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Persistence Studies with the Herbicide, Haloxyfop-Methyl, in Prairie Field Plots

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The experimental herbicide haloxyfop-methyl (methyl 2-[4-((3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy]propanoate) is currently being evaluated on the Canadian prairies at rates up to 0.5 kg/ha, as postemergence treatments for the control of annual and perennial grasses in broad-leafed crops.

Studies have shown (Ryder et al. 1983; Smith 1985a) that the herbicidal ester was rapidly hydrolysed in soil to haloxyfop acid, providing the moisture levels were above those of the wilting points. The haloxyfop acid was, in turn, degraded in the soils with a half-life of between 27 and 100 days depending upon the soil type (Ryder et al. 1983; Smith 1985a). Investigations with [14C]haloxyfop-methyl in moist nonsterile soil have revealed that the phenoxy ring system of haloxyfop acid is cleaved with the evolution of [14C]carbon dioxide (Smith 1985a).

Persistence studies with haloxyfop-methyl have not been reported under field conditions in western Canada, and the work to be described was undertaken to determine the persistence of the herbicide, using a small plot technique, at three Saskatchewan locations.

MATERIALS AND METHODS

The composition and physical properties of the clay (C), clay loam (CL) and sandy loam (SL) used in these studies have already been described (Smith 1985a).

Haloxyfop-methyl and haloxyfop acid, with purities of over 99%, were provided by Dow Chemical Canada Inc., Sarnia, ONT. These compounds were dissolved in methanol to yield separate solutions each containing 1.0 mg of ester, or acid, per mL. A commercial formulation, containing 240 g/L of active ingredient, was used for the field persistence studies.

For the field treatments, separate field plots (20 x 20 cm, 400 cm^2) at Regina (clay), Melfort (clay loam) and White City (sandy loam), Saskatchewan, were treated with a freshly prepared aqueous suspension of the formulated product (2.0 mL, containing 2 mg haloxyfop-methyl) during the last week of May 1984, 1985 and 1986, as described for similar studies with other herbicides (Smith 1971, 1972; Smith and Hayden 1976; Smith and Hsiao 1985). These treatments, equivalent to an application rate of 0.5 kg/ha, were not incorporated. The plots remained fallow and were hand-weeded as necessary. Four replicate treatments were sampled during the last week of May, 12 months following application, by removing the soil from the 0-5 and 5-10 cm soil levels, as described (Smith 1971, 1972; Smith and Hayden 1976; Smith and Hsiao 1985). After air drying at room temperature to constant weight, the individual soil samples were weighed, mechanically ground and thoroughly mixed in a laboratory mixer for 20 minutes. Portions of the soils were then solvent extracted and any haloxyfop acid remaining was determined gas chromatographically.

Soil from each field sample (20 g) was weighed into a 125-mL glass-stoppered flask and shaken on a wrist-action shaker for 1 hour with extraction solvent (50 mL) consisting of a mixture of acetonitrile, water and ammonium hydroxide (30% w/v) in the proportions 80:10:10 (v/v/v). After shaking, the soil was allowed to remain in contact with the extraction solvent overnight before being shaken for a further 1-hour period. The soil extracts were then centrifuged at 2000 x g for 10 minutes and portions (25 mL, equivalent to 10 g soil) evaporated to approximately 5 mL using a rotary evaporator with a water bath at 40°C. The residue was transferred with portions of 5% aqueous sodium bicarbonate (2 x 50 mL) to a separatory funnel and acidified with concentrated hydrochloric acid (10 mL). The acidified solution was extracted with diethyl ether (2 x 50 mL) and the aqueous phase discarded. The combined ether extracts were re-extracted with 5% aqueous sodium bicarbonate solution (2 x 50 mL) and the organic layer discarded. Following addition of concentrated hydrochloric acid (10 mL) to the combined bicarbonate extracts, the acidified solution was shaken with diethyl ether (2 x 50 mL) to recover any haloxyfop acid present. The combined etherial extracts were evaporated to dryness at 30°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 residue was transferred with methanol (2 x 5 mL) to a 50-mL glass tube and the methanol removed, under reduced pressure, at 30°C, prior to methylation.

Methylation was accomplished by the addition of borontrifluoride/methanol reagent (5 mL, 14%) to the tube, which was then heated in a fume hood at 65°C for 1 hour. After cooling to room temperature, excess reagent was destroyed by the addition of saturated sodium chloride solution (10 mL). Methyl ester of haloxyfop acid was extracted with benzene (2 x 10 mL), and the volume made up to 25 mL with the same solvent. The benzene extracts were then dried over anhydrous sodium chloride and aliquots (2 µL) examined by gas chromatography.

The gas chromatograph used was a Varian (Model 3400) equipped with a radioactive nickel detector operated at 325°C. The column was of fused silica (30 m x 530 µ i.d.) coated with 1.5 µ DB-5. Nitrogen at a flow rate of 30 mL/min was the carrier gas. With an injector temperature of 250°C and a column temperature of 230°C, the retention time of haloxyfop-methyl was 3.10 minutes. Amounts of haloxyfop-methyl present in the various solutions were calculated by comparing peak areas with those of appropriate standards prepared in benzene.

Average recoveries, based on 3 determinations, from samples (20 g) of air-dried soils fortified with haloxyfop acid at the 1.0 µg/g and 0.1 µg/g levels and following a 7-day equilibration period are compared in Table 1. Extraction of untreated soils indicated that no interfering substances were present. The analytical procedure appeared to be both satisfactory and reproducible (Table 1) and no recovery corrections were applied to the persistence data.

Table 1. Recoveries of haloxyfop acid from three prairie soils following fortification at the 1.0 and 0.1 µg/g levels 7 days prior to extraction and analysis.

Soil type	Fortification (µg/g)	Recovery (%)*
Clay	1.0	87 ± 4
Clay loam	1.0	88 ± 9
Sandy loam	1.0	102 ± 4
Clay	0.1	90 ± 5
Clay loam	0.1	97 ± 2
Sandy loam	0.1	89 ± 8

* Means and standard deviations from 3 replicate analyses.

RESULTS AND DISCUSSION

Aqueous ammoniated acetonitrile, together with the extended extraction was used to recover haloxyfop acid from soils since this procedure has proved satisfactory for the extraction of the phenoxypropanoic acids fenoxaprop, fenthiaprop, fluazifop and haloxyfop from prairie soils (Smith 1985a, 1985b, 1987). The extraction procedure results in complete hydrolysis of haloxyfop-methyl to haloxyfop acid, but this was not considered important given the very rapid hydrolysis of the ester in moist soils collected from the same three field locations reported in the present study (Smith 1985a).

Analysis of the field soils following May treatments with formulated haloxyfop-methyl indicated (Table 2) that, after 12 months, less than 5% of the initial treatment could be recovered from the 0-5 cm soil depths at the Regina (clay) and White City (sandy loam) locations. This would suggest that in the clay and sandy loam field soils haloxyfop is almost completely degraded with insignificant carry-over of residues to the next crop year. In contrast, at the Melfort site (clay loam) for each application year, approximately 20% of the initial treatment was still present as haloxyfop acid in the 0-5 cm soil level after 12 months. There was no evidence of leaching below 5 cm at any of the three locations during any of the three years (Table 2).

Table 2. Residues of haloxyfop acid recovered from the top 5 cm of field plots after 12 months at different locations following spring treatments with 0.5 kg/ha of haloxyfop-methyl.

Application date	Sampling date	Haloxyfop acid remaining (% of applied)*		
		Melfort (CL)	Regina (C)	White City (SL)
May, 1984	May, 1985	23 ± 3	**	<5
May, 1985	May, 1986	20 ± 1	<5	<5
May, 1986	May, 1987	19 ± 4	<5	<5

* Means and standard deviations from the analysis of 4 replicate plots. Less than 5% of the applied herbicide recovered as haloxyfop acid from the 5-10 cm soil depths.

** Data not available.

It is interesting to note that laboratory persistence experiments, conducted with soils taken from the same locations reported in the present study, have indicated a slower rate of [14C]haloxyfop acid degradation in the Melfort (clay loam) soil (Smith 1985a). The loss of solvent extractable radioactivity from these soils treated with [14C]haloxyfop-methyl and incubated at 20°C and at 85% of field capacity followed first-order kinetics with the half-life of haloxyfop being 27, 38 and 92 days, respectively, in the sandy loam, clay and clay loam (Smith 1985a).

Both laboratory (Smith 1985a) and field studies confirm that haloxyfop can be more rapidly degraded on lighter textured Saskatchewan soils, with about 4% organic content, than in heavier textured soil such as the clay loam with 12% organic content.

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