J. Range Manage.
45:167-170, March 1992

Observations: Potential long-term environmental impact of tebuthiuron and its metabolites in Utah juniper trees

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Abstract

The concentrations, distribution, and longevity of tebuthiuron {*N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N*,*N*'-dimethylurea} and its metabolites in Utah junipers [*Juniperus osteosperma* (Torr.) Little] killed by tebuthiuron are not known, causing concern about potential residues and their release into the environment from decaying plants or burning wood. Utah juniper trees killed by tebuthiuron at 3 north-central Arizona locations were assayed for tebuthiuron and its metabolites by gas chromatography with flame photometric detection. Foliage, twigs, stems, and litter from recently killed trees averaged 13.3 ± 0.4, 0.4 ± 0.1, 0.4 ± 0.1, and 4.0 ± 6.6 mg/kg of tebuthiuron plus its metabolites, respectively. Dead stems averaged 0.5 ± 0.4 mg/kg in sapwood, 0.1 ± 0.1 mg/kg in heartwood, and 0.4 ± 0.7 mg/kg in bark, 3 to 9 years after application. Root bark averaged 1.1 ± 1.9 mg/kg, and root wood averaged 0.5 ± 1.4 mg/kg. Although long lived, these small tebuthiuron residues should have little potential environmental harm if treated Utah juniper wood is used as firewood or fence posts.

Key Words: herbicide residues

Tebuthiuron {*N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N*,*N*'-dimethylurea} has been used in many places to kill Utah junipers [*Juniperus osteosperma* (Torr.) Little] (Clary et al. 1985, Johnsen 1987). Juniper trees are major sources of firewood and fence posts in the western United States (Barger and Ffolliott 1972, Budy and Meeuwig 1987, Fox 1987). Wood cutters often avoid junipers uprooted by bulldozing or chaining because grit embedded in the bark rapidly dulls chain saws (Barger and Ffolliott 1972). Junipers killed by herbicides are preferred as they are standing in place, the bark free of grit, and can be harvested without rapidly dulling saws. However, very little is known about the concentrations, distribution, or longevity of tebuthiuron residues in woody plants, causing concerns about potential residues and their release in the environment from decaying plants or burning wood.

The tebuthiuron is applied to the soil where it is absorbed by roots and accumulated in the top growth (Steinert and Stritzke 1977, McNeil et al. 1984). Tebuthiuron may be leached from treated plants to the soil from decaying litter, roots, and stems (Garcia and Lee 1979, Johnsen and Morton 1989). This tebuthiuron released from dead trees and juniper fence posts might affect susceptible plants growing nearby.

Tebuthiuron and its metabolites decompose at temperatures greater than 280° C (Loh et al. 1978). Flaming combustion in stoves or fireplaces commonly reaches 800 to 1,000° C, but smoldering combustion may not be as hot and small amounts of the herbicide residue might be released in the smoke (Bush et al. 1987). Burning juniper wood containing 1.9 tebuthiuron or less mg/kg plus its metabolites is considered safe since the small amount of residues is quickly oxidized during combustion (Elanco 1983).

This study was done to determine long-term concentrations of tebuthiuron and its metabolites in roots, stems, foliage, and litter from Utah junipers killed by tebuthiuron at different locations, applications rates, and periods after application.

Materials and Methods

Systematic experimental studies of tebuthiuron residues in junipers were not initially part of the efficacy trials because reliable methods to chemically determine tebuthiuron residues were not available then. Also, the residue's long-term persistence (Johnsen and Morton 1989, Johnsen and Morton 1991) was not anticipated. For this study, dead junipers on previously treated plots were sampled to obtain representative samples from different locations, soils, application rates, and years after application.

Location

Samples were obtained from dead Utah juniper trees at 3 north-central Arizona locations: Drake, Rio Verde, and Brushy Mountain. Annual rainfall means ranged from 320 mm at Drake to 380 mm at Brushy Mountain with peak amounts falling in the summer and winter. Drake and Rio Verde were lower, warmer, and drier than Brushy Mountain. Pinyon-juniper was the dominant vegetation at each location, and Utah juniper was the dominant tree.

Soils at Brushy Mountain are Barkerville sandy loam, a loamy, mixed, mesic shallow, Udorthentic Haplustoll, a Mollisol. Soils at Drake are Springerville clay, a fine, montmorillontic, mesic, Typic Chromustert, a Vertisol and Tajo loam, a fine-loamy, mixed, mesic, Petrocalcic Palueustoll, a Mollisol. Soils at Rio Verde are a Lynx loam, a fine-loamy, mixed, mesic, Cumulic Haplustoll, a Mollisol, and Barkerville sandy loam.

Herbicide Treatments

Previously established tebuthiuron efficacy trials were used. At Drake, tebuthiuron pellets were applied at rates equivalent to 2.2., 4.5, and 6.7 kg a.i./ha in a 2.74- by 2.74-m grid pattern in April 1975. At Rio Verde, tebuthiuron pellets were aerially broadcast at 2.0 and 4.9 kg a.i./ha in November 1977. At Brushy Mountain tebuthiuron pellets were aerially broadcast at 0.9, 1.8, and 4.6 kg a.i./ha in May 1979.

Plant Collections

Collections were made in the fall season. Utah juniper stems were sampled in 1982 at Brushy Mountain and Drake, in 1983 and 1984 at all locations, and in 1986 at Brushy Mountain. Samples were 30-cm long sections from 7- to 20-cm diameter main stems on 3 randomly selected standing dead trees on each plot. Stems were combined by date of collection for each plot; bark, sapwood, and heartwood were separated for assays. Also, litter under 3 randomly selected dead Utah junipers was sampled in 1984 and 1985 on each of the 1.8, 2.2, and 2.0 kg/ha plots at Brushy Mountain, Drake,

The author thanks R.D. Martin and J.F. Ruyle for conducting the assays; R.M. Madrigal and C.W. Braun for helping with the field work; the Prescott National Forest and the Rio Verde Ranch for providing the sites; and Elanco Products Co. for providing the herbicide and assay standards.
Manuscript accepted 25 July 1991.

Table 1. Total tebuthiuron plus metabolites detected in treated Utah juniper in North-Central Arizona at 3 to 9 years after treatment. Values for roots are means of roots from all soil-depth layers; values for stem sapwood and heartwood are from stem samples combined by collection date for each treatment.

Location	Rate	Plant Part	Year after application						
			3	4	5	6	7	8	9
	kg/ha		mg/kg						
Brushy Mountain	0.9	Root	0.6 ± 0.6	0.1 ± 0.1	0.3 ± 0.5	—[1]	–	–	–
		Sapwood	0.3	0.2	–	–	–	–	–
		Heartwood	ND	0.3	–	–	–	–	–
	1.8	Root	1.4 ± 0.6	0.1 ± 0.1	0.3	–	–	–	–
		Sapwood	0.1	0.1	T	–	0.5	–	–
		Heartwood	0.1	ND	ND	–	ND	–	–
	4.6	Root	3.0 ± 2.7	0.2 ± 0.2	0.4 ± 0.3	–	0.5	–	–
		Sapwood	–	0.7	–	–	–	–	–
		Heartwood	–	ND	–	–	–	–	–
Drake	2.2	Root	–	–	–	–	0.6 ± 0.6	0.1 ± 0.3	0.6 ± 0.8
		Sapwood	–	–	–	–	1.0	1.3	1.1
		Heartwood	–	–	–	–	0.3	0.2	0.2
	4.5	Root	–	–	–	–	0.8 ± 1.2	T ± 0.0	2.8 ± 0.6
		Sapwood	–	–	–	–	0.4	0.9	–
		Heartwood	–	–	–	–	–	ND	–
	6.7	Root	–	–	–	–	1.7 ± 2.6	T ± 0.0	0.1 ± 0.1
		Sapwood	–	–	–	–	0.3	1.1	–
		Heartwood	–	–	–	–	–	0.1	–
Rio Verde	2.0	Root	–	–	T ± 0.0	0.1 ± 0.1	3.0 ± 0.5	–	–
		Sapwood	–	–	–	0.3	ND	–	–
		Heartwood	–	–	–	0.3	ND	–	–
	4.9	Root	–	–	1.2 ± 0.7	ND ± 0.0	3.0 ± 3.0	–	–

[1] — = not sampled; T = less than 0.1 mg/kg; ND = neither tebuthiuron nor its metabolites detected, detection limits of 0.1 mg/kg for tebuthiuron and metabolites I and II, and 0.3 mg/kg for tebuthiuron and metabolites I and II, and 0.3 mg/kg for metabolite III.

and Rio Verde, respectively. In addition, in 1982, foliage, twigs, and stems were sampled from 3 randomly selected trees killed the year of collection on areas adjacent to plots originally treated with 1.8 tebuthiuron kg/ha at Brushy Mountain and 2.2 kg/ha at Drake. New juniper roots had been found growing in treated plots on which tebuthiuron was detected in soils 1 to 11 years after application (Johnsen and Morton 1989).

Dead Utah juniper lateral roots were sampled in 1982, 1983, and 1984 at each location; and in 1986 at Brushy Mountain. All juniper roots in soil layers in depths of 0- to 7-, 7- to 15-, 15- to 30-cm, and thereafter at 15-cm increments down to bedrock or caliche were collected from 0.5- by 3.0-m trenches dug concurrently for soil sampling (Johnsen and Morton 1989). Roots were 1- to 9-cm diameter; smaller roots rapidly disintegrated and were not collected. Woody tissues in roots collected 6 years or more after applications had decayed, leaving the root-bark in tubelike channels. Root samples were combined by depth and date for each plot, making 89 root samples. Forty-eight randomly selected root samples were separated into bark and wood for assays. Plant parts were shredded in a hammer-mill to pass a 2-mm screen, dried in a forced-air drier at 60° C for 48 hours, ground to pass a 40-mesh screen, and stored in the dark at room temperature in sealed glass bottles.

Laboratory Analyses

Concentrations of tebuthiuron and metabolites were chemically determined for whole roots, root bark, root wood, stem bark, stem sapwood, stem heartwood, twigs, foliage, and litter. Tebuthiuron and its metabolites in plants were assayed using a gas chromatograph equipped with a flame photometric detector (Loh et al. 1978). Tebuthiuron was assayed separately from its metabolites. Metabolite I, *N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N*-methylurea, and metabolite II, *N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N'*-hydroxymethyl-*N*-methylurea, were assayed together (Loh et al. 1978). Metabolite III, *N*-[5-(2-hydroxyl-1,1-dimethylethyl)-1,3,4,-thiadiazol-2-yl]-*N,N'*-dimethylurea, was assayed separately. Tebuthiuron and metabolite standards were added to untreated samples and compared to unknown samples to quantify the amounts of tebuthiuron and its metabolites. The lower detection limits were 0.1 mg/kg of tebuthiuron and metabolites I and II, and 0.3 mg/kg of metabolite III.

Calculations and Statistical Analysis

Generalized concentration means for plants parts were obtained by averaging all data for each plant part. Whole root concentration means for treatments were determined by averaging values from whole root samples from all soil layers for each treatment. Nonparametric methods were used to make comparisons because population distributions were unknown. Wilcoxon rank sum tests (Huntsberger and Billingsley 1981) were made to determine differences between matched sample pairs of plant parts. Kruskal-Wallis one-way analysis of variance by ranks (Montgomery 1984) was used to determine differences by plant parts between locations, applications rates by location, and year after application by location.

Results and Discussions

Except when discussing metabolites alone, tebuthiuron and metabolites concentrations were summed because tebuthiuron:-metabolites ratios varied widely, tebuthiuron metabolization rates are not known, and levels for tebuthiuron allowed by EPA in forage plans are based on total amounts of tebuthiuron and its phytotoxic metabolites. Widely varied tebuthiuron:metabolite ratios have been reported for other species (Ibarra 1984, Johnsen and Morton 1991).

Stems

Low concentrations of tebuthiuron and its metabolites were detected in dead Utah juniper stems 3 to 9 years after application

(Table 1). More residues were in the sapwood than in the heartwood ($P<0.05$). In sapwood combined residues averaged 0.5 ± 0.4 mg/kg (n = 16), with 1.3 mg/kg the highest concentration found, and 6% of the samples contained none. Four of 16 sapwood samples contained metabolites I and II (averaging 0.12 ± 0.06 mg/kg), no metabolite III was detected. Heartwood residues averaged 0.1 ± 0.1 mg/kg (n = 14), with a high of 0.3 mg/kg, and 50% of the samples contained none. No metabolites were found in heartwood. Stem bark residues averaged 0.4 ± 0.7 mg/kg (n = 16), similar to that of sapwood, with a high of 2.5 mg/kg, and 31% of the samples contained none (Table 1). Only 2 of 16 bark samples contained metabolites, both with metabolites I and II (0.14 and 0.18 mg/kg) and 1 with metabolite III (1.11 mg/kg). The combined residue concentrations found in this study agree with the reported juniper fuelwood value of 1.9 mg/kg (Elanco 1983).

Concentrations of residues in the stems were higher at Drake than at Rio Verde or Brushy Mountain ($P<0.01$), perhaps due to differences in application rates and soils. Residue concentrations in stems did not differ with time after application at Brushy Mountain and Drake, but were not determined for Rio Verde.

Tebuthiuron is stable (Elanco 1983); any tebuthiuron and its metabolites in the tree when it dies would remain until lost through leaching or decomposition by fire or invasive microorganisms. The low radial permeability of juniper wood (Choong and Fogg 1968) and low rainfall of semiarid pinyon-juniper rangelands indicate minimal leaching potential of tebuthiuron and its metabolites from intact juniper wood. Juniper heartwood rarely shows signs of decay, but sapwood contacting soil may decay in 5 to 15 years (Barger and Ffolliott 1972). Thus, small amounts of tebuthiuron residues in the sapwood of fence posts or fallen dead trees might be released over 5 or more years. However, residues of tebuthiuron and its metabolites may remain in juniper firewood or fence posts as long as the wood is intact.

Sapwood constitutes from about 10 to 90% of the volume of the stems most likely to be harvested for firewood or fence posts (Howell 1940, Meagher 1940). The relative ratio of sapwood to heartwood varies with stem size and growth rates, being less with larger stems and slower growing trees. Among stems of the same size, stems with the most sapwood would contain the most tebuthiuron and its metabolites. Even then, the residue amounts are very small. If we assumed that bark was 10%, sapwood 45%, and heartwood 45% of the wood volume, a cord of juniper firewood (about 2.26 m^{-3}, 1,160 kg oven dry) would contain an average of about 1.5 g of tebuthiuron plus its metabolites, most of which would be destroyed by a flaming fire as it burned. Thus, burning tebuthiuron treated juniper firewood should not be hazardous.

Roots

Juniper lateral roots averaged 0.8 ± 1.4 mg/kg tebuthiuron plus metabolites (n = 89) 3 to 9 years after applications. The highest concentration detected in roots was 7.2 mg/kg, and 27% of the samples contained no residue. Metabolites I and II were detected in 27 of the whole root samples, averaging 1.22 ± 1.69 mg/kg, but no metabolite III was found. Concentrations of tebuthiuron plus its metabolites in roots did not differ among application rates (Table 1).

Root bark had significantly higher ($P<0.01$) concentrations of tebuthiuron plus metabolites than root wood. Root bark averaged 1.1 ± 1.9 mg/kg residues (n = 48), the highest concentration was 2.5 mg/kg, and 29% of the samples contained none. Twelve of the 48 root bark samples contained metabolites I and II (2.08 ± 2.27 mg/kg), but not metabolite III. Root wood averaged 0.5 ± 1.4 mg/kg residues (n = 48), the highest concentration being 4.25 mg/kg, and 67% of the samples contained none. Nine of the 48 root wood samples contained metabolites I and II (2.32 ± 2.34 mg/kg) and 1 contained metabolite III (0.6 mg/kg).

An apparent increase in whole root residue concentrations with time at Drake and Rio Verde may be due to increased loss of root woody tissues from decay 6 years or more after applications (Table 1). Such loss would increase the root bark:wood ratio, thus shifting whole root residue concentrations higher since residue concentrations are higher in root bark than in woody tissues. Tebuthiuron released from decomposing juniper roots would be a small portion of the tebuthiuron found in soils (Johnsen and Morton 1989); however, herbicide remaining in the tubelike channels left after the root's woody tissues decomposed could damage susceptible plants whose roots grow into these channels.

Foliage and Litter

Residues in dead foliage from trees killed the year of collection on areas adjacent to treated plots averaged 13.3 ± 0.4 mg/kg (n = 3), metabolites I and II averaged 1.26 ± 1.06 mg/kg (n = 3) of this total. Stems bearing this recently killed foliage contained an average of 0.4 ± 0.1 mg/kg residues (n = 5), similar to the 0.5 ± 0.4 mg/kg residues in sapwood of stems killed several years earlier. Only 2 samples of the recently killed stems contained detectable amounts of metabolites, but only of metabolites I and II (0.02 and 0.04 mg/kg).

Residues in litter under treated trees averaged 4.0 ± mg/kg (n = 6), the highest detected was 17.2 mg/kg. Four litter samples contained metabolites I and II (0.78 ± 0.79 mg/kg) and 2 contained metabolite III (3.01 and 2.03 mg/kg).

Conclusions

Small concentrations of tebuthiuron and its metabolites were found in dead roots, stems, foliage, and litter of Utah junipers as long as 9 years after application. Similar concentrations were found in stems of trees killed the year of collection, indicating that tebuthiuron might be in undecayed wood indefinitely. Concentrations found in stems were similar to that reported by Elanco (1983), 1.9 mg/kg, which was considered safe to burn. The highest residue concentrations were in the foliage and litter. All residue concentrations detected were well below the 20 mg/kg tolerance level of tebuthiuron plus its metabolites established for forage by the Environmental Protection Agency.

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