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Measurement and Prediction of Chlorsulfuron Persistence in Soil

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Chlorsulfuron, 2-chloro-N-(((4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino)carbonyl)-benzenesulfonamide, has recently been approved in the United Kingdom for weed control in autumn-sown cereals at rates up to 20 g a.i./ha. It shows good selectivity in cereals and is highly active in the soil against a wide range of broad leaf weeds (PALM et al. 1980). Because of its high soil activity, the time for which chlorsulfuron persists in the soil is of particular importance since this could have implications for the safety of following crops. It has been shown, for example, that growth of some vegetable crops can be reduced significantly at soil concentrations equivalent to less than 0.5 g/ha (WALKER & BROWN 1982). PALM et al. (1980) reported that in the field, the half-life of chlorsulfuron in soil is between 1 and 2 months, and that persistence is strongly influenced by temperature and soil pH. The rate of degradation of most soil-applied herbicides increases with an increase in temperature, and with many compounds, soil moisture is also important in controlling rates of loss (HURLE & WALKER 1980). Because degradation rates are controlled by soil temperature and soil moisture content, persistence of any herbicide will vary from one time of application to another and from site to site. One approach to the evaluation of the variability in herbicide persistence in the field is the use of computer modelling techniques (WALKER 1978; WALKER & BARNES 1981).

The objectives of the present experiments were to measure the influence of soil temperature and soil moisture content on the rate of degradation of chlorsulfuron in the soil, to measure its persistence in the field and, using a mathematical model of persistence, to calculate possible residues of the herbicide in soil following application in different years or at different sites.

EXPERIMENTAL METHODS

The soil used was a sandy loam containing 1.2% organic carbon, 70% sand and 18% clay, with pH 7.1 and water holding capacity of 16.1% (w/w). The herbicide used was a wettable powder formulation of chlorsulfuron (80% a.i.).

Laboratory experiments

A fresh sample of soil was allowed to air dry for 48 h and then thoroughly mixed by passing several times through a 2-mm mesh sieve. Ten separate 500-g quantities of soil containing chlorsulfuron at a concentration of 4 mg/kg dry soil were prepared for incubation using the techniques described in detail previously (WALKER 1978). Duplicate samples were incubated at temperatures of 10, 15, 20, 25 and 30°C and soil moisture content of 12%. The treatments were sampled within 60 min of preparation and then at intervals during the subsequent 82 days. At each sampling time, duplicate 50-g subsamples of soil were extracted with 50 ml methanol plus water (70:30 by volume) by shaking for 1 h on a wrist-action shaker. The samples were allowed to stand until the soil had settled when the concentrations of chlorsulfuron in the clear supernatants were determined by reversed-phase isocratic high-performance liquid chromatography. A stainless steel column (20 cm x 5 mm i.d.) packed with Spherisorb (5 µm)-ODS was used and the elution solvent was methanol plus water (60:40 by volume) at a flow rate of 1.0 ml/min. The herbicide was determined using an Altex-Hitachi variable UV detector at 250 nm, and the retention time was 3.8 min. The limit of detection was 0.05 mg chlorsulfuron/kg dry soil.

The limit of detection of the HPLC method described above was not sufficiently low to detect chlorsulfuron residues in soil following application at realistic rates in the field. Further experiments were therefore made using a bioassay to measure residual concentrations. Five separate 8-kg quantities of air dry soil containing chlorsulfuron at a concentration of 0.04 mg/kg dry soil were prepared for incubation. Samples were incubated at 10, 20 and 30°C with soil moisture at 12%, and further samples were incubated at 20 and 30°C with soil moisture at 6%. Samples of 1 kg soil were removed for bioassay at intervals over 98 days. The bioassay technique used was based on the shoot growth of lettuce and was identical with that described previously by BOND & ROBERTS (1976). The limit of detection was 0.5 µg chlorsulfuron/kg dry soil.

Field experiment

Three replicate field plots (6 x 1.5 m) were sprayed with chlorsulfuron at 30 g a.i./ha on April 23 1981. On the day of herbicide application, 30 cores (2.5 cm diameter to a depth of 10 cm) were taken from each plot at random positions. The cores were bulked separately for each plot, thoroughly mixed by passing several times through a 2-mm mesh sieve and the total weights of sieved soil recorded. The samples were stored at -10°C until analysis. Further soil samples were taken at intervals of approximately 14 days during the subsequent 20 weeks. The herbicide concentrations in the soil were determined using the lettuce shoot growth bioassay of BOND & ROBERTS (1976).

RESULTS AND DISCUSSION

Examples of the results obtained in the laboratory incubation experiments are shown in Fig. 1. These data are from the treatments incubated at 12% soil moisture and temperatures of 10, 20 and $30^{\circ}C$, and are plotted as the concentrations remaining, on a logarithmic scale, against time of incubation. The straight lines shown are those of best fit calculated by linear regression analysis and the good linear relationships obtained show that the results can be interpreted using first-order kinetics.

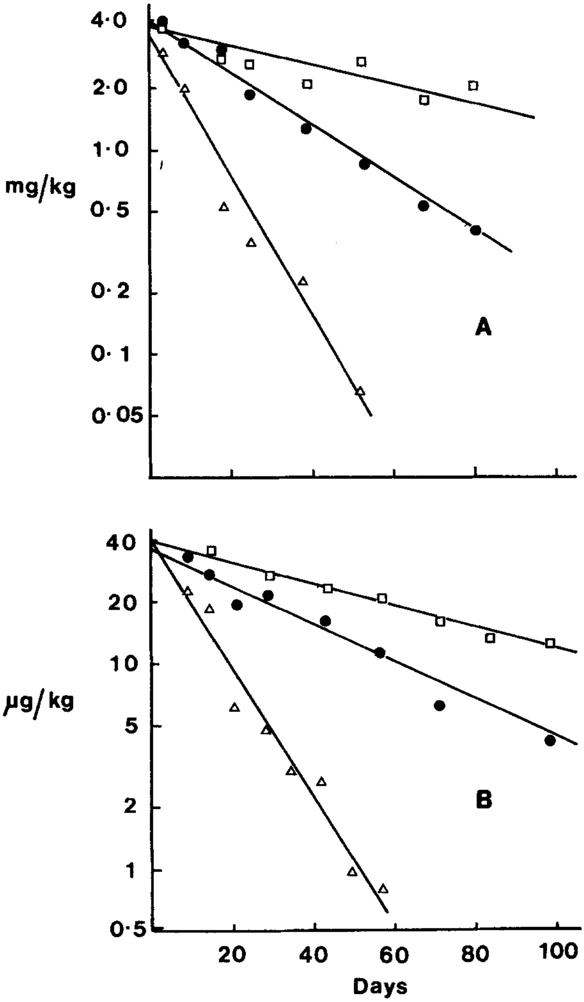

Fig. 1. Degradation of chlorsulfuron in soil at 12% soil moisture and temperatures of 10°C (□), 20°C (●) and 30°C (△). A, initial concentration 4 mg/kg, residue measurements by HPLC; B, initial concentration 0.04 mg/kg, residue measurements by bioassay.

TABLE 1

First-order half-lives for chlorsulfuron degradation in a sandy loam soil at different temperatures and soil moisture contents.

Temperature °C	Moisture %	Half-life (days) HPLC	Half-life (days) Bioassay
10	12	64.2	54.2
15	12	37.4	-
20	12	25.6	31.9
25	12	12.8	-
30	12	8.9	9.7
20	6	-	56.0
30	6	-	20.5

First-order half-lives derived from all of the laboratory data are given in Table 1. The agreement between the half-lives derived from the three treatments where residues were measured by both HPLC and bioassay is further confirmation that degradation of chlorsulfuron in soil can be described by first-order reaction kinetics. The initial concentration in the HPLC experiment was 100 times greater than that in the bioassay experiment and the results show that the rate of loss was independent of initial concentration within this range. The rate of chlorsulfuron loss was affected by both temperature and moisture content of the soil (Table 1). An increase in temperature of 10°C increased the rate of loss by a factor of between 2 and 3, and an increase in soil moisture content from 6 to 12% increased the rate of loss by a factor of approximately 2. Variations in the temperature and moisture content of the soil have similar effects on rates of degradation of many other soil-applied pesticides (HAMAKER 1972; WALKER 1978; HURLE & WALKER 1980).

The results from the measurements of persistence in the field are shown in Fig. 2. The data in the upper diagram show the patterns of residue decline in each of the three replicate plots, and the data in the lower diagram show the residues averaged across the three replicates. The time for 50% loss of the applied dose was approximately 40 days, and after 140 days, about 5% of the amount applied could be recovered from the soil. Previous experiments have shown that measurements of herbicide degradation rates under different controlled moisture and temperature regimes in the laboratory (such as those in Table 1) can be used to predict persistence in the field using a computer simulation program (WALKER 1978; WALKER & BARNES 1981). In order to use the laboratory degradation data with chlorsulfuron in this computer model, constants to describe the temperature and moisture dependence of degradation were required. In the model, the dependence of degradation on temperature is characterised using the Arrhenius equation:

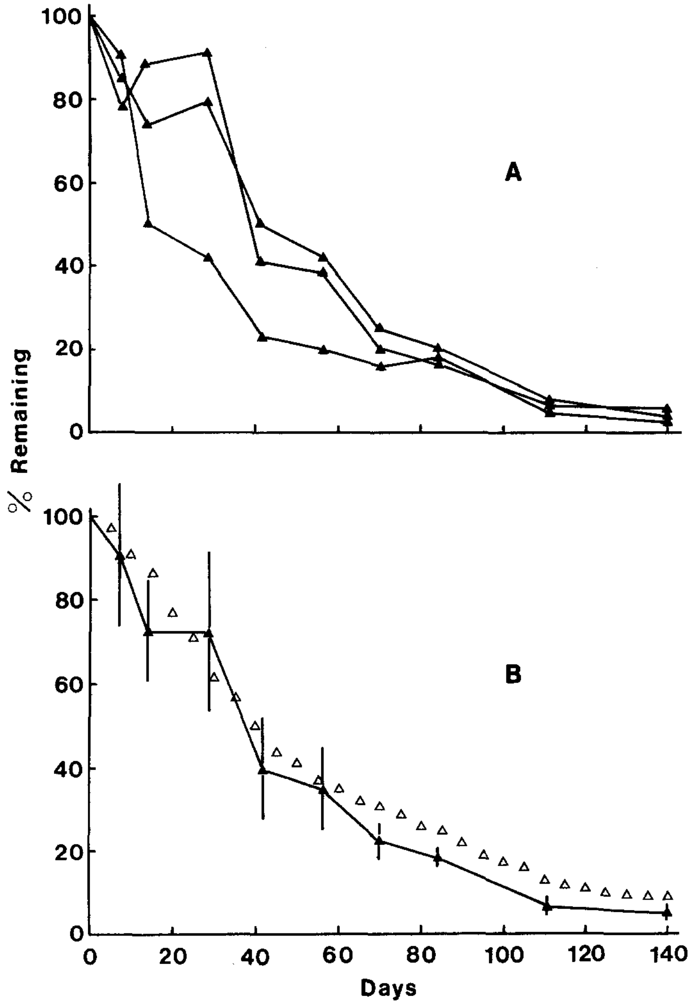

Fig. 2. Persistence of chlorsulfuron in the field following application on April 23 1981. A, residue decline in the three replicate plots; B, average soil residues; ▲ , observed data; △ , calculated data.

$$\log H_1 - \log H_2 = \frac{E}{4.575} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where H_1 and H_2 are half-lives at absolute temperatures T_1 and T_2, and E is the Arrhenius activation energy. The dependence of degradation on moisture is characterised by an empirical equation:

$$H = A M^{-B}$$

in which H is the half-life at moisture content M and A and B are constants. Values for the constants E, A and B derived from the data in Table 1 by the methods described previously (WALKER 1978) were 15918, 353.3 and 1.056 respectively. These constants were used in the computer program of WALKER & BARNES (1981) together with appropriate weather data for the period of the field experiment with the results shown in Fig. 2B. The model predicted persistence of chlorsulfuron in the field with reasonable accuracy and the average percentage deviation of calculated from observed data was ±25.2. Since the coefficient of variation in measured residues was often greater than this, this degree of correspondence is probably sufficient for practical purposes.

Since the results in Fig. 2. suggest that the computer model can give a reasonable description of the persistence of chlorsulfuron in the soil, it was used to calculate possible variations in persistence following application at different times or at different sites. Chlorsulfuron is currently recommended in the United Kingdom for weed control in autumn-sown cereals, and it is probable that this recommendation will be extended to spring-sown crops. In some cereal cropping programmes, following crops other than cereals may occasionally be sown within 6 months of spring application or within 12 months of autumn application, but more usually, these intervals will be 12 and 18 months respectively. Weather data from Wellesbourne for the years 1971 to 1981 were used in the computer model to predict soil residues of chlorsulfuron which may remain in the soil after these times following application in April or October of different years. The results are shown in Table 2. Although these calculated residue levels are generally small, some crops are sensitive to very low concentrations of chlorsulfuron in the soil (WALKER & BROWN 1982). Growth of onion, red beet and carrot, for example, was reduced significantly at soil concentrations equivalent to 0.25, 0.35 and 0.40 g/ha respectively. These concentrations represent 1.3, 1.8 and 2.0% of an initial application of 20 g/ha; of the same order of magnitude as some of the percentages shown in Table 2, even after intervals of 12 months. PALM et al. (1980) reported that initial rates of 80 g chlorsulfuron/ha and below applied in autumn have not injured sugar beet sown 18 months later, whereas spring applications of 30 g/ha have injured beet sown after 12 months. Assuming that the susceptibility of sugar beet is similar to that of red beet, damage would be expected if about 1% of the 30 g rate or 0.4% of the 80 g rate were present in the soil at the time of sowing. Comparison of these percentages with those in Table 2 shows that damage might be expected 12 months after application of 30 g/ha in the spring, but would be unlikely to occur 18 months after application of 80 g/ha in the autumn.

TABLE 2

Predicted residues of chlorsulfuron in the soil (% of initial amount) 6 and 12 months after application in April and 12 and 18 months after application in October of different years

Year	Residue remaining :			
of application	6 months after April 1	12 months after April 1	12 months after October 1	18 months after October 1
1971	4.6	0.8	1.0	0.25
1972	5.7	1.4	1.0	0.16
1973	4.0	0.7	0.8	0.13
1974	4.6	0.8	0.5	0.17
1975	3.1	1.0	2.0	0.40
1976	6.3	1.2	1.2	0.18
1977	6.2	0.9	0.6	0.15
1978	4.0	1.0	1.1	0.17
1979	4.4	0.7	0.6	0.09
1980	3.8	0.6	0.6	0.12
Average	4.7 ± 1.07	0.93 ± 0.35		0.18 ± 0.09

TABLE 3

Predicted residues of chlorsulfuron in the soil (% of initial amount) at monthly intervals following application in late April or early May at different sites

Site	Weather data from	Residue remaining after months:			
		1	2	3	4
England	1 May 1980	63	35	22	11
Holland	12 May 1980	73	45	21	10
Sweden	1 May 1980	64	33	18	8
Germany	14 May 1980	59	24	11	6
Saskatchewan	25 Apr 1980	69	37	12	5
Alberta	1 May 1980	55	24	11	6
Ontario	22 Apr 1980	59	22	8	2
British Columbia	18 Apr 1980	47	21	6	2
Colorado	19 Apr 1979	63	30	14	6
New York	8 May 1979	46	21	6	2
Mississippi	11 May 1979	34	9	2	0.6

Further results from the model are shown in Table 3. These were derived using weather data from several different sites and show calculated residues at monthly intervals following application in late April or early May. They suggest most rapid degradation in the warmer and wetter areas of North America, intermediate rates of loss in the warm but drier climates of Colorado, Saskatchewan and Alberta, and slowest degradation in the cooler climates of northern Europe. PALM et al. (1980) when summarising world-wide field experience with chlorsulfuron, suggested that its half-life in soil was generally between 1 and 2 months. Predictions from the model (Table 3) are in agreement with this observation. It must be stressed, however, that the results in Table 3 refer only to a 4-month period during summer. Relative rates of loss in winter will be different from those shown. In Alberta and Saskatchewan, for example, the soil is permanently frozen in winter and no degradation would therefore be expected. In contrast, winters in England are relatively mild, and some degradation would be expected during the winter months.

The results in Tables 2 and 3 do not take account of variations in soil type. There is evidence that rates of chlorsulfuron degradation are influenced in particular by soil pH, with slower rates of loss in more alkaline soils. A fuller evaluation of the persistence of chlorsulfuron using the computer model would require degradation data similar to those in Table 1 for other soils. Although there are limitations in interpretation of the present results, they are in general agreement with field observations and they demonstrate the potential usefulness of modelling techniques to evaluate herbicide persistence in the soil.

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