

ISSN 0103-9016



SCIENTIA AGRICOLA

Cont. ANAIS DA ESALQ

UNIVERSIDADE DE SÃO PAULO
CAMPUS "LUIZ DE QUEIROZ"
ESALQ/CENA

PIRACICABA, SÃO PAULO, BRASIL

VOLUME 54 NÚMERO ESPECIAL JUNHO 1997

ATRAZINE MOVEMENT IN A DARK RED LATOSOL OF THE TROPICS

M.D. DE SOUZA¹; L.H. BASSOI²; O.O.S. BACCHI^{3,5}; K. REICHARDT^{3,4,5}; L.C. HERMES¹; R.B. ABAKERLI¹; J.E. PILOTTO^{3,5}

¹CNPMA/EMBRAPA, C.P. 69, CEP 13820-000 - Jaguariuna, SP - Brazil

²CPATSA/EMBRAPA, C.P. 23, CEP 56300-000 - Petrolina, PE - Brazil

³Centro de Energia Nuclear na Agricultura/USP, C.P. 96, CEP: 13400-970 - Piracicaba, SP - Brazil

⁴Depto. de Física e Meteorologia-ESALQ/USP, C.P. 9, CEP: 13400-000 - Piracicaba, SP - Brazil

⁵Bolsista do CNPq.

ABSTRACT: Atrazine displacement was studied in a soil profile as a function of water movement and time after herbicide application, taking into account possible influences of preferential flow on leaching. The experiment consisted of two 7 x 7m plots of a dark red latosol (Kandudalfic Eutrudox), located at Piracicaba, S.P., Brazil (22°43'S and 47°25'W), 250km inside continent, at an altitude of 580m. One plot was previously treated with 1,000 kg/ha of lime, in order to increase base saturation to 88%, and 500 kg/ha of gypsum. Each plot was instrumented with tensiometers, neutron probe access tubes and soil solution extractors, in order to monitor water and atrazine flows. Atrazine was applied at the high rate of 6 kg/ha of active principle. Results showed intensive leaching of atrazine in the whole soil profile, up to the instrumented depth of 150cm, already at the first sampling, seven days after herbicide application. The limed plot showed much higher atrazine leaching losses than the other plot. The atrazine adsorption capacity of the soil is very low, its maximum value being of the order of 10%, for the 0-15cm surface layer.

Key Words: atrazine, leaching, preferential flow, adsorption, herbicide, tropical soil

MOVIMENTO DA ATRAZINA NUMA TERRA ROXA ESTRUTURADA EUTRÓFICA

RESUMO: O presente trabalho teve como objetivo verificar o deslocamento de atrazina no perfil do solo, em função do movimento da água e do tempo de aplicação, e possíveis influências de fluxos preferenciais sobre a lixiviação. O trabalho foi conduzido em uma Terra Roxa Estruturada eutrófica de textura argilosa, em Piracicaba (SP), no período de junho de 1992 a fevereiro de 1993. Foram instalados dois experimentos, sendo um com a cultura do milho irrigado (experimento 1) e o outro em solo nu (experimento 2). O experimento 1 foi instalado em uma área de 1000m² sobre a qual se demarcou duas parcelas de 12m x 12m separadas uma da outra por 18m. Uma parcela foi irrigada e a outra fertilizada. O experimento 2 foi instalado em duas parcelas de 7m x 7m, separadas uma da outra por 5m. Em uma das parcelas do experimento 2 aplicou-se previamente 1.000kg de calcário/ha para elevar a saturação de bases para 88%, além de 500kg de gesso/ha. Cada parcela do experimento 2 foi constituída de três linhas de instrumentos e os resultados obtidos para cada linha foram comparados entre si para verificação de fluxo preferencial. A atrazina foi aplicada na dosagem de 6,3l/ha no experimento 1 e 6kg do princípio ativo/ha no experimento 2. Os resultados mostraram intensa lixiviação da atrazina em todo o perfil do solo até 150cm de profundidade já na primeira coleta efetuada 7 dias após a aplicação. A parcela 2 do experimento 2, apesar de não ter recebido calcário, mostrou perdas de atrazina por lixiviação muito maiores que a parcela 1. O solo apresentou pequena capacidade de adsorção de atrazina (máximo em torno de 10% na camada de 0-30cm).

Descritores: atrazina, lixiviação, fluxo, preferencial, adsorção, solo tropical

INTRODUCTION

In modern agriculture, mainly under intensive land use conditions, manual and animal labors were almost totally replaced by machines and the use of agrochemicals to control pests, diseases and weeds. The use of these chemicals is, in most cases, performed in inadequate and abusive ways. A technology introduced to help the farmer increasing

productivity, can also contribute causing severe damage to the environment. Among the several agrochemicals used, atrazine was chosen for this study, since according to BAILEY *et al.* (1968), it presents base characteristics and can, therefore, be adsorbed by positively charged clay particles. According to these authors, a basic compound is 10% associated when soil pH is one unit above the value of the product pK_a, 90% associated when the pH is

one unit below pKa, and 100% associated or completely dissociated when the pH is two units above or below pKa, respectively. Although the pKa value for atrazine is 1.68, the increase of soil pH due to liming develops conditions for low atrazine adsorption because the increase in the soil cation exchange capacity is counteracted by a much stronger decrease of atrazine positive charges, and the final result is a lower adsorption. Under these conditions there is an increase in the risk of ground-water contamination through the leaching process.

According to Green & Obien (1969), in the case of soils of low adsorption capacity, changes in soil water content alter significantly the herbicide concentration in soil solution. Bacci *et al.* (1989) also observed for a given soil profile, that 130 days after the application of 2 kg/ha of atrazine, the chemical was found in all soil layers, down to the 3.2 m depth. Smith *et al.* (1992) also observed a rapid downward atrazine movement, to the 0.8 m depth, in 1.15 m long sandy soil columns, submitted to 35 mm irrigation. Guth *et al.* (1977) verified that the main atrazine transport mechanism is the aqueous phase mass transport. Zins *et al.* (1991) studied the effect of alfalfa roots on atrazine and alachlor movements, in silty soil columns, concluding that the presence of roots facilitated pesticide movement as a consequence of the development of macropores, due to root growth. This paper has the aim of studying atrazine displacement in a soil profile, as a function of soil water movement, after herbicide application, and the possible influence of preferential flow on herbicide leaching losses.

MATERIALS AND METHODS

The experiment was carried out on a dark red latosol (Kanduidalfic Eutradox), known as "terra roxa estruturada", at the county of Piracicaba, SP, Brazil (22°43'S and 47°25'W), 250km inside continent, at an altitude of 580m. Two plots of 7 x 7m, separated by a distance of 8m, were instrumented with: i) a neutron probe access tubes of 2m length, to measure soil water contents at the depths of 0.20, 0.50, 1.00 and 1.50 m; ii) 9 tensiometer sets, each composed of six tensiometers with cups at 0.35, 0.65, 0.85, 1.15, 1.35 and 1.65 m below soil surface in order to observe the direction of water flow in the different portions of the profile, and iii) 9 soil solution extractor sets, each composed of four porous cups at 0.20, 0.50, 1.00 and 1.50 m below soil surface (Figure 1).

Plot N° 1 received 1,000 kg/ha of lime and 500 kg/ha of gypsum, which were manually incorporated into the 0.10m surface layer, to increase base saturation to 88%. Plot N° 2 was left in its natural base saturation condition. Table 1 characterizes the plots from the chemical and physical points of view.

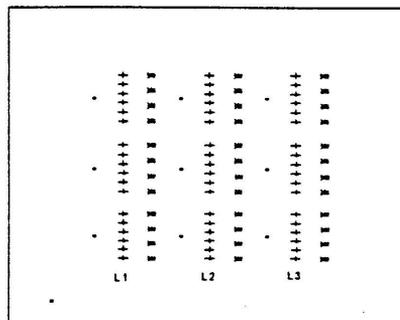


Figure 1 - Schematic design of one experimental plot, indicating on each line L the relative positions of neutron probe access tubes (.), tensiometers (+) and soil solution extractors (*).

Atrazine (2-chloro-4 ethylamino-6 isopropylamino-s-triazine) was applied to soil surface at a rate of 6 kg/ha of active principle, on 16 March 1993. At application soil was relatively wet, around field capacity. Thereafter, it was maintained wet through natural rainfall and irrigation, simulating conditions of natural agriculture (Figure 2). Soil solution samples were extracted in 15 day intervals, starting at 23 March and ending at 26 May. Due to the cost of atrazine analysis, solution samples were composed, mixing the 3 samples from each row at each depth (Figure 1). This procedure restricted the analysis of the soil variability along the lines.

Atrazine (2-chloro-4 ethylamino-6 isopropylamino-s-triazine) was applied to soil surface at a rate of 6 kg/ha of active principle, on 16 March 1993. At application soil was relatively wet, around field capacity. Thereafter, it was maintained wet through natural rainfall and irrigation, simulating conditions of natural agriculture (Figure 2). Soil solution samples were extracted in 15 day intervals, starting at 23 March and ending at 26 May. Due to the cost of atrazine analysis, solution samples were composed, mixing the 3 samples from each row at each depth (Figure 1). This procedure restricted the analysis of the soil variability along the lines.

TABLE 1 - Chemical and Physical properties of the soil at different depths, for plots 1 and 2.

Depth m	pH _{water}	pH _{CaCl₂}	H+Al	Ca me/dl	Mg me/dl	K	P ppm	MO	sand %	silt	clay
Plot 1											
0.0-0.15	5.98	5.10	1.90	4.24	1.07	0.51	68.90	2.70	39	32	29
0.15-0.30	5.95	5.03	1.70	3.55	0.87	0.33	28.00	1.62	31	32	37
0.30-0.45	6.14	5.40	1.40	3.52	0.90	0.23	19.70	1.08	27	25	48
0.45-0.60	6.28	5.63	1.40	3.54	0.95	0.23	21.50	0.72	23	27	50
0.60-0.75	6.35	5.70	1.30	3.40	0.87	0.21	25.10	0.72	23	27	50
0.75-0.90	6.38	5.76	1.30	3.44	0.84	0.20	23.30	0.54	25	47	28
0.90-1.05	6.38	5.81	1.30	3.08	0.75	0.21	20.10	0.18	26	46	28
1.05-1.25	6.45	5.87	1.20	2.96	0.73	0.24	15.40	0.72	27	33	40
1.25-1.45	6.50	5.92	1.20	2.47	0.60	0.23	10.80	0.54	29	29	42
1.45-1.65	6.57	5.97	1.20	2.40	0.63	0.24	9.30	1.08	29	28	43
Plot 2											
0.0-0.15	6.33	5.56	1.90	4.47	1.57	0.66	93.40	2.52	44	34	22
0.15-0.30	6.08	5.31	1.80	3.94	1.05	0.45	74.30	1.62	40	36	24
0.30-0.45	6.08	5.38	1.60	3.75	1.02	0.26	43.10	1.26	29	29	42
0.45-0.60	6.16	5.48	1.60	3.33	1.02	0.21	30.50	0.36	28	32	40
0.60-0.75	6.22	5.58	1.30	3.49	1.12	0.22	26.90	0.90	25	27	48
0.75-0.90	6.24	5.60	1.40	3.10	1.00	0.20	26.90	0.36	28	28	44
0.90-1.05	6.25	5.60	1.30	3.00	0.99	0.22	20.10	0.54	28	30	42
1.05-1.25	6.19	5.64	1.30	2.62	0.82	0.22	15.40	0.36	28	30	42
1.25-1.45	6.23	5.70	1.30	2.38	0.72	0.20	14.40	0.54	28	28	44
1.45-1.65	6.31	5.83	1.30	2.24	0.65	0.15	10.00	0.72	29	27	44

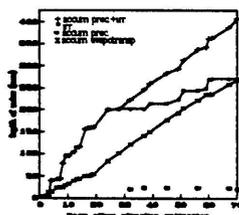


Figure 2 - Cumulative evaporation, rainfall and irrigation during sampling period.

RESULTS AND DISCUSSION

Total soil water potential head Y (cm H_2O) distributions can be seen in Figure 3. They indicate downward water flow during the whole experimental period. This was a desired condition in order to maximize pesticide leaching and have an extreme situation. Soil water content q ($cm^3 \cdot cm^{-3}$) profiles show a slight influence of the textural B horizon (0.40-0.60m) of the profile (Figure 4), due to its

higher clay content. The extreme variability of q measurements did not allow the calculation of soil water flux densities, as already discussed for this soil by Reichardt *et al.* (1993).

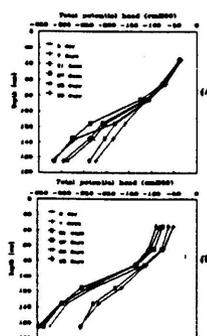


Figure 3 - Total soil water potential head for plot n° 1 (A) and plot n° 2 (B) during the five soil sampling dates (7, 21, 37, 66 and 80 days after atrazine application)

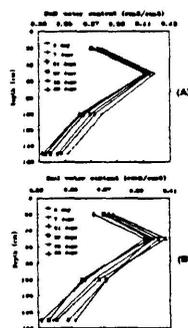


Figure 4 - Soil water content profiles for plot n° 1 (A) and plot n° 2 (B) during the five soil sampling dates (7, 21, 37, 66, and 80 days after atrazine application).

Figure 5 presents data of atrazine concentration in soil solution, for plot N° 1 at each sampling date and for each line, and also average values.

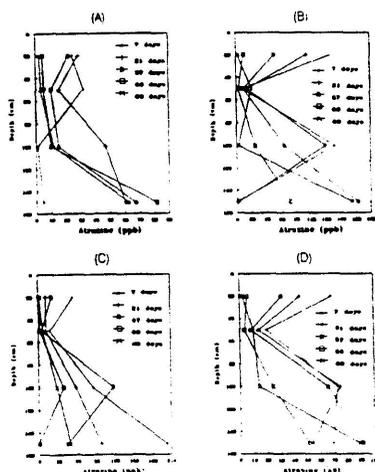


Figure 5 - Atrazine concentration for each extractor line at plot n° 1 Lines 1, 2 and 3, respectively (A), (B) and (C). Average for all lines (D).

Comparing data of the three lines, for the 1st sampling (7d), leaching of atrazine was fast and variable, reaching the depth of 1.50 m at concentrations of 5, 2 and 200 ppb for line 1, 2 and 3, respectively, with maximum of 55 ppb at depth 0.50 m for line 1, 130 ppb at depth 100 for line 2, and with no maximum for line 3. Atrazine concentration increased along time at the 1.50 m depth, for line 1 and 2, and decreased for line 3, where the highest

concentration occurred at the first sampling date. These results indicate that leaching losses were greater at the plot side corresponding to line 3, suggesting conditions of preferential flow at this side.

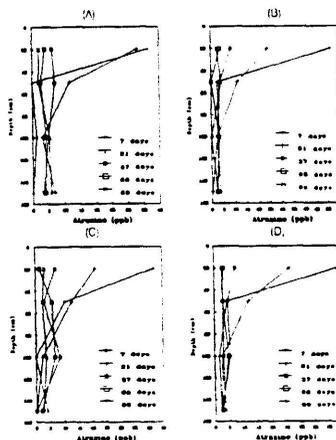


Figure 6 - Atrazine concentration for each extractor line at plot n° 2. Lines 1, 2 and 3, respectively (A), (B) and (C). Average for all lines (D).

For plot N° 2 (Figure 6) atrazine profiles show a very different behavior as compared to plot N° 1. Here, concentrations were much lower for all depths at all times. The highest concentrations were found at the depth of 0.20 m, and they decreased rapidly along time. Variation between lines was significantly lower, indicating a greater homogeneity in the leaching process.

Plot N° 1, which received lime and gypsum, presented greater leaching since, because according to BAILEY *et al.* (1968), the increase in pH reduces atrazine adsorption capacity, promoting leaching. This fact associated to the high soil water content levels, affects significantly the herbicide concentration in soil solution and contributes to fasten atrazine movement in the soil profile (GREEN & OBIEN, 1969).

Saturated hydraulic conductivity measurements, performed before herbicide application, show that the free drainage of plot No 2 is 3.5 times greater than of plot N° 1. On the 3rd and 7th day after atrazine application, plots received rainfalls of 34.4 and 34.9 mm, totalizing a water

excess of 55 mm, and it is possible that a great part of the atrazine of plot No 2 was leached to depths greater than 150 cm, by mass flow. GUTH *et al.* (1977) state that the main transport mechanism of atrazine is mass flow.

Results obtained for adsorption (Figure 7) show very low values as compared to literature. Dunigan & McIntosh (1971) found an atrazine adsorption of 77.5 mg/g in a silt-loam soil, of which 37.5 mg/g were due to the presence of organic matter (2.5%). Huang *et al.* (1984) and Reinhard *et al.* (1990) also discuss the important role of soil organic matter on atrazine adsorption. However, increasing soil pH, negative pH dependent charges found in organic matter are increased, and the final result is a reduction in adsorption. Although low, adsorption was highest in the first 30 cm of the soil profile, in which organic matter levels are higher (2.7% from 0-0.15 m, and 1.6% from 0.15-0.30 m). Using the adsorption criteria of Bailey *et al.* (1968), which adopts the K value of Freundlich's equation when the concentration of the equilibrium solution is unity, the K values found correspond to 0.91 and 0.36 mg/g, respectively for the depths of 0-0.30 and 0.30-0.60 m. These values are about 16 times lower than those found by Bailey *et al.* (1968).

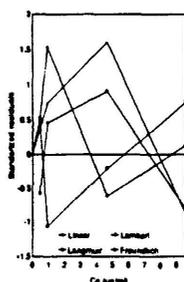


Figure 7 - Atrazine adsorption isotherms using four models.

With respect to desorption, it was observed that 65% of the adsorbed amount in soil of the 0-0.30 m layer turned free by desorption. This indicates that besides having a very low adsorption capacity, the small amounts that are adsorbed can easily be released to soil solution.

Although it was not possible to quantify atrazine flux densities, it is concluded that for the kind of soil tested, under high soil water content and pH conditions, atrazine leaching losses may be significant, reaching soil layers below root zone, with

consequent risk to groundwater contamination. The presence of preferential water flow paths increase this leaching potential.

REFERENCES

- BACCI, E.; RENZONI, A.; GAGGI, C.; CALAMARI, D.; FRANCHI, A.; VIGHI, M.; SEVERI, A. Models, field studies, laboratory experiments: an integrated approach to evaluate the environmental fate of atrazine (s-triazine herbicides). *Agriculture, Ecosystems and Environment*, v.27, p.513-522, 1989.
- BAILEY, G.W.; HITE, J.L.; ROTHBERG, T. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Science Society of American Proceedings*, v.32, n.2, p.222-234, 1968.
- DUNIGAN, E.P.; McINTOSH, T.H. Atrazine-soil organic matter interactions. *Weed Science*, v.19, n.3, p.279-282, 1971.
- GREEN, R.E.; OBIEN, S.R. Herbicide equilibrium in soils in relation to soil water content. *Weed Science*, v.17, p.514-521, 1969.
- GUTH, J.A.; GERBER, H.R.; SCHLAEPFER, T.H. Effect of adsorption, movement and persistence on the biological availability of soil-applied pesticides. *Proceedings British Crop Protection Conference-Pest and Diseases*, p.961-971, 1977.
- RALPH, G.N. Solid-size extraction of carbofuran, atrazine, simazine, anachlor, cyanazine from shallow well water. *Journal Association of Oss. Analysis Chemical*, v.73, n.3, p.438-442, 1990.
- REICHARDT, K.; BACCHI, O. O. S.; VILLAGRA, M.M.; TURATTI, A. L.; PEDROSA, Z. O. Hydraulic variability in space and time in a dark red latosol of the tropics. *Geoderma*, v.60, p.159-168, 1993.
- REINHARDT, C.F.; EHLERS, J.G.; NEL, P.C. Persistence of atrazine as affected by selected soil properties. *South African Journal of Plant and Soil*, v.7, n.3, p.182-187, 1990.
- SMITH, W.N.; PRASHER, S.O.; KHAN, S.U.; BARTHAKUR, N.N. Leaching of ¹⁴C-labelled atrazine in long, intact soil columns. *Transactions of the Asae*, v.35, n.4, p.1213-1220, 1992.
- ZINS, A.B.; WYSE, D.L.; KOSKINEN, W.C. Effect of alfalfa (*Medicago sativa*) roots on movement of atrazine and alachlor through soil. *Weed Science*, v.39, n.2, p.262-269, 1991.

Recebido para publicação em 29.04.97

Aceito para publicação em 15.05.97