*	*135*
0–5	0.94 ± 0.32[a]	0.37	0.06	n.d.
5–10	n.s.	0.11	0.02	n.d.
10–15	n.s.	0.04	0.02	n.d.
15–20	n.s.	0.03	0.02	n.d.
20–25	n.s.	0.03	0.02	n.d.
25–30	n.s.	0.04	0.02	n.d.

[a]Mean of 5 replicates ± standard deviation
n.s. = Not sampled
n.d. = Not detected at the limit of the determination of 0.01 mg/Kg

$$C(x) = k1/(x + k2)^m$$

where $k1$, $k2$ and m are constants and $C(x)$ the concentration at the soil depth x (cm). This model accounts for the changing trend of atrazine concentration for increasing soil depth.

Figures 1 and 2 show the atrazine vertical distribution in the two types of soil at three different times.

On the basis of this mathematical elaboration, at one month after soil treatment, these distributions are characterized by a very sharp decrease of atrazine concentration with increasing depth in the first soil layers (about 5–10 cm of depth), followed by a more flat trend, with atrazine levels nearly constant in the 15–30 cm deep soil layers (Figure 1, A and D; Figure 2, A and D).

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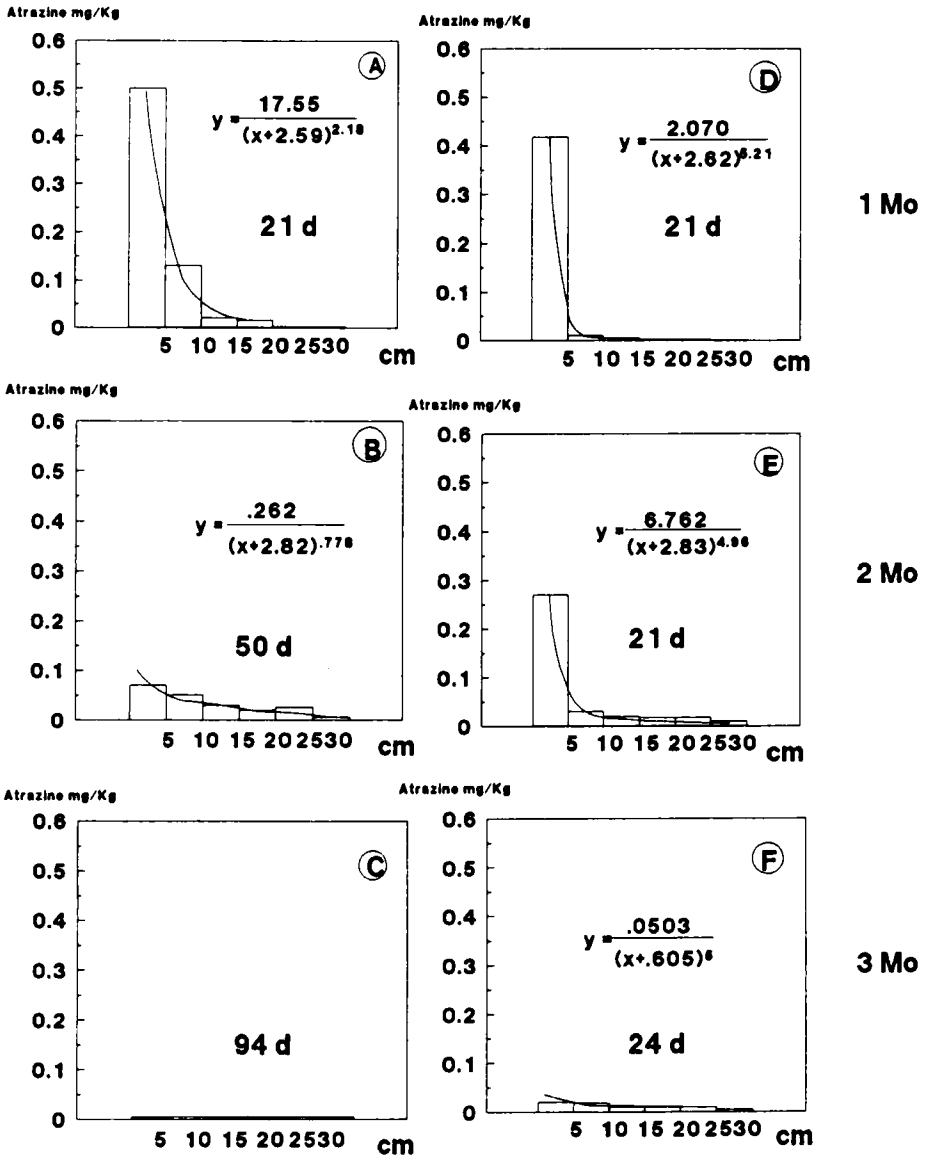

Figure 1 Vertical distribution of atrazine in loamy soil (Soil A) for the application rates 800 g a.i./ha: A, B, C and 2000 g a.i./ha: D, E, F, over several months.

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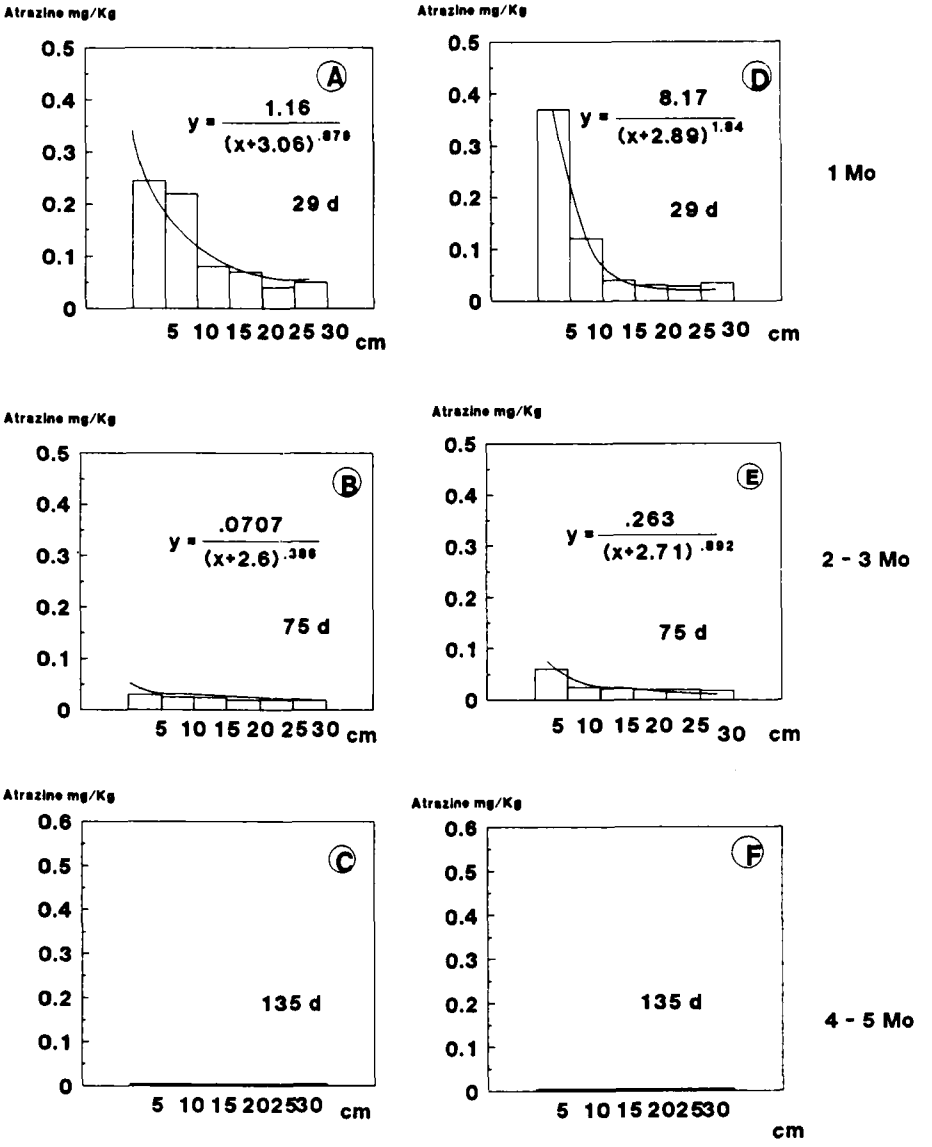

Figure 2 Vertical distribution of atrazine in loamy-sandy soil (Soil B) for the application rates 800 g a.i./ha: A, B, C, and 2000 g a.i./ha: D, E, F over several months.

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At two–three months after the soil treatment, the atrazine vertical distribution in soil progressively becomes more and more uniform (Figure 1, B–C and E–F; Figure 2, B and D), the average concentration in the whole tested 30 cm-deep soil layer progressively and significantly decreases, and the initially high concentrations in the upper 5 cm thick soil layer progressively disappear.

In the two sampling sites in the loamy soil (Figure 1) atrazine appears in the lower 10–30 cm-deep soil layer only during the second month. In the loamy-sandy soil (Figure 2) the atrazine concentration below the first 10 cm of soil is already significant during the first month.

These findings are consistent with an environmental degradation process, as well as a significant atrazine percolation process. Degradation processes seem to be responsible for the major part of atrazine dissipation in the loamy soil.

The comparison of the atrazine vertical distributions in the examined loamy and loamy-sandy soil indicate that the percolation process is significantly more effective and rapid in the loamy-sandy soil while the degradation processes seem to be more important for atrazine dissipation in loamy soil.

The parameters of the mathematical functions used to model the vertical distribution at different times and in the different soils, whose fitting to experimental data is satisfactory and statistically significant, confirm these hypotheses. Moreover, the mathematical modelling of vertical distribution allows us to extrapolate the vertical distribution trend in the first meter of soil.

This analysis indicates that the amount of atrazine estimated as present in the first meter of soil is reduced by a factor of 2–3 in the time period of about one month, in agreement with atrazine half-life available determinations.[17] Moreover, in the loamy soil at one month after the treatment, the same kind of analysis indicates that the atrazine percentage estimated to be present in the first 20 cm-deep soil layer is about 93–99% of the whole estimated content in the 1 m-deep soil layer. This percentage decreases with time, reaching about 30–40% at 3 months after the treatment. In the two sampling points in the loamy-sandy soil, the same percentage is about 50% and 80% at one month after the treatment, respectively, and about 30% and 50%, respectively, at 2.5 months.

In this work, the importance of the nature of soils and the application rate in the process of downward transport of potential contaminants of groundwater such as atrazine has been demonstrated.

Further work concerning the behaviour of atrazine even in deeper layers of soil and the effects of successive applications may be useful in better understanding the process of groundwater contamination.

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