J.Pest Cont. & Environ. Sci. 10(1): 99-114 (2002)

Leaching potential of alachlor and picloram in disturbed and undisturbed soil columns

By

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Received 24/1/2002, Accepted 16/2/2002

ABSTRACT

The leaching of pesticides in soil as well as reaching groundwater is a considerable problem. It provokes a major environmental risk and pollution. Using disturbed and undisturbed soil columns was to investigate the leaching of two herbicides, alachlor and picloram and bromide as a water tracer in a German soil (Merzenhausen, MER). The tested concentration of alachlor (analytical grade substance and [U-^{14}C] alachlor) was equivalent to 1.7kg a.i./ha. and the combination of ^{14}C-labeled and unlabeled picloram yielded an application rate of 0.49 kg a.i./ha. The results showed that the picloram breakthrough curves (BTCs) in disturbed and undisturbed soil columns were identical to that of bromide (which is in a symmetrical form), but the BTCs of picloram exhibited some tailing. Alachlor was less mobile in both soil types than bromide and the BTCs of alachlor included two or

three peaks. Approximately 56 and 25 % of ^{14}C-alachlor were leached, while about 89 and 96 % of ^{14}C-picloram were leached in the case of disturbed and undisturbed soil columns, respectively. According to the above data as well as the distribution pattern of the two tested compounds in the soil layers, picloram was more leached than alachlor. The risk of picloram to reach groundwater is pronounced. Thus, the timing of irrigation during the period after picloram application must be managed.

Key words: Leaching, herbicides, alachlor, picloram, soil columns, radiotracer technique, breakthrough curves.

INTRODUCTION

The mobility of pesticides in soils is an important process involved in the environmental behavior of the compounds (Koskinen and Harper,1990). Also, the contamination of surface and groundwaters with pesticides has been a source of concern for the past several years (Sundaram, 1996). Although, the monitoring data for pesticides are generally poor in much of the world and especially in developing countries (FAO, 1996). The transport of pesticides in soil is important because it determines the extent to which pesticides reach groundwater (Boesten et al., 1989). The contamination of groundwater by pesticides is not only caused by their application to agricultural land but also by their use on non-cultivated areas (Hassink et al., 1993). The risk of water pollution by pesticides and/or their derivatives are frequently estimated using adsorption coefficient, bio-degradability indices and leaching tests through columns in the laboratory (Dousset et al., 1995).

The most definitive tests of organic chemical mobility have occurred in tracer studies where a mobile, non-adsorbing tracer such as chloride or bromide has been added simultaneously with a sorbing organic tracer whose adsorption to soil has been characterized independently through laboratory measurements (Jury and Ghodrati, 1989). Breakthrough curves (BTCs) for mobile chemicals may be retarded relative to water movement. The specific form of the BTC curve is dependent on the physicochemical properties of the chemical and soil solids, the chemical composition of the soil solution, and the structure of the soil through which the chemical moves. Macro-and micro pores influence the movement of agricultural chemicals to groundwater (Shipitalo et al., 1990). The movement of alachlor and picloram through the soil was investigated by Peter and Weber (1985), Fleming et al. (1992) and Gaber et al. (1992).

The objective of the present study is to investigate the leaching behavior of non-sorbed water tracer Br^- and the herbicides active ingredients of alachlor and picloram under flooded conditions, in disturbed and undisturbed soil cores using radiotracer technique. The distribution of alachlor and picloram in the soil layers is also including in this experiment.

MATERIALS AND METHODS

Chemicals: Alachor (99.0 %) 2-chloro-2',6'-diethyl-N-methoxymethyl-acetanilide and [U-^{14}C]alachlor (99.9 %), with specific radioactivity of 2.9210 MBq mg^{-1} were supplied by Monsanto Co. Picloram (99.4 %) 4-amino-3,5,6-trichloro-picolinic acid and [2,6-^{14}C]picloram (99.0 %), with specific radioactivity of 4.2596 MBq mg^{-1} were provided by Dow Elanco Co. Bromide was used as an inert water tracer in the chemical form of KBr.

Soil: The soil used in this study was collected from the top 20 cm layer from Merzenhausen (MER), Germany. There is no history of pesticides application in this area and the physico-chemical properties of the soil were as follows: pH 7.2; organic carbon, 1.2%; cation exchange capacity, 11.4 mmole/100g; water holding capacity, 43 ml/100g and its texture, 6.4% sand, 78.2% silt and 15.4% clay.

The soil samples were air-dried, crushed and sieved using a 2-mm sieve. The undisturbed soil samples were taken by pressing the columns in the intact soil of MER field.

Experimental procedure: Disturbed and undisturbed soil columns (three replicates each) were prepared by uniformly packing 625 g and 665 g into stainless steel columns, respectively (25-cm length, 5.2-cm diameter). The bottom end cap supported a porous stainless steel plate. The top and the bottom of the columns were connected with small tubes for the solutions exchange. The columns were preconditioned before applying the herbicide-Br^- pluse by saturation with 0.01 M $CaCl_2$ (Cox et al., 1995). The flow rate was adjusted at 0.063 ml min^{-1}. One ml of KBr solution (0.1 mmole Br^-) was applied onto the top of the column. After 10 min, 2 ml of the herbicide solution (analytical grade of picloram + ^{14}C-picloram in acetone, application rate of 0.49 kg/ha) or (analytical grade of alachlor + ^{14}C-alachlor in diethyl-ether, application rate of 1.73 kg/ha) were applied dropwise on the soil surface, then leached with 0.01 M $CaCl_2$ under the normal condition for the disturbed columns and air pressure at 750 mbar for the undisturbed columns. The leachates were collected at intervals of 30 minutes for the first day followed by 12 h intervals for the next 5 days and then once a day until day 30.

Bromide concentrations were determined by using HPLC technique (Gynkotek GINA 50, IC AN-1 column 100 x 4.6 mm, 0.1M methansulfonic acid, 1.2 ml/min and the retention time was 5.65 min.). Radio-TLC (SG 60 F 254) and radioscanner (Tracemaster 40) were used to characterize radioactivity (Arnold and Farmer, 1979 and Novick et al., 1986). The layers of soil column were dried, ground and combusted in a sample oxidizer (Packard, Tri-carb 306), then the ^{14}C-activity determined on a Liquid Scintillation Counter (Packard Tri-carb 2500 TR).

RESULTS AND DISCUSSION

Breakthrough curves:-

Disturbed soil columns: The results showed that Br^- leached rapidly in disturbed soil columns, all bromide was leached in about 500 ml. The highest concentration of bromide was found in the first 250 ml of the leachates (Fig.1). The breakthrough curves (BTCs) of alachlor showed two peaks. The first peak was small and identical to that of bromide, while the second was much larger with some tailing. Some alachlor molecules might be leached through macropores without interference with the soil matrix, giving rise to a small peak. The larger peak indicated leaching of alachlor in the soil matrix by diffusion through micropores. The concentration of ^{14}C in the leachates reached a maximum at the top of the second peak then decreased to a minimal value after the release of 2500 ml leachates. The accumulated volume of the leachates until the top of BTC was about 750 ml. It was found that the concentration of alachlor in leachates reached a maximum with one liter of leachates collected (Peter and Weber, 1985). The highest concentration of picloram was identical to the highest concentration of bromide, but the picloram BTC, showed some tailing in this case.

In general, the major amount of radioactivity was leached in the first 500 ml of leachates.

Undisturbed soil columns: The bromide BTCs observed from the undisturbed soil columns were symmetrical. The highest concentration of bromide could be leached in about 250 ml of the leachates. The radioactivity of ^{14}C-alachlor was being detected in the first 125 ml of percolate. About 100 % of applied bromide detected in all leachates up to 2000 ml of the leachates. BTC of alachlor, indicated that the release of alachlor started with the first leachates. Also, the shape of alachlor BTC was zigzag including three peaks (Fig. 2). On the other hand, breakthrough curve of ^{14}C-picloram in undisturbed soil columns was retarded relative to the bromide movement and exhibited a flatter peak and tailing.

The water tracer Br^- was leached fast and the BTCs in disturbed and undisturbed soil columns were symmetrical. Similar results were obtained from other study (Gaber et al., 1992). The rapid release of Br^- from undisturbed soil columns may be due to the use of air pressure on the soil surface. The shape of alachlor BTC in undisturbed soil columns showed several peaks. This shape might result from a reduced pressure on the soil surface when $CaCl_2$ solution was added to the columns. Breakthrough curves of picloram in disturbed and undisturbed soil columns were identical to that of bromide, but the BTCs of picloram exhibited some tailing. Also, it was showed that BTCs for mobile chemicals were having flatter peaks or longer tailings (Beck et al., 1993). Alachlor was less mobile in disturbed and undisturbed soil columns than bromide. The results obtained were in a good agreement with the results of Fleming et al. (1992).

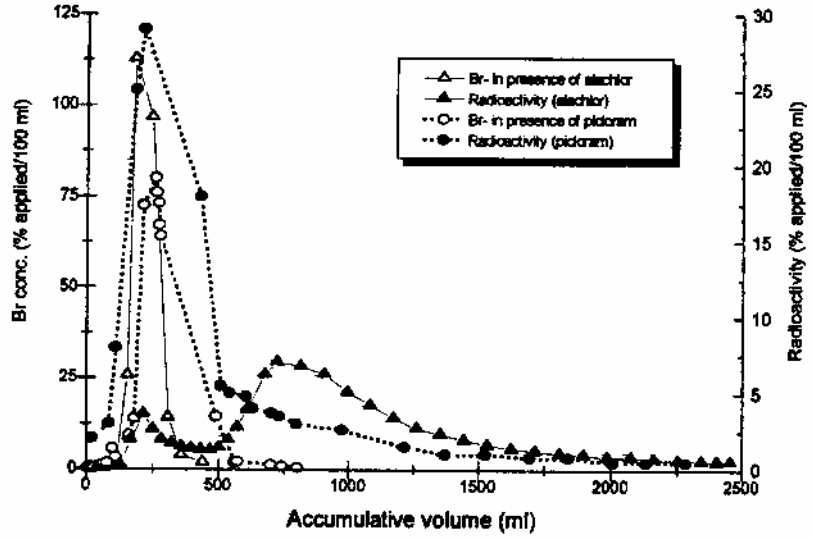

Fig. (1): Breakthrough curves of Br $^-$, alachlor and picloram in disturbed soil columns

(Applied Br $^-$, ^{14}C-alachlor and ^{14}C-picloram = 100 %)

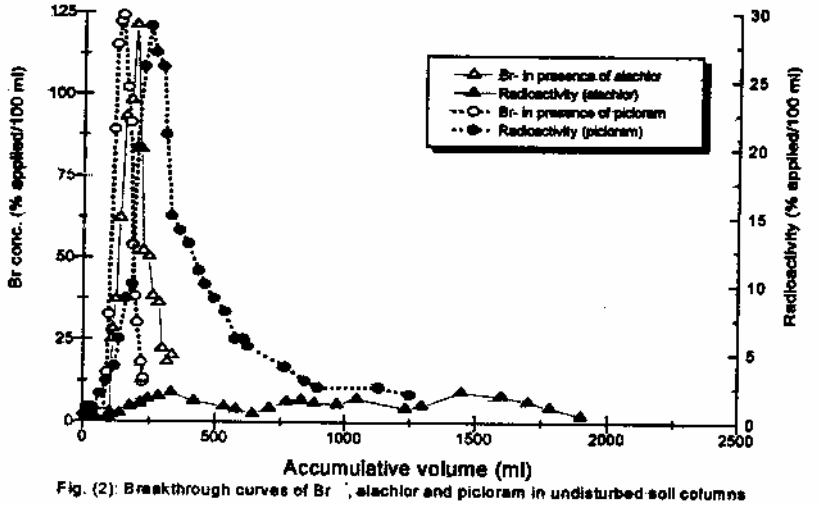

Fig. (2): Breakthrough curves of Br $^-$, alachlor and picloram in undisturbed soil columns

(Applied Br $^-$, ^{14}C-alachlor and ^{14}C-picloram = 100 %)

Balance of residual radioactivity in disturbed and undisturbed soil columns: During the leaching period of the experiment (30 days), the cumulative amount of radiocarbon leached from disturbed soil columns amounted to be 57 and 89 % of the applied alachlor and picloram, respectively. After the leaching period of alachlor, 43 % of the applied radiocarbon was detected in the disturbed soil. The radioactivity remaining in the soil treated with ^{14}C-picloram represented 11 % of the applied dose. Only 25 % of the applied radioactivity from ^{14}C-alachlor was leached during 30 days, while about 96 % of ^{14}C-picloram were leached (Fig. 3). At the termination of the leaching period, about 75 % of the applied ^{14}C-alachlor could be detected in the soil, while traces of ^{14}C-picloram residues were retained in the soil.

The leachates with the highest concentration of radioactivity (peaks of the BTC) included the parent compound and its metabolites. In the case of alachlor, 48 % were detected in the leachate fraction, while 77 % from the parent picloram were detected (Fig. 4). From the undisturbed soil columns, the results of radio-TLC analysis indicated that approximately 27 and 80 % of alachlor and picloram were identified in the leachates, respectively. In general, picloram was weakly adsorbed and did not undergo much interference with the soil matrix in disturbed or undisturbed soil columns. Our findings are in agreement with that reported by Davidson and McDougal (1973). The high quantity of alachlor as well as residual radioactivity in disturbed and undisturbed soils was attributed to the higher adsorption or to the higher degradation and binding in an undisturbed soil. The microorganisms are active in the undisturbed soil as compared to the disturbed one, because the disturbed soil was dried before the filling of the columns.

It could be stated that alachlor was moderately adsorbed in MER soil. The sorption of alachlor was moderate in a clay loam, silt loam, silt clay loam and sandy loam soils (Yen et al., 1994). Only small amount of the applied ^{14}C-alachlor leached through undisturbed soil columns. These observations are in harmony with that obtained by Zins et al. (1991).

Distribution of residual radioactivity in different soil layers: Fig. (5) represents the percentage of residual radioactivity of alachlor and picloram in different soil layers of the column. The results showed that the distribution of residual radioactivity in the soil layers was almost uniform for both the tested compounds. Only in the case of picloram, higher concentrations of ^{14}C-activity were found in the bottom layer.

The distribution of residual radioactivity in soil layers illustrated in Fig. (6) showed a distinct ^{14}C profile. High residual radioactivity of alachlor was concentrated in the top soil layers (0-4 cm) and decreased in the layers of the last 10-cm. Only about 4 % of applied radioactivity of picloram were recovered in soil. The radioactivity of picloram was concentrated at the bottom layer, which could be desorbed with $CaCl_2$ solution easily. On the contrary, the distribution of residual radioactivity of alachlor in soil layers of the disturbed soil columns was almost uniform, while in undisturbed soil columns showed higher concentrations in the upper five layers (0-10 cm). These results have supported with the results of Peter and Weber (1985). The differences in the behavior of picloram and alachlor in soil was attributed to the differences in the physicochemical properties of such herbicides, particularly their water solubility. In fact, the water solubility of picloram is twice as high as alachlor. The leaching of herbicides was affected by soil conditions, weather and their physicochemical

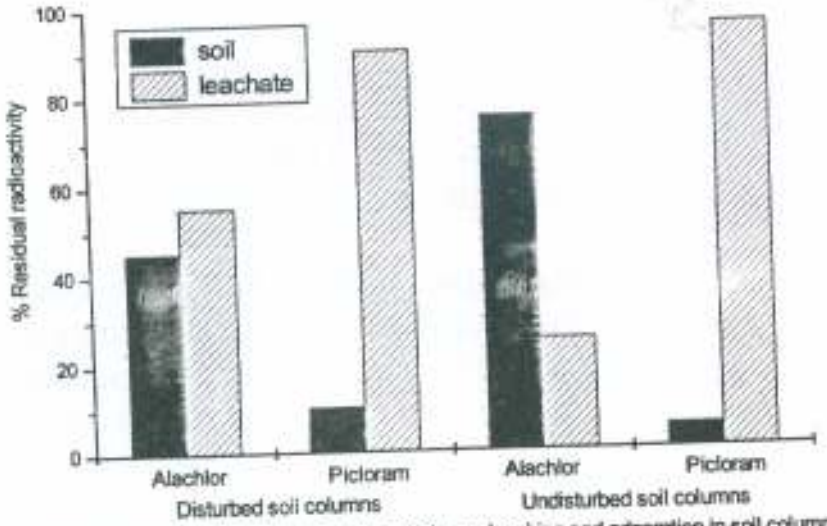

Fig. (3): Balance of residual radioactivity between leaching and adsorption in soil columns
(Applied ^{14}C-alachlor and ^{14}C-picloram = 100 %)

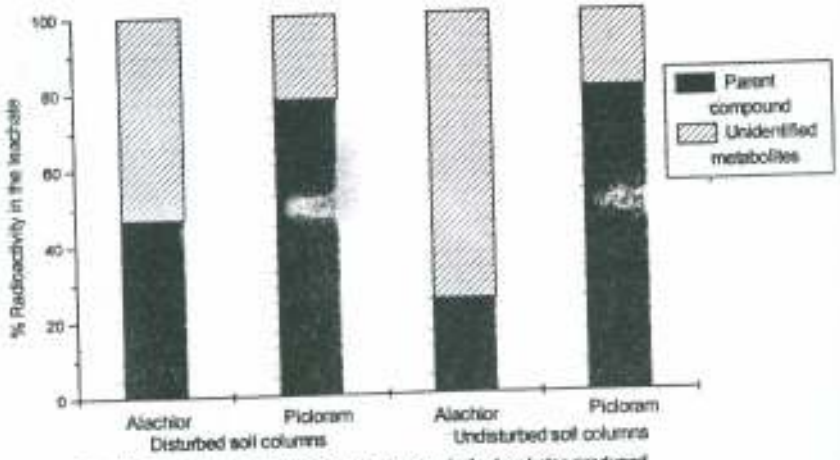

Fig. (4): Concentration of alachlor and picloram in the leachates produced the top of BTCs in soil columns
(Residual radioactivity in the leachate = 100 %)

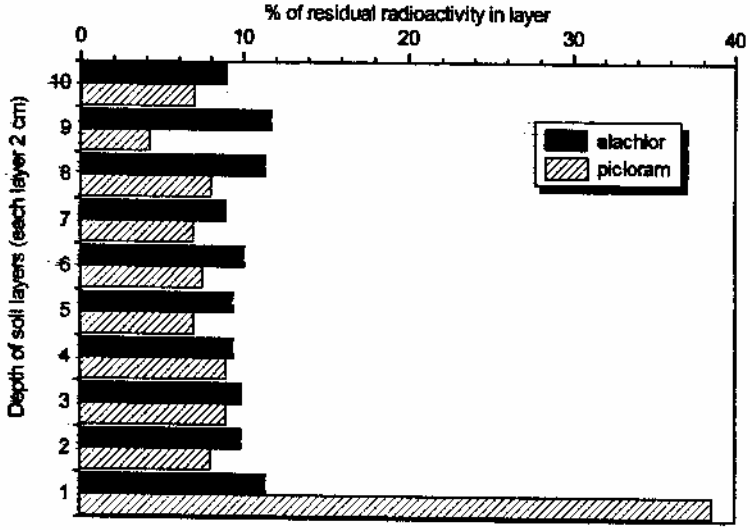

Fig. (5): Distribution of residual radioactivity in soil layers of disturbed soil columns
(Residual radioactivity in soil = 100 %)

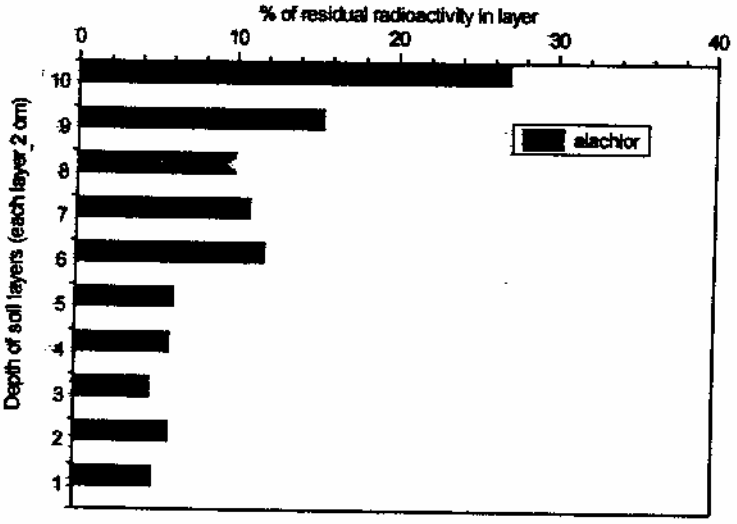

Fig. (6): Distribution of residual radioactivity in soil layers of undisturbed soil columns
(Residual radioactivity in soil = 100 %)

properties (Clay, 1993). Also, the herbicide adsorption was generally inversely related to the mobility and water solubility (Peter, 1984).

From the results obtained, it could be concluded that the BTCs of picloram in disturbed and undisturbed soil columns are identical to that of Br^-. Picloram was found to leach more than alachlor. Consequently, the risk of picloram to reach groundwater is pronounced. Thus, the timing of irrigation, particularly during the period after the picloram application must be managed.

ACKNOWLEDGEMENT

The authors would like to thank the staff in the Institute of Chemistry and Dynamic Geosphere, Radioagronomy, Research Center, Jülich, Germany.

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الملخص العربى

غسيل مبيدى الحشائش ألاكلور وبيكلورام فى أعمدة التربة المثارة وغير المثارة

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تعتبر عملية غسيل المبيدات فى التربة ووصولها للماء الأرضى من أهم مشاكل التلوث لما يمثلها من خطورة. لقد تم دراسة غسيل مبيدى الحشائش ألاكلور وبيكلورام (المركبات النقية مع المركبات النشطة إشعاعياً) ومقارنتهما مع البروميد كأحد المكونات (غير المدمصة) التى تتحرك مع السريان الطبيعى للماء وذلك باستعمال أعمدة مملوءة بتربة مثارة حيث سبق إعدادها وتربة غير مثارة أى على صورتها الطبيعية. وأظهرت النتائج أن منحنى غسيل البيكلورام كان متطابق مع منحنى غسيل البروم فى كلا نوعى التربة وكان منحنى غسيل الألاكلور يتكون من عدة قمم ، الألاكلور أقل حركية فى نوعى التربة بالمقارنة مع البروم والبيكلورام واتضح أن نسبة ٥٦ ، ٢٥ % من المكونات النشطة إشعاعياً التى تم غسيلها عبارة عن ألاكلور بينما ٨٩ ، ٩٦ % عبارة عن البيكلورام فى التربة المثارة وغير المثارة على الترتيب. هذه النتائج تشير الى خطورة البيكلورام لامكانية وصوله للماء الأرضى لذا فانه يجب الأخذ فى الاعتبار طريقة وتوقيت الرى بعد المعاملة.