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Persistence Studies with the Herbicide Fluazifop-butyl in Saskatchewan Soils Under Laboratory and Field Conditions

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Fluazifop-butyl, the butyl ester of fluazifop acid ((±)-2-[4-[[5-trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid) is currently being evaluated in western Canada, at rates up to 1 kg/ha, as a postemergence treatment for the control of annual and perennial grasses in broadleaved crops.

Although fluazifop-butyl is applied to the growing crop, some of the spray will come into contact with the soil making it necessary to determine the herbicide's persistence in soils.

It has been reported (Bewick 1986) that the enantiomers of fluazifop-butyl, as well as the racemic herbicidal ester, undergo rapid hydrolysis in soils to fluazifop acid, with hydrolysis being over 97% complete within 24 hours. It has also been shown (Bewick 1986) that fluazifop acid undergoes rapid breakdown in moist soils under laboratory conditions. Under field conditions, herbicidal activity was noted (Anon 1985) for between 3 to 6 weeks after application, depending upon soil temperature and moisture.

In the studies to be described, the hydrolysis of fluazifop-butyl to fluazifop acid was investigated in three Saskatchewan soils under laboratory conditions. Studies were also conducted to determine the persistence of fluazifop-butyl, and acid, in the same soils under field and laboratory conditions.

MATERIALS AND METHODS

The composition and physical properties of the clay, clay loam and sandy loam used in these studies have already been described (Smith 1985a). Samples of all soils were collected from the surface 5-cm horizons during September, 1984, when the moisture contents of the soils were below 10% of their field capacities. The soils were screened through a 2-mm seive and stored at room temperature until the laboratory studies were commenced in March, 1985.

Fluazifop-butyl and fluazifop acid, with purities of over 99%, were provided by Chipman Inc., Stoney Creek, ONT. These compounds were dissolved in methanol to yield separate solutions each con-

taining 2.0 mg of ester, or acid, per mL. For the field persistence studies, a commercial formulation, "Fusilade", containing 250 g/L of active ingredient was used.

For the hydrolysis studies, 20 g duplicate samples of clay, clay loam and sandy loam at 20%, 65% and 100% of their field capacity moisture levels were weighed into 125-mL glass-stoppered flasks and treated with 50 µL (100 µg) of the fluazifop-butyl solution. The application rate was equivalent to 5.0 µg/g, based on moist soil. The soils were stirred to distribute the ester, then the flasks were stoppered and incubated in the dark at 20°C. Duplicate samples of all treatments were extracted and analyzed after 24 and 48 hours, using high pressure liquid chromatography (HPLC), to determine the amounts of butyl ester remaining.

For the analysis of fluazifop-butyl, sufficient extraction solvent (acetonitrile:water:glacial acetic acid, 80:20:2.5 v/v/v) was added to each flask, so that the total volume of extractant together with the water present in the soils was equivalent to 50 mL. The flasks were then shaken on a wrist-action shaker for 1 hour, after which, the extracts were centrifuged at 2000 x g for 5 min and 25 mL of the supernatant added to a separatory funnel containing 100 mL of 5% aqueous sodium bicarbonate and 50 mL of n-hexane. Following vigorous shaking, the aqueous phase was discarded and the organic layer was collected in a 50-mL flask to which anhydrous sodium chloride was added as drying agent. The hexane solution, containing any fluazifop-butyl, was decanted into a 100-mL round bottomed flask. The sodium chloride was rinsed with two further 10-mL portions of hexane and the combined hexane extracts were evaporated to dryness at 30°C using a rotary evaporator. The residue was taken up in 5.0 mL of methanol containing 15% water, and 100 µL portions were examined by HPLC.

The liquid chromatograph used consisted of a Waters Model 510 pump, a steel column (15 cm x 3.5 mm i.d.) filled with Nova-Pak C18 reverse phase packing, and a Waters Model 490 ultraviolet-visible programmable detector. Elution solvent was methanol containing 15% (by volume) water at a flow rate of 0.5 mL/min. Under these conditions, and using the detector at a wavelength of 268 nm, the retention time for fluazifop-butyl was 4.48 min. Ester present in the extracts was quantified by comparing chromatogram peak areas with those derived from appropriate standards. Extraction of untreated soils confirmed the absence of interfering substances.

For the laboratory persistence studies, duplicate 50 g samples of the three soil types, moistened to 85% of their respective field capacities, were weighed into 175-mL polystyrene foam containers fitted with plastic lids and incubated in the dark at 20°C for 7 days. Distilled water was added, by weight, every second day to replace moisture lost by evaporation. After the equilibration period, 8 cartons of each soil were treated with the methanolic solution containing fluazifop acid (50 µL, 100 µg) to give soil concentrations of 2 µg/g, based on moist soil weights. Following

treatment, the soils were thoroughly mixed and the capped cartons incubated in the dark at 20°C. Water was added, with mixing, every second day to maintain the moisture content. Duplicate samples from the three soil treatments were extracted after 1 hour, and then after 14, 28 and 42 days, and analyzed by HPLC.

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 (acetonitrile:water:ammonium hydroxide (30% w/v), 80:10:10 v/v/v) so that the combined volume of the solvent together with the water present in the soil was equivalent to 100 mL. 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 min and 25 ml portions (equivalent to 12.5 g moist soil) evaporated to approximately 5 mL using the rotary evaporator. The residue was transferred with 2 x 50-mL portions of 5% aqueous sodium bicarbonate solution, to a separatory funnel, and acidified with 10 mL of concentrated hydrochloric acid. The acidified solution was extracted with 2 x 50-mL portions of diethyl ether and the aqueous phase discarded. The combined ether extracts were back-extracted with 2 x 50-mL portions of 5% aqueous sodium bicarbonate solution and the organic layer discarded. After addition of 10 mL concentrated hydrochloric acid to the combined bicarbonate extracts, the acidified solution was shaken with 2 x 50-mL aliquots of diethyl ether to recover any fluazifop acid present. The combined etherial solution was evaporated to dryness at 30°C, using the rotary evaporator, and traces of moisture were removed by azeotopic distillation following the addition of 20 mL of a 1:1 mixture of 2-propanol and benzene to the evaporation flask. The residue was transferred using 2 x 5-mL portions of methanol to a 50-mL glass tube and the methanol removed under reduced pressure prior to methylation.

Methylation was achieved by the addition of 5.0 mL borontrifluoride/methanol reagent (14%) to each tube, which was then heated at 65°C for 1 hour in a heating block in a fumehood. After cooling to room temperature, excess reagent was destroyed by the addition of 10 mL saturated aqueous sodium chloride solution. Any methyl ester of fluazifop acid was extracted with 2 x 10-mL portions of benzene. The combined benzene extracts were then dried over anhydrous sodium chloride, and the dried extracts decanted into a 100-mL round bottomed flask. The sodium chloride was rinsed with two further 10-mL portions of benzene, and the combined extracts evaporated to dryness at 30°C. The residue was dissolved in 5.0 mL of 25% aqueous methanol and 200 µL portions examined by HPLC.

The experimental conditions for the detection of fluazifop-methyl by HPLC were the same as those described above for the measurement of fluazifop-butyl, except that the elution solvent was 25% aqueous methanol. The retention time for fluazifop-methyl was 5.2 min. Methyl ester present in the extracts was quantified by comparing the sample chromatogram peak areas with those derived from standards prepared from appropriate amounts of fluazifop acid that

had been methylated with borontrifluoride/methanol reagent exactly as described above. Extraction of untreated soils indicated that no interfering substances were present.

For the field persistence studies, 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 "Fusilade" (2.0 mL, containing 4 mg fluazifop-butyl) during the last week of May 1984 and 1985, as described for similar studies with other herbicides (Smith 1971, 1972; Smith and Hayden 1976). These treatments, equivalent to a rate of 1 kg/ha, were not incorporated; the plots remained fallow and were hand weeded as necessary. Three replicate treatments were sampled during the last week of the May following application (52 weeks) by removing the soil from the 0-5 and 5-10 cm levels, as described (Smith 1971, 1972; Smith and Hayden 1976). After air-drying at room temperature, the individual soil samples were weighed, ground and mixed. Soil aliquots of 20 g were extracted with 50 mL of the aqueous ammoniated acetonitrile and the methylated extracts analyzed for fluazifop-methyl using HPLC, exactly as described above.

Average recoveries, based on 4 determinations, from 20 g samples of air-dried soils fortified with fluazifop acid at the 1.0 µg/g level and following a 7-day equilibration period, were in excess of 90%. The average recoveries of fluazifop acid from soils similarly fortified at a 0.2 µg/g rate, were slightly lower and ranged from 80 to 85%.

RESULTS AND DISCUSSION

Aqueous acidic acetonitrile was used to recover fluazifop-butyl from the soils since this extractant has proved most satisfactory for the recovery of many herbicidal esters from the soil types used in the present studies (Smith 1977, 1985a, 1985b). HPLC was used for the quantification since the ester was insensitive to detection by electron-capture gas chromatography.

Table 1. Hydrolysis of fluazifop-butyl in moist soils at 20°C after 24 and 48 hours.

		% Fluazifop-butyl remaining		
Soil type	Time	20% of FC	65% of FC	100% of FC
Clay	24 h	90	23	9
	48 h	97	6	<2
Clay loam	24 h	101	15	14
	48 h	96	8	8
Sandy loam	24 h	94	4	3
	48 h	90	<2	<2

Average from two replicates, variation <5%.

The results of the experiments comparing the hydrolysis of fluazifop-butyl in the three soils are summarized in Table 1 and there was excellent agreement between data from the two replicate analyses.

The results from the hydrolysis study indicated (Table 1) that in all soils at 65% and 100% of their field capacities, a rapid loss of fluazifop-butyl occurred, so that after 48 hours less than 8% of the original ester was recoverable. In the air-dry soils (20% of field capacity) over 90% of the applied ester was recovered after 24 and 48 hours (Table 1). It was thus considered that in soils with moistures in excess of 65% of field capacity, almost complete hydrolysis of fluazifop-butyl to fluazifop acid had occurred after 48 hours. These findings are therefore similar to those reported by Bewick (1986) for British soils. Thus, fluazifop-butyl behaves similarly to the herbicidal esters diclofop-methyl, fenoxaprop-ethyl, fenthiaprop-ethyl and haloxyfop-methyl all of which possess a phenoxypropanoate grouping ($OC_6H_4OCH(CH_3)CO_2C..$) like fluazifop-butyl (Smith 1977, 1985a, 1985b).

Aqueous ammoniated acetonitrile, together with the extended extraction, was selected for recovery of fluazifop acid from soils since this procedure has proved satisfactory for extraction of the phenoxypropanoic acids fenoxaprop, fenthiaprop and haloxyfop from prairie soils (Smith 1985a, 1985b). This extraction procedure resulted in complete hydrolysis of the fluazifop-butyl to fluazifop acid. However, this was not considered important given the rapid hydrolysis of the ester in moist soils (Table 1).

Table 2. Recovery of fluazifop acid from soils initially treated at a rate of 2 µg/g following incubation at 20°C and 85% of field capacity.

	% Fluazifop acid remaining				
Soil type	1 h	14 d	28 d	42 d	Half-life (days)
Clay	90	63	42	21	23
Clay loam	93	61	33	26	21
Sandy loam	99	42	10	<5	11

Average from two replicates, variation <5%.

Results of the laboratory persistence studies with fluazifop acid are summarized in Table 2 and there was excellent agreement between the results from duplicate analyses. Breakdown of the fluazifop acid in all soils was rapid and appeared to follow first-order kinetics. Thus, the half-lives were calculated from the lines of best fit, derived by plotting the logarithm of percentage herbicide remaining against incubation time (Table 2). Degradation of fluazifop acid was more rapid in the sandy loam than in the other two soils (Table 2).

From previously published data from this laboratory (Smith 1985a), the half-life values for haloxyfop acid, incubated under identical conditions and in the same soils used in the present studies, were calculated. These were 36, 72 and 25 days in the clay, clay loam and sandy loam, respectively. Thus, it would appear that, in all three soils, the degradation rates of fluazifop acid were much faster than for haloxyfop acid, whose structure differs from that of the former compound only by a chlorine atom in the pyridine ring.

Both years, analysis of field soils following May treatments with fluazifop-butyl, showed that after 52 weeks, at all three locations, less than 5% of the initial treatment could be recovered from any of the 0-5 or 5-10 cm soil depths.

Both the laboratory and field studies confirmed that fluazifop acid is rapidly degraded in Saskatchewan soils, so that carry-over problems with soil residues to the next crop year should not be expected following spring treatments with the herbicide.

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