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Persistence Studies with the Herbicide Clopyralid in Prairie Soils at Different Temperatures

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Clopyralid (3,6-dichloropicolinic acid) is being used in western Canada at rates up to 300 g/ha as a post emergence treatment for the control of weeds in oil seed crops (Anon 1988). This non-volatile herbicide is water soluble (Haagsma 1975) and exhibits low adsorption to soil colloids, so that leaching can occur under field conditions (Pik et al. 1977). Although clopyralid is degraded by microbiological processes in soil, it is relatively persistent in field soils of Alberta (Pik et al. 1977). This contrasts with a rapid loss in Belgian field soil (Galoux et al. 1985), where no clopyralid was detected in the soil 3 to 4 weeks after application.

To obtain more information about the soil degradation of clopyralid, its rate of breakdown was investigated in three Saskatchewan soils at three different temperatures under laboratory conditions, where no leaching could occur.

MATERIALS AND METHODS

The composition and physical characteristics of the clay, clay loam, and sandy loam used in the studies have already been described (Smith 1988). Samples of all three soils were collected in the fall of 1987 from the surface 10-cm soil horizon and stored at ambient temperature in wooden boxes. Prior to use, during the winter of 1988, all soils were sieved to pass through a 2-mm screen.

Clopyralid (99.3% pure) was obtained from the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina and a solution prepared containing 1 mg of clopyralid per mL methanol.

For the laboratory persistence studies, samples (50 g) of all three soils at 85% of their field capacities were weighed into 175 mL polystyrene cartons, fitted with plastic lids, and incubated in the dark at 10 ± 1, 20 ± 1, or 30 ± 1°C for 7 days. Distilled water was added (by weight) every second day to the 10°C and 20°C samples, and every day to the 30°C samples, to maintain the moisture levels. Following the equilibration period, clopyralid

solution (25 µL, 25 µg) was added to the moist soils and thoroughly mixed, by hand, to ensure distribution of the chemical. This treatment is equivalent to 0.5 µg/g, based on moist soil, and represents a field treatment of approximately 0.25 kg/ha assuming incorporation to a depth of 5 cm. All cartons were re-capped and re-incubated at either 10°C, 20°C, or 30°C, with distilled water being added as necessary to maintain moisture levels throughout the experiment. Duplicate samples of the soils incubated at 10°C and 20°C were extracted and analyzed for clopyralid remaining after 14, 28, 42, 56, and 84 days. Duplicate samples of soils incubated at 30°C were analyzed after 7, 14, 21, 28, 35, 56 and 84 days. Analyses were terminated when less than 10% of the applied herbicide remained.

The soil from each carton was transferred to a 250 mL glass-stoppered flask and shaken on a wrist action-shaker for 1 hour with sufficient extraction solvent, 90% acetonitrile and 10% ammonium hydroxide (30% w/v), so that the total volume of extractant, plus water present in the soil, was equivalent to 100 mL. In the case of air-dry soils, acetonitrile, water and ammonium hydroxide in the proportions of 80:10:10 (v/v/v), was used as the extractant. After shaking, the solvent was allowed to remain in contact with the soil overnight before being shaken for a further 1 hour period. Following centrifugation at 3000 rev/min for 5 minutes, a portion (25 mL) of the clear soil extract was evaporated to approximately 5 mL using a rotary evaporator with a water bath at 50°C.

Extracts in the evaporation flasks were transferred to a separatory funnel with portions (2 X 50 mL) of 5% aqueous sodium bicarbonate and acidified with concentrated hydrochloric acid (8 mL). The acidified solution was then extracted with diethyl ether (2 X 50 mL) and the aqueous layer discarded. The combined ether extracts were re-extracted with 5% aqueous sodium bicarbonate (2 X 50 mL) and the organic layer discarded. Following the addition of concentrated hydrochloric acid (8 ml), the solution was further extracted with portions (2 X 50 mL) of diethyl ether and the aqueous layer discarded. The combined ether extracts were evaporated to dryness at 50°C using the rotary evaporator. Traces of water were removed by azeotropic distillation following the addition of benzene (10 mL) and 2-propanol (10 ml) to the evaporation flask. The dry residue was then transferred, with methanol (2 X 5 mL), to a 50 mL glass-stoppered tube. Methanol was removed under a stream of dry nitrogen with the tube in a water bath at 40°C. Methylation was carried out by adding 14% boron trifluoride-methanol reagent (5 mL) to the dry residue in the tube, and heating at 65°C for 1 hour in a fume hood. Excess boron trifluoride was neutralized by the addition of saturated aqueous sodium chloride (10 ml), and the methyl ester of clopyralid extracted into benzene (25 mL). The benzene extract was then dried over sodium chloride (5 g), and analyzed gas chromatographically.

Gas chromatography was conducted using a Varian (model 3400) equipped with a ^{63}Ni electron capture detector operated at 325°C, and a Vista 402 chromatography work station. All injections (1 µL) were performed using a Varian series 8000 autosampler and a heated injector block at 250°C. Ultra high purity nitrogen was used as a carrier gas with a flow rate of 35 ml/min through a glass column (1.5 m X 4 mm i.d.), packed with 5% OV-17 on Chromasorb W, DMCS, 80-100 mesh. With a column temperature of 180°C the retention time for the methyl ester of clopyralid was 3.2 minutes. Amounts of clopyralid present were calculated by comparing the peak areas of the samples with those obtained from standards of known concentrations. All gas chromatographic standards were prepared by derivatizing clopyralid (25 µg), as described, at the same time as the soil extracts were being derivatized. The standard solutions thus contained the equivalent of 1 ng clopyralid per µL and were diluted with benzene as necessary.

Recoveries of clopyralid from all three soil types were determined after fortification, at the 0.50 µg/g and 0.10 µg/g levels, of triplicate air-dry soil samples. After equilibration for 24 h at 20°C, the soils were extracted and analyzed as described. The results of these recoveries are summarized in Table 1. Analysis of untreated control soils indicated that interfering substances were equivalent to <0.02 µg/g clopyralid.

Table 1. Recoveries of clopyralid from fortified soils.

Amount added (µg/g)	Recovery (%)*		
	Clay	Clay loam	Sandy loam
0.50	95 ± 4	95 ± 1	96 ± 10
0.10	90 ± 6	89 ± 4	100 ± 8

* Mean and standard deviation from 3 replicates.

RESULTS AND DISCUSSION

Aqueous sodium chloride at a pH of 7 (Pik and Hodgson 1976), calcium hydroxide solution (Cotterill 1978), and dilute aqueous sodium hydroxide (Galoux et al. 1985) have been used to extract clopyralid residues from soils prior to gas chromatographic analysis. However, none of these solvent systems resulted in reproducible recoveries of the herbicide from fortified soils described in these studies. The ammoniated acetonitrile, together with the extended extraction, was selected since this procedure has proved satisfactory for the recovery of residues of the related herbicide picloram (4-amino-3,5,6-trichloropicolinic acid) from aged field soils (Smith and Milward 1983). With this extraction procedure, the recoveries of clopyralid from soils fortified

Table 2. Persistence of clopyralid in three soils at 85% of field capacity following incubation at 10°C, 20°C, and 30°C.

Days	Percentage of clopyralid remaining*		
	Clay	Clay loam	Sandy loam
		10°C	
0	95	95	96
14	81	83	73
28	63	67	66
42	46	45	48
56	43	42	38
84	35	24	32
		20°C	
0	95	95	96
14	69	67	72
28	67	18	64
42	42	5	41
56	41	-**	38
84	23 (79)	- (85)	19 (73)
		30°C	
0	95	95	96
7	73	76	65
14	63	60	69
21	60	18	62
28	-	3	-
35	44	-	40
56	32	-	28
84	15	-	11

* Average of 2 replicates. Figures in parenthesis represent percentage of applied clopyralid recovered from soils at 20°C and 10% of field capacity (air-dried).

** Not determined.

at the 0.5 and 0.1 µg/g were greater than 89% with satisfactory reproducibility (Table 1).

The loss of clopyralid from the three soil types incubated at 10°C, 20°C, and 30°C are summarized in Table 2, and there was good agreement between the results from the two replicates at each sampling time. No recovery factors were applied to the soil persistence data. The loss of clopyralid from the soils at all three temperatures, followed first-order kinetics with correlation coefficients >0.95. The only exception occurred with the clay

loam incubated at 30°C where the correlation coefficient was 0.85. Half-life values, the time for 50% of the applied clopyralid to be degraded, in the different soils at the three temperatures are summarized in Table 3.

Table 3. Half-life values for clopyralid in soils at 85% of field capacity over an 84-day incubation period at different temperatures assuming a first-order dissipation rate.

	Half-life (days)		
Temperature	Clay	Clay loam	Sandy loam
10°C	47	42	44
20°C	38	13	36
30°C	29	10	26

From Tables 2 and 3, it is concluded that the breakdown of the herbicide was temperature dependent and similar in the clay and sandy loam. In the clay loam, the rate of clopyralid loss at 10°C was similar to those noted in the clay and sandy loam at the same temperature. However, at 20°C and 30°C the rate of loss was approximately three times faster in the clay loam than in the other two soils (Tables 2 and 3).

Thus, the breakdown of clopyralid appears to be soil dependent (Tables 2 and 3) and probably reflects the number of organisms present in the soil capable of degrading the herbicide. Such an explanation may also explain the more rapid loss of clopyralid from Belgian soils (Galoux et al. 1985) than from Albertan soils (Pik et al. 1977).

As a result of laboratory and field studies carried out with many herbicides in the soils used in the present study, it has been concluded (Smith 1987) that if the laboratory half-life of a herbicide in soil, incubated at 20°C and 85% of field capacity, is greater than 3-4 weeks, then under field conditions there is potential for the carry-over of spring treatments to the next crop year. Thus, carry-over of clopyralid residues on the clay and sandy loam field soils may be expected under Saskatchewan conditions.

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