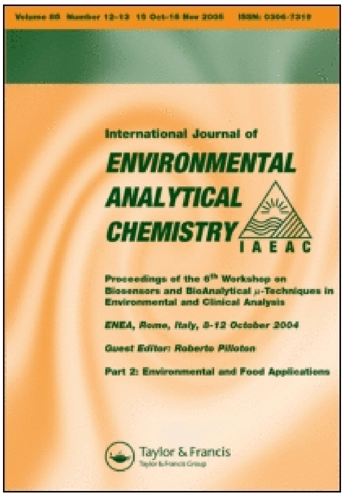

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Comparison of the Leaching Behaviour of Alachlor and its Metabolites Under Field and Laboratory Conditions

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COMPARISON OF THE LEACHING BEHAVIOUR OF ALACHLOR AND ITS METABOLITES UNDER FIELD AND LABORATORY CONDITIONS

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The aim of the investigation was to evaluate whether the results of field studies and those obtained from soil column experiments are comparable in order to describe leaching behaviour of pesticides. The fate of Alachlor and its metabolites 2,6-diethylaniline and 2-chloro-2′,6′-diethylacetanilide are described in this paper. Field leaching study and laboratory soil column experiments carried out with the formulated herbicide LASSO® gave similar results. Applied Alachlor remained mostly in the top 10 cm soil layer representing a limited mobility. Very small amounts of Alachlor in ground and percolated water indicated only a slight leaching potential. The calculated half-life of 15 days and 90% loss after 335 days demonstrate a remarkable persistence of alachlor. Only 2-chloro-2′,6′-diethylacetanilide but not 2,6-diethylaniline was detected in soil and percolated water. It is still uncertain if these residues originate from the formulated product or result partially from "metabolism".

Column experiments with the same soil carried out under undisturbed conditions are a simple alternative to field studies and allow quantitative estimations. The column experiments support the assumption that most of the alachlor that cannot be found after application is not lost by wind drifting or volatilization but due to formation of bound residues.

KEY WORDS: Pesticides, Alachlor, leaching, gas chromatography, groundwater, soil.

INTRODUCTION

In recent years, contamination of groundwater by agrochemicals has become a matter of public concern[1,2,3]. Various experiments have been carried out to examine the environmental fate of agrochemicals. Field approaches to the study of the movement of pesticides in soil are subject to numerous environmental variables[3,4]. Frequently, attempts have been made to compare results from such studies with those resulting from laboratory soil column experiments, or computer simulations. However, because of different conditions used in conducting these investigations, they are not easily compared.

The intention of these investigations was to evaluate the potential for pesticides to leach by conducting a field study, soil column experiments and computer simulations. The hypothesis to be tested was that these model experiments are suitable for the simulation of pesticides' behaviour under field conditions.

The fate of alachlor and its metabolites 2,6-diethylaniline and 2-chloro-2′,6′-diethylacetanilide are described in this paper. Alachlor was chosen because of its agricultural relevance and its potential capability to leach into groundwater.

MATERIALS AND METHODS

Field study

The field experiment was carried out on a 1.3 ha arable field in the north of Germany. The test plot was divided into a treated and a nontreated part. The soil was sandy with a humus content of 3.3%, an organic C content of 1.8% and a pH of 4–5. The groundwater level was between 3.5 and 4.5 m depending on the season; the pH of the groundwater was 5–6. A mustard crop was seeded and the herbicide applied in pre-emergence with an application rate of 2.5 kg active ingredient (a.i.)/ha. Alachlor was applied as a commercial 480 g a.i./l emulsifiable concentrate (LASSO®) purchased from Monsanto (Düsseldorf).

Groundwater was sampled by means of a peristaltic pump from wells 14, 15, 16, 17, 19, 20, 21 and 22 (see Figure 1) at the day of application and after 28, 59, 93, 105 and every following 14 days till the end of the trial. The samples were stored at 4°C until analysis. Soil samples were taken with a HUMAX auger (Max Hug, Luzern, Switzerland) down to 75 cm depth at three places (each consisting of three subsamples) from the field. Soil was sampled on the day of application and after 3, 6, 20, 28, 56, 93 and 174 days. The soil cores were frozen and segmented into 10 cm pieces before analysis.

Soil column experiments

Soil column experiments were carried out according to the official German guidelines for testing the leaching behaviour of pesticides (BBA, 1986[15]) with some modifications and three replicates each. The experimental set up is shown in Figure 2. The columns had a total length of 35 cm and an inside diameter of 5 cm and consisted of segmented glass. These segments were sealed together by silicone grease and a steel construction not shown in Figure 2. The experiments were conducted in the dark and at temperatures between 20 and 25°C. The soil was sampled from test plot. Three disturbed columns consisted of air-dried soil from the upper 30 cm of the test plot, passed through a 2 mm sieve. Three other columns contained undisturbed soil cores taken with a HUMAX auger. Quartz sand and a filter disc were placed on the top and the lower end of each column according to Figure 2. Before application of the herbicide, the soil columns were saturated by continuous application of distilled water (Millipore, Great Britain) corresponding to about 50 mm rain/day by means of a peristaltic pump. To avoid extensive loss of minerals from the soil the percolate was recycled. Alachlor was applied in amounts of 0.47 mg a.i. according to the usual application rate. Furthermore, 47 mg were applied to the undisturbed soil column simulating one

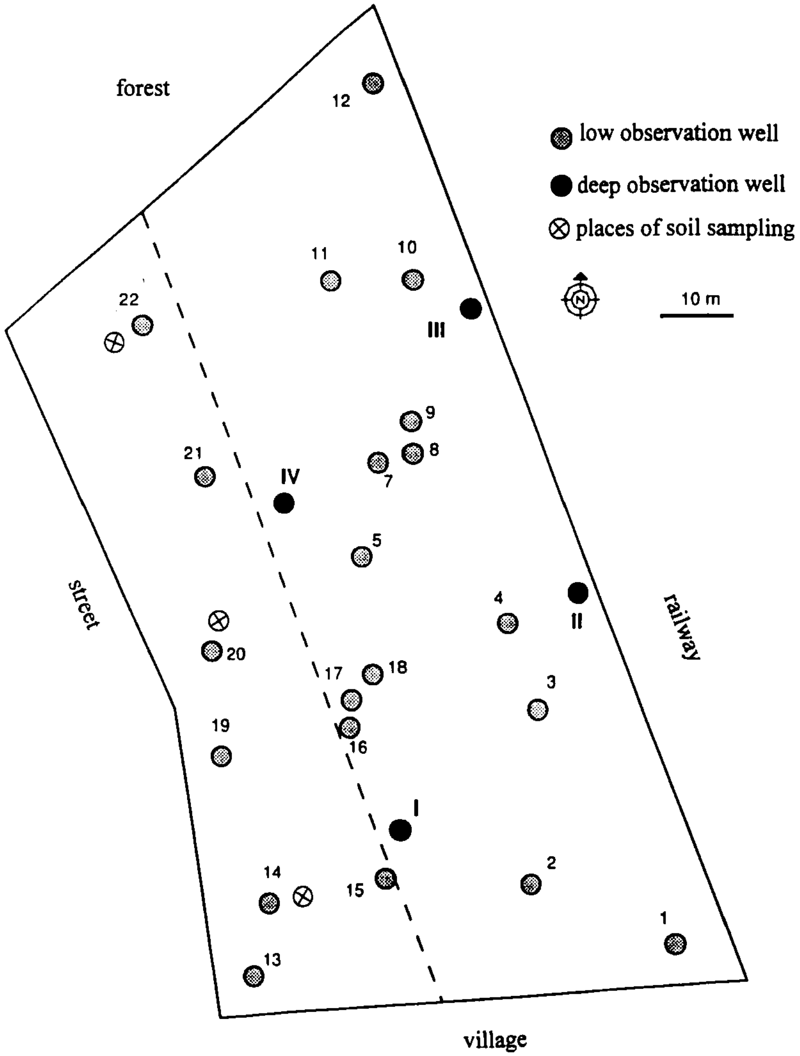

Figure 1 Description of the test plot. The groundwater flow (about 10 cm/day) is from west to east. The test plot is divided into a treated (west) and a nontreated part.

hundred times the normal field application rate. Potassium bromide was used as a tracer and detected by measurement of conductivity. Leaching was performed over 9 days simulating an average surplus precipitation of 400 mm/year in Germany, twice as much as specified in the guidelines.

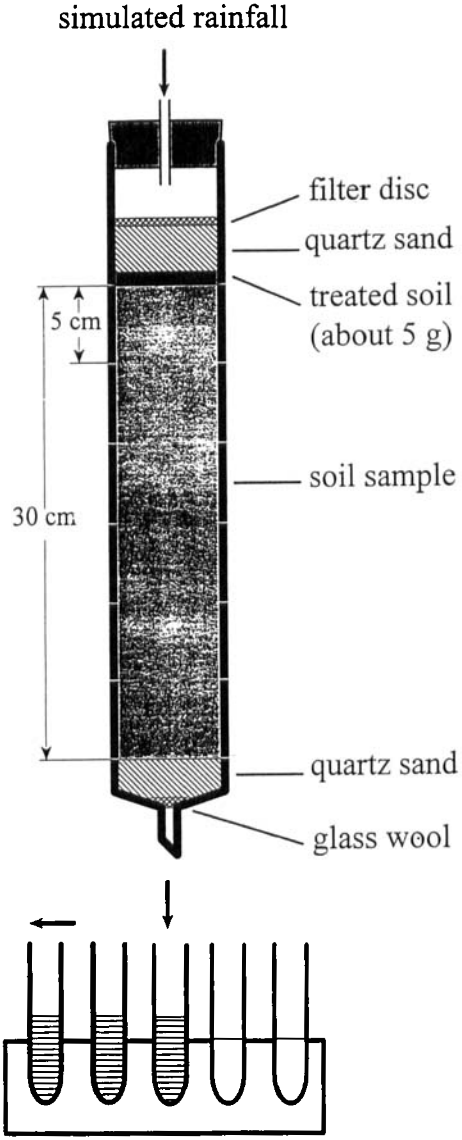

Figure 2 The soil columns for laboratory experiments. The columns consisted of segmented glass. The segments were sealed together by silicone grease and a steel construction not shown here.

Analytical methods

Soil samples were segmented into 10 cm pieces, air-dried, spiked with Metolachlor (PESTANAL, Riedel de Haen, Seelze, FRG) as an internal standard (1 mg/kg in the upper 10 cm decreasing to 0.05 ppm in the 60–75 cm soil layer). 50 g were shaken vigorously with 100 ml hexane: acetone=9:1 for two hours, vacuum filtrated, the extract evaporated to dryness and dissolved in 0.5 ml or 1 ml toluene depending on the expected concentration. Recovery tests showed 90% recovery with a standard deviation of 8%. The LODs (limit of detection) were 1 µg/g for alachlor and 2-chloro-2′,6′-diethylacetanilide and 10 µg/g for 2,6-diethylaniline. The method will be described elsewhere[5].

Groundwater samples (400 ml) were filtered, spiked with Metolachlor as an internal standard (100 ng/l) and extracted by micro-liquid-liquid-extraction[5]. The LOD was calculated to be 25 ng/l, 35 ng/l and 40 ng/l for Alachlor, 2,6-diethylaniline and 2-chloro-2′,6′-diethylacetanilide with recoveries of 85–90% and standard deviations of 5%. In the soil column experiments, two 43 ml fractions per day were analyzed. Details of the method will be exactly described elsewhere[5].

Gas chromatography

The extracts were analyzed by a HP 5890A gas chromatograph with an autosampler HP 7673A, nitrogen-phosphorus and electron-capture detector and fitted with a 25 m HP-5column (0.32 mm i.d. and 0.16 µm film thickness). The temperature programme was 100°C-1 min-30°/min-150°C C-2 min-3°/min-205°C-10°/min-260°C-20 min, the injection temperature 210°C. 2 µl were injected by hot splitless injection. Alachlor and 2,6-diethylaniline were purchased from Riedel-de Haen in PESTANAL quality and 2-chloro-2′,6′-diethylacetanilide was synthesized as a reference substance.

RESULTS AND DISCUSSION

Field study

The field study was carried out on a 1.3 ha arable field in the north of Germany which is well equipped and hydrogeologically examined to conduct field studies. This field meets important criteria of a "worst-case" situation, such as a sandy soil and a high groundwater level. It had been continuously in agricultural use. Figure 3 shows alachlor leaching with time and soil depth in the field experiment. The leaching of alachlor during the day of application represents the limitation of the chosen sampling technique with respect to cross contamination. As can easily be seen from Figure 3, Alachlor remained mainly in the upper 10 cm soil layer and seemed to leach in very low amounts continuously into groundwater. It is remarkable that only one third, namely 0.6 µg/g Alachlor, could be detected in the top 10 cm on the day of application since the applied 2.5 kg Alachlor per ha amount to about 1.9 µg/g in a loam soil layer.

Isensee *et al.*[6] pointed out that significant volatilization losses of alachlor after applying the emulsifiable concentrate were observed. Furthermore wind during the application may have reduced alachlor application. Also formation of bound residues must be taken into consideration. Since similar results were found in soil column experiments, bound residues are the most probable explanation as will be discussed later.

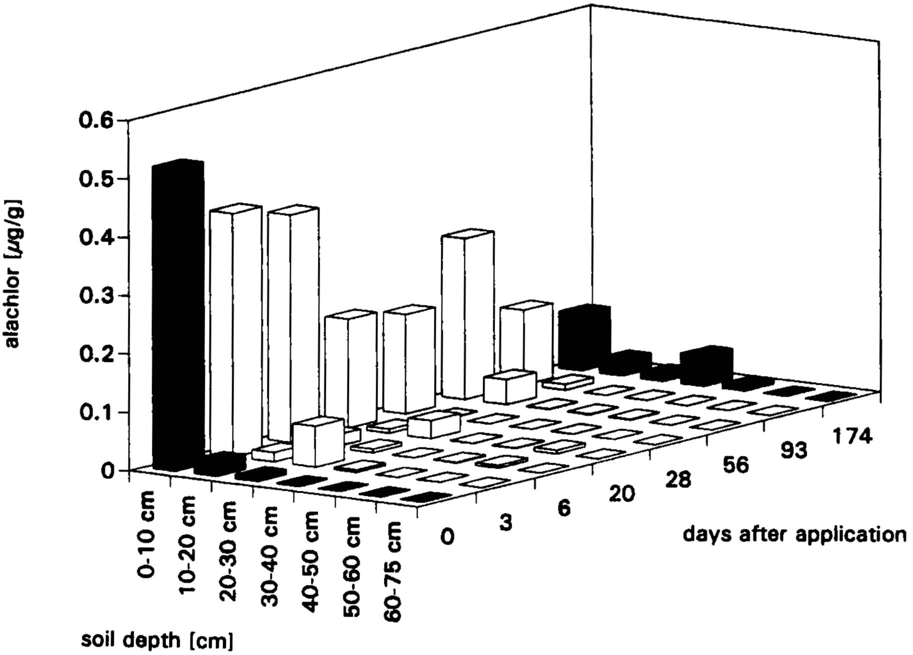

Figure 3 Leaching of alachlor with time and soil depth. Values after 174 days represent the situation after tillage

The observed "leaching" 174 days after application was due to soil mechanical treatment. Tillage was necessary according to good agricultural practice to prepare the soil for the next seeding.

Figure 3 shows the loss of extractable Alachlor in the upper 10 cm soil layer during the experiment. Alachlor is degraded primarily by microorganisms in the soil and the rate of degradation is strongly influenced by temperature and soil moisture content. Additionally, leaching into deeper soil layers and further formation of bound residues contributed to the observed decline.

A computer model derived from toxicokinetic studies (TOPFIT Vers. 1.1, Gödecke, Schering, Thomae) was used to determine the 50% and 90% loss of Alachlor. These calculations based on a two-compartment-model with linear kinetics could predict the observed residues of alachlor after application with reasonable accuracy. A half-life time DT_{50} of 15 days and a 90% loss after 335 days was calculated. Similar results of DT_{50} between 9 and 11 days had been published[7,8]. Moon and Walker[9] found an 80% loss of applied Alachlor after 168 days compared to an 80% loss after 181 days in our experiments. These results are in agreement with other authors who also reported this limited mobility of Alachlor[8,10].

It must be pointed out that these calculations are a first attempt to gain information on the half-life of Alachlor in this field experiment. They will be completed by extensive calculations in conjunction with the appropriate weather data and other variables determined

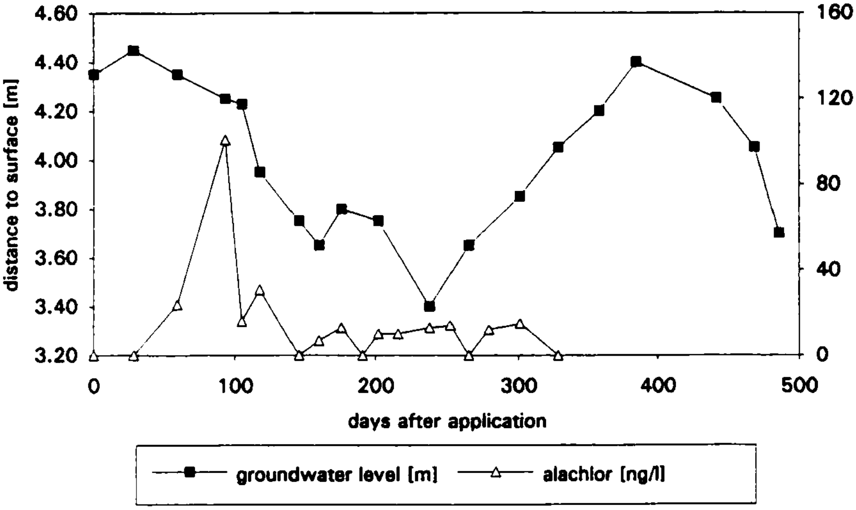

Figure 4 Breakthrough of Alachlor in well 17 in correlation to the groundwater level

(e.g. soil characteristics and degradative properties of alachlor), dependent on the prevailing field conditions.

2-chloro-2′,6′-diethylacetanilide detected at a concentration ≤10 ppb was the only metabolite in the top 10 cm soil layer. Since analysis of the spraying mixture gave a 1% content of 2-chloro-2′,6′-diethylacetanilide, no conclusions can be drawn as to whether these metabolic residues are due to application or also metabolism. Another expected metabolite reported in literature was 2,6-diethylaniline[13,14]. This compound could not be detected although the analytical procedure had been established with a LOD of 10 μg/g.

To evaluate the leaching of alachlor into groundwater, the groundwater level had been measured in representative observation wells 2, 4, 12, 17, 19 and 22 in dependence on time.

All water samples from the treated area showed a moderate break through of alachlor about 100 days after application in amounts ranging from 20 to 140 ng/l alachlor. Figure 4 shows how the observed breakthrough of alachlor correlates to the groundwater level. Well 17 was chosen to serve as representative for all the other wells. The detection of Alachlor in groundwater can be correlated to rain events causing an increase of the groundwater level but it must be emphasized that only a very low portion of the applied alachlor appeared in groundwater. It may be transported bound to a fraction of humic substances.

Similar pulses of Alachlor in groundwater shortly after herbicide application are described by Isensee *et al.*[11] who suggest preferential flow transport during rain events as a contribution to the alachlor movement. Furthermore Koskinen *et al.* discussed that alachlor possibly degraded before reaching the groundwater[12].

Soil column experiments

Three different soil column experiments were carried out to confirm the results derived from the field study and to give a comprehensive evaluation of the leaching behaviour of alachlor. As described in the experimental section three variations of the soil column experiments were chosen. Figure 5 summarizes the residue concentrations found in the soil segments at the end of the experiment. In all the experiments only one third of the applied alachlor could be detected when using a normal application rate. On the other hand 80% of the applied alachlor was found in the case of a 100 fold increased application rate. This finding indicates that the formation of bound residues contributed more to the low recovery observed just after application to the field than evaporation and transport by wind during application. The

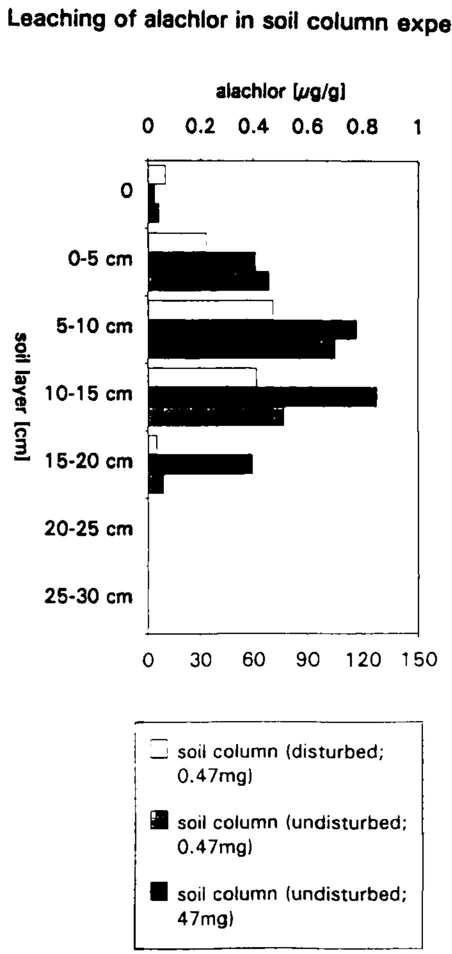

Figure 5 Concentration of Alachlor in soil segments of different columns. Bottom abscissa applies to the high Alachlor concentration resulting from the 100fold application rate. Results corresponding to the concentration of anilide are not shown.

100 times increase in the application rate did not alter the amount of alachlor in the percolate. This high application rate has no practical relevance but the results confirm the low leaching of alachlor in the soil investigated. Furthermore it can be seen that a slight leaching down to a depth of 10–15 cm occurred independent of the packing of the columns. The observed leaching in the column experiments support the results from the field study despite simulated annual rainfall over a very short period and differing temperatures.

Alachlor was detected in leachate after breakthrough of the tracer. A total of 0.6% was leached out in the disturbed column and 0.01% of applied alachlor in the undisturbed column. No increase in alachlor leaching could be observed after applying one hundred times the field rate. The very low amount of alachlor appearing in the leachate may be transported bound to a fraction of humic substances. This is in accordance to the observations made in the field study. Independent of the column packing, 2-chloro-2′,6′-diethylacetanilide was observed after addition of about 400–450 ml water. Based on calculations from residues in the spraying mixture, 9 and 6% of applied anilide were leached out in the disturbed and undisturbed case and 50% in the experiment with one hundred times the application rate. The adsorption of 2-chloro-2′,6′-diethylaniline seemed to decrease with increasing application rate. Alachlor is obviously more strongly adsorbed by the soil used than its metabolite 2-chloro-2′,6′-diethylacetanilide. As in the field study, no final conclusion can be drawn as to whether this metabolite occurs only due to application or also metabolism. The application of pure 2-chloro-2′,6′-diethylacetanilide in a separate column experiment resulted in quantities which were leached out comparable to the other column experiments. This supports the assumption of only minor contributions of metabolic breakdown.

In contrast to the field study, soil column experiments make quantitative estimations possible which obviously confirm the appearance of the minute quantities of Alachlor in the groundwater.

Summarizing the leaching experiments with formulated Alachlor

Most Alachlor remained in the top 10 cm soil layer representing a limited mobility. Small amounts of alachlor in ground and percolated water indicated only a slight leaching potential. The calculated half-life of 15 days and 90% loss after 335 days demonstrate a remarkable persistence of Alachlor. Only 2-chloro-2′,6′-diethylacetanilide but not 2,6-diethylaniline was detected in soil and percolated water. It is still uncertain if these residues originate totally from the formulated product or also result from "metabolism".

CONCLUSIONS

The hypothesis to be tested was as to whether soil column experiments with disturbed and undisturbed soil columns are suitable to simulate pesticides behaviour under field conditions. Field and laboratory soil column experiments gave similar results in the described case.

It must be pointed out that soil column experiments are a simple alternative to investigate the leaching behaviour of pesticides. When the same soil as in a field study is used, the results

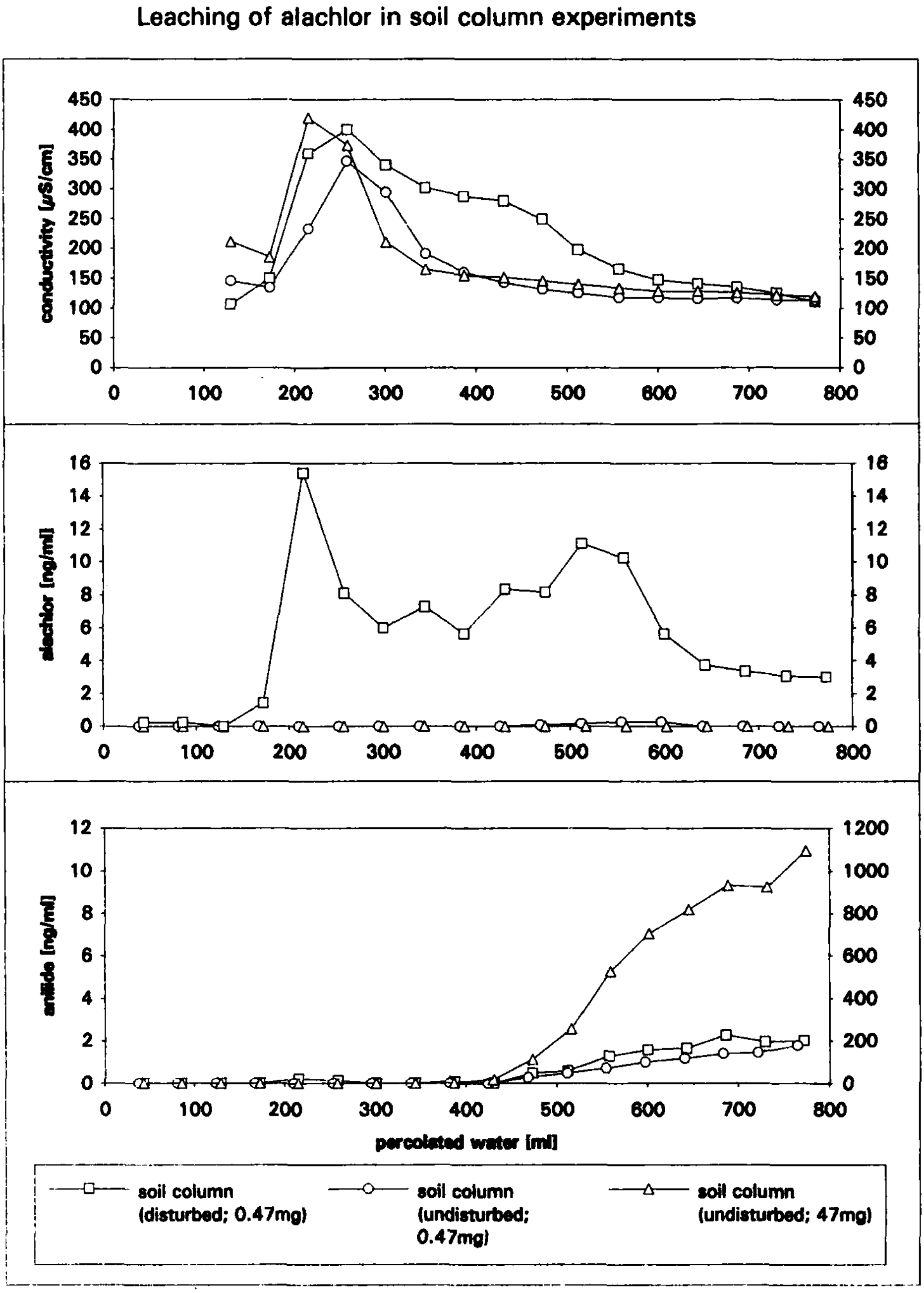

Figure 6 Concentration of alachlor in percolated water of different columns. The upper figure shows the breakthrough of the tracer potassium bromide independent of the soil structure. The figure in the middle represents the breakthrough of Alachlor. The last figure shown corresponds to the concentration of anilide in the percolate. The left ordinate applies to the normal application rate, the right to the 100fold rate. The experiments were finished after percolating 400 mm water to determine the elution profile of Alachlor in the soil columns (see Figure 5).

are comparable. Undisturbed soil columns allow a better simulation of the leaching than disturbed columns. The described column experiment can be easily carried out and enables quantitative estimations which are not possible in field studies.

Acknowledgement

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