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EFFECT OF BURNING ON HEXAZINONE RESIDUES IN FIREWOOD. P.B. Bush, D.G. Neary, C.K. McMahon, and H.L. Hendricks. University of Georgia, Athens, GA 30603; USDA Forest Service, University of Florida, Gainesville, FL 32611; USDA Forest Service, Macon, GA 31020; and University of Georgia, Athens, GA 30603.¹

ABSTRACT

Two studies were conducted in 1980 and 1982 to determine if hardwood stems killed by hexazinone were suitable for use as firewood. Mixed hardwood-pine stands, in the upper Piedmont of Georgia and in central Florida, were treated with labeled rates of hexazinone in pellet or liquid formulations.² At the Georgia site, white oak (*Quercus alba* L.), chestnut-oak (*Q. prinus* L.), hickory [*Carya glabra* (Mill.) Sweet], and sourwood [*Oxydendron arboreum* (L.) DC] stems were cut, sampled at four stem positions, and subdivided into bark and wood components for hexazinone analysis. In the Florida stand, only turkey oak (*Q. laevis* Walt.) was sampled. Composite bark and wood samples from tree bases were kept. Dark and wood tissue were analyzed for residues of hexazinone. For white and chestnut oak treated with pelleted hexazinone at the Georgia site, herbicide concentrations averaged less than 0.05 ppm 4 and 16 months after treatment. Hexazinone concentrations in hickory and sourwood were more variable but stems contained < 0.15 ppm. Turkey oak treated with the pelleted formulation averaged 0.31 ppm hexazinone at 4 months with no detectable residues at 8 months. Injection of liquid hexazinone resulted in higher residue concentrations at both 4 and 8 months (0.76 and 0.88 ppm, respectively). Wood containing hexazinone was burned under controlled heating rate and temperature conditions to determine carry over in combustion products. With slow heating to 500 C (20°/min) only 11 percent of the hexazinone residues escaped. With rapid burning, all hexazinone residues were thermally degraded at 500°C. Thus, using hardwoods killed by hexazinone for open or closed fire fuel is not likely to exceed air quality standards or produce any significant human exposure.

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² Hexazinone is currently marketed as a 25 percent active ingredient liquid formulation by E.I. DuPont de Nemours and Co., Inc., and as 5 and 10 percent granular formulations by Proserve, Inc. Use of trade and corporation names is for the reader's information and convenience. It does not constitute official endorsement or approval by the U.S. Department of Agriculture to the exclusion of any other suitable product.

INTRODUCTION

The 1978 energy crisis, which drove fuel costs upward by nearly 100 percent, created a high demand for firewood. Many households throughout the country turned to wood as a supplemental or primary heating source. One common source of firewood has been dead or cull hardwoods. One the National Forests in the South, this amounted to 550 million cubic meters (232,100 MBF) in 1980. Most of this fuelwood was taken in individual free-use-or low cost permits.

Herbicide-killed hardwoods have been a ready source of supply for growing numbers of individuals seeking low cost firewood. Toxicological information available from herbicide manufacturers did not indicate that any potential problems with exposure to residues would occur. However, very little information was available on the fate of herbicides within trees and what happens when herbicide-treated wood is burned.

Since 1980, hexazinone has been used widely in the South for site preparation and pine release (2,3,9). This soil and foliar-active herbicide has shown considerable potential as a cost-effective forestry tool. Hexazinone controls most hardwoods at rates tolerated by most Southern yellow pines and is an environmentally-compatible chemical (7,11).

The purpose of this paper is to present data on hexazinone residues in trees which could be used for firewood, and the fate of those residues when burned under controlled combustion conditions. Implications on the suitability of hexazinone-treated hardwoods for firewood and potential human exposure to residues are discussed.

METHODS

Sites

Data from two hexazinone studies are used in this paper. The first study, established in 1980, was located in Habersham County, Georgia, on the Chattahoochee National Forest.

The Georgia study was located in terrain typical of the upper Piedmont. A 60- to 70-year-old mixed hardwood pine stand was selected. Predominant species included shortleaf pine (Pinus echinata Mill.), white oak (Quercus alba L.), black oak (Q. velutina Lam.), southern red oak (Q. falcata Michx.), blackjack oak (Q. marilandica Muenchh.), red maple (Acer rubrum), dogwood (Cornus florida L.), sourwood [Oxydendrum arboreum (L.) DC], and hickory [Carya glabra (Mill.) Sweet]. Stand composition, basal area, and hexazinone efficacy are discussed in greater detail by Neary et al. (10). Two areas were treated with 1.68 kg/ha (1.5 lbs/ac) of hexazinone as the 10 percent active ingredient (a.i.) 2 cc pellet in April 1979 and in June 1980.

The Florida site selected for the study was a longleaf pine (*P. palustris* Mill.) stand which had insufficient seed trees for natural regeneration. Merchantable longleaf stems were removed leaving scattered turkey oak (*Q. laevis* Walt.), live oak (*Q. virginiana* Mill. var. *virginiana*) and sand pine [*Pinus clausa* (Chapm. ex. Engelm) Vasey ex. Sarg.]. Liquid hexazinone (25 percent a.i.) was injected into each turkey oak stem at a rate of 1 ml of undiluted herbicide per incision. The incisions were spaced 10 cm (4 inches) apart about 5 cm (2 inches) from groundline. A pelleted formulation of hexazinone was applied by hand at the rate of two 1 cc pellets (20 percent a.i.) per inch of d.b.h. The pellets were scattered within 1-2 m (3-6 ft) of each tree base. Other details on stand characteristics and herbicide efficacy are discussed by Cantrell et al. (1).

Firewood Sampling Processing

The basic design for the Georgia study consisted of three treatments (control, 4 months post application, and 16 months post application), four hardwood species (chestnut oak, white oak, sourwood, and hickory), four stem locations (base, midstem, top stem, and branches), and three tissue types (bark, sapwood, and heartwood). Five individual trees of each species were cut in 1980 4 and 16 months after hexazinone application. Only one tree of each species was cut from untreated control plots. After felling, subsamples were cut out of the base, midstem, upper stem, and crown branches. Samples were subdivided in the laboratory into bark, sapwood, and heartwood components, ground in a Model 4 Wiley mill to pass a 1 mm mesh screen, and frozen until analyzed for hexazinone residue content. Stem subsamples were also taken to determine percent moisture using standard methods.

The Florida study design consisted of five replications of two herbicide treatments which were individually sampled in 1982, 4 and 8 months after application (1). Composites of bark and wood tissue from the base of each sampled tree were obtained using a series of close-spaced chain saw cuts. Subsamples were kept separate for moisture determination. Kerf samples taken from the bottom 30 cm (1 ft) of each sampled stem were further reduced by grinding in a Wiley mill to pass a 1 mm mesh screen. Samples were then frozen at 0°C for storage prior to residue analysis at the University of Georgia.

Residue Extraction Analyses

Residues of hexazinone and its two major metabolites (A and B) were extracted from wood samples and measured quantitatively following the procedure developed by Holt (4). However, soxhlet extraction with chloroform and methyl acetate was substituted for blending and centrifugation. A representative 30 g sample was weighed into a soxhlet thimble and extracted with 250 ml of chloroform for 12 hours followed by 12 hours soxhlet extraction with 250 ml of ethyl acetate. The chloroform and ethyl acetate extracts were combined and cleaned up by liquid-liquid partitioning.

Levels of hexazinone and the two metabolites were determined by nitrogen sensitive gas **chromatography** after reaction of the metabolites with **trifluoroacetic anhydride (4,11)**. Hexazinone and **metabolite** levels were determined by **comparison** of peak height in sample chromatograms to those of an analytical standard. A reagent blank and spiked **sample** were included with each set of analyses, and percent recovery values were used to correct sample concentrations.

Combustion Procedures. --

A laboratory procedure was selected which **would simulate** the wide range of conditions under which herbicide-treated wood could be burned. Since wood burns differently in fireplaces than in stoves, or under conditions of **smoldering** and **flaming combustion**, a horizontal tube furnace was selected which would allow small samples to be burned with controlled **combustion and** air flow rates (8). This type of furnace also permitted quantitative **sampling** of **combustion** gases and smoke particulates.

Woody fuels burn under conditions which produce a combination of flaming or **smoldering** combustion. Both processes take place in burning, but one or the other dominates depending on fuel and atmospheric conditions.

Flaming combustion is an efficient, rapid process in which about 1 percent of the fuel is **converted into a black**, sooty visible smoke. Smoldering **combustion** is a slow, inefficient process in which about 10 percent of the fuel is converted to condensed tars appearing as gray or white smoke. Preliminary laboratory studies indicated that flaming conditions could be simulated by rapidly inserting fuel samples into the tube furnace preheated to **500°C**. For smoldering conditions, the samples were slowly heated (**20°C/min**) to 500°C.

Swamp chestnut oak (***Q. mi chauxii* Nutt.**) was selected for the combustion study fuel. Samples were dried to a constant weight and ground in a Wiley mill to pass a **40** mesh screen. Sample units for each test burn of 0.5 g were spiked with **415 ppm hexazinone**. Combustion gases were cooled and the herbicide residues and particulates collected in a glass transfer tube, glass fiber filter, and polyurethane foam plug system (**5,6,12**). **Components** of the sampling system were stored at **0°C** and transferred to the University of Georgia for analyses.

Combustion Residue Analysis

The glass transfer tubes, glass fiber filters, and foam plugs were Soxhlet extracted with ethyl acetate and concentrated on a rotary evaporator. **Hexazinone** was quantified on a gas chromatograph using nitrogen sensitive **chromatography (8)**. Precision, recovery, and accuracy were **examined** using lab control tests.

RESULTS

Stem Moisture Content

The four hardwood species sampled at the Georgia site showed considerable variability in weighted **stem** moisture contents 4 and 16 months after **hexazinone**

application. White oak and hickory stems uniformly dried to a moisture content of less than 28 percent by 16 months (Figure 1). Chestnut oak did not dry out to an appreciable extent by 16 months, although the smaller diameter tops and branches had dried down to 30 percent moisture. Sourwood stems were appreciably wetter after 4 and 16 months. This species was not completely killed by hexazinone and many stems were exuding sap and had epicormic sprouting (10). Most stems were sufficiently sound at 16 months to cut without any major safety hazards. However, precautions should be taken with cutting herbicide-killed trees since small to medium branches begin to fall out of the crowns after 4 months.

Hexazinone Residues in Firewood

Residues of hexazinone and its two primary metabolites were found in 21 and 35 percent of all samples taken from treated hardwoods at the Georgia and Florida study sites, respectively. The frequency of hexazinone residue detection was affected by the efficiency of herbicide uptake and the formulation. Lower detection frequencies were associated with low herbicide efficacy and use of pelleted formulations. Metabolite B was the primary residue detected in 17 percent of the hardwood tissue analyzed from the Georgia site. Hexazinone was detected half as frequently and then only in stem bark and wood. The parent chemical translocated into the crowns evidently was metabolized or degraded rapidly.

An index of hexazinone residue variability in bark, sapwood, and heartwood tissues was obtained by separate analyses of five individual chestnut oak stems 4 and 16 months after the herbicide application on the Georgia site. Chestnut oak was selected because of the large number of stems in the stand and its desirability for firewood. Samples collected 4 months after hexazinone application were fairly free of residues (Table 1). Two of the five trees were completely free of detectable residues (detection limit of 0.01 ppm). Two other stems contained hexazinone and both metabolites in base and top stem samples at concentrations of 0.06 to 0.11 ppm. Note that in most instances the standard deviation is two to three times the mean. After 16 months, the dominant hexazinone residue was still metabolite B, and most detected residues were in basal sapwood and the upper stem (Table 2). Again, many trees did not have detectable amounts of hexazinone or its metabolites and standard deviations were high. In basal sapwood, concentrations ranged from ND to 0.26 ppm. Metabolite A was not detected in any 16 month samples.

The weighted hexazinone residue concentrations in samples collected at the Georgia site 16 months after application varied considerably between stem position and tree species (Figure 2). Except for sourwood, the base and midstem sections--portions most likely used for firewood--were less than 0.05 ppm total residue content. None of the stem sections or branches contained residues above 0.20 ppm. This level is the allowable residue concentration for food at which no health effects will occur.

Samples taken from the bases of turkey oak at the Florida site had the highest hexazinone residue levels (Table 3). Mean concentrations were higher with

the injected liquid formulation and did not show any decrease **between** the 4 and 8 month samplings. Turkey oak treated with the pellet **formulation** of hexazinone had residue levels only 40 percent of the liquid treatment. By 8 months, **hexazinone** and its **metabolites** were not detectable. Injection of the liquid herbicide directly into the base of each turkey oak stem resulted in relatively high concentrations. With soil application of the pellet **formulation**, hexazinone was evidently translocated through the stems and into the **crowns**. Smaller **amounts** of the herbicide were retained in the stem tissue.

Hexazinone Combustion

Hexazinone appears **to thermally** decanpose fairly readily even in smoldering fires (Table 4). With slow heating, **11** percent of the residues in spiked samples were recovered in canbustion products (8). Under flaming conditions, no hexazinone residues were carried over in **smoke**. Hexazinone behaves similarly to picloran when burned than to **dicamba** which has high carry over. rates under both **combustion** conditions (Table 4). Data reported by **McMahon** et al. (8) indicates that temperatures of **600°C** produce greater thermal decomposition than at **500°C**. Thus, carry over rates at the **800** to **1000°C** temperatures found in well-developed stove or fireplace fires are likely to be much lower than those listed in Table 4.

DISCUSSION

Exposure to hexazinone (or other herbicide) residues from burning wood in a home fireplace or wood stove is virtually nonexistent for several reasons. By the time trees obviously killed by herbicides are collected and stored, residue concentrations are likely to be **below** detection limits. When residues **were** detected in the Georgia study, most **were below** the allowable levels for food crops. Higher concentrations were measured in the Florida study but were generally below an average value of 1.00 **ppm**. Canbustion gases and **particulates** are normally vented to the outside via a chimney or stovepipe and are not retained in the **heated** roan. **Any** residues of hexazinone still remaining in firewood **would** be thermally decanposed in a **well-developed** fire. Only 11 percent of the **hexazinone** residues would be carried over in a smoldering fire.

The TLV (Threshold Limit Value) for chemical substances in the **work environment** is 10 **mg/cubic** meter for most herbicides. This is an 8 hour time weighted air quality standard applied to manufacturing environments **where** herbicides are produced.

The **TLV** is not likely to be reached under any realistic conditions where hexazinone treated-trees **are** used for firewood. For example, if 1 metric ton of firewood containing 1 **ppm** hexazinone was burned with an 11 percent carry over and contained within a 6 x 9 m (20 x 30 ft) living roan, the effective air concentration would be **0.9 mg/cubic** meter. This value is only 9 percent of the **TLV**. The example cited above is unrealistic since most of the combustion products **would** be vented to the outside atmosphere. **Thus**, the safety factor is **well** in excess of 1,000.

CONCLUSIONS

These results clearly suggest that burning of hexazinone-treated hardwoods in wood stoves or fireplaces does not pose any significant herbicide residue exposure hazard. Low levels of hexazinone in wood coupled with 90 to 100 percent thermal decomposition rates greatly reduce potential exposure. A cautious approach would be to limit burning of hexazinone-treated firewood to well-developed, hot fires and use other fuel sources for starting fires or maintaining slow burning ones. As a note of caution, this paper has discussed an organic herbicide. Wood samples treated with inorganic herbicides or pesticides like copper **chrome** arsenate should not be burned.

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Table 1. Mean **residues of hexazinone** and **metabolites A and B** in chestnut oak at four stem positions 4 months after herbicide application, Georgia study site, 1980.

Stem position	Tissue type	Residues			
		Hexazinone	Metabolites		
			A	B	
----- ppm -----					
Base	Bark	ND ^{1/} + 0.0	ND + 0.0	ND + 0.0	ND + 0.0
	Sapwood	.02 + 0.04	ND + 0.0	.02 + 0.05	
	Heartwood	ND + 0.0	ND + 0.0	ND + 0.0	
Midstem	Bark	ND + 0.0	ND + 0.0	ND + 0.0	
	Sapwood	ND + 0.0	ND + 0.0	ND + 0.0	
	Heartwood	ND + 0.0	ND + 0.0	ND + 0.0	
Top	Bark	.01 + 0.03	.02 + 0.04	.02 + 0.04	
	Wood	ND + 0.0	ND + 0.0	.01 + 0.03	
Branches	Bark and wood	No + 0.0	No + 0.0	ND + 0.0	

^{1/} ND indicates mean residue concentrations < .001 ppm.

Table 2, Mean residues of hexazinone and metabolites A and B in chestnut oak at four stem positions 16 months after herbicide application, Georgia study site, 1980.

Stem position	Tissue type	Residues			
		Hexazinone	Metabolites		
			A	B	
----- ppm -----					
Base	Bark	ND ^{1/} ± 0.0	ND ± 0.0	No ± 0.0	
	Sapwood	ND ± 0.0	ND ± 0.0	.06 ± 0.11	
	Heartwood	ND ± 0.01	No ± 0.0	.04 ± 0.04	
Midstem	Bark	ND ± 0.0	ND ± 0.0	No ± 0.0	
	Sapwood	No ± 0.0	ND ± 0.0	ND ± 0.0	
	Heartwood	ND ± 0.0	ND ± 0.0	ND ± 0.0	
Top	Bark	ND ± 0.0	ND ± 0.0	T ± 0.02	
	wood	ND ± 0.0	ND ± 0.0	T ± 0.01	
Branches	Bark and wood	ND ± 0.0	ND ± 0.0	T ± 0.02	

^{1/} ND indicates mean residue concentration < .001 ppm and T indicates mean concentration > .001 ppm and < .01 ppm.

Table 3. Mean residues of hexazinone and metabolites A and B in turkey oak 4 and 8 months after application of liquid and granular herbicide, Florida study site, 1982.

Hexazinone formulation	Time from herbicide application			
	4 months		8 months	
----- ppm ¹ -----				
Pellet	0.31 ± 0.61	ND ± 0.0		
Liquid	0.76 ± 0.67	0.88 ± 0.93		

¹ Oven dry weight basis

Table 4. Recovery of hexazinone, **picloram**, and dicamba residues from wood heated to 500°C under two burning conditions, McMahon et al., 1985.

Herbicide	Hexazinone recovery at 500°C	
	Slow heating ^{1/}	Rapid heating ^{2/}
Hexazinone	11 + 2.3	0
Picloram	0	0
Dicamba	92 + 5.1	32 + 30

¹ Heating rate of 20°C/min
² Immediate insertion into furnace at 500°C

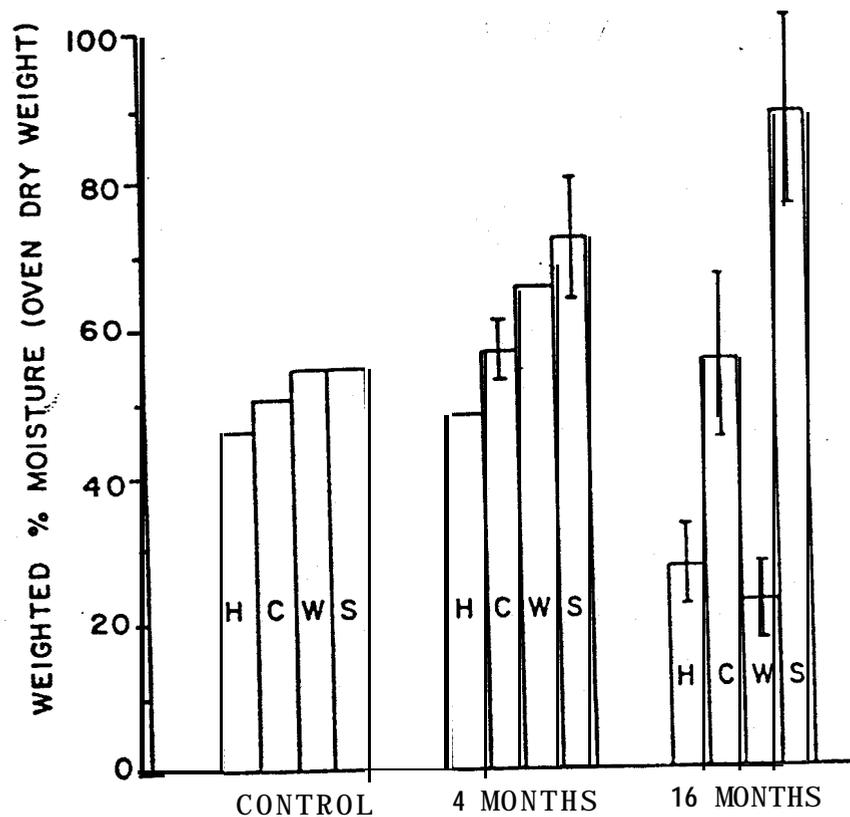


Figure 1. Weighted percent moisture of base sections of hickory (H), chestnut oak (C), white oak (W), and **sourwood** (S) stems 4 and 16 months after treatment with 1.7 kg/ha a.i. hexazinone, Georgia study site, 1980.

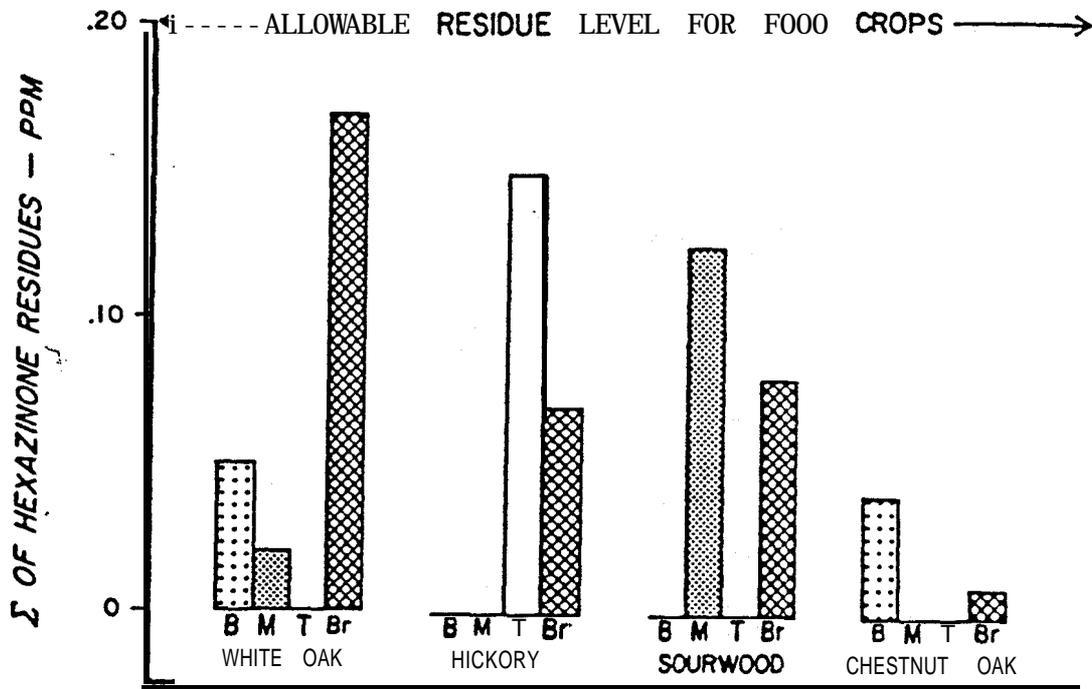


Figure 2. Weighted **sum** of hexazinone and **metabolite** concentrations in **fire-wood** samples taken **from** base (B), **midstem** (M), top (T), and branches (Br) of four hardwood species 16 months after herbicide treatment, Georgia study site, 1980.