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2,4-D DISSIPATION IN FIELD SOILS AFTER APPLICATIONS OF 2,4-D DIMETHYLAMINE SALT AND 2,4-D 2-ETHYLHEXYL ESTER

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Abstract—2,4-Dichlorophenoxyacetic acid (2,4-D) was first registered in 1947 as an agricultural herbicide, and it is still the most widely used herbicide worldwide. End-use products, however, are generally formulated as inorganic or amine salts, or as esters. Because of the various forms available, there was concern that by testing only one form, the environmental profile generated might be insufficient to represent all forms. Therefore, as part of the 2,4-D reregistration process in the U.S., 30 soil dissipation studies were conducted with 2,4-D dimethylamine salt and 2,4-D 2-ethylhexyl ester over a 2-year period. Trials were located in seven states and included four cropping practices and bare soil. The results, averaged over all conditions, showed equivalent rates of 2,4-D dissipation in soil when applied as either the amine salt or ester forms. These results also confirm data from earlier field studies in Canada and Washington state showing equivalent 2,4-D dissipation in soil from applications of isooctyl ester, dimethylamine salt, and mixed amine salt forms. The data from the current and former studies show that ester and amine forms have little effect on the rate of dissipation of 2,4-D per se because they are converted rapidly to the same anionic form.

Keywords—2,4-D Dissipation Degradation Persistence Soil

INTRODUCTION

2,4-Dichlorophenoxyacetic acid (2,4-D) is the parent herbicidal moiety in all registered end-use products that contain it as an active ingredient. The acid form, however, is usually not formulated as the end-use product. Most often commercial formulations contain 2,4-D as an inorganic or amine salt, or as an ester.

Because numerous chemical forms are available, a single set of data requirements on 2,4-D may not provide a sufficient environmental profile for all registered products. Previous field studies providing soil residue data from applications of both 2,4-D amine and ester forms have been limited. Results of two former studies, however, indicated that rates of breakdown of 2,4-D in soil from applications of amine and ester forms were very similar [1,2]. Therefore, as part of the 2,4-D reregistration process required by the United States Environmental Protection Agency (USEPA), Industry Task Force II on 2,4-D Research Data (AGRO-GOR, DowElanco, Rhône-Poulenc, NUFARM, USA) conducted soil dissipation studies during 1993 and 1994 comparing typical end-use product formulations containing 2,4-D dimethylamine salt (2,4-D DMA) and 2,4-D 2-ethylhexyl ester (2,4-D 2-EHE). The studies were conducted under diverse soil and environmental conditions, and 26 of the 30 trials were direct comparisons of the amine and ester forms. The results obtained are summarized, discussed, and compared to data from previous studies in this report.

MATERIALS AND METHODS

Fourteen field soil dissipation studies were conducted during 1993, and an additional 16 studies were conducted in 1994. All studies were designed and executed in accordance with current USEPA Environmental Fate Guidelines and followed USEPA Good Laboratory Practice Standards. Each test substance was characterized prior to use. The treatments applied were consistent with product label directions and agronomic practices for the crops and uses of interest. For each crop and use, maximum labeled rates and treatment sequences were applied. In some of the trials, bare soil test plots were established along with test plots in cropped areas. In these cases, the bare soil plots were adjacent to the cropped test plots.

In 1993, test sites were established in Colorado, North Carolina, and Texas. Commercial liquid formulations of either 2,4-D DMA or 2,4-D 2-EHE were applied as diluted sprays in separate trials at each site. Colorado and North Carolina test plots included wheat and turf cropping practices with adjacent bare soil treatments in each trial. Texas plots represented a pasture cropping practice.

The wheat and adjacent bare soil treatments consisted of 1.40 kg acid equivalents (a.e.)/ha applied in May and again in July. In Colorado, soil texture was a sandy clay loam with 1.27 to 1.77% organic matter (OM) and 7.8 to 8.1 pH. Total precipitation plus irrigation ranged from 32.0 to 36.3 cm. In North Carolina soil texture was a sand with 0.77 to 1.43% OM and 5.4 to 6.9 pH. Total precipitation plus irrigation ranged from 51.8 to 85.6 cm. Turf and adjacent bare soil treatments in North Carolina and pasture treatments in Texas consisted of 2.24 kg a.e./ha applied in May and again in June. In Texas, soil texture varied from sandy loam to silt loam with 1.46 to 1.57% OM and 6.0 to 6.1 pH. Total precipitation plus irrigation ranged from 93.7 to 94.2 cm.

In 1994, test sites were established in California, Nebraska, North Dakota, and Ohio. Spray treatments were applied with both the amine salt and ester forms to bare soil following a treatment regime for corn (Nebraska and Ohio), wheat (North Dakota), and pasture, bare soil, and turf (California). A commercial granular formulation of 2,4-D DMA was applied to

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bare soil and turf in North Dakota, and a 2,4-D 2-EHE granular formulation was applied to bare soil and turf in Ohio.

The treatments to bare soil following a corn treatment regime consisted of the following applications: 2.24 kg a.e./ha in May, 1.12 kg a.e./ha in June, 0.56 kg a.e./ha in July, and 1.68 kg a.e./ha in September/October. In Nebraska, soil texture was a silt loam with 2.9 to 3.5% OM and 5.7 to 6.7 pH. Total precipitation plus irrigation was 79.5 cm. In Ohio, soil textures included a silty clay loam, clay loam, and silt loam with 2.0 to 5.0% OM and 6.5 to 7.1 pH. Total precipitation plus irrigation was 47.4 to 97.1 cm. The wheat treatments consisted of 1.40 kg a.e./ha applied in June and again in August. In North Dakota, soil textures varied from a sandy loam to loam with 2.9 to 6.4% OM and 5.9 to 7.7 pH. Total precipitation plus irrigation ranged from 32.7 to 33.6 cm. Turf, pasture, and adjacent bare soil treatments consisted of 2.24 kg a.e./ha applied in March through July with second applications in April through August. In California, soil texture varied from sandy loam to loamy sand with 0.7 to 3.9% and 6.3 to 7.9 pH. Total precipitation plus irrigation ranged from 67.1 to 142.2 cm.

Field experimental design

At all test sites, plots were established in areas with <3% slope in any direction to minimize potential runoff. For each treated plot, cropped or bare soil, there was a corresponding untreated control plot. Treated plots were separated from untreated plots by a buffer sufficient to prevent contamination by drift (at least 30 m). Treated plots were downslope to untreated plots. Commercial cropping practices were followed, but no mechanical cultivations were made after the first 2,4-D applications and for the duration of the studies. At least monthly, irrigations supplemental to natural precipitation were made, if required, to provide at least 110% of monthly normal precipitation (10-year average).

Ground spray application equipment fitted with standard pesticide nozzles was calibrated before and utilized in each application of liquid test substances. Granular test substances were applied with drop spreaders calibrated prior to use. Application procedures followed label instructions regarding stages of crop growth, and rates and number of treatments were the maximums allowed on the product labels. The test substances applied in the studies were commercial liquid and granular formulations containing either 2,4-D DMA or 2,4-D 2-EHE. The liquid formulations contained 0.46 kg 2,4-D a.e. per liter for both the amine salt and ester forms. The granular products contained 1.0% by weight of 2,4-D a.e. for both the amine salt and the ester forms.

The following meterological/hydrological data were taken or obtained at each test site: daily rainfall, daily irrigation and amount, soil temperature at every soil sampling event or more frequently (usually at a 10-cm depth), daily maximum and minimum ambient air temperature, ''normal'' monthly average precipitation and temperature for the area (10-year average), water table depth at least to a depth of 1.4 m on dates of sampling and within 2 d after a rain/irrigation of 10 cm or more, and daily pan evaporation data.

Soil core sampling

In 1993, soil cores were sampled as follows. Inside each treated plot, five sampling areas were established, each at least 3 m × 30 m. Inside each untreated control (UTC) plot, there were three sampling areas, each at least 1.5 m × 30 m. Alleys separated the sampling areas. Each sampling area was divided into 20 sampling lines (at least 1.5 m apart) along which one UTC core or three treated cores could be taken. Three UTC and five treated sampling lines were randomly designated to be used per sampling date. At each sampling event there were three stations (A, B, and C replicates) per each of the five specified sampling lines in the treated plot and one station per each of the three specified sampling lines in the UTC plot. Soil core sampling equipment at each test site consisted of a zero-contamination, plastic-lined, hydraulic push-probe system. Cores 4.45 cm in diameter were taken from 0 to 120 cm soil depth in the UTC plots. Cores from treated plots were 5.71 cm in diameter for 0 to 15 cm soil depth and 4.45 cm in diameter for 15 to 120 cm soil depth on days of test substance applications. At other sampling intervals treated cores were 4.45 cm in diameter from 0 to 120 cm in soil depth. All soil cores were immediately placed in coolers and frozen as soon as practical. Subsequent processing consisted of cutting cores into 15-cm increments and compositing by treatment and depth prior to extraction for residue analysis. The eight core increments corresponded to soil depths of 0 to 15, 15 to 30, 30 to 45, 45 to 60, 60 to 75, 75 to 90, 90 to 105, and 105 to 120 cm. Soil core sampling events were 1 to 5 d before each test substance application, within 4 h after each test substance application, and at scheduled intervals after that up to a possible maximum of 540 d after the last test substance application.

In 1994, the soil core sampling procedure was modified as follows. Treated plots were divided into three areas that served as replicates for sampling. The replicated sampling areas were separated by treated areas of the plot not designated for soil core sampling. At each sampling interval, five cores were taken from each replicate area and composited into one sample. Sampling sites were selected randomly within each replicate for each sampling interval. The UTC plot was sampled at each sampling interval by taking five soil cores at randomly selected points within the plot and then compositing into one sample.

Analysis of soil cores for 2,4-D

In addition to 2,4-D, the analytical method employed was designed to extract and determine the ester 2,4-D 2-EHE, 2,4-dichlorophenol (2,4-DCP), and 2,4-dichloroanisole (2,4-DCA). The latter two were identified as relevant in soil metabolism studies. All analytes were extracted from soil sample aliquots by a combination of three solvent systems and sonication. The combined extracts were diluted with water and concentrated on a C18 solid-phase extraction cartridge. The analytes were eluted sequentially from the cartridge using two specific solvent systems that yielded two eluents. The first eluent, containing 2,4-D 2-EHE, 2,4-DCP, and 2,4-DCA, was chromatographed without derivatization. The second eluent contained 2,4-D that was methylated with BF_3/methanol and then partitioned into hexane. The first eluent and the hexane solution were combined into a single solution for injection into a gas chromatograph using mass selective detection (MSD) in the selected ion monitoring mode. Residue concentrations were determined by comparing the peak areas of the test samples with the peak areas of a series of calibration standards prepared from known analytical standards. Method recoveries of 2,4-D from fortified soil ranged from 91% at 0.01 parts per million (ppm) to 76% at 10.0 ppm. The limit of quantitation (LOQ) was 0.01 ppm.

Calculation of 2,4-D half-lives in soil

Half-lives ($t_{1/2}$) for 2,4-D in soil were calculated from the soil residue data obtained. For each trial, a regression analysis was performed using the concentration of 2,4-D found (ln conversion) versus days after application. Half-lives were then calculated using the equation $t_{1/2} = \ln 2/-k$, where k is the slope of the previously determined regression equation. Calculations were performed in spreadsheets developed using Microsoft Excel Version 5.0 (Microsoft Corporation, Redmond, WA, USA).

Normalization of soil moisture data

Moisture content is an important factor influencing the rate of degradation of 2,4-D in soil [3, 4]. The trials reported here were conducted in various soil types; therefore, the moisture content of each trial required standardization in order to allow meaningful comparisons between and among the various trials. The following procedure was applied to soil moisture data to allow standardization. Dry soil sample weight was subtracted from the sample wet weight and divided by the dry weight to give the moisture content of the sample. The soil field capacity (expressed as percent) was then divided by the percent moisture content of the sample to give a moisture value for the sample relative to the field capacity for the particular soil.

RESULTS AND DISCUSSION

Application verification techniques in general showed applications to be close to targeted levels. Soil half-life ($t_{1/2}$) values were calculated using only the residues found in the 0- to 15-cm soil layer. The residues in the lower layers were not added because they were generally low in absolute value (0 or <10% of the 0–15-cm layer), and the rate of degradation has been shown to decrease with increasing soil depth. Such decrease is due, at least in part, to lower numbers of aerobic microbial degraders [5]. This is of special importance with a compound such as 2,4-D for which the primary mode of degradation is by microbiological action.

Under laboratory conditions 2,4-D DMA dissociates rapidly in water (<3 min) to 2,4-D anion and dimethylammonium cation (unpublished report, The Dow Chemical Company). Data from a monitoring study of applications of 2,4-D DMA to aquatic environments support rapid dissociation in water under field conditions [6]. Because 2,4-D DMA is the salt of a weak acid, it would be expected to undergo dissociation in soil [4]. Adsorption and leaching studies have shown that in moist soils 2,4-D [^{14}C]DMA underwent dissociation with the [^{14}C]DMA cation becoming strongly adsorbed to soil colloids, but adsorption of both the free acid and DMA salt was low. This can be explained on the basis of dissociation to the ionic forms expected under the near neutral conditions of the soils studied [7]. The pH of the five soils in the adsorption study ranged from 5.9 to 7.8 and are similar to the pH range for the various soils in this study. In view of the above, a $t_{1/2}$ based on 2,4-D residues versus time is a reasonable index of 2,4-D DMA dissipation.

The rates of hydrolysis of 2,4-D esters have been studied under laboratory conditions and found to vary depending on the alcohol function of the ester [8,9]. The isopropyl and *n*-butyl esters of 2,4-D were completely hydrolyzed within 24 h at soil moistures above the wilting point, but greater than 48 h was required for complete hydrolysis of the isooctyl ester. Studies in a field soil have shown detectable isooctyl ester residues up to 14 DAT when applied at the very high rate of 31.4 kg a.e./ha but none at 1 DAT when applied at a more typical (but still high) rate of 7.8 kg a.e./ha [1]. Additionally, simultaneous isooctyl ester hydrolysis and microbial degradation of hydrolyzed 2,4-D have been shown in a wheat field [10]. These field studies demonstrate that the ester hydrolysis process, although fairly rapid, is slower than simple dissociation, and for a short period of time after application ester hydrolysis and microbial 2,4-D degradation can occur concomitantly. Therefore, rather than using involved calculations to determine hydrolysis of ester and simultaneous degradation of 2,4-D, regression analyses for 2,4-D 2-EHE applications were based on the amount of ester residue remaining (expressed as 2,4-D a.e.) and the amount of 2,4-D residue found.

Tables 1 and 2 show 2,4-D representative residues found at various sampling intervals after application for the 1993 and 1994 trials, respectively. The data shown are solely for the maximum number of treatments applied per trial. Hence, they represent only one-third of total soil residue data taken in 1993 and one-fourth of the total taken in 1994. For the 2,4-D 2-EHE treatments, the residue data consist of the sum of 2,4-D residues plus remaining 2,4-D 2-EHE residues expressed as 2,4-D a.e. Half-life ($t_{1/2}$) values in days are also included for each trial. The values shown were determined from regression analyses using all sampling time intervals, and also from analyses using the highest residue value found as the initial time point for the analysis. When a range for $t_{1/2}$ is shown, the first value represents analysis using all sampling time intervals and the second represents analysis using the highest residue found as the initial time point.

As previously mentioned, moisture content is an important factor influencing degradation rate of 2,4-D in soil. Standardization of soil moisture content for comparative purposes was accomplished by determining soil moisture as a percentage of field capacity for each trial, and these data are summarized in Tables 3 and 4.

All $t_{1/2}$ values determined are summarized in Table 5 for the 1993 trials, Table 6 for 1994 trials applied as sprays, and Table 7 for 1994 trials applied as granules. For the 2,4-D 2-EHE treatments, residue data consisted of both 2,4-D residues, and, as shown in Tables 1 and 2, the sum of 2,4-D residues plus remaining 2,4-D 2-EHE residues expressed as a.e. Regression analyses were performed with each set of residue data, and the resulting $t_{1/2}$ values for each are shown in the summary tables. In Tables 5, 6, and 7 these are identified by the letter "D," which represents 2,4-D residues, and "D+," which represents 2,4-D plus 2,4-D 2-EHE residues. The $t_{1/2}$ values were summarized by determining the average $t_{1/2}$ and standard deviation (SD) for each treatment set. Any $t_{1/2}$ value greater than two SD from the average was eliminated and the remaining $t_{1/2}$ data were resummarized. This procedure was repeated until the average $t_{1/2}$ values remained unchanged. All $t_{1/2}$ values eliminated by this process were confined to a portion of the 1994 spray solution treatments. Information for the eliminated treatments was analyzed to determine the possible causes for the outlier $t_{1/2}$ found, and these are summarized as follows.

Bare soil—Nebraska; corn treatment regime; treatment no. 3 (0.56 kg a.e./ha): soil temperature was 55°C on the day of treatment and remained high through the sampling period for this timing.

Bare soil—Ohio; corn treatment regime; treatment no. 1 (2.24 kg a.e./ha): soil was dry at ~60% of field capacity and

Table 1. 2,4-D residues (ppm) and $t_{1/2}$ (d) for 1993 trials applied as sprays

			Days after application						
Trial	Form	$t_{½}$	0	1	3	7	14	30	64
Bare soil	Amine	5.1–4.3	0.353[a]	0.380	0.357	0.529	0.047		
Wheat-CO	Ester	2.2	0.515[b]	0.483	0.347	0.156	0.007		
Bare soil	Amine	3.0	0.299	0.276	0.116	0.135	0.009[d]		
Wheat-NC	Ester	3.0–2.5	0.189	0.297	0.343[c]	0.053	0.009[d]		
Wheat	Amine	9.3–7.1	0.201	0.306	0.233	0.273	0.080		
CO	Ester	2.6–2.3	0.215	0.308	0.284[e]	0.043	0.008		
Wheat	Amine	3.1–2.9	0.262	0.278	0.102[e]	0.172	0.009[d]		
NC	Ester	6.1–6.5	0.121	0.123	0.167[c]	0.058[f]		0.005	
Bare soil	Amine	2.5	0.893	0.378	0.157[c]	0.032[g]	0.013		
Turf-NC	Ester	1.7	0.623	0.627	0.364[c]	0.031[g]	0.003		
Turf	Amine	2.3	0.875	0.566	0.128[c]	0.095[g]	0.009		
NC	Ester	3.9	0.626	0.381	0.386[c]	0.036[g]	0.008	0.001[h]	
Pasture	Amine	10.7	0.438	0.383	0.207	0.151	0.093[d]	0.054	0.005
TX	Ester	12.8	0.327	0.290	0.220	0.095	0.049[i]	0.050	0.008

[a] Residue values for amine applications are 2,4-D acid residues.
[b] Residue values for ester applications are the sum of 2,4-D acid residues plus 2,4-D 2-EHE residues converted to 2,4-D acid equivalents.
[c] Two days.
[d] Fifteen days.
[e] Four days.
[f] Eight days.
[g] Five days.
[h] Thirty-five days.
[i] Twenty-five days.

Table 2. The 2,4-D residues (ppm) and $t_{1/2}$ (d) for 1994 trials applied as sprays and granules

			Days after application								
Trial	Form	$t_{½}$	0	1	3	7	14	30	60	90	120
Bare soil	Amine	2.8	0.585[a]			0.322	0.045				
Corn-NE	Ester	4.1	0.518[b]			0.214	0.127	0.003			
Bare soil	Amine	16.1–15.9	0.467	0.746	0.730	0.496	0.442	0.073	0.014	0.006	0.009
Corn-OH	Ester	6.7–5.2	0.585	0.594	0.866	0.775	0.481	0.028			
Wheat	Amine	4.5	0.637	0.531	0.211	0.111	0.070	0.005			
ND	Ester	5.3	0.508	0.488	0.385	0.185	0.089	0.009			
Pasture	Amine	30.6–31.2	0.336	0.560	0.395	0.131	0.146	0.088[c]	0.041[d]	0.050[e]	0.010[f]
CA	Ester	25.6–27.5	0.286	0.343	0.153	0.086	0.078	0.077[c]	0.040[d]	0.017[e]	0.007[g]
Turf	Amine	7.5	0.123	0.093	0.076	0.209	0.023				
CA	Ester	8.5	0.145	0.132	0.042	0.091	0.019	0.014[h]			
Bare soil	Amine	2.3–2.1	0.833	1.403	0.817	0.132	0.021				
Turf-CA	Ester	11.0	0.423	0.288	0.302	0.280	0.146				
Granular product application											
Turf ND	Amine	5.1–4.0	0.102	0.110	0.742	0.071	0.016	0.004			
Bare soil Turf-ND	Amine	14.6–14.5	1.209	1.563	1.933	1.667	0.890	0.269	0.028[k]	0.011	0.019[i]
Turf OH	Ester	295.7–84.0	0.179	0.739	0.280	0.245	0.193	0.066[j]	0.009[d]		
Bare soil Turf-OH	Ester	9.9	1.611	1.058	1.289	1.264	1.496	0.045[j]	0.014[d]	0.004[l]	

[a] Residue values for amine applications are 2,4-D acid residues.
[b] Residue values for ester applications are the sum of 2,4-D acid residues plus 2,4-D 2-EHE residues converted to 2,4-D acid equivalents.
[c] Twenty-nine days.
[d] Fifty-eight days.
[e] Ninety-two days.
[f] One hundred twenty-one days.
[g] One hundred seventy-nine days.
[h] Twenty days.
[i] One hundred fifteen days.
[j] Thirty-one days.
[k] Sixty-two days.
[l] Ninety-three days.

Table 3. Soil moisture as percentage of field capacity and $t_{1/2}$ (d) for 1993 trials applied as sprays

			Days after application						
Trial	Form	$t_{½}$	0	1	3	7	14	30	64
Bare soil	Amine	5.1–4.3	60	50	49	46	72		
Wheat-CO	Ester	2.2	50	40	61	57	59		
Bare soil	Amine	3.0	170	161	122	105	153[b]		
Wheat-NC	Ester	3.0–2.5	170	153	124[a]	124[e]	156[b]		
Wheat	Amine	9.3–7.1	32	25	36	29	53		
CO	Ester	2.6–2.3	39	65	55[c]	73	58		
Wheat	Amine	3.1–2.9	163	129	93[c]	104	124[b]		
NC	Ester	6.1–6.5	206	176	137[a]	118[e]	141[b]	204	
Bare soil	Amine	2.5	276	179	177[a]	179[d]	198		
Turf-NC	Ester	1.7	324	228	272[a]	248[e]	166		
Turf	Amine	2.3	233	163	128[a]	140[d]	197		
NC	Ester	3.9	290	222	300[a]	350[d]	264	264[g]	
Pasture	Amine	10.7	188	186	182	176	116[b]	53	88
TX	Ester	12.8	190	215	177	121	87[f]	38	152

[a] Two days.
[b] Fifteen days.
[c] Four days.
[d] Five days.
[e] Eight days.
[f] Twenty-five days.
[g] Thirty-five days.

temperatures were low for the period, average minimum 8°C and average maximum 20°C.

Bare soil—Ohio; corn treatment regime; treatment no. 3 (0.56 kg a.e./ha): residue data available for days 0 and 1 only.

Bare soil—Ohio; corn treatment regime; treatment no. 4 (1.68 kg a.e./ha): soil was dry at ~60% of field capacity.

Pasture—California; pasture treatment regime; treatment no. 2 (2.24 kg a.e./ha): soil was dry at ~60% of field capacity,

Table 4. Soil moisture as percentage of field capacity and $t_{1/2}$ (d) for 1994 trials applied as sprays and granules

			Days after application								
Trial	Form	$t_{½}$	0	1	3	7	14	30	60	90	120
Bare soil	Amine	2.8	75			87	87				
Corn-NE	Ester	4.1	75			97	89	97			
Bare soil	Amine	16.1–15.9	62	60	59	58	58	73	68	73	122
Corn-OH	Ester	6.7–5.2	72	71	66	66	84	80			
Wheat	Amine	4.5	128	94	86	86	85	94			
ND	Ester	5.3	100	97	96	87	87	97			
Pasture	Amine	30.6–31.2	57	54	65	114	95	68[a]	116[b]	69[c]	105[d]
CA	Ester	25.6–27.5	58	62	65	92	104	98[a]	94[b]	116[c]	122[e]
Turf	Amine	7.5	152	151	130	171	133				
CA	Ester	8.5	305	215	144	80	148	228[f]			
Bare soil	Amine	2.3–2.1	127	137	115	148	108				
Turf-CA	Ester	11.0	179	153	137	112	161				
Granular product applications											
Turf ND	Amine	5.1–4.0	116	105	101	96	107	97			
Bare soil Turf-ND	Amine	14.6–14.5	95	96	92	86	99	89	104[i]	91	110[g]
Turf OH	Ester	295.7–84.0	59	59	55	44	42	97[h]	92[b]		
Bare soil Turf-OH	Ester	9.9	73	64	61	54	43	81[h]	65[b]	79[j]	

[a] Twenty-nine days.
[b] Fifty-eight days.
[c] Ninety-two days.
[d] One hundred twenty-one days.
[e] One hundred seventy-nine days.
[f] Twenty days.
[g] One hundred fifteen days.
[h] Thirty-one days.
[i] Sixty-two days.
[j] Ninety-three days.

Table 5. Half-life ($t_{1/2}$) values (d) from regression analyses using 2,4-D acid residues for 2,4-D DMA applications and 2,4-D acid alone or plus 2,4-D 2-EHE residues[a] for 2,4-D 2-EHE applications (1993 trials applied as sprays)

			Regression analyses using all time points			Regression analyses using initial time point with highest residue		
				2-EHE			2-EHE	
Trial	Treat-ment	kg a.e./ha	DMA D	D	D+	DMA D	D	D+
Bare soil	1	1.40	6.1	8.9	8.5	5.7	8.6	8.4
Wheat-CO	2	1.40	5.1	2.4	2.2	4.3	2.4	2.2
Bare soil	1	1.40	2.5	6.2	6.1	2.2	5.8	5.7
Wheat-NC	2	1.40	3.0	3.2	3.0	3.0	2.5	2.5
Wheat	1	1.40	9.5	9.3	8.2	4.6	4.8	6.0
CO	2	1.40	9.3	2.8	2.6	7.1	2.1	2.3
Wheat	1	1.40	4.3	9.3	8.9	3.6	9.3	8.9
NC	2	1.40	3.1	6.4	6.1	2.9	7.9	6.5
Bare soil	1	2.24	3.3	2.7	2.4	3.1	2.3	2.1
Turf-NC	2	2.24	2.5	1.7	1.7	2.5	1.8	1.7
Turf	1	2.24	3.2	4.4	4.4	3.2	4.5	4.5
NC	2	2.24	2.3	3.9	3.9	2.3	3.9	3.9
Pasture	1	2.24	7.4	4.2	4.0	7.4	3.6	3.5
TX	2	2.24	10.7	13.1	12.8	10.7	13.1	12.8
Average $t_{½}$			5.2	5.6	5.3	4.5	5.2	5.1
SD			2.9	3.4	3.3	2.5	3.4	3.2
Minimum			2.3	1.7	1.7	2.2	1.8	1.7
Maximum			10.7	13.1	12.8	10.7	13.1	12.8
Average + 2 SD			17.9	21.4	20.4	14.3	20.7	20.1

[a] D+ = 2,4-D + 2,4-D 2-EHE.

the site was flood irrigated on the fourth day after treatment (DAT), and residues were increasing at day 14. The next sampling date (30 DAT) showed a residue of 0.01 ppm, which is at the LOQ.

The remaining 1994 spray treatment $t_{1/2}$ data (Table 6) gave an average of 4.3 d for the 2,4-D DMA treatments and 5.3 d for the 2,4-D 2-EHE treatments. The data for 1993 (Table 5) resulted in an average $t_{1/2}$ of 4.5 d for 2,4-D DMA treatments and 5.1 d for 2,4-D 2-EHE treatments. The $t_{1/2}$ determinations for each of the 2 years support each other and indicate that there was essentially no difference in the rate of degradation and dissipation of 2,4-D when applied as either the DMA or 2-EHE forms.

A previous study conducted in Canada by Stewart and Gaul [1] compared the persistence in soil of 2,4-D residues from applications of a commercial isooctyl ester formulation versus a commercial formulation of mixed amines. The study results indicated that small percentages of the applied isooctyl ester could persist in the study soil for several weeks. However, this occurred only at a very high application rate of 31.4 kg a.e./ha and not at the somewhat lower rate of 7.8 kg a.e./ha. At 1 DAT no 2,4-D isooctyl ester was detected at 7.8 kg a.e./ha showing that hydrolysis of the ester form was very rapid at the soil concentration resulting from that rate of application. The 2,4-D residue data reported for the 7.8-kg a.e./ha ester application and a 5.6-kg a.e./ha mixed amine treatment have been subjected to regression analyses to determine $t_{1/2}$ values in a manner analogous to those determined for the trials reported here. Using residue data from 1 DAT up to 70 DAT (when 2,4-D soil residues were 0.03 ppm for the ester and 0.04 ppm for mixed amines), the $t_{1/2}$ value was 11.7 d for the isooctyl ester treatment and 13.4 d for the mixed amines treat-

Table 6. Half-life ($t_{1/2}$) values (d) from regression analyses using 2,4-D acid residues for 2,4-D DMA applications and 2,4-D acid alone or plus 2,4-D 2-EHE residues[a] for 2,4-D 2-EHE applications (1994 trials applied as sprays)

			Regression analyses using all time points			Regression analyses using initial time point with highest residue		
				2-EHE			2-EHE	
Trial	Treat-ment	kg a.e./ha	DMA D	D	D+	DMA D	D	D+
Bare soil	1	2.24	8.9	51.3	11.5	4.7	9.4	6.6
Corn-NE	2	1.12	3.7	3.5	3.4	2.5	2.1	2.1
	4	1.68	2.8	4.4	4.1	2.8	4.4	4.1
Bare soil	2	1.12	5.4	5.4	5.1	4.4	2.9	2.9
Corn-OH	3	0.56	16.6	1.2	1.0	16.6[b]	1.1	1.0
	4	1.68	16.1	7.0	6.7	15.9[b]	5.3	5.2
Wheat	1	1.40	4.0	6.1	5.2	4.0	4.9	4.8
ND	2	1.40	4.5	6.4	5.3	4.5	5.0	5.3
Pasture	1	2.24	5.7	10.6	8.6	5.2	10.0	8.6
CA								
Turf	1	2.24	29.1	6.2	5.6	3.1	5.4	5.3
CA	2	2.24	7.5	9.0	8.5	7.5	9.0	8.5
Bare soil	1	2.24	6.8	4.4	3.9	6.8	4.4	3.9
Turf-CA	2	2.24	2.3	15.0	11.0	2.1	15.0	11.0
Summary of spray treatment $t_{½}$								
Average $t_{½}$			8.7	10.0	6.1	43	6.1	5.3
SD			7.6	12.9	3.0	1.7	3.8	2.8
Minimum			2.3	1.2	1.0	2.1	1.1	1.0
Maximum			29.1	51.3	11.5	16.6	15.0	11.0
Average − 2 SD			0	0	0.1	0.9	0	0
Average + 2 SD			24.0	35.8	12.2	7.8	13.7	10.9

[a] D+ = 2,4-D + 2,4-D 2-EHE.
[b] Considered outlier values.

Table 7. Half-life ($t_{1/2}$) values (d) from regression analyses using 2,4-D acid residues for 2,4-D DMA applications and 2,4-D acid alone or plus 2,4-D 2-EHE residues[a] for 2,4-D 2-EHE applications (1994 trials applied as granules)

			Regression analyses using all time points			Regression analyses using initial time point with highest residue		
				2-EHE			2-EHE	
Trial	Treat-ment	kg a.e./ha	DMA D	D	D+	DMA D	D	D+
Turf	1	2.24	10.3			4.4		
ND	2	2.24	5.1			4.0		
Bare soil	1	2.24	16.7			15.5		
Turf-ND	2	2.24	14.6			14.5		
Turf	1	2.24		[b]	222.9		[b]	22.5
OH	2	2.24		12.7	11.1		11.6	10.1
Bare soil	1	2.24		[b]	295.7		[b]	84.0
Turf-OH	2	2.24		15.5	9.9		10.9	9.9
Summary of granule treatments								
Average $t_{½}$			13.5	10.8	134.9	9.6	8.7	31.6
SD			5.1	5.9	146.7	6.3	4.4	35.4
Minimum			5.1	4.2	9.9	4.0	3.6	9.9
Maximum			16.7	15.5	295.7	15.5	11.6	84
Average + 2 SD			23.8	22.6	428.3	22.1	17.6	102.5

[a] D+ = 2,4-D + 2,4-D 2-EHE.
[b] Half-life ($t_{1/2}$) value was negative due to the continued release of material from the granules during the short time course.

ment. The highest soil residues occurred at 14 DAT and the authors attributed this to rapid hydrolysis of the ester on grass foliage and leaching into the soil from dead grass by rainfall. There was 13.5 cm of rain at 14 DAT and 70.1 cm at 70 DAT, and the residue data indicated that 2,4-D resulting from the application of either the ester or amine forms was affected similarly by the rainfall. In view of the above, regression analyses were also conducted on the residue data using the highest residue at 14 DAT as the initial time point, analogous to the procedure followed with the current studies. The results of these calculations were $t_{1/2}$ values of 9.8 d for the isooctyl ester treatment and 10.6 d for the mixed amines treatment. Both sets of regression analyses of the 2,4-D residue data in the Canadian study confirm the results obtained here, namely that there was essentially no difference in the rates of degradation and dissipation of 2,4-D resulting from applications of the ester and amine forms studied.

The fate of 2,4-D in soil under winter wheat and fallow cropping schemes was also studied previously by Wilson and Cheng under the field conditions of eastern Washington state using DMA salt and isooctyl ester formulations [2]. The rapidity of 2,4-D breakdown decreased gradually with time, and at the end of 6 months, an average of 0.04 ppm of 2,4-D remained in the sampled soil profile regardless of formulation, application rate, or cropping scheme. The 2,4-D residue data from this study have also been subjected to regression analyses. Using 0 to 43 DAT residue data for a 1.1-kg a.e./ha application rate in test year 1973, the $t_{1/2}$ for the DMA salt and isooctyl ester were 7.8 d and 8.0 d, respectively. The $t_{1/2}$ for the DMA salt applied at 11.2 kg a.e./ha was 8.1 d. Because only 9% of the 2,4-D (a.e.) applied remained in the sampled soil profile 1 h after application, a $t_{1/2}$ for the isooctyl ester was not calculated for the higher rate. The authors attributed the low recovery to possible sampling error and/or actual loss by drift during application. Using 0 to 46 DAT residue data for the 1974 crop year the following $t_{1/2}$ values were calculated: (1) for an application rate of 8.9 kg a.e./ha the $t_{1/2}$ was 18.0 d for the DMA salt and 16.7 d for the isooctyl ester; (2) for an application rate of 0.9 kg a.e./ha the $t_{1/2}$ was 14.9 d for the DMA salt and 16.8 d for the isooctyl ester. These analyses reinforce Wilson and Cheng's conclusion that over a growing season, ester and amine form apparently have little effect on the breakdown of 2,4-D in the soil, as both would be converted rapidly in the soil to the same anionic form.

Confirmation of the essential equivalence of the degradative capability of soils treated with ester or amine forms has been reported by Smith et al. [11]. Under laboratory conditions, the breakdown of added [^{14}C]2,4-D to soils treated for 40 years with amine and ester formulations of 2,4-D was rapid with no significant difference between the forms applied at either high or low field application rates.

The data obtained with the granular formulations are limited; however, the apparent soil dissipation of 2,4-D when applied as either DMA or 2-EHE granules appears to be a slower process than when applied as sprays (Tables 6 and 7). This may be due to the time required to release the herbicides from the granules into the soil matrix.

All the soil moisture data for both study years indicated that when soil moisture was at about field capacity the half-life of 2,4-D was about 5 d. Other factors, such as soil temperature, soil OM, rate of application, etc., will also influence degradation rate, and, indeed, inspection of the soil moisture data in Tables 3 and 4 contain exceptions to the statement made above. However, as stated previously, the data shown in the tables represent only one-third and one-fourth, respectively, of all the data taken in each of the 2 study years. The need for and importance of adequate soil moisture to effect microbial degradation of 2,4-D is well documented [3–5,12,13]. In these studies soil moisture content appeared to be the most

important soil parameter influencing the rate of 2,4-D dissipation.

CONCLUSIONS

Comprehensive GLP studies with direct comparisions of 2,4-D DMA and 2,4-D 2-EHE conducted for 2 years in seven states with a total of four cropping treatment regimes plus bare soil show equivalent rates of 2,4-D dissipation in soil for the two forms applied. The results obtained are similar to data obtained in previous field studies in Canada and eastern Washington state that compared 2,4-D dissipation in soil from applications of isooctyl ester, DMA salt, and mixed amine formulations. Laboratory results showing equivalent degradation rates of radiolabeled 2,4-D in soils sampled from fields treated for 40 years with 2,4-D amine and ester formulations support the current and former field studies. Collectively, the data confirm short and similar half-lives in soil for 2,4-D from applications of amine salt and ester forms.

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