## Dicamba Residues in Streams After Forest Spraying<sup>1</sup>

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Control of hardwoods is vitally important in the establishment of Douglas-fir seedlings on Pacific Northwest forest lands. In reducing the competition of these brushy species, herbicides have become nearly an indispensable tool. However, with the increasing awareness of the importance of a clean environment, it has become apparent that the safe use of these chemicals requires a knowledge of their behavior, particularly with respect to water contamination (NORRIS 1971).

2,4,5-T (2,4,5-trichlorophenoxyacetic acid)<sup>2/</sup> is a particularly effective brush control agent, but concern about its possible hazards has caused foresters to consider alternative chemicals. Dicamba (3,6-dichloro-o-anisic acid) is an auxin-type herbicide that has been suggested as a possible replacement for 2,4,5-T. Dicamba is both soil and foliage active and is relatively low in toxicity (SWANSON 1969; NEWTON 1972; BRADY 1971). However, before dicamba can be extensively used for brush control, its behavior in various parts of the forest environment must be determined. In this study, we measured the concentrations of dicamba in streams flowing from forest lands which had received aerial application of herbicide.

Herbicide can enter forest streams through direct application to stream surfaces, in overland flow during periods of intense precipitation, or by leaching through the soil profile. Direct application to stream surfaces can be minimized through use of buffer strips between treated areas and streams (NORRIS 1967). The probability of overland flow or leaching of herbicide to streams depends largely on the persistence and movement characteristics of the chemical on and in the soil.

 $<sup>\</sup>pm$ / We acknowledge the invaluable assistance of Don Wood, Hebo Ranger District, Siuslaw National Forest, in sample collection.

 $<sup>\</sup>frac{2}{}$  This paper reports research involving pesticides. It does not contain recommendations for their use nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended.

Dicamba is more persistent than 2,4-D (2,4-dichlorophenoxyacetic acid). FRIESEN (1965) found complete detoxification of 1.12 kg per ha of 2,4-D in sandy loam in 2 weeks, but 0.56 kg per ha of dicamba remained active after 12 weeks. Dicamba persistence is markedly influenced by soil pH, organic matter content, moisture level, and temperature. CORBIN and UPCHURCH (1967) report complete detoxification of 14 ppm dicamba at pH 5.3 in 4 weeks at 26 C, but considerably longer persistence at pH 7.5. From 70 to 90 percent of a 1 ppm dicamba treatment remained in a silt loam soil incubated at 15 or 20 C for 9 months when the moisture content was 13 percent of field capacity, but only 10 percent remained after 4 months when the moisture content was 80 percent of field capacity (BURNSIDE and LAVY 1966). Favorable conditions for dicamba dissipation exist in the moderately acid, high organic matter forest soils in the high rainfall zone of the Pacific coast.

Dicamba is one of the most mobile herbicides in soil. HARRIS (1967), HELLING (1971a), and other investigators report dicamba moves rapidly through many soils. Movement is most extensive in coarse soils with low organic matter, but HELLING (1971b) showed dicamba moves near the wetting front even in soils containing 8 percent organic matter and 50 percent clay. The ready entry of dicamba to the soil profile reduces the probability of the herbicide entering streams by overland flow except during the first intense storms after application.

## MATERIALS AND METHODS

In early June 1971, several small tracts of brush-infested U.S. Forest Service land near Hebo, Oregon, were sprayed by helicopter with 1.12 kg dicamba and 2.24 kg 2,4-D per ha in 37.8 liters of water. Treatment units ranged in size from 14 to 67 ha. Water samples were collected in 2-liter glass jugs which contained 15 g sodium hydroxide to prevent microbial decomposition of the herbicide. Sampling stations were located on streams near three units.

Principal attention was given to the Farmer Creek treatment unit (Fig. 1). The unit contains predominantly the Astoria-Hembre soil association which is characterized by deep, well-drained silt clay loams over well-fractured sedimentary parent material. In this instance, 67 ha of a 244 ha watershed were treated, and samples were taken at three stations located at various distances downstream from the unit. The stream varied from 0.6 to 1.5 m in width and from 2.5 to 45 cm in depth where it flowed near the treated area, and the stream banks were relatively free of brush. Stream discharge volume at the time of application was estimated at 57, 142, and 197 liters/s at sampling stations one, two, and three, respectively.

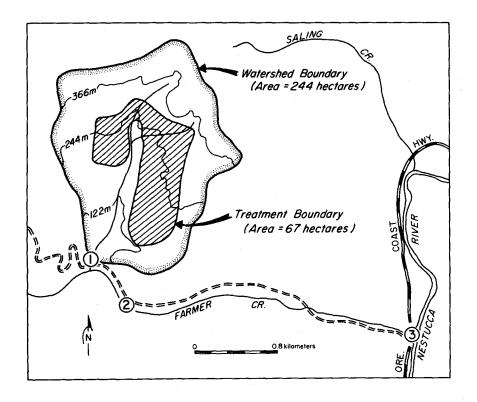


Figure 1. Farmer Creek tributary watershed, treatment area, and sampling points one, two, and three.

Water samples were analyzed only for dicamba because extensive information on entry of 2,4-D to forest streams is already available (NORRIS 1967, 1971). For chemical analysis, a 500 ml aliquot of streamwater was acidified to pH 1 with HCl and extracted with three 150 ml portions of ether. Ether extracts were concentrated to 20 ml and methylated with diazomethane in ether. The ether extracts were then concentrated to 1 ml and injected into a Varian 2100 gas chromatograph equipped with an Infotronics C-200B microcoulometric detector. The 1.8 m x 6.25 mm glass column was packed with 60/80 mesh gas chrom Q coated with 6 percent OV-1. The column was operated at 165 C with a nitrogen flow of 68 ml/min. Dicamba retention time was 2.6 min.

 $<sup>\</sup>frac{3}{}$  Mention of product by name does not imply endorsement by U.S. Department of Agriculture.

Average dicamba recovery was 87 percent (range 85-89 percent) from streamwater spiked at 1 ppb which was the minimum level which could be detected quantitatively. This method also measures the dicamba metabolites 3,6-dichlorosalicylic acid and 5-hydroxydicamba (BROADHURST et al. 1966). Methylation converts the former to dicamba, while the latter has a retention time of 6.6 min. Prespray stream samples did not contain any contaminants which would interfere with the dicamba analysis.

Precipitation patterns were recorded at Cloverdale, Oregon, approximately 6 km SSW from the Farmer Creek treatment unit (U.S. DEPARTMENT OF COMMERCE 1971, 1972).

## RESULTS AND DISCUSSION

Dicamba residues from the Farmer Creek treatment unit were found at sampling point one about 2 hours after the start of the application period (Table 1). Residue levels rose sharply to a maximum of 37 ppb in about 5.2 hours and then declined slowly to background levels by 37.5 hours. Sampling point one lies approximately 1.3 km from the point where the sample stream enters the treatment unit. Residues detected at point one during the first 30 hours after application probably resulted from a combination of drift and direct application of herbicide to exposed surface water.

Small additional amounts of dicamba entered the stream between June 10 and June 18, probably in connection with the precipitation that fell during this period. The source of these residues is not certain, but we suspect they represent rain washings of foliage which overhangs the stream or mobilization of residues on rocks or forest floor material immediately adjacent to the stream. Stream contamination from these mechanisms was slight.

Samples of water from point one were collected periodically for nearly 14 months after application, but no dicamba residues were found more than 11 days after application. Several collections were made shortly after intense storms in the early fall when maximum opportunity existed for movement of surface residues to the stream (Fig. 2). Other samples were collected in the late spring when streamflow would consist largely of ground water, at least some of which had moved through the soil profile of the treated area. Despite the persistence and leaching characteristics of dicamba and the potential for overland flow and movement through the soil profile, measurable dicamba residues were not detected in Farmer Creek.

Water samples were also collected over a 10-day period after application of dicamba to two other areas near Hebo. Opportunities for drift and direct application of spray to these streams were limited, and no detectable dicamba residues were found.

TABLE 1 CONCENTRATION OF DICAMBA IN FARMER CREEK

	S	Sample po	point one		Sample point tv	two	Sample point three	ee:
Sampling date and hours after application	date after on	$ppb^{1/}$	Sampling date	$ppb\frac{1}{2}$	Sampling date and hours after application	$ppb^{1/2}$	Sampling date and hours after application	$ppb^{1/2}$
6-5-71 (P	(Prespray)	0	6-10-71	2	6-5-71 (Prespray)	0	6-5-71 (Prespray)	0
	0.3	0	6-11-71	7	6-7-71 0.4	0	6-7-71 0.5	0
	9.0	0	6-13-71	6	0.7	0	6.0	0
	1.0	0	6-16-71	0	1.1	0	1.2	0
	1.2	0	6-18-71	2	1.5	0	1.6	0
	1.7	0	6-21-71	0	1.8	0	2.0	0
	2.1	Н	6-30-71	0	2.2	0	2.4	0
	2.5	0	7-8-71	0	2.6	0	3.2	0
	2.7	0	7-9-71	0	3.0	0	3.7	0
	3,3	က	8-11-71	0	3.5	0	4.2	0
	3.8	12	8-25-71	0	4.0	ო	4.7	0
	4.3	16	8-20-71	0	4.5	4	5.2	0
	4.8	28	9-1-71	0	5.0	7	5.7	0
	5.2	37	9-2-71	0	5.5	6	6.5	0
	6.2	33	9-7-71	0	6.3	10	7.2	0
	8.9	30	9-29-71	0	6.9	6	8.2	-
	7.8	27	10-19-71	0	7.9	<b>∞</b>	9.2	4
	8.8	24	11-17-71	0	6.8	9	10.6	9
	10.2	16	11-29-71	0	10.3	4	13.5	3
	13.1	11	12-22-71	0	13.2	ო	23.1	0
	22.8	9	5-18-72	0	23.0	1	30.1	0
			6-8-72	0	30.0	0	4.114	
6-8-71	30.1	7	6-30-72	0				
	37.5	0	7-28-72	0			-	
6-9-71	50.2	0						

 $\frac{1}{2}$  0 means less than 1 ppb.

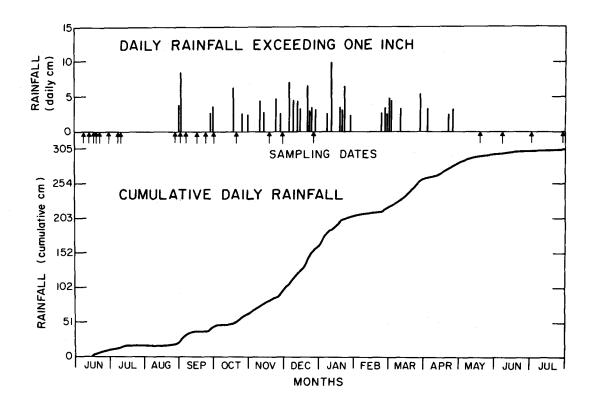


Figure 2. Rainfall patterns and sampling dates, Farmer Creek. Rainfall records for Cloverdale, Oregon.

TRICHELL et al. (1968) studied dicamba runoff from sloping sod plots in Texas. They found up to 6.5 percent of the applied dicamba was recovered in runoff water when 1.27 cm artificial rain was applied 24 hours after the herbicide. No dicamba was found in runoff water from a similar artificial rain application 4 months later after 21.6 cm natural rainfall. Approximately 8 percent of the artificial rain was recovered as runoff. The infiltration capacity of most forest soils is so very high that there is little overland flow except during periods of extremely heavy precipitation.

With respect to other pesticides, dicamba is considered highly mobile in soil. Thus, while many insecticides and herbicides remain in the surface few centimeters of the soil, dicamba may leach 0.5 m or more. Relative to the distance from a treated area to a nearby stream, however, leaching of 0.5 m or so is not important. In terms of potential for leaching to streams, we think dicamba is not particularly mobile in the forest floor and soil.

Water samples were also collected at sampling points two and three on the main branch of Farmer Creek. These points were, respectively, 0.6 and 3.7 km downstream from sampling point one. The concentration of dicamba in the stream was markedly reduced with downstream movement (Fig. 3). There is a sizable increase in stream discharge between points one and two because point one is on a tributary of the main branch of Farmer Creek. We assume the 1.4-fold increase in stream discharge between points two and three is from ground water because there is little contribution from side streams.

Integration of the curves of dicamba concentration revealed a total of 58, 35, and 26 g dicamba passed sampling points one, two, and three, respectively, the first 37.5 hours after application. Dicamba was apparently rapidly adsorbed by stream sediments and detritus or taken up by aquatic biota. The travel time for peak dicamba concentrations between points one, two, and three is roughly proportional to the distance between points, however, which suggests rapid attainment of equilibrium of dicamba distribution between streamwater and sites of chemical uptake. We were surprised at the apparent interaction between dicamba and stream bottom materials in view of the limited interaction between dicamba and soil.

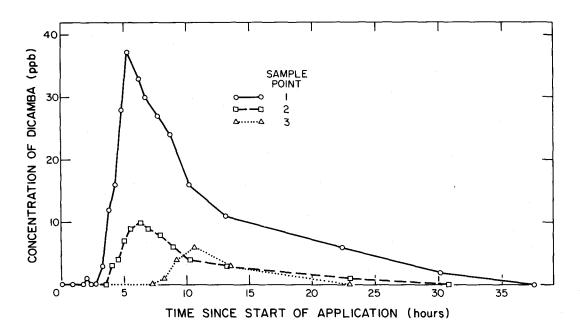


Figure 3. Concentration of dicamba in Farmer Creek after aerial application of 1.12 kg dicamba per ha to 67 ha of a 244-ha watershed.

Dicamba is relatively low in toxicity to fish and mammals (BRITISH CROP PROTECTION COUNCIL 1971). The 48-hour LC  $50\frac{4}{}$  is 465 ppm for small carp (dicamba, dimethylamine salt), and the 96-hour LC 50 (dicamba, acid) is 28 ppm for rainbow trout and 23 ppm for bluegill. Dicamba produced no effect on rats fed 500 ppm or dogs fed 50 ppm in their diet for 2 years. Thus, the levels found in our study were several orders of magnitude below the threshold response levels.

Based on the toxicity characteristics of dicamba, we conclude the dicamba residues in the Farmer Creek stream system posed no acute hazard to aquatic organisms or to downstream water users, and the short persistence of the herbicide in the water precluded chronic exposure. We believe dicamba can be used for brush control on forest lands with little or no impact on aquatic environment if direct application to surface waters is minimized by using appropriate spray application techniques.

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 $<sup>\</sup>frac{4}{}$  Concentration of chemical which will kill 50 percent of the exposed population in 48 hours.