Triclopyr Persistence in Western Oregon Hill Pastures

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Triclopyr effectively controls many woody plants and is increasingly important for vegetation management (Byrd et al. 1975). We determined the movement and persistence of triclopyr and its principal metabolites in grass, soil, and water to provide a better basis for evaluating environmental risks associated with using this herbicide in western Oregon.

MATERIALS AND METHODS

This study was conducted at two western Oregon sites: a hill-pasture near Coquille (Site I) which could be managed for either timber or forage but which was being used for grazing at the time of the study, and (2) a hill-pasture near Corvallis (Site II) suited for grazing. Site I is near the Oregon coast. Site II is in the Willamette Valley. At Site I, triclopyr (3.4 kg acid equivalent/ha with 1.2 L polyglycol surfactant and enough water to give 93.5 L/ha total solution) was applied as the isopropylamine salt on May 24 by helicopter to 2.5-ha which included all of a 1.74-ha watershed. The site averages 34% slope and has Etelka (1 to 2% organic matter) and Whobrei (2 to 5% organic matter) silt clay loam soils. There was no buffer zone along the intermittent stream, which is quite small and does not flow during summer.

Soil was sampled 0, 180, 270, and 365 days after triclopyr application at six random locations on a line that paralleled the stream channel. Soil was collected at 0 to 5, 5 to 15, 15 to 30, 30 to 45, 45 to 60, 60 to 75, and 75 to 90 cm deep from three vertical face of a soil pit dug at each location; soil from a given depth from the six pits was composited by sampling date and frozen.

A stream-water monitoring station was installed at the lower end of the watershed. The stream was dammed with interlocking aluminum panels driven at least 60 cm into the stream bottom, and 35 cm into the sides of the stream bank. A 90° V-notch weir was

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sealed to the dam, and the bottom of the catchment basin was packed with bentonite clay to minimize seepage loss.

Stream stage and rainfall were continuously recorded. An automatic sampler took individual water samples from the small pool behind the dam every 30 min to every 12 h during and shortly after triclopyr application and every 6 h in September and October during the first post-treatment storms; each sample was placed in a separate bottle. Otherwise, samples were collected every 6 h, and four consecutive collections composited into a single 500-ml bottle to obtain a daily-average sample. Each bottle contained 4 g NaOH to insure sample stability. Stream-water sampling terminated 13 months after herbicide application.

At Site II, triclopyr (10.1 kg ae/ha in 372 L water) was applied with a compressed-air-powered, 3-m, hand-held boom to three 6.1- by 30.5-m plots on June 24. The site has a 15% slope and Hazelair (3.8% organic matter) silty clay loam soil. In each plot, grass was clipped at three random locations and composited in a 1.5-kg sample 0, 7, 14, 18, 56, 158, and 365 days after triclopyr application. Soil samples (15-cm increments to 45-cm at six random locations per plot) were collected with a hydraulic corer on the same dates. Samples from a given plot and depth were composited on each date. Grass and soil samples were frozen until analyzed. There was no stream in this area.

Triclopyr and its metabolites (3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine) were extracted from grass, soil, or water and chemically analyzed by the McKellar (1977) method with some minor modifications (analytical method available from M.L.M. on request). The recovery from fortified soils averaged 89% triclopyr at 0.1 mg/kg, 98% 3,5,6-trichloro-2-pyridinol at 0.05 mg/kg, and 84% 2-methoxy-3,5,6-trichloro-pyridine at 0.05 mg/kg.

RESULTS AND DISCUSSION

Residues on grasses from Site II were highest immediately after application (527 mg/kg), but decreased rapidly with time (Table 1). There was some conversion of triclopyr to the pyridinol metabolite but very little to the pyridine metabolite, and neither metabolite accumulated.

The disappearance of triclopyr in grass can be described by the first-order equation: $\ln Y = 4.79 - 0.0136X$, ($r^2 = 0.776$); where Y = milligrams of ae triclopyr per kilogram of grass and X = days after application, however, it substantially underestimates the initial rapid rate of loss.

Triclopyr concentration likely decreases from grass because of the simultaneous action of many processes (metabolism, growth dilution, wash-off, volatilization and photodegradation) which do not proceed at the same rate; thus, the kinetics are not

Table 1. Residue[a] (mean ± standard deviation) of triclopyr and metabolites in grass after triclopyr application (10.0 kg ae/ha, as the isopropylamine salt) by hand-held boom sprayer near Corvallis, OR, June 24 (Site II).

Time after application	Triclopyr		3,5,6-trichloro-2-pyridinol	2-methoxy-3,5,6-trichloropyridine[b]
(day)			------------------ (mg/kg) -------------------	
0	527	± 117	2.9 ± 1.8	0.12 ± 0.16
7	158	± 26	2.4 ± 0.8	< 0.1
14	40	± 18	1.4 ± 1.1	ND
28	99	± 50	1.2 ± 0.9	ND
56	37	± 18	1.2 ± 0.8	ND
158	5.3 ± 1.8		0.29 ± 0.18	ND
365	1.3 ± 1.4		0.07 ± 0.02	ND

[a]Corrected for recovery, controls, and moisture level to oven-dry basis.
[b]ND=no detectable difference between treated samples and controls.

necessarily represented by a single rate constant. We found a biphasic first-order rate model more accurately describes the data as follows:

For 0 to 14 days: $\ln Y = 6.276 - 0.1868X$, ($r^2 = 0.941$); and for 14 to 365 days: $\ln Y = 4.089 - 0.0109X$ ($r_2 = 0.834$).

The biphasic model shows a 50% loss of triclopyr in 3.7 days and a 90% loss in 40 days. Between 14 and 365 days the rate of loss decreased sharply with a (50% loss in 63 days). The pyridinol metabolite levels were low and decreased with time. The pyridine metabolite levels were barely detectable the first week after application and not detectable after 14 days (Table 1)..

In a greenhouse study, Bovey et al. (1979) found slower dissipation of triclopyr in huisache [Acacia farnesiana (L.) Wild] than in grass in our study, but photodecomposition (McCall and Gavit 1986) was probably not a factor in the greenhouse. Bovey et al. (1979) reported triclopyr residue levels of 9 to 37 mg/kg in leaves and stems immediately after application and 1 to 18 mg/kg 30 days later; no data were given for the metabolites.

The initial level of triclopyr in soil was higher at Site II than Site I, presumably reflecting the lower application rate and much denser overstory vegetation at Site I (Table 2). Between the first and second sample collections at both sites, triclopyr residues in the uppermost soil depth (0 to 5 cm) increased, probably because of wash-off from the vegetation. In the 0- to 15-cm soil depth, triclopyr residues decreased with time, following first-order kinetics.

Table 2. Residues[a] of triclopyr and its metabolites in soil after triclopyr application (at two rates, as the isopropylamine salt) on two western Oregon sites.

Time after application	Soil depth	Triclopyr[b]	3,5,6-tri-chloro-2-pyridinol[b]	2-methoxy-3,5,6-trichloro-pyridine[b]
(days)	(cm)	------------ (mg/kg) ------------		
Near Coquille (3.4 kg ae/ha, May 24, Site I)				
0	0-5	0.02	0.01	0.01
180	0-5	0.93	0.26	0.04
	5-15	0.07	0.02	0.01
	15-30[c]	0.01	0.01	ND
270	0-5	0.49	0.19	0.06
	5-15	0.01	0.02	0.01
	15-30[c]	ND	0.01	ND
365	0-5	0.18	0.12	0.05
	5-15[c]	0.01	0.02	0.01
Near Corvallis (10.1 kg ae/ha, June 24, Site II)				
0	0-15	0.55	ND	0.01
28	0-15	3.1	0.48	0.05
	15-30	0.03	0.04	ND
	30-45	0.04	0.03	ND
112	0-15	1.0	0.66	0.09
	15-30	0.06	0.06	0.01
	30-45	0.01	ND	ND
265	0.15	0.10	0.18	0.02
	15-30	0.01	0.09	0.03
	30-45	0.01	0.05	0.01
477	0-15	0.14	0.04	ND
	15-30	0.04	ND	ND
	30-45	0.01	ND	0.01

[a]Corrected for recovery, controls, and moisture level to oven-dry basis.
[b]ND=no detectable difference between treated sample and controls.
[c]No residues detected at depths between 30 and 90 cm at 180 and 270 days or between 15 and 90 cm at 365 days at Site I.

At Site I: $\ln Y = 7.555 - 0.00917X$, ($r^2 = 0.995$);
at Site II: $\ln Y = 8.049 - 0.00855X$, ($r^2 = 0.973$), where Y = micrograms of ae triclopyr per kilogram of soil, and X = days after application. On the basis of these relationships, the half-life of triclopyr in soil was 75 days at Site I and 81 days at Site II.

Despite the rapid disappearance of triclopyr from soil, only trace amounts of either metabolite were detected. Concentration

of 3,5,6-trichloro-2-pyridinol was highest 0 to 5 cm deep 180 days after application at Site I.

Triclopyr disappeared from soil more slowly at our study sites than has been noted by researchers at other sites. In the laboratory, Regoli and Laskowski (as reported in Hamaker and Goring 1976) found that triclopyr had a half-life of about 45 and 12 days in two soils (0.8 and 4.2% organic matter) when incubated at 35 C and 33 kPa moisture. In a Texas field study (Miller clay), Moseman and Merkle (1977) noted that triclopyr applied in fall persisted about 6 months, whereas most of that applied in summer was dissipated in 3 months. Schubert et al. (1980) reported that triclopyr residues in soil decreased from 18 to 0.8 mg/kg in soil in 28 days and to 0.1 mg/kg in 166 days in a West Virginia watershed. The more rapid disappearance of triclopyr in West Virginia probably reflects their wet summer in contrast to the dry Oregon summer.

Residues of triclopyr and metabolites were essentially confined to the top 30 cm (principally in the top 15 cm) of soil in our study (Table 2). Only trace amounts (0.04 mg/kg or less) were detected below 30 cm. Soils on our sites have 2 to 5% organic matter and substantial microbial degradation probably occurs before herbicide is leached deep in the soil profile.

Maximum concentration of triclopyr in stream water (95 µ/L) the first 20 h after application at Site I (Figure 1) was about the same as that observed when other herbicides were applied directly to forest stream surfaces (Norris 1981; Norris et al. 1982, 1984). During application, only a trickle of water was entering the pond at the stream-monitoring station, and water was not deep enough to overflow the weir. The reduction in concentration the first 20 h after application is attributed largely to photodecomposition. McCall and Gavit (1986) reported a midday, midsummer half-life of triclopyr in water at 2.1 h. Dilution and adsorption on sediments could also be factors. The pool was dry 24 days after application, and sampling was suspended until fall.

In September, during the first significant rains after application (in May), triclopyr residues (12 µg/L maximum) were found in the small pond behind the dam at Site I. Very little streamflow (< 2 L/h) entered the pool behind the dam (at any time in September or October, evaporation and seepage offsetting inflow--water depth varied from 1 to 15 cm. The water level did not reach the 25-cm depth needed to overflow the weir until the first heavy storm of the season, which began November 6. On November 7, more than 6 cm of rain fell; triclopyr concentrations increased to 15 µg/L, stream discharge was 6500 L, and triclopyr discharge was ~ 100 mg (Figure 2). Even more stream water was discharged on November 9, but the triclopyr concentration was much lower. Water samples collected November 11 were the last that had detectable triclopyr levels. Sampling continued daily through the following June (13 months after treatment), but no further residues were detected. About 5840 g
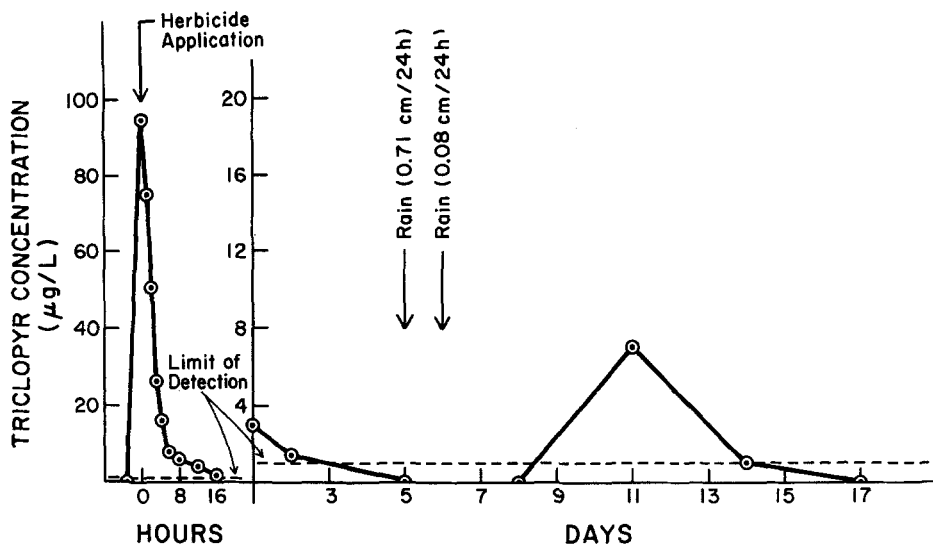
Figure 1. Triclopyr concentration in stream water the first 17 days after application near Coquille, OR., (Site I).
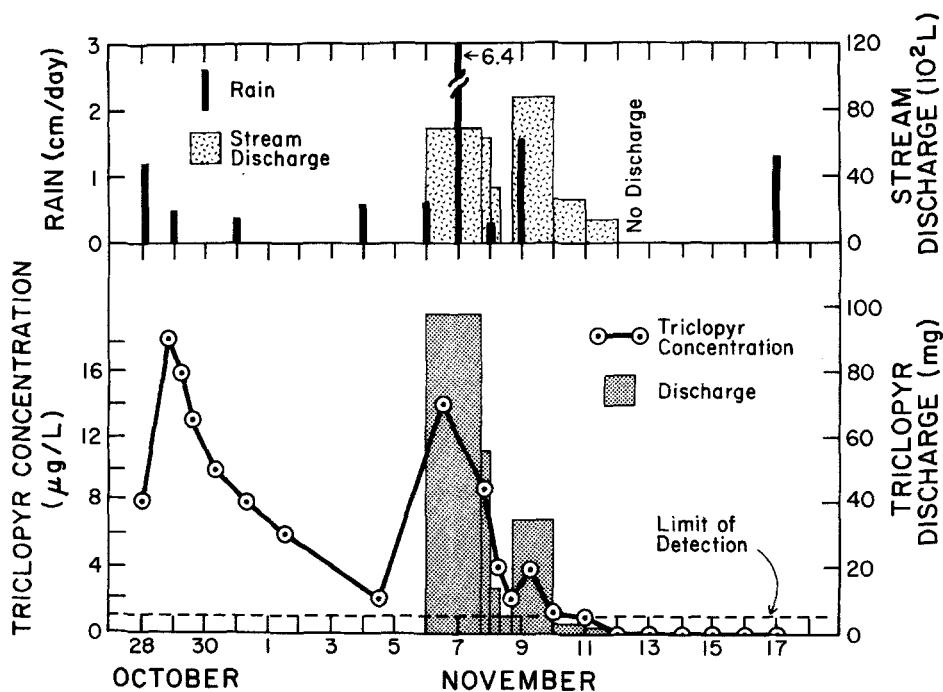

Figure 2. Dynamics of triclopyr concentration and discharge in stream water during the first major (fall) storm after herbicide application the previous May near Coquille, OR (Site I)..

of triclopyr were applied to the watershed at Site I, but only 0.2 g (~ 0.003% of that applied) were recovered in streamflow, virtually all of it during the heavy November 7-9 storm.

Even though present in the soil, triclopyr was not detected in stream water during subsequent periods of heavy precipitation, or during periods of base (low).flow. Thus it appears neither long distance overland flow nor leaching introduced significant amounts of triclopyr to the stream at this site. We believe most or all of the triclopyr detected--that found in September after the first fall rains and that detected subsequently--had originally been applied to either the dry stream channel (~ 0.36% of the watershed area) or its banks and was mobilized by overland flow from those spots.

The proportion of the applied triclopyr we recovered in streamflow at Site I was about the same as reported for 2,4,5-T (0.017%) and 2,4-D (0.014%) and substantially less than for picloram (0.35%) (Norris et al. 1982, 1984) in similar types of studies. Schubert et al. (1980) reported triclopyr residues ranging from nondetectable to 80 µg/L in stream water in a West Virginia watershed (average slope 8%) treated with triclopyr at 11.2 kg/ha. They detected no triclopyr metabolites in water and concluded that "no significant amount of triclpyr moved from the site of application," although streamflow was not directly measured, and most of the watershed was not treated. On the basis of this study and other published research on triclopyr, we conclude its use in western Oregon, according to the label, offers little opportunity for toxicologically-significant exposure to non-target organisms or downstream water users.

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