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Persistence of 2,4-D, 2,4,5-T, and Dicamba in Range Forage Grasses[1]

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Abstract. The herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 2-methoxy-3,6-dichlorobenzoic acid (dicamba) each labeled in the carboxyl position were sprayed on a pasture consisting of a mixture of silver beardgrass (*Andropogon saccharoides* Swartz.), little bluestem (*A. scoparius* Michx.), and dallisgrass (*Paspalum dilatatum* Poir.) and a sideoats grama (*Bouteloua curtipendula* [Michx.] Torr.) pasture over a 3-year period. Plant samples were harvested at intervals between 1 hr and 16 weeks after treatment and residues determined by radioassay. No important differences were found in the persistence of herbicides or of different formulations of the same herbicide. Rainfall was the most important factor influencing the persistence of the herbicides. The little bluestem-silver beardgrass-dallisgrass samples harvested 1 hr after treatment with the butoxyethyl ester of 2,4,5-T contained both this ester and the acid of 2,4,5-T. One week after treatment, the acid of 2,4,5-T and unknown metabolites were found but no ester.

INTRODUCTION

A VARIETY of herbaceous and woody plants are controlled by 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 2-methoxy-3,6-dichlorobenzoic acid (dicamba). Although the phenoxy acids have been registered and are used for weed control on lands devoted to forage production, the substituted benzoic acids have restricted usage on these areas. Little direct evidence of the persistence of these compounds in forage grasses has been published. Glastonbury *et al.* (3) sprayed peas (*Pisum sativum* L. var. Onward) with the sodium salt of 4-(2-methyl-4-chlorophenoxy)butyric acid (MCPB) and found that the half-life of the retained chemical was 3 days. Gutenmann and Lisk (4) sprayed the diethylamine salt of 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB) on a pasture containing birdsfoot trefoil (*Lotus corniculatus* L.) and timothy (*Phleum pratense* L.) and found a rapid decrease in herbicide concentration in the forage after rainfall. Concentrations of 2,4-DB in the forage immediately after application of 1.5 and 3.0 lb/A rates were about 70 and 160 ppm, respectively, but were 0.32 and 0.80 ppm, respectively, after 48 days.

Klingman *et al.* (5) sprayed a Kentucky bluegrass (*Poa pratensis* L.) pasture with either the butyl ester or the 2-ethylhexyl ester of 2,4-D and found that most of the butyl and about 75% of the 2-ethylhexyl ester were hydrolyzed to the 2,4-D acid within ½ hr after spraying. Total concentrations of 2,4-D residues from the butyl and 2-ethylhexyl esters dropped from 58.4 and 48.4 ppm ½ hr after treatment to 5.0 and 15.1 ppm, respectively, 7 days after treatment.

The investigation reported herein was conducted to determine the persistence of 2,4-D, 2,4,5-T, and dicamba in range forage grasses, to compare the persistence of amine and acid formulations of 2,4,5-T, and to determine the influence of rate of application on the persistence of 2,4-D and 2,4,5-T.

MATERIALS AND METHODS

Two field sites were fenced for the study. One was at College Station, Texas, in a pasture in which silver beardgrass (*Andropogon saccharoides* Swartz.), little bluestem (*A. scoparius* Michx.), and dallisgrass (*Paspalum dilatatum Poir.*) were the dominant species. The other was at Spur, Texas, in a pasture in which sideoats grama (*Bouteloua curtipendula* [Michx.] Torr.) was the dominant species. Different areas were treated at each site each year.

Herbicides labeled in the carboxyl position with carbon-14 were mixed with technical grade herbicides in the proportions necessary to give the specified radioactive levels as well as the specified rate of herbicide per acre. In all experiments, sprays were applied at volumes equivalent to 20 gpa with a compressed air sprayer. Two replications of each treatment were used. In 1962, the plots were 2 by 10 ft and they were 2 by 12 ft in 1963 and 1964.

In 1962, we applied butoxyethyl ester of 2,4,5-T at rates equivalent to ½ and 2 lb/A. Sprays were applied June 11 and June 19 at Spur and College Station, respectively, which contained 5 μc of radioactivity per plot. The carrier consisted of 7 parts water and 1 part diesel fuel (v/v).

In 1963, we applied 2,4-D and 2,4,5-T acids to the silver beardgrass-little bluestem-dallisgrass pasture June 14. Each solution contained 50 μc of radioactivity and sufficient herbicide to provide ½ or 2 lb/A rate. The carrier was acetone-water (1:1) containing 0.5% (v/v) surfactant[3].

In 1964, we applied dimethylamine salt of 2,4-D, dimethylamine salt of dicamba, and triethylamine salt of 2,4,5-T to the silver beardgrass-little bluestem-dallisgrass pasture July 1. We applied both the amine and acid of 2,4,5-T and dicamba to the sideoats grama pasture July 7. The carrier was water containing 0.5% (v/v) surfactant[3] for amine salt formulations and acetone-water (1:1 v/v) for the acid of 2,4,5-T. Each solution contained 60 μc of radioactivity and sufficient herbicide to provide a rate of 1 lb/A.

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[3]Surfactant contained alkylarylpolyoxyethylene glycols, free fatty acids and isopropanol.

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In all years, we sampled the treated plots 1 hr (0 week), 1, 2, 4, and 8 weeks after treatment. An additional sampling was obtained on the fourteenth and sixteenth weeks in 1963 and 1964, respectively. We harvested 2-sq-ft subplots from each main plot by clipping the grass plants at ground level. The clipped plants were separated into those tissues produced during the current year, designated green tissues, and those tissues produced during previous seasons, designated litter tissues. Partially decomposed plant tissues were gathered from the soil surface of the subplots and were added to the litter tissues. After separation, the samples were placed in polyethylene bags, sealed with rubber bands, weighed, and stored at −10 C. Samples harvested as Spur were transported to College Station in an ice chest for analysis.

The harvested samples were shredded, and a 20-g portion was homogenized in a blender with 80% ethanol and filtered. The homogenization was repeated until the radioactivity of the residue was less than two times background. The filtrates were combined, reduced in volume under vacuum in a rotary evaporator, and brought to volume in a 25-ml volumetric flask. Duplicate 1-ml samples of each concentrated filtrate were dried in 1-in planchets, weighed, and the radioactivity assayed with a Geiger-Müller tube. Counts were converted to weight of herbicide from standard curves with appropriate corrections for background and self-absorption. The quantity of herbicide recovered on and in the forage was calculated for each subplot and converted to parts per million equivalents of fresh weight.

In 1962 and 1963, identification and characterization of the radioactive compounds in the concentrated ethanolic extracts were made by descending chromatography on Whatman No. 1 filter paper. An isopropanol:ammonium hydroxide:water (10:1:1 v/v/v) developer was used. After development and drying, each chromatogram was scanned with an autoscanner to determine the location of radioactive substance or substances on the chromatogram. Chromatograms of the ester of 2,4,5-T treating solutions contained radioactive butoxyethyl ester of 2,4,5-T and small amounts of acid. Identifications of the butoxyethyl ester of 2,4,5-T, and acids of 2,4,5-T and 2,4-D were made by co-chromatography of the ethanolic extracts and standard solutions of these compounds.

Results and Discussion

Recovery of herbicides from sprayed plots. The amount of herbicide recovered from grass tissues harvested 1 hr after treatment, calculated as a percentage of the amount applied, varied from 28% (20% green tissue and 8% litter tissue) to 102% (42% green tissue and 60% litter tissue) (Table 1). In all but two plots, greater quantities of the herbicides were recovered from the green tissues than from the litter tissues. Although the silver beardgrass-little bluestem-dallisgrass stands were relatively uniform, the plants and litter did not cover all of the plot areas. The low recovery percentages were due to sparse stands and the higher recoveries to dense plant and litter cover.

Experiments in 1962. Figure 1A presents a semilogarithmic graph of the concentrations of the ester of 2,4,5-T in green tissues of silver beardgrass, little bluestem and

Table 1. Percentage of herbicides recovered in green and litter tissues of silver beardgrass, little bluestem, and dallisgrass and sideoats grama harvested 1 hr after treatment.[a]

Herbicide	Treatment rate	Silver beardgrass-little bluestem-dallisgrass		Sideoats grama	
		Green tissue	Litter tissue	Green tissue	Litter tissue
	lb/A	1962			
Ester of 2,4,5-T	0.5	42	5	33	8
Ester of 2,4,5-T	2.0	34	16	30	10
		1963			
Acid of 2,4-D	0.5	32	17	—	—
Acid of 2,4-D	2.0	50	24	—	—
Acid of 2,4,5-T	0.5	48	26	—	—
Acid of 2,4,5-T	2.0	20	8	—	—
		1964			
Amine salt of 2,4-D	1.0	44	34	—	—
Amine salt of 2,4,5-T	1.0	42	60	54	28
Acid of 2,4,5-T	1.0	—	—	64	20
Dicamba	1.0	34	44	52	20

[a]Average of two replications.

dallisgrass harvested at five dates after treatment. The lines for the two rates are essentially parallel, indicating that the rate of disappearance was not affected by rate of application. Concentrations of the ester of 2,4,5-T residues decreased rapidly during the second week after treatment when 2.18 in of rainfall occurred. The apparent half-life of the ester of 2,4,5-T (half-life equals average length of time necessary for one-half of herbicidal residue to disappear) under the conditions of this experiment averaged 2.6 weeks. Concentrations of ester of 2,4,5-T in the green tissues 8 weeks after treatment were 25 and 7 ppm, respectively, at the 2.0 and 0.5 lb/A rates.

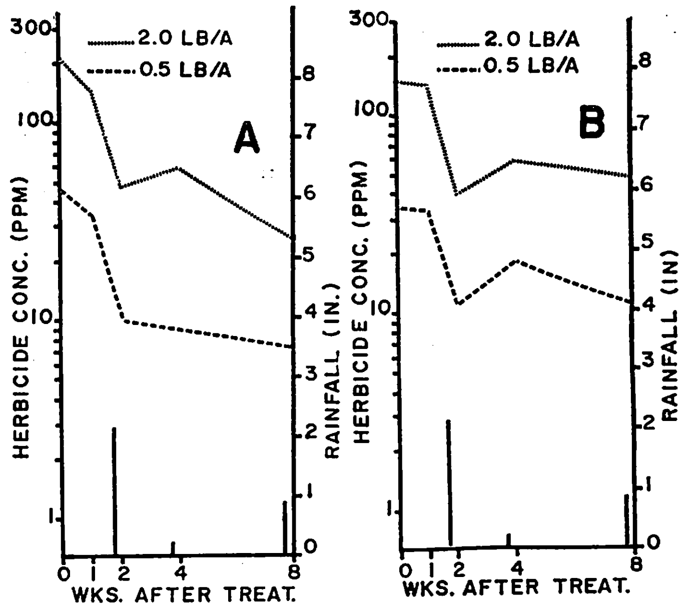

Figure 1. Concentrations of ester 2,4,5-T residues found in silver beardgrass-little bluestem-dallisgrass tissues harvested at five dates after treatment June 19, 1962 at 0.5 and 2.0 lb/A at College Station. (A) Green tissues, (B) litter tissues. Solid vertical lines indicate rainfall which occurred during the indicated interval after treatment.

Figure 1B is a semilogarithmic plot of the ester of 2,4,5-T concentrations in the litter tissues of silver

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beardgrass, little bluestem, and dallisgrass. Disappearance was most rapid during the second week after treatment. The rate of disappearance in litter tissues was slower than in the green tissues. The apparent half-life of ester of 2,4,5-T in the litter tissues was about 4 weeks under the conditions of this experiment. Two factors were important in the slower rate of disappearance. First, growth of the green tissues would have diluted the herbicide, but the litter samples were composed of non-living tissues and growth was not a factor in lowering the concentrations in these samples. Second, conditions for microbial decomposition of the herbicide were unfavorable due to the low rainfall.

Figure 2 presents a semilogarithmic plot of the apparent ester of 2,4,5-T concentrations in the green and litter tissues of sideoats grama. The ester of 2,4,5-T disappeared more rapidly from sideoats grama than from

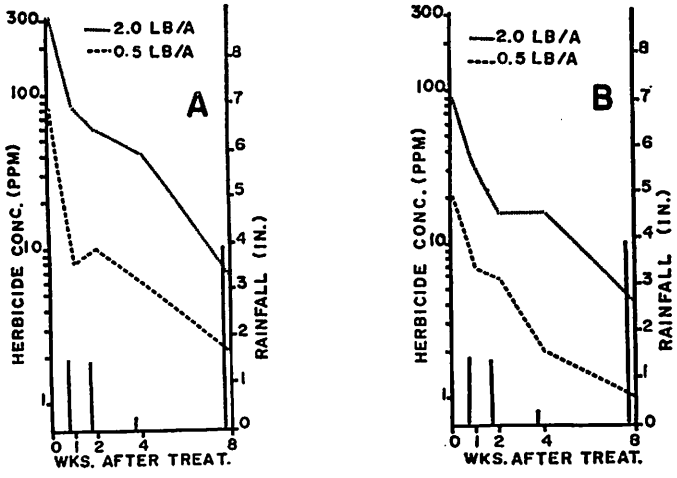

Figure 2. Concentrations of ester of 2,4,5-T residues found in sideoats grama tissues harvested at five dates after treatment June 11, 1962, at 0.5 and 2.0 lb/A at Spur. (A) Green tissues, (B) litter tissues. Solid vertical lines indicate rainfall which occurred during the indicated interval after treatment.

silver beardgrass, little bluestem, and dallisgrass. More rain fell on the sideoats grama than on the silver beardgrass, little bluestem, and dallisgrass. The apparent half-life of the herbicide averaged 1.6 weeks in the green tissues and 1.7 weeks in the litter tissues. The amount and frequency of the rainfall were conducive to leaching, microbial decomposition of the herbicide, and growth of sideoats grama plants. All of these factors contributed to a rapid reduction in herbicide concentrations.

Experiment in 1963. The concentrations of 2,4-D and 2,4,5-T residues found in green and litter tissues of silver beardgrass, little bluestem and dallisgrass harvested at six dates after treatment June 18 are shown in Figure 3. A 0.69-in rain occurred during the first week after treatment, and the concentrations of both herbicides in green and litter tissues decreased rapidly. No rainfall occurred during the second week after treatment and the rate of herbicide disappearance was slower in most of the plots than it was during the first week. During the third and fourth weeks after treatment, 1.58 in of rain occurred and the rate of herbicide disappear-

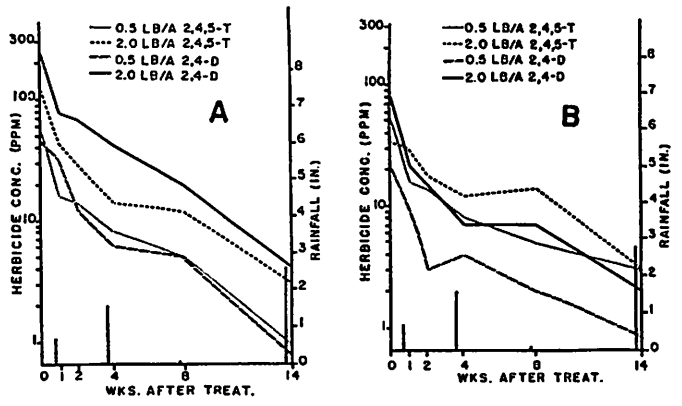

Figure 3. Concentrations of 2,4-D and 2,4,5-T residues found in silver beardgrass-little bluestem-dallisgrass tissues harvested at six dates after treatment June 14, 1963 at 0.5 and 2.0 lb/A at College Station. (A) Green tissues, (B) litter tissues. Solid vertical lines indicate rainfall which occurred during the indicated interval after treatment.

ance was more rapid in most of the plots than during the second week. During the fourth through the eighth weeks after treatment, only 0.08 in of rainfall occurred and relatively small decreases in herbicide concentrations were found. The 2.78 in of rainfall which occurred during the eighth through the fourteenth weeks after treatment probably was the primary factor responsible for the rapid rate of herbicide disappearance during this interval. The average half-life for 2,4-D in green and litter tissues was 2.3 and 2.8 weeks, respectively. The average half-life of 2,4,5-T in green and litter tissues was 2.9 and 3.4 weeks, respectively.

Experiments in 1964. Residues of amine salts of 2,4-D, 2,4,5-T, and dicamba disappeared from silver beardgrass, little bluestem, and dallisgrass tissues at about the same rate (Figure 4). The apparent average half-life for each

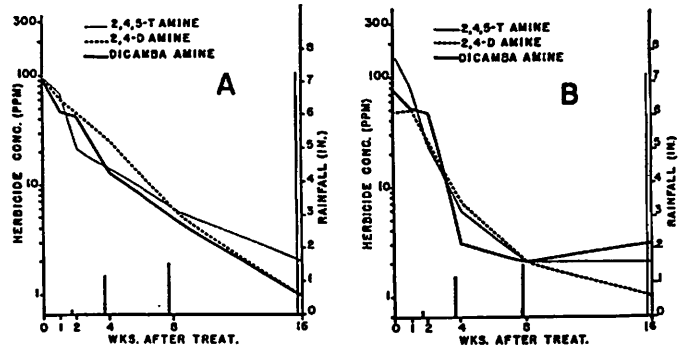

Figure 4. Concentrations of amine of 2,4-D, amine of 2,4,5-T, and dicamba residues found in silver beardgrass-little bluestem-dallisgrass tissues harvested at six dates after treatment July 1, 1964, at 1 lb/A at College Station. (A) Green tissues, (B) litter tissues. Solid vertical lines indicate rainfall which occurred during the indicated interval after treatment.

of the three compounds in green tissues was 2.0 weeks under the conditions which existed during the experiment. Because of heavy rainfall during the fifteenth week after treatment, the concentrations of the three compounds were reduced to 1 or 2 ppm in the green

tissues. Concentrations of the three herbicides decreased rapidly in the litter tissues during the first 8 weeks after treatment (Figure 4B) when frequent rainfall kept the soil and litter tissues moist. The average half-lives of 2,4-D, 2,4,5-T, and dicamba in the litter tissues were 2.8, 2.7, and 2.6 weeks, respectively.

A relatively slow disappearance rate was found for all three herbicides in the green and litter tissues of sideoats grama (Figure 5). This slow disappearance occurred during a period of low rainfall. Although considerable variability occurred in the concentrations of the three herbicides at each sampling date, all herbicides had essentially the same rate of disappearance during the 16-week duration of the experiment. Concentrations of the acid of 2,4,5-T, amine of 2,4,5-T, and dicamba were 6, 5, and 4 ppm, respectively, in the green tissues at the time of final sampling 16 weeks after treatment. The concentrations of the three herbicides in litter tissues of sideoats grama are shown in Figure 5B. The acid of 2,4,5-T disappeared more slowly than the amine of 2,4,5-T and dicamba in litter tissues during weeks 2 to 4, but all three compounds were present after 8 weeks in approximately equal concentrations.

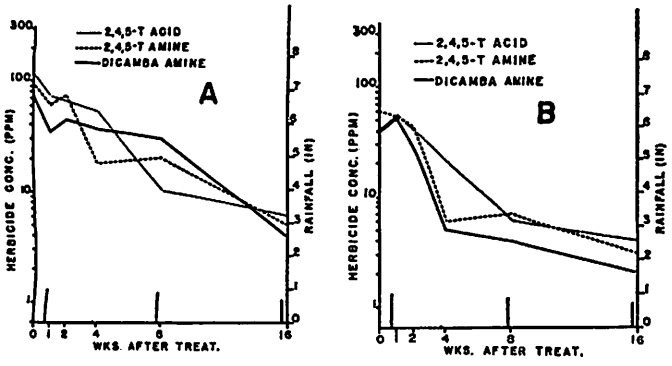

Figure 5. Concentrations of acid of 2,4,5-T, amine of 2,4,5-T, and dicamba residues found in sideoats grama tissues harvested at six dates after treatment July 7, 1964, at 1 lb/A at Spur. (A) Green tissues, (B) litter tissues. Solid vertical lines indicate rainfall which occurred during the indicated interval after treatment.

Data indicate that formulation had no significant effect upon the persistence of 2,4,5-T in the tissues of silver beardgrass, little bluestem, dallisgrass, and sideoats grama. While there were minor differences in the rates of disappearance of the three herbicides applied at College Station and Spur, their persistence in forage tissues appears to be essentially the same after several weeks. The most important factor influencing the persistence of these herbicides was rainfall. Both amount and frequency of rainfall were important.

Even when rainfall did not occur, there was a gradual reduction in the herbicide concentrations in the green tissues, particularly if rainfall had occurred prior to the interval when herbicide concentration was being measured. Dilution of the herbicides by plant growth was an important factor during the intervals after rainfall had occurred and soil moisture was adequate for growth of the plants. Important reductions in the concentrations of the herbicides were not found in the litter tissues when no rainfall occurred. This is evident in Figures 1B, 3B, and 5B. The exception to this statement is found in Figure 4B when a reduction in the concentration of the amine of 2,4,5-T from 146 ppm to 78 ppm occurred during the first week after treatment.

It is not surprising that formulations had no influence on the persistence of 2,4,5-T. Phenoxy herbicides deposited on the surfaces of plant leaves as ester formulations are hydrolyzed to the acid in a relatively short period of time (1, 2, 5).

Identification of herbicide residues. Attempts to identify the radioactive components in the ethanolic extracts by paper chromatography were only partly successful. All extracts from silver beardgrass, little bluestem, and dallisgrass green tissues harvested 1 hr after treatment with ester of 2,4,5-T contained the applied herbicide and the acid of 2,4,5-T. The Rf values ranged from 0.69 to 0.75 and 0.85 to 0.89, respectively, for the acid and ester of 2,4,5-T. Approximately 10% of the radioactivity was attributed to the ester and 90% to the acid of 2,4,5-T. These data confirm the results of Klingman *et al.* (5) who found rapid hydrolysis of the ester of 2,4-D by Kentucky bluegrass. Extracts of green tissues of silver beardgrass, little bluestem, and dallisgrass harvested 1 week after treatment contained the acid of 2,4,5-T and unidentified metabolites which had Rf values ranging from 0.10 to 0.30 but no ester of 2,4,5-T. Approximately 50% of the radioactivity was attributed to the acid of 2,4,5-T and 50% to the unknown metabolites.

The extracts of green tissues of silver beardgrass, little bluestem, and dallisgrass harvested 1 hr after treatment with acid of 2,4-D or acid of 2,4,5-T yielded only the acids of 2,4-D or 2,4,5-T. Tissues harvested 1 week after treatment contained both the acid and unknown metabolites. The metabolites of 2,4,5-T had Rf values ranging from 0.10 to 0.30, and those of 2,4-D had Rf values ranging from 0.07 to 0.25.

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