Residues of Trichlorfon and Lauroyl Trichlorfon in Douglas-fir, Willow, Grass, Aspen Foliage, and in Creek Water after Aerial Application

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Monitoring residue levels after aerial spraying can be useful in a study of possible harmful effects of an insecticide on wildlife. Such a study was conducted in the summer of 1971 in the Pike National Forest near Colorado Springs, Colorado, by the U. S. Forest Service's Pacific Southwest Forest and Range Experiment Station and the U. S. Bureau of Sport Fisheries and Wildlife's Denver Wildlife Research Center. The study sought to determine residue levels of trichlorfon (TCF) and lauroyl trichlorfon (TCF-12) in foliage of Douglas-fir, willow, grass, and in creek water as a function of location and time. TCF-12 residues were also analyzed in aspen foliage. TCF is 0,0-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate. TCF-12 is 0,0-dimethyl 2,2,2-trichloro-1-n-dodecanoyloxyethyl phosphonate, the lauric acid ester of TCF.

TCF-12 is an experimental insecticide under development by the U. S. Forest Service. It has higher insecticidal activity but lower mammalian toxicity than TCF. Both are potential insecticides for the control of the spruce budworm, a major forest defoliator (CRISP 1971).

Methods[1/]

Four 160-acre plots were established, each with a central 40-acre intensive study area which included a small creek. The vegetation consisted primarily of ponderosa pine, Douglas-fir, aspen, and spruce, with a grass willow complex bordering the creeks.

[1/] Certain elements of the sample preparation and gas chromatography procedures were taken from methods established by the Chemagro Corporation, Kansas City, Mo., in Reports 21811 and 21386.

[2/] This paper reports research involving pesticides. It does not report recommendations for their use or imply that any uses described have been registered. All uses of pesticides must be registered by appropriate State or Federal agencies, or both, before they can be recommended.

[3/] Trade names and commercial enterprises or products are mentioned solely for information. No endorsement by the U. S. Department of Agriculture is implied.

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The insecticides were sprayed from a helicopter[2/]. TCF (as Dylox 80% ASP, produced by Chemagro Corp.)[3/] was formulated in Orchex 796 oil (Humble Oil and Refining Co.) in a concentration of 1 lb in 5.35 pints and was to be applied on two plots designated "long" and "west creek" at a rate of one and two lbs per acre, respectively. Owing to repeated clogging of the nozzles, the spray was applied unevenly, and each plot received one lb of TCF per acre. TCF-12 was formulated in Orchex 796 oil in a concentration of one lb in 5.35 pints. It was applied to the third plot -- designated "Manchester" -- at a rate of one lb per acre. The fourth plot served as an unsprayed control.

Sampling. Three foliage samples for TCF and TCF-12 residue analysis were taken from Douglas-fir, willow, and grass (Festuca sp.) on each sampling day. TCF-12 residues were also studied on aspen. In addition, water was sampled from three locations along the creek within each plot. Foliage samples were taken immediately after spraying and on day 1, 7, and 14. Water samples were collected immediately after spraying and on day one. All samples were packed in dry ice and shipped to the laboratory in Berkeley, California.

Sample Preparation. The TCF water samples were slightly acidified with HCl in the field to prevent hydrolysis of the insecticide.

For TCF residue analysis, 20 g of foliage were homogenized with 200 ml 0.1 N H_2SO_4 in a Waring blender and then filtered through two layers of cheese cloth. The homogenizing and filtering process was repeated and the combined liquid portion was centrifuged to remove particulate material. The supernatant was decanted into a separatory funnel containing 50 g NaCl. The aqueous phase was extracted three times with 70 ml portions of analytical grade chloroform. Centrifugation was used to separate the phases whenever emulsions occurred. The chloroform extracts were combined and filtered through anhydrous Na_2SO_4 to remove water and then evaporated just to dryness under reduced pressure in a rotary evaporator. The residue was dissolved in 10 ml benzene.

Each TCF water sample was extracted as follows: 50 g of NaCl were added to 400 ml sample water in a separatory funnel. The water was then extracted three times with 70 ml portions of chloroform. The chloroform extracts were combined and passed through anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was dissolved in 10 ml benzene.

For TCF-12 residue analysis, 20 g of foliage were placed in a pint jar and extracted three times by shaking with 80 ml of n-hexane and decanting. The combined hexane extracts were filtered through anhydrous Na_2SO_4. A drop of mineral oil was added to prevent evaporative loss of TCF-12 during the subsequent removal of hexane in a rotary evaporator. The residue was then taken up in 10 ml benzene.

The procedure for extraction of TCF-12 water samples was the same as that of TCF except that cyclohexane was used instead of chloroform. A drop of mineral oil was added before concentration of the cyclohexane extract.

Gas Chromatography. The prepared samples were analyzed for TCF with a Tracor gas chromatograph equipped with a flame photometric detector in the phosphorus mode and a 6-ft. column, 4 mm i.d., packed with 16% XF 1150 on 60/80 Chromosorb W, A.W. Operating temperatures (°C) were: column (180), detector (195), injector block (255), and venting valve (200). Nitrogen was the carrier gas. The gas flows (ml per minute) were: nitrogen (80), hydrogen (310), oxygen (55) and air (35). After proper dilutions with benzene, 10 µl of the extract were injected onto the column. Measurements were based on peak height. Under these conditions, it was possible to detect 0.5 ng of TCF.

The gas chromatographic part of TCF-12 analysis was similar to that of the TCF analysis except for these conditions: An 18-inch column was packed with 6% DC 200 (12,500 C.S.) on 60/80 chromosorb W, A.W. The nitrogen gas flow was 165 ml per minute. Temperatures (°C) were: column (220), detector (200), injector (175), and venting valve (200). Under these conditions, it was possible to detect 5.0 ng of TCF-12.

Recoveries. To obtain recovery figures, foliage and water samples collected before spraying were fortified at these levels (ppm): TCF, foliage (2.50), TCF, water (0.125), TCF-12, foliage (1.00), TCF-12, water (0.05). TCF was added as a solution in 0.1 N H_2SO_4 and TCF-12 was dissolved in hexane. After fortification the samples were allowed to stand for 1 hour. The remainder of the analytical procedure was the same as described for the residue samples.

Results and Discussion

The large variability in TCF residue figures reflects the uneven application of the insecticide due to clogging of the spray nozzles (Table 1). However, it was clear that a fairly rapid decline of TCF residues on foliage took place during the two weeks. In general, residues taken from grass and willow which grow in exposed areas showed a greater deposit. Greater exposure also seemed to be correlated with a faster disappearance of the insecticide. TCF was still present in water samples after one day, but in much reduced amounts (Table 1).

TABLE 1

Residues of trichlorfon (TCF) and lauroyl trichlorfon (TCF-12) on foliage and in water after aerial spraying, by day of application and days thereafter, Pike National Forest, Colorado.

Sample	Sampling point	Day 0	Day 1	Day 7	Day 14
		ppm[1/]			
		Plot: "Long", TCF at 1 lb/acre			
Douglas-fir	1	22.4	13.5	1.5	0.8
Douglas-fir	2	6.5	12.4	2.2	0.4
Douglas-fir	3	8.8	5.3	1.5	0.8
Average	-	12.6	10.4	1.6	0.67
Willow	4	121.2	90.9	7.3	0.2
Willow	5	87.1	80.8	4.0	0.0
Willow	6	36.9	6.6	0.5	0.0
Average	-	81.7	59.4	3.9	0.07
Grass	7	101.7	39.0	5.9	2.9
Grass	8	11.3	16.4	12.4	1.4
Grass	9	226.0	17.0	0.5	2.0
Average	-	113.0	24.1	6.3	2.1
Water	Lower	0.0230	0.0092	---	---
Water	Middle	0.0115	0.0123	---	---
Water	Upper	0.0358	0.0148	---	---
Average	-	0.0234	0.0121	---	---

[1/] Value of one measurement.

TABLE 1

Residue of trichlorfon (TCF) and lauroyl trichlorfon (TCF-12) on foliage and in water after aerial spraying by day of application and days thereafter. Pike National Forest, Colorado, continued

Sample	Sampling point	Day 0	Day 1	Day 7	Day 14
		ppm[1/]			
		Plot: "West Creek", TCF at 1 lb/acre			
Douglas-fir	10	8.6	3.0	1.3	0.3
Douglas-fir	11	11.8	7.1	0.5	<0.1
Douglas-fir	12	12.8	1.2	0.6	<0.1
Average	-	11.1	3.8	0.8	---
Willow	13	80.0	48.0	9.1	<0.1
Willow	14	70.7	37.9	1.9	0
Willow	15	53.0	34.9	2.5	0
Average	-	68.2	40.3	4.5	<0.1
Grass	16	44.1	22.8	4.6	2.1
Grass	17	57.6	47.3	5.4	1.9
Grass	18	27.7	19.8	5.4	<0.1
Average	-	43.1	30.0	5.1	<2.1
Water	Lower	0.0265	0.0080	---	---
Water	Middle	0.0296	0.0098	---	---
Water	Upper	0.0996	0.0084	---	---
Average	-	0.0519	0.0087	---	---

[1/] Value of one measurement.

TABLE 1

Residues of trichlorfon (TCF) and lauroyl trichlorfon (TCF-12) on foliage and in water after aerial application by day of application and days thereafter, Pike National Forest, Colorado, continued.

Sample	Sampling point	Day 0	Day 1	Day 7	Day 14
		ppm[1/]			
		Plot: "Manchester", TCF-12 at 1 lb/acre			
Douglas-fir	19	27.4	48.9	4.8	1.0
Douglas-fir	20	7.9	7.9	0.1	0.0
Douglas-fir	21	12.4	64.1	9.3	0.0
Average	-	15.9	40.3	4.7	0.3
Willow	22	29.7	2.8	1.0	0.0
Willow	23	9.2	16.0	2.4	3.2
Willow	24	6.1	2.7	1.3	3.8
Average	-	15.0	7.2	1.6	2.3
Aspen	25	62.6	15.0	4.1	0.3
Aspen	26	7.8	8.9	2.7	1.6
Aspen	27	30.4	7.8	0.1	2.2
Average		33.6	10.6	2.3	1.4
Grass	28	40.3	6.9	0.7	0.3
Grass	29	6.6	8.3	0.0	0.2
Grass	30	17.2	8.6	1.1	0.7
Average	-	21.4	7.9	0.6	0.4
Water	Lower	0.2465	0.0445	---	---
Water	Middle	0.0056	0.0723	---	---
Water	Upper	0.0723	0.0612	---	---
Average	-	0.1081	0.0593	---	---

[1/] Value of one measurement.

TCF-12 residues on foliage declined at about the same rate as those of TCF (Table 1). TCF-12 disappeared more slowly from water than TCF, possibly by adherence to organic matter present in the streams.

The percent recovery from fortified samples ranged from 83 to 99 in TCF and from 71 to 100 in TCF-12:

	TCF	TCF-12
	Percent	
Sample		
Douglas-fir	83	70
willow	99	100
Aspen	--	95
grass	89	100
water	83	71

These values are based on averages of two replications.

Acknowledgment

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REFERENCES

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