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Disappearance of Oxyfluorfen (Goal) from Onions and Organic Soils

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Annually about 2500 ha of onions are produced in Ontario worth an estimated value of $13 to 25 million depending on the market price which has been shown to fluctuate widely from year to year (OMAF 1986, 1987). Production is largely confined to the marsh areas where the land has been cleared and is intensively cultivated for vegetables. Most of these marshes are below natural surface water levels. Banks, canals and ditches have been constructed to control flooding and facilitate irrigation and drainage of the areas. Water being removed from the systems is pumped from ditches to rivers or canals above the marsh. Tolman et al. (1986) have shown that a critical part of onion production is the control of weeds. Onions have been shown to be weak competitors with weeds and without herbicides it is difficult to produce any marketable crop. Over the last decade several major herbicides, used for controlling broadleaf weeds, have been deregistered because of health concerns or removed from the marketplace because of low sales volumes. These include: (1) allidochlor (Randox), (2) nitrofen (Tok), (3) ioxynil (Totril) and (4) aziprotryn (Masoranal). Research into the efficacy of oxyfluorfen (Goal) has shown this herbicide to be an effective replacement for the control of broadleaf weeds in the emerged crop (Yih and Swithenbank, 1976; Beste et al., 1983). However there is a lack of data on the dissipation of residues on onions and in organic soils under Canadian conditions. This study was intended to address some of these needs.

METHODS AND MATERIALS

Field experiments 1 and 2 were conducted during 1985 and 1986. The onion, cultivar, Rocket, was seeded into plots on an organic soil at the Research Station, Kettleby on the Holland Marsh north of Toronto. Plots 10 m x 3.4 m were included in a randomized block of four replications. Seeding

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occurred on 3rd and 4th May respectively in the two years using a four row precision planter, plots consisted of 8 rows 0.4 m apart. Onions emerged during May and were in the six leaf stage on 12 and 10 July respectively in 1985 and 1986 when oxyfluorfen was applied. Oxyfluorfen was formulated as an emulsifiable concentrate sold under the trade name of Goal^{R} and contained 192 g ai L^{-1} of oxyfluorfen. The rates of application of oxyfluorfen was 120 and 240 g ha^{-1} in 1985 and 60 and 120 g ha^{-1} in 1986 (Table 1). The treatments were applied with a boom-type sprayer that delivered 550 L ha^{-1} of water at a pressure of 140 kpa. Onions were pulled at several stages of development up to normal harvest time at day 70 after treatment and analysed for residues (Table 1). Onions were also sampled from storage and analysed. Soils were collected at the same time onions were sampled in the

Table 1. Residues of oxyfluorfen on onions grown on organic soils following application on 12 July 1985, 10 July 1986 and 29 June 1987 in the six leaf stage, Research Station, Kettleby, Ontario (field experiment 1, 2, 4).

Days after	1985 oxyfluorfen residue in onions mg kg^{-1}	
Application	120 g ha^{-1}	240 g ha^{-1}
0	0.63±0.06[2]	1.10±0.23
10	<0.05	<0.05
70[1]	<0.05	<0.05
	1986	
	60 g ha^{-1}	120 g ha^{-1}
0	0.33+0.05	0.38±0.4
11	<0.05	<0.05
40	<0.05	<0.05
70[1]	<0.05	<0.01
	1987	
	60 g ha^{-1}	120 g ha^{-1}
0	0.15±0.02	0.71±0.14
10	<0.05	<0.05
25	<0.05	<0.05
100[1]	<0.05	<0.05

[1]In 1985 samples taken in storage on days 109, and 139 after treatment, residues <0.05 mg kg^{-1}, in 1986 additional samples were taken on days 20, 34, and 56 in field and days 105 and 133 in storage and residues were <0.05 mg/kg, in 1987 additional samples were taken on days 50 and 75 in the field and no residues were detected.
[2]Mean ± SEM

field and sent for chemical analyses. The depth of sampling was 0 to 5 cm. Onion and soil samples were stored frozen at -20 C until analysed.

Four sites were selected for field experiment 3 on four separate farms located on the Holland Marsh where onions had been planted on four separate dates 19 and 25 April and 4 and 5 May 1987 (Table 2). Sites 1 and 2 were sprayed with oxyfluorfen at 120 g ai ha^{-1} on 29 May when the onions were in the first and second true leaf stages respectively. Site 3 and 4 were sprayed on the 9 June with 120 g ai ha^{-1} of oxyfluorfen (625 ml ha^{-1} of Goal^{R}) when onions were in the third and fourth true leaf. The herbicide was applied in 550 L of water per ha at site 3 and 800 L ha^{-1} at the other three sites. Onions and soil samples were taken between day 0 and 10 following treatment.

Cultivar Rocket was seeded into replicated plots in field experiment 4 at the Research Station, Kettleby on 1 May 1987. The same early procedures were followed as in Experiments 1 and 2. Onions emerged during May and were in the second true leaf stage when the first application of oxyfluorfen was made on 9 June with 60 g and 120 g ai ha^{-1} (312, 625 ml ha^{-1} of Goal^{R}). Applications were repeated at the two rates on 15, 23 and 29 June 87 at which time the onions were in the 4-5 true leaf stage. Samples of onions were taken following the fourth application and then at intervals up to harvest (Table 2). Samples of organic soil were taken before and after the

Table 2. Residues of oxyfluorfen on onions grown on organic soils following treatment with oxyfluorfen on 29 May (1-2 leaf stage) and 9 June (3-4 leaf stage) 1987, and 21 June (3-4 leaf stage) 1988, Muck Research Station, Kettleby, Ontario (field experiment 3, 5).

	Oxyfluorfen in onions				
Days after treatment	1987 mg kg^{-1} (120 g ha^{-1})[2]	Accumulated rainfall (mm)	Days after treatment	1988 mg kg^{-1} (60 g ha^{-1})	Accumulated rainfall (mm)
0	1.22 ± 0.22[1]	1	0	0.19 ± 0.03	0
1	0.51 ± 0.08	1	1	0.09 ± 0.01	11
2	0.33 ± 0.04	3	2	0.06 ± 0.02	11
4	0.16 ± 0.03	20	3	0.06 ± 0.01	11
6	<0.05	26	4	0.04 ± 0.01	11
8	<0.05	31	5	0.03 ± 0.01	11
10	<0.05	39	6	<0.01	11
Half life disappearance	1.6 d			1.7 d	
Regression equation	log y = -0.048 - 0.190 x			= -0.772 - 0.177 x	
	F = 71 r^2 = 0.97			F = 55 r^2 = 0.96	

[1]Mean ± SEM Residue
[2]Rate of application

Table 3. Residues of oxyfluorfen in organic soil following applications on 12 July 1985, 12 July 1986 and 29 June 1987, Research Station, Kettleby, Ontario (field experiments 1, 2, 4)

Year (Soil depth) Number applications	Days after after application	Oxyfluorfen in soil (mg kg^{-1}) 120 kg ha^{-1}	240 kg ha^{-1}	Accumulated rainfall (mm)
1985: 12 July	0	0.32 ± 0.07	0.77 ± 0.15	0
0–15 cm	10	0.35 ± 0.05	0.78 ± 0.22	55
one	40	0.25 ± 0.06	0.67 ± 0.12	150
treatment	70	0.20 ± 0.07	0.60 ± 0.11	250
	120	0.13 ± 0.04	0.34 ± 0.11	331
	Log y =	=0.459–0.004x	–0.077 – 0.003x	
	F = 124, r^2 = 0.99		F = 34, r^2 = 0.96	
	Half life	86	103	
		60 kg ha^{-1}	120 kg ha^{-1}	
1986: 10 July	0	0.69 ± 0.07	0.92 ± 0.18	0
0–5 cm	11	0.66 ± 0.07	0.94 ± 0.12	63
one	20	0.45 ± 0.03	0.55 ± 0.05	89
treatment	34	0.31 ± 0.05	0.39 ± 0.02	165
	40	0.30 ± 0.01	0.43 ± 0.01	197
	56	0.14 ± 0.02	0.30 ± 0.04	258
	70	0.13 ± 0.02	0.20 ± 0.03	375
	105	0.05 ± 0.01	0.13 ± 0.02	507
	133	<0.05	0.05 ± 0.01	527
	Log y =	–0.154–0.010 x	= –0.021–0.009 x	
	F = 254, r^2 = 0.99		F = 279, r^2 = 0.99	
	Half life	30 d	33 d	
		60 kg ha^{-1}	120 kg ha^{-1}	
1987: 29 June				
(0–15 cm)	Pre	0.13 ± 0.03	0.21 ± 0.05	
four	0	0.34 ± 0.02	0.55 ± 0.08	0
treatments	10	0.25 ± 0.02	0.39 ± 0.10	0
	25	0.21 ± 0.02	0.31 ± 0.03	60
	50	0.19 ± 0.03	0.24 ± 0.01	135
	75	0.19 ± 0.04	0.26 ± 0.06	163
	100	0.11 ± 0.01	0.19 ± 0.03	218
	(301)	(0.11 ± 0.02)	(0.18 ± 0.04)	(593)
	Log y =	–0.525–0.004x	= –0.291–0.004x	
	F = 24, r^2 = 0.93		F = 19, r^2 = 0.901	
	Half life	78 d	69 d	

four applications and then at various intervals up to harvest and again in the spring of 1988. Cultivar Rocket was seeded into replicated plots in field experiment 5 at the Research Station Kettleby on 3 May 1988. The same procedures were followed as in Experiments 1 and 2. Onions emerged during mid May and were in the 3-4 true leaf stage when treated with oxyfluorfen on 21 June with 240 g ai ha^{-1} (1260 ml ha^{-1} Goal^{R}). Onion samples were collected daily following application for the first 7 days (Table 2).

Organic soil at the Research Station Kettleby was treated with oxyfluorfen at 720 g ai ha^{-1} on 21 June 1988 in field experiment 6. Samples were collected prior to treatment to determine if any residues were present on the site. A replicated randomized design was used and application was made using the spray equipment described above under Experiments 1 and 2. Samples of organic soils were collected from three depths, namely 0-5, 5-10 and 10-15 cm. Water samples were collected at weekly intervals between 7 July and 10 August 1988 from a manhole draining the plot area on the Research Station.

Thirty grams of onions and 50 g of air dried organic soil were extracted twice with dichloromethane by shaking. Air dried organic soil contained 64-70% moisture. The extracts were then cleaned up on a neutral aluminum column. The purified extracts were taken up in benzene after evaporation and residues were determined on a Perkin Elmer 8320B capillary gas liquid chromatograph equipped with a nitrogen phosphorus detector. The column was a DB-5 fused silica capillary column 0.25 mm x 30 m with a 0.25 m coating thickness and programmed over the range of 60 to 225 C.

Recoveries of oxyfluorfen from both onion and soil samples fortified at levels of 0.12 and 0.24 mg kg^{-1} were 80 to 95%. The limit of detection was 0.05 mg/kg for both onions and soil samples. Residues in soil were corrected for moisture content.

RESULTS AND DISCUSSION

The results of analyzing onions in field experiments 1, 2, 3 and 5 conducted in 1985, 1986, 1987 and 1988 respectively, appear in Table 1 and 2. On day 0 residues of oxyfluorfen were detected on onions in all four years. Initial residues varied between 0.15 and 1.22 mg kg^{-1} and were correlated to rate of application which varied from 60 to 240 g ha^{-1}. In experiments 1, 2 and 4 the second sampling date was between 10 days following treatment and residues of oxyfluorfen were already below the detection limit of 0.05 mg kg^{-1}. No residues were detected subsequently following sampling up to harvest time and taken from storage.

In experiments 3 and 5 initial residues of 1.22 and 0.19 mg

kg^{-1} declined below the detection limit in six days. A half residue disappearance was calculated at 1.7 days with a first order regression equation (Table 2). The residue decline did not appear to be correlated to rainfall. In both experiments residue appeared to decline the greatest when no rainfall occurred.

Oxufluorfen residues in organic soil varied with the rate of application between 60 and 720 g ha^{-1} and the depth of sampling between 0-15 cm. The data collected appear in Tables 3 and 4. The organic soil had a density between 0.2 and 0.3 g ml^{-1} and the soil weighed between 0.30 and 0.45 x 10^6 kg ha^{-1} to a depth of 15 cm. The theoretical concentration in the upper 15 cm of organic soil was 0.30 or 1.02 mg kg^{-1} in the upper 5 cm from an application of 120 g ha^{-1}. Initial concentrations indicated there was little or no loss during application.

Table 4. Residues of oxyfluorfen in organic soils following a treatment of 720 g on 21 June 1988, Research Station, Kettleby (Experiment 6).

Days[1]	Oxyfluorfen residues in organic soils (mg kg^{-1})				Accumulated
	0-5 cm	5-10 cm	10-15 cm	0-15 cm	rainfall (mm)
- 5	<0.05	<0.05	<0.05	<0.05	
0	4.5	0.93	0.41	1.96 ± 0.15	0
10	3.98	1.45	0.82	2.08 ± 0.17	11
30	3.85	1.45	0.82	2.04 ± 0.14	53
50	2.03	0.82	0.77	1.21 ± 0.05	106
99	1.65	0.48	0.26	0.80 ± 0.05	265
134	1.03	0.48	0.29	0.60 ± 0.08	346
				Half life 70 d	
Log y				0.345 - 0.004x	
				F = 71, r = 0.97	

[1]Weekly samples of water collected from tile drainage were below 0.1 mg L^{-1} during June and August inclusive.

Regression analysis showed that a best fit for the disappearance of oxyfluorfen was a Log y = a + bx equation. The half life disappearance from the upper 15 cm of the soil ranged from 30 to 103 days and varied with the year. The diappearance appeared rapid in 1986 at 30 days while in 1985 the time was considerably longer at 86 and 103 days.

Oxyfluorfen used as a post emergence herbicide on onions and weeds declined to non detectable levels within six days of application at rates between 60-120 g ai ha^{-1}. Half residue disappearance was within 1.7 days. Fadayomi and Warren (1977b) reported that there was very little movement of oxyfluorfen from the roots to the shoots of pea (Pisum sativum L.) or sorghum (Sorghum bicolor (L.) Moench) and almost all the applied herbicide to the foliage of green bean (Phaseolus vulgaris L.)

and soybean (Glycine max (L.) Merr.) remained at the point of application. This would explain the fact that while residues were present in the soil residues did not appear in onions once the foliar treatments disappeared. It was also reported that oxyfluorfen was very resistant to removal by rain and it was not readily metabolized in plants (Beste et al., 1983). The rapid loss from onions suggested either rapid metabolism or volatilization from the plant.

Fadayomi and Warren (1977a) reported that oxyfluorfen was readily adsorbed into muck soils and this resulted in a rapid loss of its bioactivity. The half life disappearance in the upper 15 cm of the soil profile ranged from 69-103 days. The fact that a shorter half life disappearance in the surface 0-5 cm suggested movement vertically contributed to disappearance. It was evident in one experiment that when soils were analysed in October and then in April the following year no decline in residue occurred over the winter months.

A preliminary report indicated that microbiological degradation was not a major route of breakdown and half life in soil was 30 to 40 days (Beste et al., 1983) however this appeared to be on mineral soils.

Fadayomi and Warren (1977a) reported that oxyfluorfen was held tightly against desorption on muck soils and less than 2% of the parent material was found in leachate. In this study no residues of oxyfluorfen were found in the tile drainage water leaving the treated area.

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