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The Relative Persistence in Soil of Five Acetanilide Herbicides

Allan Walker and Pauline A. Brown

National Vegetable Research Station, Wellesbourne,
Warwick CV35 9EF, England

Propachlor (2-chloro-N-isopropylacetanilide) is used as a surface-applied pre-emergence herbicide for weed control in a number of vegetable crops. It is of short persistence in the soil which, under conditions which favour degradation, can lead to an inadequate level of weed control (Walker and Brown 1982). Experiments have been made at the National Vegetable Research Station in England to compare the activity and selective phytotoxicity of a number of other acetanilide herbicides with that of propachlor to determine whether any of them can be used as an alternative treatment (Roberts and Bond 1983). As part of these experiments, measurements were made of the persistence of residues in the soil. Results from comparative persistence experiments with acetanilide herbicides have been reported previously. For example, Beestman and Deming (1974) showed an order of persistence of propachlor<alachlor<butachlor, and Zimdahl and Clark (1982) showed an order of persistence of propachlor<alachlor<metolachlor. The herbicides examined in the present experiments were propachlor, alachlor, dimethachlor, metazachlor and metolachlor. Rates of degradation in soil were compared under different incubation conditions in laboratory experiments, and persistence was measured following application at different times in the field.

MATERIALS AND METHODS

The soil used was a sandy loam containing 70% sand, 19% clay, and 0.65% organic carbon, with pH 6.4. The herbicides were wettable powder or emulsifiable concentrate formulations of propachlor, alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide), dimethachlor (2-chloro-N-(2,6-dimethylphenyl)-N-(2-methoxyethyl)acetamide), metazachlor (2-chloro-N-(1-pyrazolylmethyl)-aceto-2',6'-xylidide) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide) together with analytical grade samples of the different compounds.

A fresh sample of soil was passed through a 2-mm mesh sieve and allowed to air dry for 24 h. A suspension of the commercial formulation of each herbicide in water was incorporated into a separate 3-kg amount of soil to give an initial herbicide concentration of 4.0 mg/kg dry soil. Six 500-g subsamples of each herbicide treatment were transferred to loosely-capped polypropylene bottles. Individual samples for each herbicide were incubated at temperatures of 5, 15 and 25°C with soil moisture at 12% w/w (approximately 75% of water holding capacity), and further samples were incubated at 25°C with soil moisture at 6, 9 and 15% w/w. Full details of the sample preparation methods have been described previously (Walker 1978). Soil moisture levels were maintained by periodic additions of water. All of the treatments were sampled at intervals during the subsequent 35 to 70 days to give a total of seven sampling times per treatment. At the appropriate sampling times, duplicate 30-g amounts of soil were extracted with methanol (50 ml) by shaking for 1 h on a wrist-action shaker, and the concentrations of herbicide in the methanol extracts were determined by gas-liquid chromatography as described previously (Walker et al. 1983a).

Separate field experiments were prepared at adjacent sites on April 24 and June 8 1982. On each occasion, two plots (4 x 1.5 m) were prepared for each herbicide. Alachlor, dimethachlor and metazachlor were applied at a rate equivalent to 1.0 kg a.i./ha, metolachlor was applied at 2.5 kg a.i./ha and propachlor at 4.0 kg a.i./ha. All of the herbicides were applied using a knapsack sprayer in a spray volume of 1000 l/ha. All plots were maintained vegetation-free by occasional hand weeding. On the day of herbicide application, 20 cores (2.5 cm diameter to a depth of 10 cm) were taken from each plot at random positions. The cores from each plot were bulked together, thoroughly mixed by passing several times through a 2-mm sieve and the total weight of sieved soil recorded. The samples were stored at -10°C until analysed. Further soil samples were taken at intervals during the subsequent 50 to 90 days. Herbicide residues in the soils were determined by gas-liquid chromatography as before (Walker et al. 1983a).

RESULTS AND DISCUSSION

The results from the incubation studies are shown in Table 1. It was assumed that degradation of all five herbicides followed first-order kinetics and the data in Table 1 are presented as half-lives. These were derived from the slopes of the lines of best fit calculated by linear regression analysis of the logarithm of the concentrations remaining against time of incubation. For all thirty treatments, the correlation coefficient (r) was greater than 0.95 and was statistically significant at $P=0.001$, suggesting that over the concentration changes examined, the assumption of first-order kinetics was valid.

There were consistent differences between the herbicides in their rates of degradation in the different treatments.

Table 1. First-order half-lives for degradation of five acetanilide herbicides in a sandy loam soil

	Half-life for degradation (days)					
Temperature (^oC)	25	25	25	25	15	5
Moisture (% w/w)	6	9	12	15	12	12
Propachlor	7.7	4.6	4.2	3.7	9.2	21.7
Alachlor	23.0	8.3	7.4	5.7	16.5	38.6
Dimethachlor	21.4	9.8	7.4	5.8	14.4	35.7
Metazachlor	24.2	18.1	13.2	11.6	29.2	77.0
Metolachlor	80.6	41.8	23.9	20.9	47.4	107.8

Propachlor degraded the most rapidly under all of the incubation conditions studied, and metolachlor degraded the least rapidly. The other three herbicides were intermediate in rates of loss with metazachlor somewhat more persistent than alachlor or dimethachlor. In previous experiments, Beestman and Deming (1974) reported half-lives for propachlor and alachlor in a silt loam soil incubated moist at 22°C of 4.4 and 7.8 days respectively; very similar to those recorded at 25°C and 12% soil moisture in the present experiments. Zimdahl and Clark (1982) showed that the half-lives of propachlor, alachlor and metolachlor at 20°C and 80% of field capacity were 3.3, 18.8 and 33.4 days respectively in a sandy loam and 4.1, 11.1 and 15.8 days respectively in a clay loam. These half-lives are again of similar magnitude and in the same relative order as those in Table 1.

The effects of temperature on rates of loss (Table 1) were similar for the different herbicides with an increase in temperature of 10°C reducing the half-life by a factor of between 1.9 and 2.5. Temperature effects on herbicide degradation can often be characterised by the Arrhenius equation (Hurle and Walker 1980), and the Arrhenius activation energies derived from the data in Table 1 are 57.0, 57.0, 54.5, 60.8 and 52.0 kJ/mol respectively for propachlor, alachlor, dimethachlor, metazachlor and metolachlor. These values confirm the similarity in temperature dependence of degradation of the five herbicides. The activation energies derived from the present data are also similar to those reported by Walker and Zimdahl (1981) for metolachlor degradation in other soils.

Soil moisture content also influenced degradation of the different herbicides with slower rates of loss in drier soil. The half-life in soil at 6% moisture was between 2 and 4 times greater than that at 15% moisture (Table 1). In previous experiments, the effects of soil moisture on herbicide degradation rates have been characterised using an empirical equation:

$$H = AM^{-B}$$

where H is the half-life at moisture content M, and A and B are constants (Walker 1978; Walker and Zimdahl 1981). The constant B gives a measure of the moisture dependence of degradation and appropriate values derived from the data in Table 1 are 0.79, 1.46, 1.41, 0.83 and 1.54 for propachlor, alachlor, dimethachlor, metazachlor and metolachlor respectively. These values suggest that degradation of propachlor and metazachlor in this soil was somewhat less dependent on soil moisture than was degradation of the other three compounds. This result is not consistent with that of Zimdahl and Clark (1982) who showed that the rate of propachlor degradation in two different soils was considerably more sensitive to fluctuations in soil moisture level than was the rate of degradation of either alachlor or metolachlor. Similar large variations in the moisture dependence of degradation between different soils were reported by Walker et al. (1983b) in studies of simazine degradation and persistence.

The results from the field experiments are shown in Fig. 1. Data from a previous experiment at the same site which involved measurements of residues of the five herbicides (Walker et al. 1983a) have been included for comparative purposes. All of the data are plotted as percentages of the applied dose recovered from the soil against time after application. There were marked variations in rates of loss between herbicides and between the different times of application. In general, the order of persistence in the field was similar to that observed in the laboratory experiments. Propachlor was the least persistent and the time for 50% loss of the applied dose varied from 10 to 15 days. Metolachlor was the most persistent with the time for 50% loss varying from 40 to 70 days. The other herbicides were intermediate between these extremes with the time for 50% loss varying between 15 and 45 days. When comparing between different times of application, all of the herbicides were least persistent when applied in June 1982. Differences in the rates of residue decline between the other two times of application were small.

Zimdahl and Clark (1982) suggested that rates of degradation of propachlor, alachlor and metolachlor, measured in the laboratory, gave a reliable indication of persistence of these compounds in the field. Half-lives in a clay loam soil incubated at 20°C and 80% of field capacity, for example, were 4.1, 11.1 and 18.1 days for propachlor, alachlor and metolachlor respectively, and similar values derived from a field experiment in summer were 4, 9 and 17 days respectively. Agreement between laboratory and field half-lives in a sandy loam soil was not so

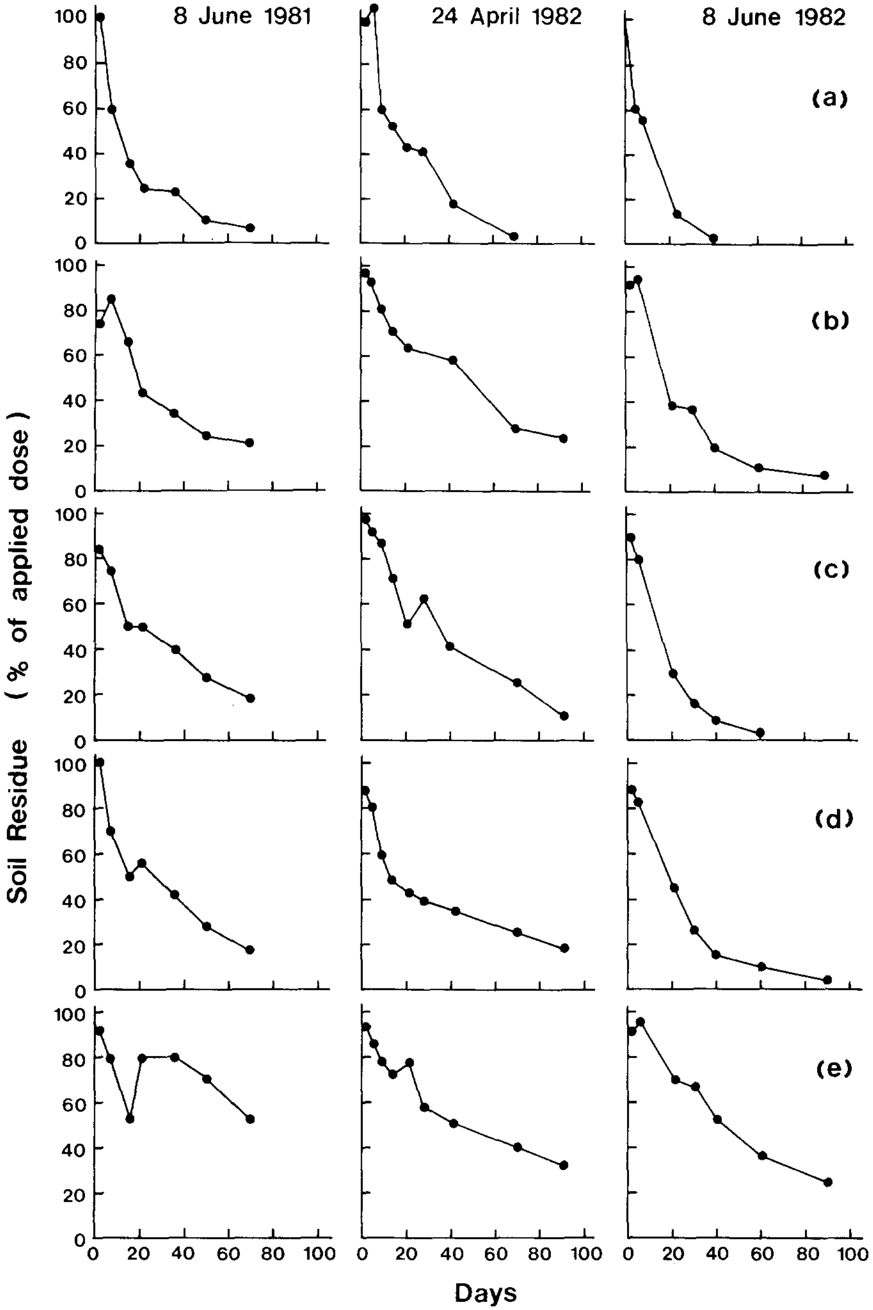

Figure 1. Persistence in soil of (a) propachlor, (b) alachlor, (c) dimethachlor, (d) metazachlor and (e) metolachlor in experiments prepared on 8 June 1981, 24 April 1982 and 8 June 1982

Table 2. Calculated times for 50% loss (DT50, days) and 80% loss (DT80, days) of five acetanilide herbicides in three field experiments.

Herbicide	Time (days) in experiment prepared on:					
	8 June 1981		24 April 1982		8 June 1982	
	DT50	DT80	DT50	DT80	DT50	DT80
Propachlor	12	22	11	20	7	14
Alachlor	24	48	21	37	11	21
Dimethaclor	24	48	21	37	11	21
Metazachlor	35	67	32	58	19	53
Metolachlor	70	165	52	105	39	95

good, but the relative rates of loss in the two situations were still similar. The extent to which the half-life data obtained in the present experiments (Table 1) could be used to predict field persistence of the different herbicides (Fig. 1) was examined using the computer model described by Walker and Barnes (1981). This model uses weather records of air temperature and rainfall to predict the fluctuations in soil temperature and soil moisture content in the field. These data are combined with appropriate constants derived from the laboratory half-lives in order to predict rates of loss and hence persistence in the field. The times for 50% and 80% loss of the different herbicides calculated using the model are shown for the three field experiments in Table 2. The calculated time for 50% loss of propachlor varied from 7 to 12 days, that of metolachlor from 39 to 70 days, and that of the other compounds from 11 to 35 days. These data are in good agreement with those observed. The model also predicted most rapid degradation following application in June 1982 and slowest degradation following application in June 1981, which once more is in general agreement with the observed results (Fig. 1).

The results from these experiments therefore show marked differences between acetanilide herbicides in their soil peristence. With any one compound, there are also differences in rates of loss following application in the field at different times. Their relative persistence can be well defined by measuring rates of degradation under standard laboratory conditions, and when rates of loss are measured at a range of temperatures and soil moisture contents the results can be used in conjunction with weather records to predict persistence in the field.

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