Bull. Environ. Contam. Toxicol. (1995) 54:562–569

Environmental Contamination and Toxicology

Influence of Leaching Rates on ^{14}C-Metolachlor Mobility

M. J. Sánchez-Martín,[1] T. Crisanto,[1] L. F. Lorenzo,[1] M. Arienzo,[2] M. Sánchez-Camazano[1]

[1]Instituto de Recursos Naturales y Agrobiología de Salamanca, C.S.I.C. Apdo 257, 37071 Salamanca, Spain
[2]Dipartimento di Scienze Chimico-Agrarie, Universita di Napoli "Federico II", Via Universita 100-I, 80055 Portici, Italy

Received: 15 July 1994/Accepted: 29 August 1994

Metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide) is a herbicide from the chloroacetanilide group that has been widely used in recent years (22 million Kg are used annually in the United States) for the control of weeds in soybean, corn and many other crops. Recent studies addressing the monitoring of pesticides in ground water have demonstrated the presence of metolachlor residues (Chesters et al., 1989). Additionally, occasional carryover of metolachlor in soils has also been reported (Braverman et al., 1985). These observations point to the need to gain deeper insight into the factors affecting the leaching of this compound when applied to soils. This knowledge is of great interest as an index of the risk of contamination of ground water.

Some works in the literature have demonstrated the influence of soil texture and soil organic matter content in the mobility of metolachlor (USEPA, 1980; Dynamac, 1986). However, despite the great importance of water flow applied and its application rate in the mobility of herbicides, this aspect has not received much attention for herbicides in general (Weber and Whitacre, 1982) or metolachlor in particular (Chesters et al., 1989). Only Obrigawitch et al. (1981), using a bioassay, has demonstrated that the mobility of metolachlor was gre ater when 18 cm of water were applied to a soil column than when 9 cm of water were applied. In a previous work (Crisanto et al., 1994) a study was made of the mobility of metolachlor by soil TLC in 33 soils with low organic matter content from irrigated zones of the province of Salamanca (Central-West Spain). It was observed that the compound is moderately mobile in 78% of the soils under saturated flow conditions, which is how leaching occurs in TLC. Since metolachlor is widely used for differents types of crops in this irrigated area, it was thought to be of interest to study the mobility of the herbicide in other leaching conditions.

In the present work the effect of water flow and its rate of application on the mobility of metolachlor were studied in three soils by studies of leaching in soil packed columns and using ^{14}C-labelled metolachlor. Three water flows in a non-saturated regimen were applied, one of them was also applied in a saturated-non-saturated regimen.

Correspondence to: M. Sánchez-Camazano

MATERIALS AND METHODS

Three soil samples from irrigated zones of the province of Salamanca (Central-West Spain) were used (Table 1).

Table 1. Characteristics of the soils

Soil	Soil Texture	pH	OM%	Sand%	Silt%	Clay%	Clay Mineralogy[a]
3	Sandy Clay Loam	7.0	1.56	61.40	14.30	24.30	I,K,S
6	Loamy Sand	5.9	0.94	78.40	10.00	11.60	I,K,V
16	Sandy Clay Loam	7.6	2.04	56.00	21.35	22.20	I,K,S

[a] I, Illite; K, Kaolinite; S, Smectite; V, Vermiculite.

^{14}C-labelled metolachlor of 1.94 MBq mg^{-1} specific activity and 99% purity and unlabelled metolachlor of 99.7% technical purity was supplied by Ciba-Geigy Corporation (USA). Metolachlor is a liquid with a water solubility of 530 mgL^{-1}; the compound is also soluble in most organic solvents (Worthing and Walker, 1987).

Leaching columns were constructed from polyvinylchloride (PVP) pipe and were 35 cm long x 5 cm inner diameter. They were prepared according to Weber (1986). Each column was packed with 600 g of dry soil and then saturated by placing them in a tank and increasing the water volume in the tank ever 24 h for one week until it topped the columns. Then each column was allowed to drain free for 24 h. Five mL of a 200 $\mu g\ mL^{-1}$ ethanol solution of metolachlor of 13.8 KBq mL^{-1} specific activity were added to the top of each column. The columns were washed with flows corresponding to 9.2 cm, 36.7 cm and 71.3 cm of water; the first two were applied in a non-saturated regimen (daily washings with 10 ml or 40 mL over 18 days) and the third was applied in a non-saturated regimen (leachings of 40 mL over 35 days) and in a saturated-non-saturated regimen (leachings of 200 mL over 7 days).

The column leachates were monitored daily for herbicide content using 1 mL of sample for measuring activity (DPM). After draining for some time, the columns were cut breadthwise at 5 cm intervals. The soil contained in each segment was turned over and weighed. Then, five samples of 1 g each were taken from each segment. Two such samples were used to determine the moisture content of the soil from the weight loss measured on heating at 80°C for 12 h. The other three samples were employed to determine the ^{14}C content on a Harvey OX-500 biological oxidizer. The activity of the radioactive solutions containing $^{14}CO_2$ was determined with a Beckman LS 1800 scintillation counter by measuring the DPM for each sample. The experiments were performed in duplicate and a contrasted column for each soil was subjected to the whole process in parallel to determine its natural radioactivity for reference purposes.

RESULTS AND DISCUSSION

Figure 1 shows the percolation curves of metolachlor in the columns of the three soils after the application of 9.2 cm of water. These represent the concentrations and accumulated amounts of metolachlor (% of applied) in the leachates of the columns as a function of the volume of leached water. The curves are similar for all three soils and indicate that initially there is no leaching of the herbicide in the columns and that its concentration is very low when the leachate volume is 120 mL. Thereafter, its concentration slowly rises, but with no maximum concentration peak. The amount of metolachlor accumulated in the leachate water rose from 0.88% in soil 16 to 2.22% in soil 6 (Table 2).

The retention of metolachlor in the columns is also very similar for all three soils. The percentages of compound retained are shown in Table 2 and indicate that most of the compound is retained in the columns of the three soils when these are subjected to a low water volumen (9.2 cm) and under non-saturated conditions (0.5 cm day^{-1} over 18 days). The distribution of the herbicide across the three columns (Table 2) shows that the compound is accumulated in the upper two segments at greater amounts for soils 3 and 16 (81.13% and 62.67%, respectively) with a greater content in clay and organic matter than for soil 6 (41.35%). This stronger accumulation of metolachlor in the upper segments of the columns of soils 3 and 16 is consistent with the values of the Freundlich adsorption constants (K) determined by the authors in a previous work (Crisanto et al., 1994); these are, 1.52 and 1.34 for soils 3 and 16 and 0.39 for soil 6. Obligawitch et al. (1981) using a bioassay, also found an accumulation of metolachlor in the first two segments of the columns of three soils with an organic matter content of less than 1% after application of 9 cm of water.

The percolation curves obtained after application of 36.7 cm of water to the columns of the three soils assayed are shown in Figure 2. The concentration of leached compound is very low for low leachate volumes and increases progressively, although no maximum peak is observed. The curves corresponding to the three soils are similar as regards shape, although the maximum concentration of metolachlor obtained in the leachates is greater for soil 6 (4.04%) than for soil 3 (2.11%) and soil 16 (1.58%). The accumulated amounts of herbicide also vary in the same sense, ranging from 15.38% to 7.82%(Table 3).

The percentages of metolachlor retained in the soil columns (Table 3) show that as in the above case most of the compound remains in the column after leaching. The distribution of metolachlor in the columns of the three soils shown in Table 3 indicates that in this case, too, the compound is accumulated in the upper segments of the columns of soils 3 and 16 (56.88% and 41.49%, respectively) while in the column corresponding to soil 6 the distribution is homogeneous across all segments.

Figure 3 shows the percolation curves after application of a water flow of 71.3 cm in a non-saturated regimen. These curves differ from those obtained when lower

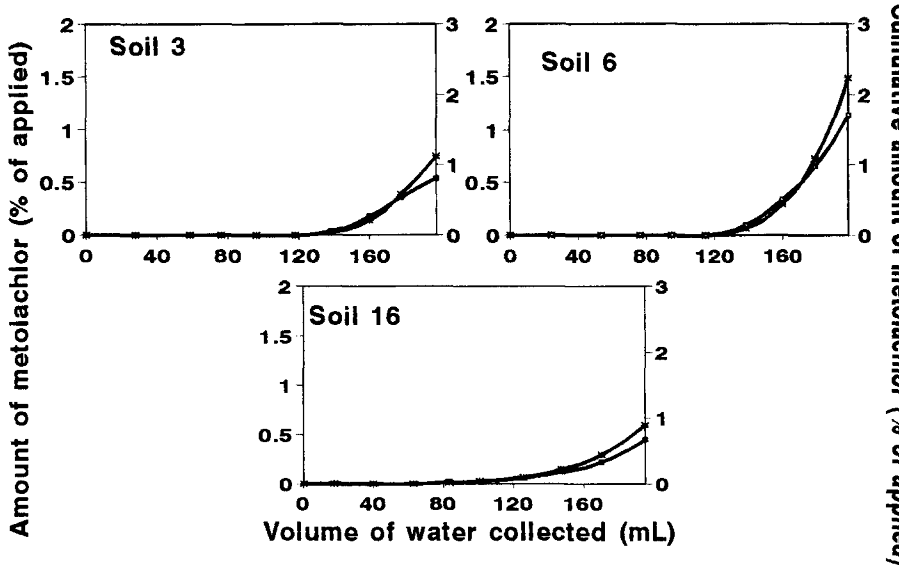

Figure 1. Breakthough and cumulative curves for ^{14}C-metolachlor in soils leached with 9.2 cm of water (non-saturated flow).

Table 2. Amounts of ^{14}C-metolachlor retained and leached (% of applied) in the soil columns leached with 9.2 cm of water (non-saturated flow)

Soil depth (cm)	Soil 3	Soil 6	Soil 16
0 to 5	45.99	20.85	37.15
5 to 10	35.13	20.49	20.51
10 to 15	7.68	17.27	7.61
15 to 20	4.48	8.05	5.19
20 to 25	4.51	6.66	3.00
25 to 30	3.24	6.29	2.35
Total column	101.27	79.63	75.83
Total leached	1.13	2.22	0.88
Total recovered	102.20	81.85	76.33

LSD (0.05 %), within soils and depth = 4.14

water flows are employed. The concentration of metolachlor in the leached water of soil 6 increases until a maximum defined at 6.83% is reached for a leachate volume of 495 ml while in the leached water of soils 3 and 16 the concentration of metolachlor remains practically constant across the curve, reaching a poorly-defined peak of maximum concentration at 3.90% and 4.35% for both soils, respectively, in a leachate volume of 890 mL. The delay in the peak of soils 3 and 16 with respect to that of soil 6 is 395 mL. The amount of metolachlor accumulated in the leachates is higher in soil 6 (64.54%) and lower in soils 3 (40.08%) and 16 (37.12%).

Application of this water flow results in a decrease in the amount of residual metolachlor in the columns with respect to application of lower water flows. The

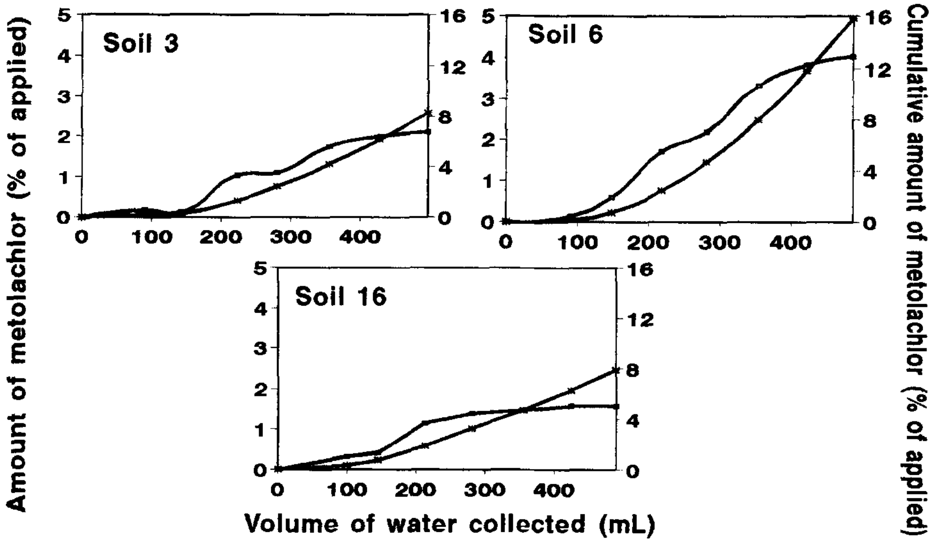

Figure 2. Breakthough and cumulative curves for ^{14}C-metolachlor in soils leached with 36.7 cm of water (non-saturated flow).

Table 3. Amounts of ^{14}C-metolachlor retained and leached (% of applied) in the soil columns leached with 36.7 cm of water (non-saturated flow)

Soil depth (cm)	Soil 3	Soil 6	Soil 16
0 to 5	31.12	15.64	25.81
5 to 10	25.76	16.36	15.67
10 to 15	16.84	11.81	7.93
15 to 20	11.62	10.86	7.54
20 to 25	6.68	9.67	6.90
25 to 30	3.71	7.65	5.13
Total column	95.74	72.01	69.00
Total leached	8.27	15.83	7.82
Total recovered	104.01	87.84	76.80

LSD (0.05 %), within soils and depth = 6.39

amount retained ranges between 26.77% for soil 6 and 43.64% for soil 3 (Table 4); additionally, it is distributed homogeneously in the column of soil 6 while in the columns corresponding to soils 3 and 16 the greatest concentration of the compound is found in the upper segments of the column.

Figure 4 shows the percolation curves obtained when this same washing flow (71.3 cm) is applied to the soil columns under a saturated -non-saturated regimen (10.2 cm day^{-1} over 7 days). The concentrations of metolachlor accumulated in the leachates fluids of the three soils are slightly higher (except in soil 16, which is lower) than those obtained when the same flow is applied in a non-saturated regimen (Table 5). The curves exhibit a maximum metolachlor concentration peak at 10.23%, 23.87% and 8.86% for soils 3, 6 and 16, respectively. These

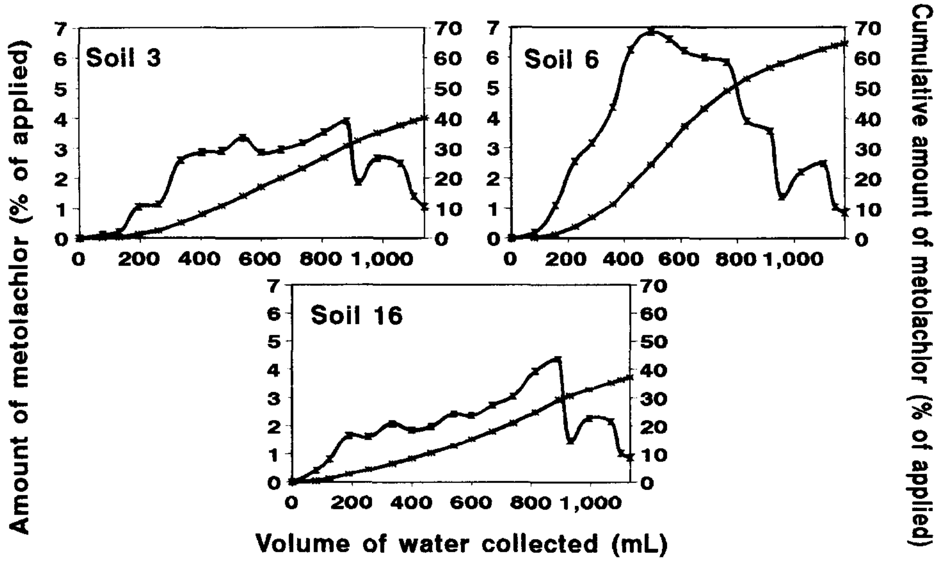

Figure 3. Breakthough and cumulative curves for ^{14}C-metolachlor in soils leached with 71.3 cm of water (non-saturated flow).

Table 4. Amounts of ^{14}C-metolachlor retained and leached (% of applied) in the soil columns leached with 71.3 cm of water (non-saturated flow)

Soil depth (cm)	Soil 3	Soil 6	Soil 16
0 to 5	9.33	5.54	11.50
5 to 10	9.42	5.16	4.21
10 to 15	9.89	5.47	5.53
15 to 20	6.58	4.53	5.40
20 to 25	4.54	2.65	5.66
25 to 30	3.88	3.32	5.03
Total column	43.64	26.77	37.33
Total leached	40.08	64.54	37.12
Total recovered	83.72	91.31	74.45

LSD (0.05 %) within soils and depth = 2.86

concentrations are higher than those obtained in the previous case and are obtained for lower leachate volumes (540, 340 and 360 ml., respectively). Metolachlor percolation curves similar to these were obtained by Peter and Weber (1985) when the herbicide was washed out in a soil column with 51 cm of water under non-saturated flow conditions.

Application of this water flow gives rise to a decrease in the amount retained in the columns of soils 3 and 6, but not in soil 16 (Table 5). In soil 6, the distribution of the herbicide along the column is similar, while in soils 3 and 16 there continues to be an accumulation of the herbicide which in soil 3 occurs in the lower segments and in soil 16 in the first segments.

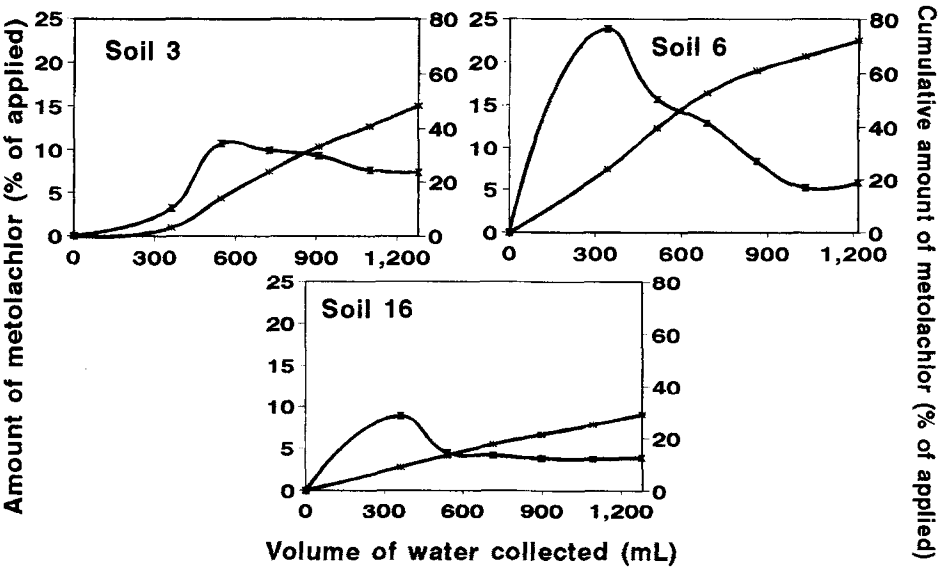

Figure 4. Breakthough and cumulative curves for ^{14}C-metolachlor in soils leached with 71.3 cm of water (saturated-non saturated flow).

Table 5. Amounts of ^{14}C-metolachlor retained and leached (% of applied) in the soil columns leached with 71.3 cm of water (saturated-non saturated flow)

Soil depth (cm)	Soil 3	Soil 6	Soil 16
0 to 5	3.80	2.82	21.51
5 to 10	4.14	2.24	12.05
10 to 15	6.36	2.40	8.06
15 to 20	6.82	2.67	8.58
20 to 25	8.01	3.64	6.77
25 to 30	8.98	3.70	6.83
Total column	38.04	17.47	63.78
Total leached	48.31	71.08	29.06
Total recovered	86.35	88.55	92.84

LSD (0.05 %), within soils and depth = 2.73

Both under these saturated-non-saturated flow conditions and in the previous non-saturated flow conditions the leaching of the herbicide is greater in the column of soil 6 than in the columns of soils 3 and 16. These results are consistent with the R_f values obtained for the mobility of metolachlor in the three previous soils by soil TLC (R_f=0.35, 0.48 and 0.38 for soils 3, 6 and 16, respectively (Crisanto et al., 1994)

The results obtained indicate the importance of the flow of water and the rate of application in the leaching of metolachlor in soils. It may be concluded that metolachlor is always leached more than 30 cm in the columns of the three soils used, regardless of the volume of water applied to the columns and the rate of its application. The percentage of herbicide leached increases with the water flow; it varies between 0.88%-2.22% of the herbicide applied when flow is low (9.2 cm) and increases up to 29.06%-71,08% when the volume of water applied is higher (71.3cm). The leaching of the compound with the same volume of water but applied at a different rate yields similar results as regards the concentration of herbicide accumulated in the leachate. However, the maximum herbicide concentration increases from 3.90%-6.83% of the herbicide applied when washing is performed with 2.1 cm day^{-1} up to 8.86%-23.87% when an amount of 10.2 cm day^{-1} is used. This maximum herbicide concentration appears at a lower leachate volume when washing is performed more rapidly. These results show that rapid application of large volumes of water could lead to point contamination of the compound in ground water.

Additionally, the effect of the water flow on the mobility of metolachlor in soil depends on the composition of the soil; the content in organic matter and clay of the soil favours the adsorption of the herbicide and its retention, especially in the first segments of the column. Accordingly, when these soil parameters are high, the herbicide only could be mobile when the volumes of water applied are also high.

Acknowledgments. This work was financially supported by the "Junta de Castilla y León" (Spain) as a part of Projet No. 0611-90.The authors wish to thank Ciba-Geigy AG, Barcelona (Spain) for kindly supplying of the chemical employed.

REFERENCES

Braverman MP, Lavy TL, Talbert RE (1985) Effects of metoclachlor residues on rice. Weed Sci 33: 819-824.

Chesters G, Simsiman GV, Levy J, Alhajjar BJ, Fathulla RN, Harkin JM (1989) Environmental fate of alachlor and metolachlor. Rev Environ Contam Toxicol 110: 1-74.

Crisanto T, Sánchez-Martín MJ, Arienzo M, Sánchez-Camazano M (1994) Adsorption and mobility of metolachlor in surface horizons of soils with low organic matters content. Sci Total Environ (In Press).

Dynamac Corporation (1986) Metolachlor final registration standard and tolerance reassessment. Final Rept Contract No 68-02-4266 Submitted to USEPA, Arlington.

Obrigawitch T, Hons FM, Abernathy JR, Gipson JR (1981) Adsorption, desorption, and mobility of metolachlor in soils. Weed Sci 29: 332-336

Peter CJ, Weber JB, (1985) Adsorption, mobility, and efficacy of alachlor and metolachlor as influenced by soil properties. Weed Sci 33: 874-881.

USEPA (1980) Metolachlor: pesticide registration standard NTS No PB81-123820 US Environmental Protection Agency Washington DC 183 pp.

Weber JB, Whitacre DM (1982) Mobility of herbicides in soil columns under saturated- and unsaturated- flow conditions. Weed Sci 30: 579-584.

Weber JB (1986) Herbicide mobility in soil leaching columns. In: Camper ND (ed) Research Methods in Weed Science. Southern Weed Science Society, Champaign p 201.

Worthing CR, Walker SB (1987) The pesticide manual. The Lavenham Press Limited, Suffolt England p 568.