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Loss of Enhanced Biodegradation of 2,4-D and MCPA in a Field Soil Following Cessation of Repeated Herbicide Applications

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Soils previously treated with phenoxyalkanoic acid herbicides can develop an enhanced ability to degrade these chemicals, seemingly due to an increase in the numbers of microorganisms adapted to their metabolism (Roeth 1986; Smith and Lafond 1990; Smith et al. 1991). Increased rates of loss of 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid) following repeated use have been reported from field studies (Kirkland 1967; Fryer and Kirkland 1970; Torstensson et al. 1975; Fryer et al. 1980; Smith et al. 1989; Smith and Aubin 1991a). Soils from such treated fields can retain their ability to rapidly degrade these herbicides for extended periods. Soil from field plots receiving 2 annual applications of MCPA for 7 years maintained enhanced ability to rapidly degrade fresh additions of the herbicide for at least 5 years after receiving the final herbicide treatment (Fryer et al. 1980). Soil from field plots in Saskatchewan that had received 43 annual treatments of 2,4-D formulations and 37 annual applications of MCPA amine, retained enhanced degradation of the respective herbicides, compared to untreated control plots, for at least 48 weeks after the last treatment (Smith and Aubin 1991a).

The present study was undertaken to investigate, over a 4-year period, the ability of soils from the Saskatchewan plots to retain their populations of 2,4-D- and MCPA-degrading organisms, and thus their enhanced breakdown of these herbicides, after cessation of herbicide applications. After 4 years, an enumeration of 2,4-D- and MCPA-degrading organisms was conducted on soils from the treated and control plots.

MATERIAL AND METHODS

The field study at the Agriculture Canada Experimental Farm at Indian Head, Saskatchewan where plots have been

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receiving annual applications of 2,4-D amine and ester formulations since 1947, and MCPA amine treatments since 1953, have already been reported (McCurdy and Molberg 1974; Smith et al. 1991). These sources also give full details regarding soil type, herbicide treatments, and crop rotations. After the final herbicide treatments 1989, following 43 annual applications of 2,4-D formulations and 37 annual treatments of MCPA amine the study area was seeded to grass.

Untreated control plots, and treated plots that had received applications of 2,4-D amine and ester, and MCPA amine, formulations at rates of 1.12 kg/ha, were sampled. These plots were the same as those sampled in previous degradation studies (Smith et al. 1989; Smith and Aubin 1991a). For each herbicide and formulation, samples were collected from three replicate treatment plots. Sampling was carried out during late April or early May of 1991, 1992, and 1993 100, 152, and 204 weeks, respectively, after cessation of 2,4-D and MCPA treatments, by taking 5 samples from the 0- to 2.5-cm depth at 3-m intervals down the centre of each plot using a garden trowel as described (Smith and Aubin 1991a). The soil samples from each individual plot were pooled, mixed, and used immediately in the persistence studies as before (Smith and Aubin 1991a).

Laboratory persistence studies in which the breakdown of chain-labeled ^{14}C-2,4-D and carboxyl-labeled ^{14}C-MCPA at rates of 2.0 μg/g were studied in the soils from the variously treated, and control, plots at 85% field capacity and 20 ± 1°C were identical to those described earlier (Smith et al. 1989; Smith and Aubin 1991a). One fortified soil sample from each replicate plot treatment was solvent extracted with aqueous acetonitrile containing acetic acid and analyzed radiochemically for ^{14}C-2,4-D and ^{14}C-MCPA remaining after 4 and 8 days, exactly as reported (Smith and Aubin 1991a).

Enumeration of 2,4-D- and MCPA-degrading organisms in the respectively treated, and control, plots was conducted on soils collected in the spring of 1993, 204 weeks after the final herbicide treatment. The procedure used, based on that of the most probable number (MPN), has been described (Smith and Aubin 1991b).

RESULTS AND DISCUSSION

It has been noted that enhanced breakdown of ^{14}C-2,4-D still occurred in soils from plots treated with 2,4-D amine and ester formulations, compared to untreated control plots, for at least 48 weeks after the last herbicide application (Smith and Aubin 1991a). A similar

effect was observed for the breakdown of ^{14}C-MCPA in soils from the plots that had received continuous applications of MCPA amine formulation (Smith and Aubin 1991a).

The degradation of ^{14}C-2,4-D and ^{14}C-MCPA after 4 and 8 days of incubation in soils at 85% field capacity and 20°C following collection from the appropriately treated plots 100, 152, and 204 weeks after the last 2,4-D or MCPA field treatment are summarized in Table 1. At all sampling times, the degradation of ^{14}C-2,4-D in the 2,4-D treated plots was faster than that of ^{14}C-MCPA in the MCPA treated plots (Table 1). The data also indicated that the rate of breakdown of ^{14}C-2,4-D was not the same at each sampling date, being considerably more rapid in the soils sampled 152 and 204 weeks after the final 2,4-D field treatments than those sampled after 100 weeks. This phenomenon was not as apparent with the ^{14}C-MCPA studies.

Table 1. Breakdown of added ^{14}C-2,4-D and ^{14}C-MCPA during incubation after 4 and 8 days at 20°C and 85% of FC in soil from field plots collected 100, 152, and 204 weeks after the 43rd annual application of 2,4-D formulations or 37th annual treatment with MCPA amine

	4-Day incubation			8-Day incubation		
Treatment	100	152	204	100	152	204
	Applied ^{14}C-2,4-D remaining (%)*					
Control	49a	9a	14a	3a	- **	-
2,4-D amine	12b	4b	6b	2a	-	-
2.4-D ester	7b	5b	6b	2a	-	-
	Applied ^{14}C-MCPA remaining (%)*					
Control	55a	37a	37a	31a	22a	19a
MCPA amine	58a	33a	27a	26a	4b	4b

* Mean amounts in soils from three plots. Means within a particular column followed by a common letter are not significantly different at the 0.05 level according Duncan's multiple range test.
** Not determined.

From the data (Table 1) it was concluded that at all sampling dates the breakdown of ^{14}C-2,4-D over the first 4 days was significantly faster in soils receiving the 2,4-D amine and ester formulations than in soils from untreated control plots. After 8 days of incubation, recovered 2,4-D, in all plots, accounted for less than 5% of that applied. In contrast, at all sampling dates the breakdown of ^{14}C-MCPA in both untreated control soils and

soils from the MCPA treated plots was statistically similar after 4 days (Table 1). After 8 days of incubation, there were significant differences in the soils collected 152 and 204 weeks after the final MCPA treatment.

The soil enumeration studies indicated that 204 weeks after the 43rd annual application of 2,4-D amine and ester formulations, the numbers of 2,4-D-degrading organisms ranged from 250 to 450 per g (based on oven dry soil) and were not significantly different from those in the soil from the untreated control plots. Similarly, there was no significant difference in the numbers (less than 50 per g oven dry soil) of MCPA-degrading organisms in the soil collected from the plots 204 weeks after the 37th annual MCPA amine treatment compared to those in the control plots.

Previous studies conducted with the Indian Head study have indicated (Cullimore 1981) that after 32 years of 2,4-D treatments there were significantly higher numbers of 2,4-D-degrading organisms than in soils from the control plots. Similar studies by Fournier (Smith et al. 1991) have reported that the numbers of 2,4-D metabolizing organisms in the soil of plots after 35 annual treatments of 2,4-D were 20-fold greater (7200 organisms/g soil) than in soil from the control plots (300 organisms/g).

Recent enumeration studies (Holben et al. 1992) carried out on soil from these 2,4-D-treated plots collected several months after the 42nd 2,4-D treatment revealed that such soils did not have significantly higher numbers of 2,4-D-degrading organisms than did the control soils. However, it was also noted (Holben et al. 1992) that in response to laboratory amendments with 2,4-D, both the previously treated soils and those with no prior history of the herbicide exhibited a dramatic increase (over 10,000 fold) in the number of 2,4-D-metabolizing organisms. This was attributed to the selection and maintaining of a dominant 2,4-D-degrading population in these soils. In the present study (cf Table 1) the breakdown of 2,4-D in the soils collected 152 and 204 weeks after cessation of herbicide treatments was very rapid with little difference in data from treated and control plots. However, there may have been some contamination of the control soils with that from the treatments after termination of the experiment and sowing the grass cover.

Thus, it would appear that following cessation of 2,4-D applications the soil microflora maintain the ability to rapidly degrade 2,4-D for at least 204 weeks, whereas the ability of the enhanced microflora to degrade MCPA is

maintained for between 48 and 100 weeks after the last MCPA field treatment. This latter contrasts with earlier studies (Fryer et al. 1980) who, using a sorghum bioassay procedure, observed that plots repeatedly treated with MCPA maintained an enhanced ability to degrade the herbicide for 5 years following the final application.

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