Persistence of 2, 4-D, 2, 4, 5-T and Dicamba in a Dykeland Soil[1]

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The increasing use of herbicides for brush and weed control renders the accidental spraying of nearby crop land more likely. The present investigation was prompted by one such local accident on dykeland which resulted in extensive litigation involving rather tenuous claims re long persistence and potent biological effects of 2,4-D, 2,4,5-T and dicamba. ALTOM and STRITZKE (1973) reviewing the persistence of toxic concentrations of herbicides in soil give ranges of 7-98 days for 2,4-D, 47-300 days for 2,4,5-T and 30 days to more than 1 year for dicamba. These wide ranges in persistence were due to variations in many factors such as application rate, soil type, soil temperature, rainfall, vegetative cover and microbial populations. Thus it is still difficult to predict the persistence of a herbicide in soil and it is often necessary to conduct a local study to determine the rate of breakdown. This study reports the soil residues over a 55-week period resulting from surface application of 2,4-D, 2,4,5-T and dicamba to dykeland in a humid, temperate climate.

MATERIALS AND METHODS

Soil treatments and sampling

On August 30, 1973, 14 plots, each 1.5 x 1.5 m, in a randomized block design were established on a silt loam soil of the Acadia Soil Complex (NOWLAND and MACDOUGALL, 1973) at the Nappan Experimental Farm. The soil consisted of 19% sand, 56% silt, 25% clay. Organic matter was 2.6%, pH 5.8, and cation exchange capacity 12.0 meq/100 g. The herbicide formulations were applied at the rates given in Table 1.

A single spray was applied to the appropriate plot on August 30, 1973 using a 1.52 m boom sprayer accurately calibrated to deliver the required volume of

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solution. Soil samples were collected on August 31 approximately 13 hours after application and at 14, 28, 42, 56, 70, 265 and 385 days. A composite sample of ten 2.5 cm diameter cores was taken from each plot at each sampling date. These samples were air-dried, passed through a 20-mesh sieve and stored at -15°C until analyzed. The 0-10 cm depth only was sampled on the first 3 dates, the 0-10 and 10-20 cm depths on the next 3 dates and the 0-10, 10-20, and 20-30 cm depths on the last 2 sampling dates.

TABLE 1

Rates and formulations of herbicides applied to experimental plots

Treatment	Formulation	Active ingredient	Rate kg/ha A.E.*
1	Chipman 2,4,5-T 76 Reg. No. 3961	iso-octyl esters of 2,4,5-T	1.1
2			2.1
3			4.3
4	Co-op Brush Killer 112 Reg. No. 7527	iso-octyl esters of 2,4-D and 2,4,5-T	7.8**
5			15.7**
6			31.4**
7	Chipman 2,4-D amine 80 Reg. No. 2238	mixed amines of 2,4-D	5.6
8			11.2
9			22.4
11	Velsicol Banvel D Reg. No. 8631	dicamba amine salt	1.1
12			2.2
13			4.5
10	Check		
14	Check		

*Acid equivalent

**Rate of each ingredient

Climate

The plot site has a humid, temperate climate. A summary of weather data (1914-1965) is as follows: mean annual precipitation 99 cm, of which 20 cm is snow; average daily temperature 5.3°C; average total degree days (4.4°C base) May to September - 1570. The soil at the site remains frozen for most of the period December through March.

Extraction and derivatization of residues

Herbicide esters - 10.0 g soil samples were extracted with hexane/acetone in Soxhlet extractors (STEWART and CAIRNS, 1974), the extracts evaporated to dryness on a rotary evaporator, the residues dissolved in hexane/acetone (1:1) and refrigerated until analyzed.

Herbicide acids - A 50.0 g soil sample was shaken vigorously with 75 ml distilled water, 5 ml 6N H_2SO_4 and 100 ml peroxide-free diethyl ether for 2 1/2 hours on a rotary shaker. The mixture was then centrifuged and 75 ml of the ether layer collected. The acids were removed from the ether layer by shaking with 5% $NaHCO_3$ solution, and then re-extracted into ether after acidifying the aqueous solution with dilute sulphuric acid. The acids were methylated with an ether solution of diazomethane, the ether removed on a rotary evaporator and the residues dissolved in hexane/acetone (1:1) and refrigerated until analyzed.

Recoveries of known amounts of herbicides (acids) added to untreated soil and carried through the extraction and analytical procedures averaged 102% for 2,4,5-T (0.2-1.0 ppm level), 109% for 2,4-D (0.4-4.0 ppm level) and 110% for dicamba (2.0 ppm level).

Residue determinations

Residues of 2,4-D, 2,4,5-T and dicamba (methyl esters) were determined by gas chromatography using a Micro Tek 220 with a ^{63}Ni electron capture detector operated in the pulse mode. The pulse rate was 270 μ sec and the pulse width 3 μ sec. The column was 75 cm x 0.64 cm Pyrex glass packed with 3% OV-17 on Gas Chrom Q, 100-120 mesh. Carrier gas was argon containing 5% methane. The oven temperature was 180°C for 2,4-D and 2,4,5-T methyl esters, with a carrier gas flow rate of 60 cc/min. For dicamba methyl ester the oven temperature was 170°C and the carrier gas flow rate 45 cc/min. For determination of iso-octyl esters of 2,4-D and 2,4,5-T an oven temperature of 185° and a carrier gas flow of 75 cc/min was used.

Known concentrations of methyl esters of 2,4-D, 2,4,5-T and dicamba, and iso-octyl esters of 2,4-D and 2,4,5-T were compared to the unknowns to determine the herbicide levels present. Standard curves were prepared daily by plotting peak area (as determined by an Infotronics CSI-208 electronic integrator) versus amounts of standards injected.

RESULTS AND DISCUSSION

Ester persistence in soil

The iso-octyl ester of 2,4,5-T applied at rates of 1.1-4.3 kg/ha (Treatments 1-3) did not result in detectable residues of the unchanged ester in soil 13 hours after application. When applied at higher rates, 7.8-31.4 kg/ha (Treatments 4-6), together with the 2,4-D ester, trace residues of the 2,4,5-T ester could be detected in the 42-day sample while the 2,4-D ester persisted only 14 days (Table 2).

TABLE 2

Persistence of 2,4-D and 2,4,5-T iso-octyl esters in soil

Days after application	ppm ester					
	Treatment 4		Treatment 5		Treatment 6	
	2,4-D	2,4,5-T	2,4-D	2,4,5-T	2,4-D	2,4,5-T
	0-10 cm		0-10 cm		0-10 cm	
1	ND	ND	.01	.02	.11	.30
14	ND	ND	ND	.01	.01	.12
28	ND	ND	ND	ND	ND	.03
42	ND	ND	ND	ND	ND	Tr

ND - not detected; sensitivity of method ∿ .005 ppm
Tr - trace, detected at level < 0.01 ppm

These results indicated that a small percentage of the applied iso-octyl esters of 2,4-D and 2,4,5-T can persist for several weeks in this soil. SMITH (1972) showed that although the iso-propyl and n-butyl esters of 2,4-D hydrolyzed almost immediately, the iso-octyl ester persisted several days in soil.

2,4,5-T iso-octyl ester (Treatments 1-3)

In the present study the major residue in the soil following the application of 2,4,5-T iso-octyl ester was the free phenoxy acid.

The major portion of the 2,4,5-T soil residues disappeared within 50 days of application (Table 3). Only small amounts of 2,4,5-T penetrated to the 10-20 cm depth and residues were not detected in the 20-30 cm depth. Residues of ∿ .01 ppm were detected 265 days after application in the 0-10 cm depth.

TABLE 3

2,4,5-T residues in soil following application of 2,4,5-T iso-octyl ester

	2,4,5-T acid (ppm)					
Days after treatment	Tr 1 1.1 kg/ha		Tr 2 2.1 kg/ha		Tr 3 4.3 kg/ha	
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm
1	.06	-	.39	-	.26	-
14	.05	-	.28	-	1.08	-
28	.03	-	.09	-	.59	-
42	.01	.01	.02	.02	.21	.11
56	.01	.01	.02	.02	.08	.05
70	.01	.01	.02	.01	.05	.05
265	.01	.Tr	.01	Tr	.01	Tr
385	Tr	ND	Tr	ND	Tr	ND

2,4-D/2,4,5-T iso-octyl esters (Treatments 4-6)

The major residues in the soil following the application of the 2,4-D/2,4,5-T iso-octyl ester formulation were the respective free phenoxy acids.

The maximum soil residues of 2,4-D from Treatments 4-6 occurred in the 14-day samples (Table 4). The time at which the highest 2,4,5-T soil residues occurred depended on the rate of application - 14 days with Treatment 4, 28 days with Treatment 5, and 42 days with Treatment 6. A possible explanation for the time lag in reaching maximum soil residues is that the phenoxyacetic esters were rapidly converted to the free acids on the foliage (CRAFTS, 1960), the grass died due to the high rates of application and rain gradually leached the free acids into the soil. The hydrolysis of the small amounts of ester in the soil (Table 2) cannot account for this phenomenon.

Rainfall during the 1st day was 0.2 cm, 2-14 days 1.9 cm, 15-28 days 1.42 cm, 28-42 days 0.99 cm, 42-56 days 0.59 cm, 56-70 days 5.75 cm.

2,4,5-T residues were more persistent than 2,4-D residues at all 3 application rates. Residues were principally in the 0-10 cm depth, small amounts were found in the 10-20 cm depth and none in the 20-30 cm depth.

TABLE 4

2,4-D and 2,4,5-T residues (ppm acid) in soil following application of a 2,4-D/2,4,5-T iso-octyl ester formulation

Days after treatment	Treatment 4				Treatment 5				Treatment 6			
	7.8 kg/ha 2,4-D		7.8 kg/ha 2,4,5-T		15.7 kg/ha 2,4-D		15.7 kg/ha 2,4,5-T		31.4 kg/ha 2,4-D		31.4 kg/ha 2,4,5-T	
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm
1	.59	-	.28	-	.82	-	.42	-	3.66	-	1.16	-
14	.87	-	1.05	-	1.47	-	1.32	-	12.4	-	7.1	-
28	.14	-	.92	-	.28	-	3.60	-	.60	-	8.9	-
42	.06	.03	.26	.22	.50	.14	2.39	.76	.39	.03	10.9	.22
56	.01	.06	.84	.18	.05	.09	1.20	.59	.28	.06	7.2	.18
70	.03	.02	.11	.10	.11	.03	.81	.19	.24	.02	7.5	.10
265	.01	ND	.02	.01	.05	Tr	.11	.01	.10	ND	1.2	.01
385	ND	ND	Tr	Tr	ND	ND	Tr	Tr	ND	ND	.02	ND

After 70 days 1% of the applied 2,4-D remained in the soil from Treatment 4, 2% from Treatment 5 and 1% from Treatment 6; 4% of the 2,4,5-T remained from Treatment 4, 9.5% from Treatment 5 and 36% from Treatment 6. After 55 weeks 2,4-D could not be detected from any of the 3 treatments. No 2,4,5-T was detected after 55 weeks from the 7.8 kg/ha and 15.7 kg/ha applications but a small residue of 0.02 ppm remained in the 0-10 cm depth from the 31.4 kg/ha application.

2,4-D amine salts (Treatments 7-9)

The maximum soil residues were found in the 14-day samples (Table 5). It appears probable that, as was postulated for Treatments 4-6, appreciable amounts of the amine formulation were absorbed by the grass and later leached into the soil by rain and dew. The maximum soil residues in the 2,4-D ester plots (Treatments 4-6) also occurred in the 14-day samples (Table 4).

TABLE 5

2,4-D residues in soil following application of 2,4-D amine formulation

Days after treatment	2,4-D acid (ppm) Tr 7 5.6 kg/ha 0-10 cm	Tr 7 5.6 kg/ha 10-20 cm	Tr 8 11.2 kg/ha 0-10 cm	Tr 8 11.2 kg/ha 10-20 cm	Tr 9 22.4 kg/ha 0-10 cm	Tr 9 22.4 kg/ha 10-20 cm
1	0.87	-	1.61	-	4.41	-
14	1.84	-	4.82	-	6.94	-
28	.31	-	.96	-	2.15	-
42	.10	.02	.12	.21	.42	.56
56	.10	.08	.15	.22	.48	.55
70	.04	.02	.22	.07	.18	.18
265	ND	ND	.04	Tr	.08	.01
385	ND	ND	.01	ND	.05	Tr

Rapid decomposition of 2,4-D from the amine formulation occurred in the 14-42 day period after application and less than 5% remained at the end of 70 days. Small amounts of 2,4-D were still present from Treatments 8 and 9 after 385 days. During the experiment small amounts of 2,4-D penetrated to the 10-20 cm depth but none were found in the 20-30 cm depth.

Dicamba (Treatments 11-13)

The loss of dicamba was rapid with approximately

5% of that applied present after 42 days (Table 6).

TABLE 6

Dicamba residues in soil following application of a dicamba amine formulation

Days after application	Dicamba acid (ppm) Tr 11 1.1 kg/ha 0-10 cm	10-20 cm	Tr 12 2.2 kg/ha 0-10 cm	10-20 cm	Tr 13 4.5 kg/ha 0-10 cm	10-20 cm
1	.43	-	.75	-	.85	-
14	.23	-	.61	-	3.08	-
28	.05	-	.10	-	.50	-
42	.05	.02	.08	.03	.16	.12
56	.03	.01	.08	.03	.24	.12
70	.02	.01	.09	.02	.13	.04
265	.01	.01	.03	Tr	.07	.03
385	Tr	Tr	Tr	ND	Tr	Tr

Small amounts of dicamba leached to the 10-20 cm depth but none were detected in the 20-30 cm depth. Small residues (.07 ppm) were detected the next spring (265 days) but at 385 days only traces (< .01 ppm) were still present. The persistence of dicamba in soil was very similar to that of 2,4,5-T (Table 3) when the latter was applied as the iso-octyl ester at the same rate. Soil residues of dicamba due to Treatment 13 (4.5 kg/ha) rose to a maximum at 14 days as did the 2,4,5-T residues due to 2,4,5-T iso-octyl ester, Treatment 3. The lower rates of dicamba (Treatments 11, 12) and 2,4,5-T iso-octyl ester (Treatments 1, 2) did not result in a maximum but soil residue levels fell continuously from time of application (Tables 3, 6).

In the present study more than 90% of the amounts of applied herbicides had disappeared within 70 days (with the exception of the highest rate of 2,4-D/2,4,5-T iso-octyl esters) even though relatively large amounts were applied compared to usual agricultural practice. After 55 weeks 3 treatments had residues of approximately 0.1% of the initial application and the rest had undetectable or trace residues. The biological effects of these small quantities of herbicide are not likely to be significant.

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