Bull. Environ. Contam. Toxicol. (1993) 50:506–513

Environmental Contamination and Toxicology

Biodegradation of Liquid and Microencapsulated Formulations of Alachlor in a Clay Loam Soil

Ettore Capri[1] and Allan Walker[2]

[1]Istituto di Chimica Agraria ed Ambientale, Università Cattolica del Sacro Cuore, Facoltà di Agraria, 29100 Piacenza, Italy and [2]Horticulture Research International, Wellesbourne, Warwick CV35 9EF, United Kingdom

Alachlor (2-chloro-N-2,6-diethyl-N-(methoxymethyl) acetanilide) is a herbicide used widely in many countries. It is available mainly as an emulsifiable concentrate formulation, but in recent years it has also been available as a microencapsulated formulation in the USA and Italy. Both formulations are used primarily in pre-emergence and applied to the soil surface. It has been reported that alachlor is degraded mainly by microorganisms in the soil (Sun et al., 1991; Chester et al., 1989) and that the rate of degradation is influenced by temperature and soil moisture content. Walker and Brown (1985) reported that half-lives in a sandy loam soil at 12 % soil moisture varied from 7.5 days at 25 °C to 39 days at 5 °C; and at 25 °C varied from 6 days at 15 % soil moisture content to 23 days at 6 %. The formulation controls the amount of active ingredient available to microorganisms and consequently reduces or promotes degradation rate. Recent studies have demonstrated different behaviour of different formulations in field and laboratory studies (Gennari et al., 1991; Peterson and Shea, 1989; Peyton et al., 1988).

The present experiments were done to gain further information on the effects of alachlor formulation on its degradation rate in an Italian soil. Rates of degradation were compared under different incubation conditions in the laboratory. Detailed studies were done of the effects of temperature, soil moisture and the depth in the soil profile on rates of loss under laboratory conditions.

MATERIALS AND METHODS

The soils used were from Tencara (45.11 N, 9.47 E; Cremona - Italy) and samples were collected from the 0-20 and 30-50 cm horizons of profile pits at two different positions in the field. The chemical and physical properties were determined using standard techniques of analysis (Società Italiana Scienza del Suolo, 1985); microbial biomass - was measured using the Jenkinson and Poulson method (1976) where the proportion of fumigated organisms was taken as 0.41

Send reprint request to Ettore Capri at the above address.

(Anderson and Domsch, 1978; Lynch and Panting, 1980). Soil moisture contents at applied pressures of 0.05, 0.33, 2 and 15 bar, were determined with a pressure membrane apparatus. The soil when collected was sieved immediately (3 mm mesh) and then stored for about 10 days at low temperature and humidity, until the incubation experiments had been prepared.

The herbicides used were: 1) a commercial emulsifiable concentrate formulation of alachlor (48% AI); 2) a commercial microencapsulated formulation (43% AI); 3) analytical grade alachlor (British Greyhound Ltd, Birkenhead).

For each treatment a suspension of the herbicide in water was added to eight separate 1-kg amounts of fresh soil, to give an initial concentration of 8.0 mg/kg of dry soil. Further water was added to adjust soil moisture content to a nominal value of 19.24 (top soil) or 19.44 % w/w (subsoil). Samples of soil (500 g) were transferred to loosely-capped polypropylene containers (800 ml capacity) while soil moisture contents corresponding with those required (Table 1) were obtained by adding of water. When lower soil moisture contents were required, the soils were spread in trays on the laboratory bench until sufficient water had evaporated. The samples were incubated at constant temperatures of 15, 20, 25 and 30 °C for the samples at soil moisture corresponding to 0.33 bar, and at 25 °C only for the samples at soil moisture corresponding to 0.05, 2 and 15 bar. Soil moisture contents were maintained by the addition of water followed by shaking as necessary. The soils were sampled at intervals during the subsequent 47 days, when 40 g were removed and analyzed immediately. To extract alachlor residues, 40 g from the laboratory samples were shaken with acetone (50 ml) for 1 hr on a wrist action shaker. The soil was allowed to settle, and the concentrations of the herbicide in the clear supernatant were measured by glc. All samples were analyzed using an Analytical Instruments model 93 gas liquid chromatograph with nitrogen flame ionisation detector. A glass column (1.5 m x 3 mm i.d.) packed with 5 % OV-1 was used and the operating temperatures of injection port, column and detector were 225, 220 and 235 °C respectively.

RESULTS AND DISCUSSION

Tencara soil from the 0-20 cm depth was similar to that at 30-50 cm in terms of chemical and physical properties (Table 1). However there was a small difference in degradation rate (Table 2) with faster degradation in the subsoil then in the topsoil by a factor varying from 1.1 to 1.5.

Temperature had a pronounced effect on degradation with an accelerated loss at higher temperature (Table 2). When the incubation temperature was varied from 15 to 30 °C (the extremes used in this experiment), the half-life decreased from 32.5 days to 6.7 days for the

Table 1. Chemical and physical characteristics of the soil used.

Properties		Depth (cm) 0 - 30	30 - 50
Sand	(%)	21.7	21.9
Silt	(%)	48.3	46.7
Clay	(%)	30.0	31.4
Texture Class		Clay Loam	Clay Loam
pH		7.9	7.8
Organic Matter	(%)	2.3	2.2
C.E.C.	(meq/100 g)	20.3	19.9
Soil Moisture Content	(% w/w) at:		
	0.05 bar	27.03	32.04
	0.33 bar	22.17	22.68
	2.00 bar	19.24	19.44
	15.00 bar	15.16	15.55
Microbial Biomass	(mgC/kg)	298	341

top soil and from 28.1 to 4.7 days in the sub soil. An increase in temperature of 5 °C reduced the half-life by a factor of between 1.3 and 1.9, with the greatest difference resulting from a change in temperature from 15 to 20 °C. Walker and Brown (1985) reported that increasing the temperature by 10 °C between 5 and 25 °C with 12 % soil moisture, reduced the half-life by a factor of 2.2-2.3. The present results are slightly different, giving a factor of 3.6 with a temperature increase from 15 to 25 °C.

Temperature effects on degradation of herbicides are often characterised by the Arrhenius equation (Walker, 1978; Hurle and Walker, 1980; Walker and Brown, 1985). The fit of the Arrhenius equation to the present data was derived by linear regression analysis of the logarithm of the half-life against the reciprocal of the absolute temperature: the regression coefficients were 0.935 for the topsoil, and 0.981 for the sub soil; both were statistically significant ($P < 0.001$). The mean activation energy derived from the fit of the Arrhenius equation was 78.28 KJ/mol for the topsoil and 83.16 KJ/mol for the sub soil. The values are somewhat higher than those of 57.0 and 70.6 KJ/mole reported previously by Walker and Brown (1985) and Moon and Walker (1991).

Soil moisture content also affected the degradation of alachlor with slower rates of loss in drier soil. Half-lives at different soil moisture contents are shown in Table 2. A change in soil moisture from 27.0 % (0.05 bar) to 15.5 % (15 bar) decreased the half-life by a factor between 2.3 and 2.5. In previous experiments (Walker, 1978; Walker and Brown 1985), the effects of moisture on herbicide degradation rates were characterized using the empirical equation $H = A \times M^{-B}$ in which

Table 2. Half-life ($t_{1/2}$) coefficient of determination (R^2) and degradation rate (K_{deg}) of alachlor in soil.

Treatment		LIQUID						MICROENCAPSULATED		
		Top Soil			Sub Soil			Top Soil		
(°C)	(bar)	$t_{1/2}$ (days)	R^2	K_{deg} (days^{-1})	$t_{1/2}$ (days)	R^2	K_{deg} (days^{-1})	$t_{1/2}$ (days)	R^2	K_{deg} (days^{-1})
15	0.33	32.5	0.94	0.0214	28.1	0.93	0.0255			
20	0.33	16.7	0.98	0.0430	12.6	0.97	0.0558			
25	0.05	7.9	0.98	0.0893	6.1	0.99	0.1155			
25	0.33	9.0	0.96	0.0773	8.4	0.98	0.0834			
25	2	11.9	0.99	0.0598	9.5	0.99	0.0732			
25	15	20.1	0.98	0.0352	14.0	0.99	0.0499	43.3	0.97	0.0098
30	0.33	6.7	0.99	0.1080	4.7	1.00	0.1488	71.4	0.87	0.0160

Degradation parameters are calculated only where there was close correspondence to first-order reaction kinetics. The values are means of two replicates.

H is the half-life at moisture content M, A and B are constants. The slope of the line (B) gives a measure of the moisture dependence of degradation and the values of B derived from the fit of the empirical equation ($R^2 = 0.92\text{-}0.94$; $P < 0.001$) were 1.65 for the top soil and 1.13 for the sub soil. The values were similar to that of 1.42 reported previously by Walker and Brown (1985) and 1.47, by Moon and Walker (1991). The values of the constant A were 1836 and 292, for the top soil and sub soil respectively.

Predictions of half-lives using the Arrhenius equation and the empirical moisture relationship indicate further the usefulness of these equations and the particulary strong association of alachlor degradation with soil temperature (Figure 2).

The other main comparison is between formulations. There is evidence that alachlor in liquid formulation degrades more rapidly than alachlor in micro-encapsulated formulation. Half-lives of alachlor in liquid formulation at temperatures of 15-20-25 and 30 °C (0.33 bar) were 32.5-16.7-9.0-6.7 days respectively (Table 2). Alachlor in the microencapsulated formulation was still present in large amounts at the sampling time of 47 days following treatment (71, 66, 62 and 55 % of the initial amount respectively at 15, 20, 25 and 30 °C). Identical behaviour was found at different soil moisture levels where alachlor liquid formulation showed half-lives of 7.9, 9.0, 11.9 and 20.1 days respectively at 0.05, 0.33, 2 and 15 bar pressure (25 °C) while alachlor residues from the microencapsulated formulation after 47 days still represented 59.6, 62.1, 58.3 and 42.2 % of the initial amount.

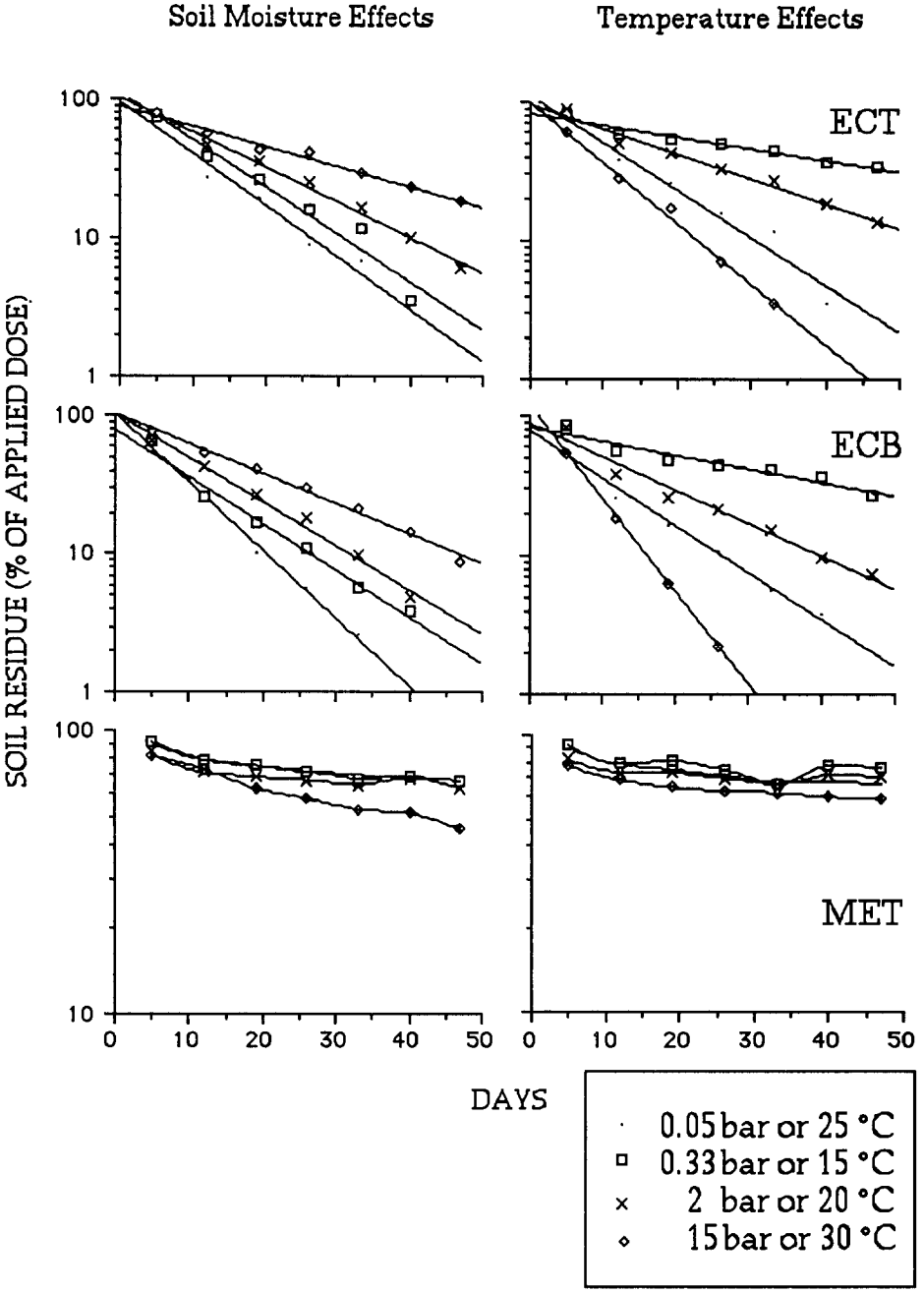

Figure 1. Comparison of the temperature and soil moisture effects on degradation rates of alachlor in soil treated with liquid formulation (ECT top and ECB sub soil) and with microencapsulated formulation (MET top soil only). Values are the mean of the two replicates.

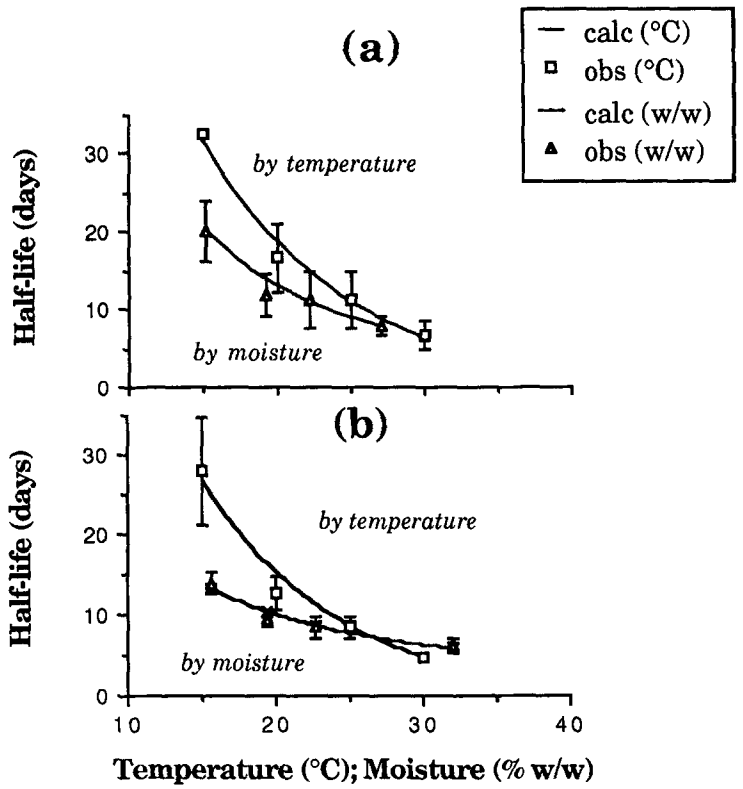

Figure 2. Comparison between half-lives observed and calculated for (a) top soil and (b) sub soil. The bars are standard deviations from the mean of two replicates.

These results agree with those of Petersen et al. (1988), who reported that more than 75 % of the alachlor remained in the microencapsulated formulation after 56 days at 15 °C and 15 % soil moisture. They also reported a half-life greater than 56 days at 24 °C and 33 % soil moisture.

When microencapsulated, alachlor was always more persistent and the rate of loss was less influenced by temperature and soil moisture than in the liquid formulation.The results also indicate that there was more degradation of the microencapsulated formulation at the higher temperature and under drier soil conditions where the percentages of the initial amount remaining after 47 days were 42.2 and 55.4 % respectively (Fig 1). Only in these cases was it possible to calculate a first-order half-life from the appropriate linear regression (Table 2). This unusual behaviour in dry conditions is not consistent with the diffusion process that is assumed to be the main mechanism of active ingredient release from the capsule (Petersen and Shea, 1989). On the other hand, Peyton et al. (1988) found that in air-dry soil the activity of

microencapsulated alachlor was enhanced, while no effect was seen on that of alachlor in liquid formulation. These observations suggest an influence of moisture content on breakdown of the microcapsule walls.

The results of these experiments confirm that soil moisture exerts a strong influence on the rate of alachlor degradation especially when it is in liquid formulation. The effects of temperature, expressed by activation energy equation, which includes both chemical and biological reactions, are also proportionally significant. Microencapsulated formulation of alachlor can have a marked effect on the rates of degradation in soil by decreasing the amount of active ingredient available for environmental factors but dry soil and high temperature seem enhancing the degradation rates. Further studies are required to examine the underlying mechanism involved.

Acknowledgement. Ettore Capri thanks the Crop Protection Department of HRI, Wellesbourne, for the facilities to carry out this work.

REFERENCES

Anderson J P, Domsch K H (1978) Mineralization of bacteria and fungi in chloroform-fumigated soil. Soil Biol Biochem 10: 207-213.

Chesters G, Simsiman G V, Levy J, Alhajjar B J, Fathulla R N, Harkin J M (1989) Environmental fate of alachlor and metolachlor. Rev Environ Contam Toxicol 110: 1-74.

Gennari M, Negré M, Raimondo E (1991) Degradation of the herbicide alachlor in soil under different conditions. Poster presented at 4th International Workshop Chemical, Biological and Ecotoxicological Behaviour of Pesticides in the Soil Environment. Rome, May 29-31, 1991.

Hurle K, Walker A (1980) Persistence and its prediction. In: Interactions Between Herbicides and the Soil, R.J. Hance (Editor), London: Academic Press, pp 83-122.

Jenkinson D S, Poulson D S (1976) The effects of biocidal treatments on metabolism in soil. V. A method for measuring soil biomass. Soil Biol Biochem 8:209-213.

Lynch J M, Panting L M (1980) Variations in the size of the soil biomass. Soil Biol Biochem 12:547-550.

Moon Y, Walker A (1991) The degradation and mobility of alachlor in a sandy loam soil. In Proceedings 1991 Brighton Crop Protection Conference - Weeds, vol 2, 499-506.

Petersen B B, Shea P J (1989) Microencapsulated alachlor and its behaviour on wheat (Triticum aestivum L) straw. Weed Sci 37: 719-723.

Petersen B B, Shea P J, Wicks G A (1988) Acetanilide activity and dissipation as influenced by formulation and wheat stubble. Weed Sci 36: 243-249.

Peyton J D, Wilson H P, Hantzios K K (1988) Comparative efficacy of two formulations of alachlor and metolachlor. Weed Sci 36: 221-226.
Società Italiana di Scienza del Suolo (1985) Metodi normalizzati di analisi dei suoli. Edagricole, Bologna, pp 185.
Sun H L, Sheets T J, Corbin F T (1990) Trasformation of alachlor by microbial comunities. Weed Sci 38: 416-420.
Walker A (1978) Simulation of the persistence of eight soil-applied herbicides. Weed Res 18: 305-313.
Walker A, Brown P A (1985) The relative persistence of five acetanilide herbicides. Bull Environ Contam Toxicol 34: 143-149.

Received May 24, 1992; accepted October 15, 1992.