

# Alachlor Dissipation in Soil As Influenced by Formulation and Soil Moisture

Michèle Nègre,\*† Mara Gennari,† Emanuele Raimondo,† Luisella Celi,† Marco Trevisan,† and Ettore Capri†

Dipartimento di Valorizzazione e Protezione delle Risorse Agroforestali, Sezione Chimica Agraria, Università degli Studi di Torino, Via Pietro Giuria 15, 10126 Torino, Italy, and Istituto di Chimica Agraria ed Ambientale, Facoltà di Agraria, Università Cattolica del Sacro Cuore di Piacenza, Via Emilia Parmense, 29100 Piacenza, Italy

The persistence of alachlor applied as pure active ingredient (ALA), emulsifiable concentrate formulation (Lasso EC), and two microencapsulated formulations (Lasso ME and Chloral ME) in a clay loam soil was examined under laboratory standard conditions at 25 °C, at various moisture levels. The order of persistence of alachlor was as follows: Lasso ME > Chloral ME > Lasso EC > ALA at 50 and 75% of field moisture capacity (FMC) and Lasso ME > Lasso EC > Chloral ME > ALA at 25% of FMC. The half-life of ALA increased from 5 to 13 days with decreasing moisture percent. The rates of degradation of Lasso EC were about the same at 50 and 75% of FMC ( $t_{1/2}$  = 10 and 9 days), whereas it was much lower at 25% of FMC ( $t_{1/2}$  = 38 days). In contrast, both microencapsulated formulations were more persistent at high moisture levels ( $t_{1/2}$  > 56 days), while at 25% of FMC the half-life was 49 days for Lasso ME and 34 days for Chloral ME. Field experiments on the persistence of Lasso ME indicated that alachlor concentration was <25% of the initial dose 18 days after application. No alachlor was detectable below a 10-cm depth. Alachlor was detected in soil solution and gravitational water up to a 60-cm depth but at very low concentrations (1.13 and 0.22 µg/L).

## INTRODUCTION

Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide] is an acetanilide preemergence herbicide that controls a large spectrum of weeds by altering protein synthesis. It is used in a wide variety of crops, including corn, soybeans, rice, peanuts, and potatoes. Commercial formulations are granular, emulsifiable concentrates, and microencapsulated. The microencapsulated formulation has been developed to improve safety in handling and minimize environmental contamination (Marrs and Seaman, 1978; McFarlane and Pedley, 1978; Meghir, 1984). Microencapsulation has been recently used for alachlor.

The environmental fate of alachlor has been largely reviewed by Chesters et al. (1989) and Sharp (1988). Alachlor degradation in soil appears to be mainly mediated by aerobic microorganisms, though just a small part of the applied product is mineralized. Several metabolites have been identified which are probably strongly bound to soil components. Half-lives of alachlor applied as pure ingredient or as emulsifiable concentrate in laboratory experiments are in the range of 6-43 days and are strongly influenced by soil type, temperature, and moisture (Beestman and Deming, 1974; Walker and Brown, 1985; Zimdahl and Clark, 1982; Pothuluri et al., 1990; Jones et al., 1990). Microencapsulation has been observed to increase the persistence of alachlor in soil (Petersen et al., 1988; Huang and Ahrens, 1990).

However, most of the studies of alachlor degradation in soil concern the pure active ingredient or the emulsifiable concentrate; there is little information on the influence of the microencapsulation on the persistence of the herbicide. The objectives of this study were to compare the degradation rate of alachlor applied to soil as pure ingredient (ALA), emulsifiable concentrate formulation (Lasso EC),

and two types of microencapsulated formulations (Lasso ME and Chloral ME) under laboratory controlled conditions; to determine the effect of soil moisture level on alachlor dissipation in each formulation; and to compare the persistence of Lasso ME under field and laboratory conditions.

## MATERIALS AND METHODS

**Chemicals.** Alachlor (99.3% pure) was from Erhenstorfer (Ausborg, D). Alachlor emulsifiable concentrate (48% ai) (Lasso) was from Monsanto. Alachlor microencapsulated (43.2% ai) (Lasso Microtech) was from Monsanto, and alachlor microencapsulated (41.5% ai) (Chloral) was from Du Pont. All other chemicals were of analytical reagent or HPLC grade.

**Soil.** The Tencara clay loam soil was used for both field and laboratory studies. It contained 30% clay and had a cation-exchange capacity of 16.7 mequiv/100 g. The organic matter content was 1.5%, the pH in water was 8.1, and the field moisture capacity (FMC) was 43.5% of the dry weight.

The soil used for laboratory experiments was sampled to a depth of 0-25 cm, dried to 10% water content (w/w), sieved to obtain a <2-mm fraction, and stored at room temperature in black PVC bags.

**Laboratory Studies. Incubation Conditions.** The soil was incubated in closed systems based on that described by Laskowsky et al. (1983). Each incubation system consists of a two-compartment apparatus. The soil sample (50 g dry weight) was placed in the first compartment, and 75 mL of 0.5 N NaOH was placed in the second one to trap the carbon dioxide produced by the respiratory process. The systems were connected to an oxygen supply to replace the oxygen consumed.

Alachlor was added to soil at 5 µg/g as aqueous solution, emulsion, or suspension. Soil moisture was adjusted to 25, 50, and 75% of field moisture capacity (FMC). The closed systems maintain the desired soil moisture throughout the experiment (Gennari et al., 1986). Incubation was conducted in the dark at 25 °C. Three individual incubation systems were removed at 0, 1, 3, 7, 14, 28, and 56 days for alachlor and CO<sub>2</sub> determination.

**Alachlor Extraction.** The soil samples were transferred to 250-mL polyethylene bottles and extracted twice with 50 mL of ethanol. After centrifuging, the combining extracts were filtered

† Università degli Studi di Torino.

† Università Cattolica del Sacro Cuore di Piacenza.

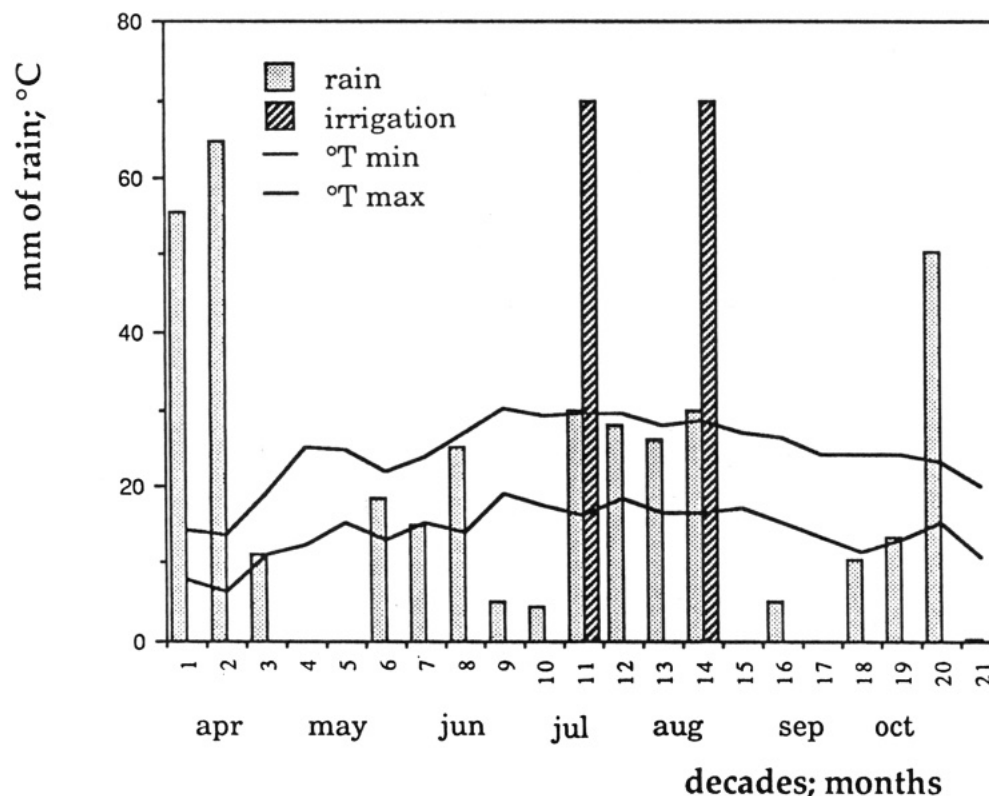


Figure 1. Climatic data for the period April–September 1990.

and evaporated on a rotary evaporator at 30 °C to remove the ethanol. The remaining aqueous solution was diluted to 10 mL with a solution of acetonitrile–water 8:2 (v/v), filtered through a 0.45- $\mu$ m filter, and analyzed by HPLC.

**HPLC Analysis.** Analyses of sample extracts were conducted by utilizing a Varian 5000 HPLC equipped with a variable-wavelength detector (Varian UV 100) set at 220 nm and a 10- $\mu$ L Rheodyne valve injector. The mobile phase was water–acetonitrile (20:80 v/v ratio) at a flow rate of 1 mL/min. The column was a C<sub>18</sub> (Merck Lichrospher 100 RP-18, 10  $\mu$ m, 25 cm  $\times$  4 mm).

Recoveries were 76.2  $\pm$  4.6, 77.9  $\pm$  3.3, 76.0  $\pm$  2.8, and 64.5  $\pm$  4.9% for ALA, Lasso EC, Lasso ME, and Chloral ME, respectively. The lower limit of detectability in the soil was 0.02 mg/kg (signal-to-noise 2:1).

**CO<sub>2</sub> Determination.** The concentration of CO<sub>2</sub> in the incubation systems was determined by titration with 0.5 N HCl using an automated titrator (Radiometer TTT 85, Copenhagen).

**Field Studies.** These studies were conducted in 1990. The experimental field was divided in three 250-m<sup>2</sup> plots. Lasso ME at 3.87 kg of ai/ha was preemergence applied on May 7 without mixing with other herbicides, following Good Field Practices (GI-FAP, 1977; IUPAC, 1988). The treatments were carried out by using a tractor-mounted sprayer calibrated to distribute 220 L/ha of water. Soybeans (Rosada variety) were planted on May 5, and the plant density was about 90 plants/m<sup>2</sup> (22.5  $\times$  5 cm). The field was irrigated by dispersion on July 15 and August 17. The crop was harvested on September 29. Figure 1 shows climatic data for the period April–September 1990. The irrigations were considered equivalent to 70 mm of rain and added to the measured rainfall.

**Soil Sampling.** Five soil cores (length 50 cm, diameter 5.8 cm) were taken by means of a continuous sampling tube, which fits within an electrical hollow-stem auger column, 18, 42, 74, and 157 days after the treatment. The cores were cut into three sections corresponding to 0–10, 20–30, and 40–50 cm of depth. Samples for each plot were mixed, sieved through a 5-mm mesh sieve, and immediately frozen at –20 °C until analysis. The moisture content of the samples was determined before analysis.

**Water Sampling.** In each plot four water samplers were installed at 30- and 60-cm depths. These suction samplers were used to collect the soil solution flowing in the unsaturated zone, under a negative pressure of between 40 and 80 cbar. The samples

collected at the same depth for each plot were mixed to obtain the final sample for examination.

A free drainage type lysimeter was set up in the middle of the experimental field to collect gravitational water when the precipitation exceeded the FMC requirements or when there was a large water input to the soil (Deviny et al., 1990). The gravitational water was removed for analysis after the irrigations and the main rainfalls.

**Alachlor Extraction.** Alachlor residues in soil samples were extracted with acetone following the method reported by Del Re et al. (1991). Alachlor residues in water were extracted by solid-phase extraction on an SPE C<sub>18</sub> column (Baker) (Trevisan et al., 1991).

**GLC Analysis.** A Dani Model 3800 gas chromatograph equipped with a NPD detector, a PTV injector, and an autosampler set to inject 2  $\mu$ L was used. The column was a Supelco Sup-Herb wide-bore capillary column. The oven temperature was 60 °C for 1 min, raised to 280 °C at 16 °C/min. The carrier gas was helium at a flow rate of 5 mL/min. The detection limit was 2  $\mu$ g/kg in soil and 0.01  $\mu$ g/L in water. The mean recoveries were 95 and 85% for soil and water, respectively.

## RESULTS AND DISCUSSION

**Laboratory Studies.** The order of persistence of alachlor was Lasso ME > Chloral ME > Lasso EC > ALA at 50 and 75% of FMC and Lasso ME > Lasso EC > Chloral ME > ALA at 25% of FMC (Figures 2–4).

The degradation of ALA and Lasso EC was a first-order reaction at all moistures levels (Table I). The half-lives of ALA increased from 5 to 13 days proportionally with decreasing moisture percent ( $R^2 = 0.962$ ) and are consistent with those obtained by Beestman and Deming (1974) in a silty clay soil. The rates of degradation of Lasso EC were similar at 50 and 75% of FMC (half-life = 10 and 9 days), whereas it was much lower at 25% of FMC (half-life = 38 days). Similar results were obtained by Walker and Brown (1985) in a sandy loam soil and by Zimdahl and Clark (1982) in a clay loam soil. At 25% of FMC, Lasso EC was much more persistent than ALA. These

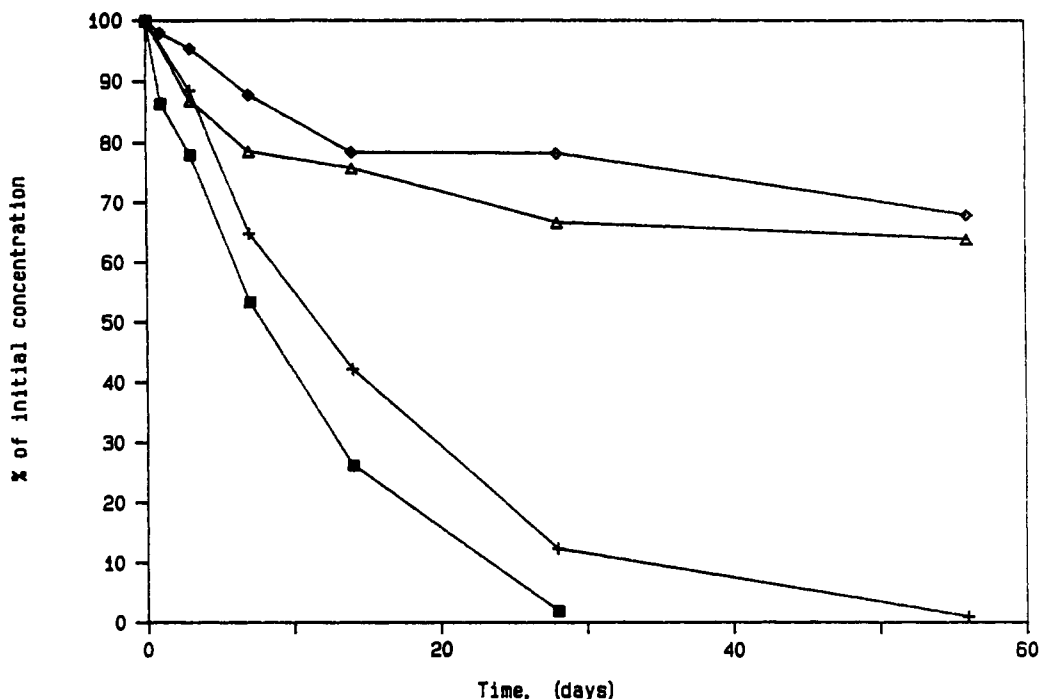


Figure 2. Degradation of ALA (■), Lasso EC (+), Lasso ME (◇), and Chloral ME (△) in soil at 75% of field moisture capacity. (Average from triplicate samples. Standard deviation <6%.)

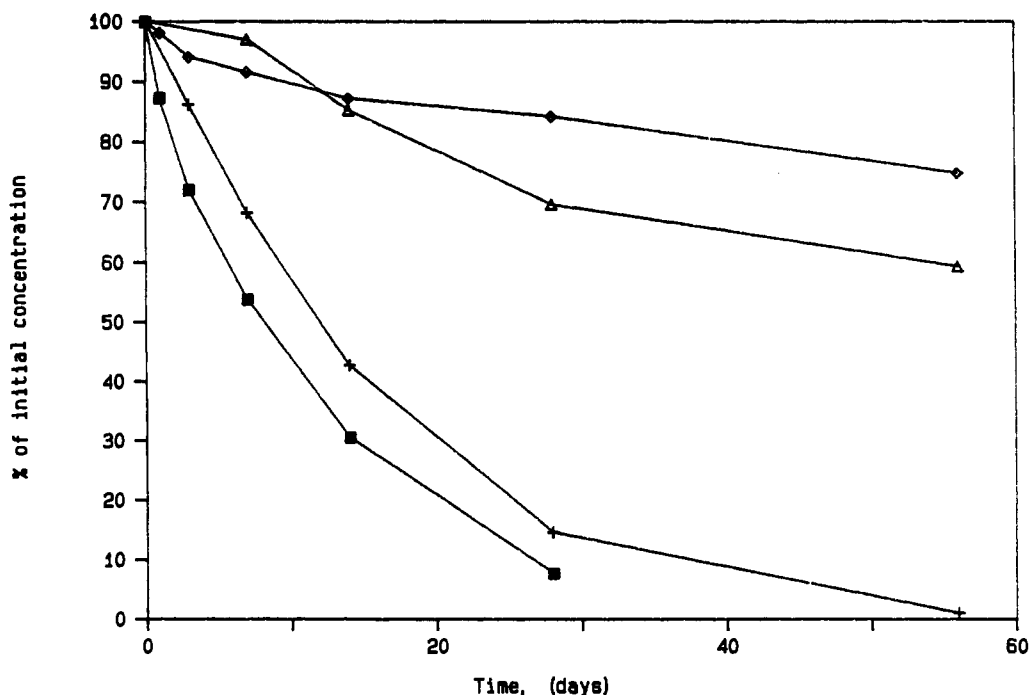


Figure 3. Degradation of ALA (■), Lasso EC (+), Lasso ME (◇), and Chloral ME (△) in soil at 50% of field moisture capacity. (Average from triplicate samples. Standard deviation <6%.)

results suggest that at low moisture level the coformulants affect the microbial activity mainly responsible for alachlor degradation.

In contrast, both microencapsulated herbicide formulations were more persistent at high moisture levels: at 75 and 50% of FMC, the half-life exceeded 56 days, while at 25% of FMC the degradation was much faster (half-life = 49 days for Lasso ME and 34 days for Chloral ME) and followed a first-order kinetics. The reason for these results is that only the small fraction of pesticide that is constantly released by the capsule is exposed to environmental action and the release does not occur as long as water surrounds the capsule (Meghir, 1984). These results are only in

partial agreement with those obtained by Petersen et al. (1988) in a silty clay loam soil, who found that the half-life of the microencapsulated alachlor exceeded 56 days at 15 and 33% (w/w) moisture content. It is possible that the soil moisture contents considered by Petersen were not low enough to promote the sufficient release of the active ingredient from the capsule and the consequent increasing of the degradation rate observed in our experiment at 25% of FMC.

Differences in the characteristics of the polymer membrane of the capsule could be responsible for the increased persistence of Lasso ME as compared to that of Chloral ME. For example, as observed by Meghir (1984), in the

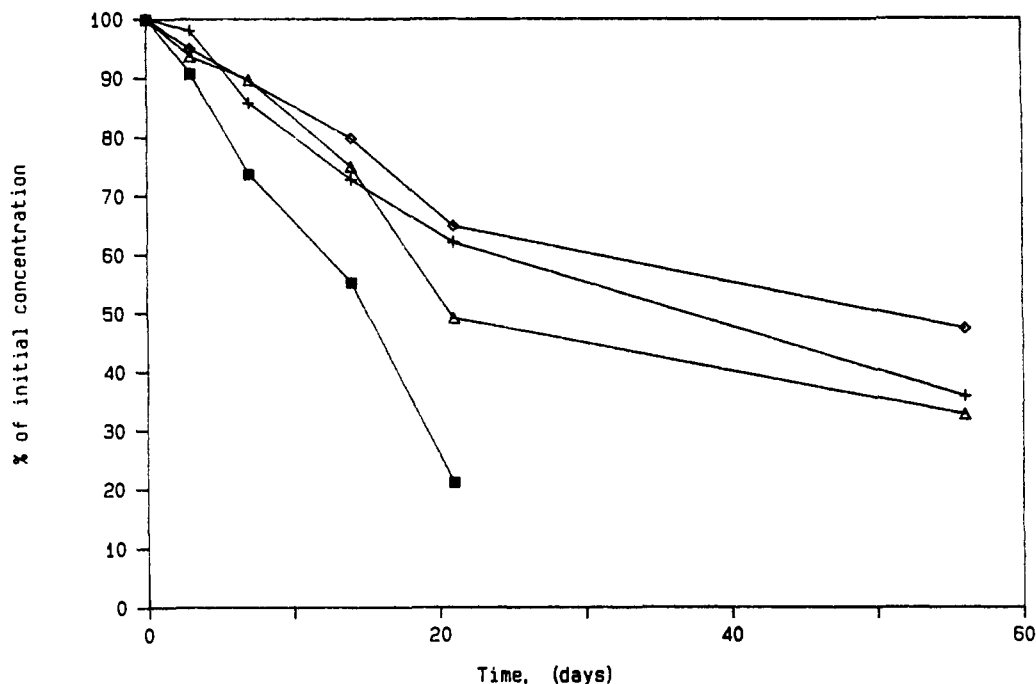


Figure 4. Degradation of ALA (■), Lasso EC (+), Lasso ME (◇), and Chloral ME (△) in soil at 25% of field moisture capacity. (Average from triplicate samples. Standard deviation <6%.)

Table I. Half-Life of Alachlor in Various Conditions Calculated from First-Order Kinetics Equations ( $n = 18$ ,  $P < 0.01$ )

formulation	% of field capacity	$t_{1/2}$ , days	$R^2$
ALA	75	5	0.9710
	50	8	0.9936
	25	13	0.9703
Lasso EC	75	9	0.9831
	50	10	0.9920
	25	38	0.9843
Lasso ME	75	>56	<i>a</i>
	50	>56	<i>a</i>
	25	49	0.9691
Chloral ME	75	>56	<i>a</i>
	50	>56	<i>a</i>
	25	34	0.9575

<sup>a</sup> Non-first-order kinetics.

Table II. Alachlor Residues in Soil at Various Depths

days after application	alachlor concn, $\mu\text{g}/\text{kg}$					% of initial concn <sup>a</sup> at 0-10 cm		
	0-10 cm			20-30 cm	40-50 cm	plot 1	plot 2	plot 3
	plot 1	plot 2	plot 3					
18	486	522	422	ND <sup>b</sup>	ND	23.6	25.3	20.5
42	321	268	123	ND	ND	15.6	13.0	6.0
74	50	42	49	ND	ND	2.4	2.0	2.4
157	21	8	12	ND	ND	1.0	0.4	0.6

<sup>a</sup> The initial concentration was calculated by taking into account the amount distributed ( $38.7 \mu\text{g}/\text{cm}$ ) and the apparent density of the soil ( $1.5 \text{ g}/\text{cm}^3$ ). <sup>b</sup> ND, <  $2 \mu\text{g}/\text{kg}$ .

case of the microencapsulated parathion-methyl, the persistence of the pesticide increases by increasing the cross-linking of the polymer.

A similar overall amount of  $\text{CO}_2$  was evolved from the soil contaminated with the different formulations, independent of the moisture level.

**Field Studies.** The results for soil degradation are shown in Table II. No detectable alachlor residues were found in soil samples taken at a depth >10 cm. Other

authors, in field experiments on the pure active ingredient or the emulsifiable concentrate formulation, concluded that leaching does not contribute significantly to the dissipation of alachlor: Beestman and Deming (1974) observed that <1% of the applied herbicide was detected below the upper 4-cm depth in a silty clay soil. Jones et al. (1990) observed that the average depth of detectable alachlor did not exceed 8.4 cm in a sandy loam soil. In contrast, Huang and Ahrens (1991) found residues of alachlor both from emulsifiable and from microencapsulated formulations at the 4-8 in. (10.2-20.3 cm) depth in a sandy loam soil. Furthermore, the results of these authors seem to show that alachlor is less leachable when it is applied as a microencapsulated formulation than when it is used as an emulsifiable concentrate formulation.

Patruno et al. (1990), in studies with soil columns, found that microencapsulated alachlor was less mobile than the emulsifiable concentrate.

Eighteen days after application, alachlor concentration was <25% of the initial dose. These results are consistent with those obtained by Petersen et al. (1988), who observed that most of the field degradation of Lasso ME occurred during the first 10 days after application at 4.5 kg of ai/ha in a silty loam soil.

The degradation rate of Lasso ME was higher than in laboratory experiments, in contrast with results obtained by Walker and Brown (1985) and Zimdahl and Clark (1982) on Lasso EC, which indicated good agreement between laboratory and field experiments. In the case of the microencapsulated herbicide, the succession of dryness and humidity in the field, which induces the opening of the capsules (Petersen and Shea, 1989), is likely to be responsible for the faster degradation of alachlor as compared to that in laboratory experiments, where humidity is constant throughout the experiment.

Alachlor concentration in soil after 157 days ranged from 8 to 21  $\mu\text{g}/\text{kg}$  and was much lower than that observed by Huang and Ahrens (1991) in the soil upper layer 4 months after application (from 71.2 to 207.9  $\mu\text{g}/\text{kg}$  depending on application rate), indicating that the dissipation rate of the microencapsulated alachlor is influenced by soil type

**Table III. Alachlor Residues in Soil Solution and in Gravitational Water**

days after application		alachlor concn, $\mu\text{g/L}$			
		soil solution		gravitational water	
		30 cm	60 cm	30 cm	60 cm
79	plot 1	1.02	1.13	0.32	
	plot 2	0.96	ND <sup>a</sup>		
	plot 3	1.17	ND		
95				0.39	
155				0.38	0.22
183	plot 1	ND	ND	ND	ND
	plot 2	ND	ND		
	plot 3	ND	ND		

<sup>a</sup> ND, <0.01  $\mu\text{g/L}$ .

and climatic conditions. Residues of alachlor in water are reported in Table III. Alachlor was detected in the samples of soil solution and gravitational water up to a 60-cm depth but at very low concentrations (1.13 and 0.22  $\mu\text{g/L}$ , respectively). No alachlor was detected after 183 days in the soil solution or in the gravitational water. The amounts are in the range previously reported by Isensee et al. (1988) for alachlor (0–0.3  $\mu\text{g/L}$ ) in ground water sampled at a 90-cm depth below treated soils and confirm the low vertical mobility and persistence of the herbicide.

#### ACKNOWLEDGMENT

We are grateful to Dott. Gianni Comba for technical assistance. This work was supported by a grant from Regione Piemonte, Assessorato Sanità, P.f. 186.

#### LITERATURE CITED

- Beestman, G. B.; Deming, J. M. Dissipation of acetanilide herbicides from soils. *Agron. J.* 1974, 66, 308–311.
- Chesters, G.; Simsman, G. V.; Levy, J.; Alhajjar, B. J.; Fathulla, R. N.; Harkin, J. M. Environmental fate of alachlor and metolachlor. *Rev. Environ. Contam. Toxicol.* 1989, 110, 1–74.
- Del Re, A. A. M.; Capri, E.; Bergamaschi, E.; Trevisan, M. Herbicide movement and persistence in soil: comparison between experimental data and prediction of a mathematical model. In *Pesticides in soil and water: current perspectives*; Walker, A., Ed.; BCPC Monograph 47; British Crop Protection Council: Coventry, U.K., 1991.
- Devinny, J. S.; Everett, L. G.; Lu, J. C. S.; Stollar, R. L. *Subsurface migration of hazardous wastes*; Environmental Engineering Series; Van Nostrand Reinhold: New York, 1990; p 387.
- Gennari, M.; Cignetti, A.; Nègre, M. Evaluation of a laboratory method to determine the behaviour of pesticides in soil. *Abstracts of Papers*, Sixth International Congress of Pesticide Chemistry, Aug 1986, Ottawa, Canada; pp 6B–20.

- GIFAP. *Guidelines on pesticide residues trials to provide data for the registration of pesticides and the establishment of maximum residue limits*; Technical Monograph; 1977; p 47.
- Huang, Q. L.; Ahrens, J. F. Residues of alachlor in soil after application of controlled release and conventional formulations. *Bull. Environ. Toxicol.* 1990, 47, 362–367.
- Isensee, R. A.; Helling, C. S.; Gish, T. J.; Kearney, P. C.; Coffman, C. B.; Zhuang, W. Ground water residues of atrazine, alachlor and cyanazine under no-tillage practices. *Chemosphere* 1988, 17 (1), 165–174.
- IUPAC. Recommended approach to the evaluation of the environmental behaviour of pesticides. *Pure Appl. Chem.* 1988, 60 (6), 901–932.
- Jones, R. E., Jr.; Banks, P. A.; Radcliffe, D. E. Alachlor and metribuzin movement and dissipation in a soil profile as influenced by soil surface condition. *Weed Sci.* 1990, 35, 589–597.
- Laskowsky, D. A.; Swann, R. L.; MacCall, P. J.; Bidlack, H. D. Soil degradation studies. *Residue Rev.* 1983, 85, 139–147.
- Marrs, G. J.; Seaman, D. Practical considerations in the control of bioavailability. *Pestic. Sci.* 1978, 9, 402–410.
- McFarlane, N. R.; Pedley, J. B. Some fundamental considerations of controlled release. *Pestic. Sci.* 1978, 9, 411–424.
- Meghir, S. Microencapsulation of insecticides by interfacial polycondensation: the benefits and problems. *Pestic. Sci.* 1984, 15, 265–267.
- Patruno, A.; Cavazza, L.; Catizone, P.; Flori, P.; Vitali, G.; Vicari, A. Use of microencapsulated herbicides. *Inf. Agrar.* 1990, 17, 47–50.
- Petersen, B. B.; Shea, P. J. Microencapsulated alachlor and its behaviour on wheat. *Weed Sci.* 1989, 37, 719–723.
- Petersen, B. B.; Shea, P. J.; Wicks, G. A. Acetanilide activity and dissipation as influenced by formulation and wheat stubble. *Weed Sci.* 1988, 36, 243–249.
- Pothuluri, J. V.; Moorman, T. B.; Obenhuber, D. C.; Wauchope, R. D. Aerobic and anaerobic degradation of alachlor in samples from a surface-to-ground water profile. *J. Environ. Qual.* 1990, 19, 525–530.
- Sharp, D. B. Alachlor. In *Herbicide, Chemistry, Degradation and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; Vol. 3, pp 301–333.
- Trevisan, M.; Montepiani, C.; Ragozza, L.; Bartoletti, C.; Del Re, A. A. M. Pesticides in rainfall and water in Italy. *Environ. Pollut.* 1992, submitted for publication.
- Walker, A.; Brown, P. A. The relative persistence in soil of five acetanilide herbicides. *Bull. Environ. Contam. Toxicol.* 1985, 34, 143–149.
- Zimdahl, R. L.; Clark, S. K. Degradation of three acetanilide herbicides in soil. *Weed Sci.* 1982, 30, 545–548.

Received for review November 8, 1991. Accepted February 14, 1992.

Registry No. Alachlor, 15972-60-8.