Bull. Environ. Contam. Toxicol. (1991) 46:519–526

Bulletin of Environmental Contamination and Toxicology

Dissipation of Alachlor under *In Situ* and Simulated Vadose Zone Conditions

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The detection of pesticides in groundwater continues to concern the general public. Several reports have indicated that as many as 73 pesticides have leached to groundwater in 34 states (Cohen et al. 1980, Williams et al. 1988). Our knowledge of the fate of pesticides in the tilled or root-zone-depth soil is extensive, whereas much less is known about their fate in subsoil and underlying unsaturated (vadose) zones. Pesticides must leach through the vadose zone to reach ground-water. Subsurface aquifer materials have been shown to contain extensive microbial populations and bio- degradation of organic compounds does occur there, but usually at rates much slower than in surface soils (Ghiorse and Wilson 1988). Microbial degradation of the herbicide metribuzin in subsoil has been shown, for example, to proceed at a much slower rate than in surface soil (Moorman and Harper 1989). This slower rate of biodegradation would be expected since both microbial population density and soil organic matter content decrease with depth (Focht and Joseph 1973, Roeth et al. 1969). Additional conditions likely to exist in the unsaturated zone include lower and less variable temperature, higher and more uniform moisture content and lower oxygen levels. These conditions would likely affect the type and activity of the microbial population, but their overall impact on pesticide degradation is unclear. Few experiments have been conducted to determine how the conditions in the subsoil and underlying unsaturated zones affect pesticide fate.

The purpose of the present study was to determine how in situ and simulated subsoil conditions affect the dissipation of alachlor in groundwater solution.

MATERIALS AND METHODS

A field study was conducted to determine the effect of in situ conditions 0, 30, and 100 cm below the soil surface on the degradation of alachlor in a groundwater solution. An apparatus, designed to expose solutions to the ambient conditions at 30 and 100 cm depths, is shown in Figure 1. The apparatus consists of (1) a housing made from 4.8 cm ID aluminum pipe and (2) a glass vessel (4.5 cm dia x 25 cm long) that contains the groundwater

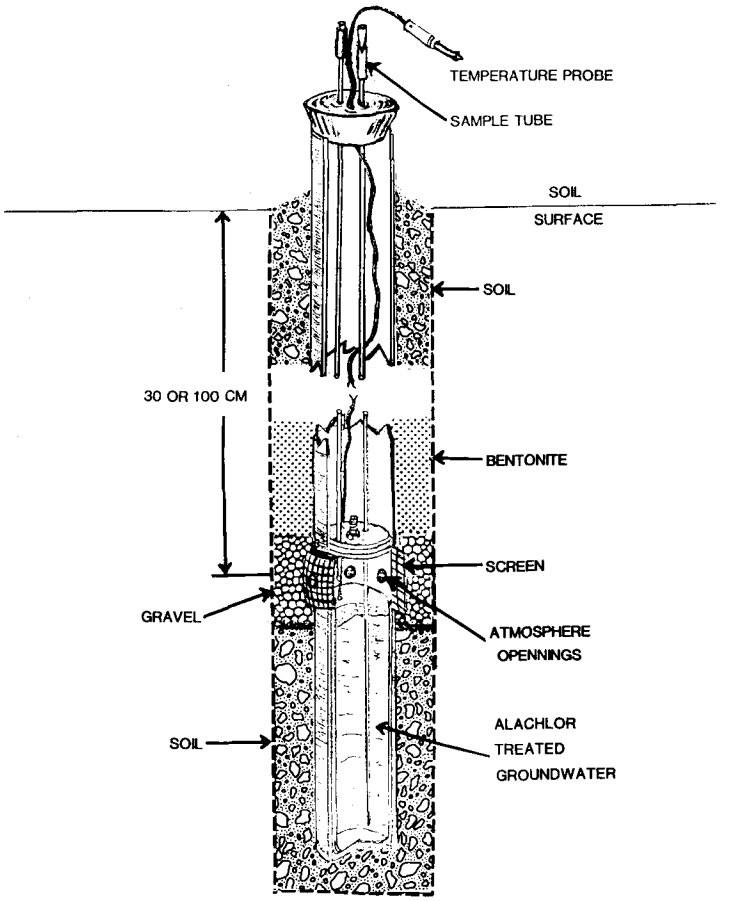

Figure 1. Apparatus used to expose alachlor solution to in situ subsurface atmosphere conditions.

solution. Sections of aluminum pipe were cut at 75 or 150 cm lengths, capped at one end and 1.3 cm dia "soil atmosphere vent" holes were drilled 30 cm from the capped end. The vent holes were covered with metal screen (0.5 cm openings) and the housing (pipes) were inserted into 8 cm diameter holes (that had been augured into the soil to a depth of 60 or 130 cm). The vent holes were 30 or 100 cm below the soil surface with about 15 cm of pipe above the soil surface. Layers of soil, gravel, and bentonite clay were packed around the pipe as shown in Figure 1. The gravel pack outside the vent holes prevents soil from entering the tubes and provides a soil atmosphere "head space". Pipes (3 each depth) were located in two rows each spaced about 2 m apart. Glass vessels were inserted into the housing followed by an air-tight seal fitted with Teflon sampling and vent tubes and a temperature probe. The seal was positioned 3 cm above the housing vent holes. Groundwater (obtained from a 3 m deep well near the field site) was filtered (glass fiber) to remove any suspended solids, but not

microorganisms. Estimates of bacterial populations (CFU's) were made by performing serial dilutions of the filtered groundwater and spread plating onto diluted nutrient broth (1 g/L) agar. Total CFU's were counted after 5 days incubation at 27 C. The pH of the water was 5.8. The filtered water (2500 ml) was treated with (ring-^{14}C) alachlor (7.08 uCi/mg, 96% purity) at 0.1 ppm. The alachlor treated groundwater (270 ml) was poured into each glass vessel through the sampling tube. A 0 cm treatment was also prepared by adding 270 ml of alachlor treated groundwater to 500 ml Erlenmeyer flasks. These flasks, each fitted with a sampling tube and a vent open to the atmosphere, were designed to expose the alachlor to the temperature and atmospheric conditions that exist at the soil surface and were positioned between the pipes. The flasks and pipes were each covered with inverted white plastic pots to reduce solar heating and photolysis. Three replications of each treatment were run at the same time.

Temperature was recorded daily and 20 ml water samples were taken after 1, 7, 14, 28, 42, and 56 days. Triplicate 1 ml subsamples were analyzed for total ^{14}C by liquid scintillation analysis (LS) and the remaining water (17 ml) was extracted using C18 Sep-Paks (Waters Associates, Inc.) 3. The ^{14}C-alachlor plus metabolites was extracted from the Sep-Paks with 10 ml methanol (extraction efficiency from water was 99%). Extracts were spotted on thin-layer-chromatography (TLC) plates (FG-254, E. Merck, Darmstadt) and developed 10 cm using toluene:methanol (95:5 v/v).

A laboratory experiment was conducted to determine the effect of oxygen content and soil on the degradation of alachlor in groundwater. Surface and subsurface soil (27 g quantities) was placed in 500 ml Erlenmeyer flasks which were designed to maintain aerobic and anaerobic (N_2 gas) head-space conditions. An additional set of flasks did not have any soil added. A set of sterile topsoil controls (aerobic only) was also prepared. All treatments were replicated three times. Soil was obtained from the 0-10 cm (surface) and 90-100 cm (subsurface) depths at the field in situ location. The sand, silt, clay, and organic carbon contents of the surface and subsurface soils were 28.6, 50.5, 20.9, and 2.44% and 41.1, 35.2, 23.7, and 0.24%, respectively. The soil was sieved to <1 mm and air dried to 4% moisture before placement in the flasks. Six liters of groundwater (obtained and filtered as described above) were treated with (ring-^{14}C) alachlor (7.1u Ci/mg, 96% purity) at 0.1 ppm. Alachlor treated water (270 ml) was added by pouring through the sampling tubes. The flasks were fitted with rubber stoppers through which glass sampling and vent tubes were inserted. The bottom of the sampling tubes were bent in a "U" shape (to prevent intake of soil) and when in place just touched the bottom of the flasks. The stoppers were fitted with either one or two vent tubes. The single vent in half the flasks was left open to the air to simulate aerobic conditions. Anaerobic conditions were maintained in the remaining flasks (fitted with two vent tubes) by flushing the head space with N_2 for 10 min after the addition of the alachlor solution, during

sampling and once each week. All tubes were stoppered immediately after flushing in the anaerobic flasks.

Water samples were taken for up to 169 days (see Figure 3 for time periods). Triplicate 1-ml samples were analyzed by LS for total ^{14}C and 15 ml samples were extracted using C18 Sep-Paks as described above. The herbicide was eluted from the Sep-Paks as described above. Extracts were analyzed by TLC as described above. Water remaining in the flasks at the end of the experiment was analyzed by LS for total ^{14}C. The saturated soil was washed from the flask with 100 ml H_2O into a buchner funnel. Total ^{14}C in the filtrate was determined by LS. The moist soil was shake extracted for 1 hr with 100 ml acetonitrile and filtered. Soil was extracted two more times with 100 ml acetonitrile. Extracts were combined and analyzed by LS and TLC as described above. Extracted soil was air dried, mixed and samples oxidized to determine bound ^{14}C.

RESULTS AND DISCUSSION

Alachlor dissipation at 0, 30, and 100 cm depths in the field is shown in Figure 2. Essentially no degradation occurred in flasks exposed to surface conditions (0 cm depth), while average half-life of alachlor at 30 and 100 cm depths was in excess of 56 days. This half-life was much longer than the reported half-life in soil of less than 10 days (Beestman and Deming 1974). The slow rate of alachlor dissipation in this study suggests that microbial degradation may have been limited by the microbial population (4.4×10^4 CFC/ml) and the dissolved organic carbon (DOC) content of the groundwater. The capability of the microorganisms present in the groundwater to degrade alachlor is unknown and the DOC content of the groundwater (0.83mg/L) may have been too low support a very high degradation rate.

By Day 56, alachlor and polar compounds constituted an average of 88 and 3, 58 and 20, and 70 and 16% (based on TLC) of the extracted ^{14}C in containers maintained at the 0, 30, and 100 cm depths, respectively. The somewhat higher amount of degradation at the 30 compared to the 100 cm depths was not significantly different (standard deviation values overlapped). Maximum daily temperature fluctions were 10-17, 2-4 , and <0.1 C at soil depths of 0, 30, and 100 cm, respectively. Temperature maxima and minima were, respectively, 38 and 13 C at the surface, 27 and 17 C at the 30 cm depth and 22 and 20 C at the 100 cm depth over the 56-day experiment. It is not known if these temperature differences, particularly at the surface compared to the 30 and 100 cm depths, affected degradation. However, the surface temperatures apparently did not affect the 0 cm treatments since degradation rate in a control set of solutions maintained in the lab at 20 C (data not shown) was identical to the degradation rate in the field. The substantial loss of alachlor at the 30 and 100 cm depths compared to the 0 cm depth suggest that some form of microbial enhancement from the surrounding soil (treatments were open to and in equilibrium with the soil atmosphere) may have

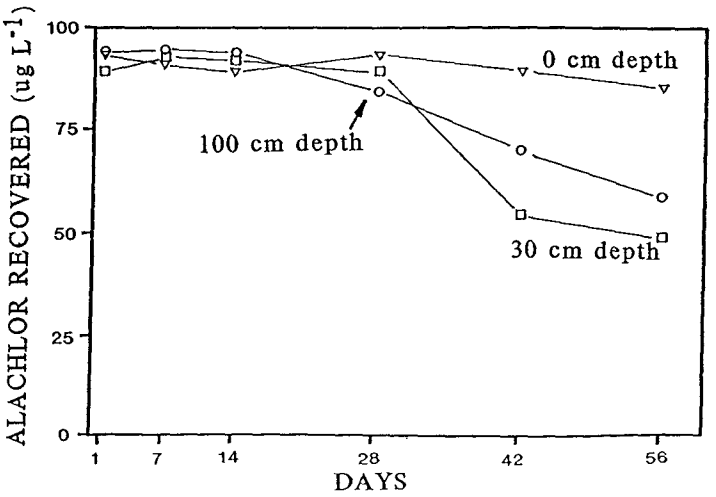

Figure 2. Recovery of ^{14}C - alachlor from groundwater exposed to in situ subsurface conditions. Standard deviation values for the 0, 30, and 100 cm depths were 3, 13, and 17 (Day 42) and 1, 12, and 23 (Day 56), respectively. Values for all other dates were < 4.

occurred. However, overall degradation rate was much lower than found in soil (Beestman and Deming 1974).

The field experiment indicated that some dissipation of alachlor (in a groundwater solution) occurs in the vadose zone, but the mechanism of loss was unclear. A laboratory experiment was therefore conducted to evaluate alachlor dissipation under more controlled conditions.

The effect of oxygen level and soil on the degradation of alachlor in groundwater solutions is shown in Figure 3. Alachlor degraded much more rapidly when in contact with topsoil compared to subsoil. Oxygen level (air vs nitrogen atmosphere) did not affect the overall degradation rate. The estimated half-life of alachlor (if a first order degradation is assumed) was about 10 and 200 days for the topsoil and subsoil treatments, respectively. Alachlor degradation rate in the topsoil was nearly identical to the reported half-life under field conditions (Beestman and Deming 1974, Zimdahl and Clark 1982), but was considerably longer in the subsoil than the 60 day half-life reported for aquifer material (Novich et al. 1986). No degradation occurred in the no-soil treatments or in a sterile surface soil treatment (data not shown for sterile control). The lack of degradation in both the no-soil and sterile topsoil treatments indicate that the microbial population in the soil rather than in the groundwater was responsible for alachlor degradation.

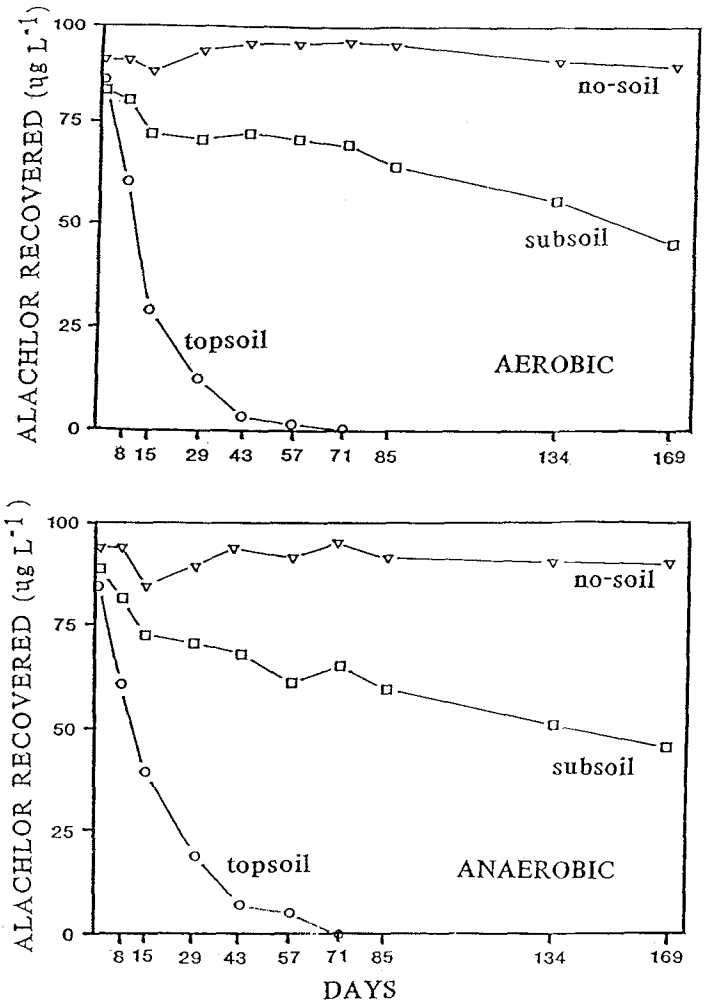

Figure 3. Effect of soil on the degradation of ^{14}C - alachlor in groundwater solutions under aerobic or anaerobic (N_2 - atmosphere) conditions. Standard deviation values for all dates and treatments were < 7.

The topsoil treatments were terminated after 71 days (because all of the alachlor was degraded to polar metabolites) and the subsoil and no-soil treatments after 169 days. Total recovery of ^{14}C in water and soil was determined (Table 1). While oxygen level (air vs nitrogen atmosphere) did not affect the overall degradation rate, relative distribution of ^{14}C between water and soil was affected. About 66 and 49% of the radioactivity added at the start of the experiment was recovered (in water) in the topsoil-air and topsoil-N_2 treatments, respectively. Most of the difference is accounted for by the increased amount of ^{14}C bound to soil under the N_2 atmosphere. The reason for this increase is between the two oxygen levels. A metabolite chromatographically

Table 1. Distribution of ^{14}C-alachlor between groundwater and soil after 169 days[a]

Treatment Atmosphere	Soil	^{14}C Recovered (%)[b]			
		H_2O	Soil Extracted[d]	Bound[e]	Total
N_2	Top	48.7[c]	9.8	28.9	87.4
N_2	Sub	76.8	13.7	5.4	95.9
N_2	None	96.7	--	--	96.7
Air	Top	66.3	7.1	14.2	92.6
Air	Sub	77.3	13.8	4.6	95.7
Air	None	95.4	--	--	95.4

[a] Top-soil treatments terminated after 71 days; sub and no soil treatment after 169 days.
[b] Expressed as % of ^{14}C-alachlor added at the start of the experiment.
[c] Average of three replications.
[d] ^{14}C-extracted with acetonitrile.
[e] ^{14}C-remaining in soil after extraction.

identical to hydroxyalachlor accounted for about 8 and 4% of the ^{14}C extracted from water (for all samplings) under the N_2 and air atmospheres, respectively (data not shown). The hydroxyalachlor unknown, but may reflect differences in metabolite formation may be more strongly adsorbed to soil than the polar metabolites. Oxygen level did not affect overall distribution of ^{14}C in the subsoil treatments as indicated by the near identical amounts of ^{14}C in water and soil between the subsoil-air and subsoil-N_2 treatments. However, there was again about twice as much hydroxyalachlor present in solutions exposed to N_2 as air throughout the sampling period (Day 15-169). Much less ^{14}C was bound to the subsoil than topsoil, which would be expected since the subsoil contained 1/10 as much organic carbon as topsoil.

The results of this study indicate that alachlor, in a groundwater solution exposed to in situ or simulated subsoil conditions, undergoes nearly no degradation unless a biologically active soil is also present. The microbial population in the groundwater apparently did not contain microbes capable of degrading alachlor. Oxygen level had very little effect on overall degradation rate, but appears to have a minor effect on metabolite formation. The implication of these results is that if alachlor is leached below the root zone then its persistence and potential for groundwater contamination will be increased.

Acknowledgments. The author thanks Monsanto Company for the generous gift of ^{14}C-labled alachlor and T. Nelson for his valuable assistance.

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Received July 16, 1990; accepted October 1, 1990.