PERSISTENCE, MOBILITY AND DEGRADATION OF HEXAZINONE IN SILT LOAM SOILS IN THE PEACE RIVER AREA, BRITISH COLUMBIA

File Report No. 76

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June 1986

ABSTRACT

A white spruce plantation near Stewart Lake, Peace River area, British Columbia was treated with hexazinone, 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, at 4.3 kg ai/ha by a helicopter equipped with a MICROFOIL® boom. Soils from within, and at 20 and 40 m (5-10% gradient) outside of the treatment block were monitored for 104 days after treatment for residues of hexazinone and its metabolites A, 3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione and B, 3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione. Soil samples, subdivided into surface organic, and 0-15 cm and 15-30 cm mineral layers, were collected before and at 0, 9, 23, 55, 70, 104 days after application. Hexazinone degradation was rapid, decreasing from 7.12 μg/g (9 days) to 2.09 μg/g (104 days). Metabolite A and B concentrations (30-50% and 0-12% that of hexazinone, respectively) indicated higher hydroxylation than demethylation activity in this silt loam soil. Leaching of hexazinone from the surface organic to the underlying 0-15 cm mineral soil layer was found only in the 55-day sample. No residues were detected for other sampling dates in this mineral layer and the layer below (15-30 cm). No positive evidence of lateral movement was found in samples from 20 m and 40 m outside of the treated block.

INTRODUCTION

Herbicide treatment for site preparation and conifer release is an important tool in forest renewal and production operations. The lack of adequate forestry herbicides and need for new forestry herbicides were identified by the Forest Pest Management Institute (FPMI) (FPMI 1984, 1985). One essential element in herbicide research associated with the registration of new forestry herbicides and the development of their responsible use is the study of their persistence, mobility and degradation in forest soils.

The herbicide hexazinone has shown good potential for forest vegetation management. It received temporary forestry registration for ground application in 1984 and 1985, with the proviso that Canadian terrestrial and aquatic fate data would be provided so a full forestry registration could be given. Hexazinone has been studied intensively (Sung *et al.* 1985; WSSA 1983; Rhodes 1980a,b; Rhodes and Jewell 1980; Dao *et al.* 1982; Bouchard and Lang 1983) in the laboratory and field in the U.S.A. A study to investigate its behaviour and kinetics in forestry soils was conducted in eastern Canada. However, a data gap remained for western Canadian soils. To fill this gap a field trial was conducted by Du Pont in the Peace River area, British Columbia, in consultation with Dr. P. Reynolds. The objectives of the study reported here were to investigate the persistence, degradation leaching and lateral movement in silt loam soils in the Peace River area, British Columbia.

MATERIAL AND METHODS

Site Description and Herbicide Application

The 5.6 ha experimental site was located at Stewart Lake, Peace River area, British Columbia. The original aspen stand was cut, windrowed and partially burned in 1981, and planted with white spruce in the spring of 1982. The site was typical of areas requiring conifer release in Northern Alberta and the Peace River area of British Columbia. The silt loam soil (sand 23%, silt 58%, clay 19%) contained 1.5% organic matter and was covered with duff and humus of varying thickness (5-10 cm). Hexazinone (Velpar® L[1], 240 g ai/L) was applied May 5, 1984 at a rate of 4.3 kg ai/ha by a Bell-47 helicopter with a MICROFOIL® boom[2] equipped with 1.5 mm (0.06 inch) hayrack nozzles. Weather was dry at the time of application, with 6°C air temperature, 80% relative humidity, 5 kmph wind and soil moisture near field capacity. First rain (1.27 cm) occurred on the next day and lasted for 4 days (total 3.64 cm).

Experimental Plots and Soil Sampling

Experimental plots (12 x 12 m) were established within the treated area for persistence and leaching studies, and at 20 m and 40 m downslope of the treated area on a 5-10% gradient for lateral movement studies. Pooled soil samples up to 4 kg were taken with a 2.5 cm diameter soil auger, and collected separately at 3 layers, including the organic layer and depths 0-15 and 15-30 cm in the underlaying mineral

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[1] Registered trademark of DuPont.

[2] Registered trademark of Union Carbide, Ambler, Pa.

soils. Sampling intervals included prespray and 0, 9, 23, 55, 70, 104 days after treatment.

Residue Analysis

Preanalysis Soil Processing: Field samples were stored at -14°C at the FPMI analytical laboratory prior to preanalysis soil preparation (Feng and Klassen 1986). An insulated drying room was equipped with a dehumidifier, metal shelves, styrofoam insulation board [to maintain room temperature (22°C) and to block out sunlight], and disposable cardboard trays (35 x 50 cm) with aluminum foil linings. Frozen soil samples were placed on separate disposable trays in the drying room. After thawing and drying overnight, large soil clumps were crumbled to fine pieces and air drying was continued. One day was normally required to reduce the moisture content to approximately 10%, and 2-4 days to reduce it to 5%. Air dried soils were pulverized by using a 4 L heavy duty stainless steel Waring blender (Waring No. S-61643-50), and sieved with a 2 mm mesh brass sieve with cover and pan (Tyler No. 10) (Feng and Klassen 1986).

Extraction and Cleanup: Holt's (1981) method was modified and used for the extraction and cleanup of hexazinone and its metabolites A and B from soils. The method is briefly summarized as follows. An aliquot of 25 g processed air dried soil was weighed in a 250 mL Nalgene bottle (Nalge 2107), wetted with 15 mL of distilled water, capped tightly and shaken horizontally on an Eberbach reciprocating shaker at 280 excursions per minute for 15 min. Sixty mL of acetone was then added. After being shaken for another 15 min, the sample was centrifuged at 350 x g (1150 rpm, rotor radius 23.8

cm) for 10 min. The extracts were filtered through a Millipore Filter Apparatus (47 mm) with Mitex disc filter (5 μm, Millipore LSWP 04700) under reduced pressure. Soils were extracted twice more each with 75 mL of an acetone-water solution (80 : 20 v/v). They were shaken for 2 min and centrifuged for 10 min, similar to that described above. The extracts were filtered and combined, and the acetone was flash-evaporated in a vacuum rotary evaporator at 60°C. The remaining aqueous solution (40 mL) was washed and extracted three times, each with 50 mL of n-hexane and 75 mL of chloroform, respectively. Chloroform extracts were combined, passed through anhydrous sodium sulfate, and flash-evaporated to dryness. The residues were re-dissolved in 50 mL of acetonitrile and washed twice each with 50 mL of n-hexane. The acetonitrile phase was combined and flash-evaporated to dryness. The residues were finally dissolved in 10 mL of ethyl acetate and filtered with Millex SR (0.5 μm) filter unit (Millipore SLSR 025 NB) before gas chromatographic (GC) analysis. If a sample extract contained residues more than twice the concentrations of that in the mix-standards (see Gas Chromatography) after preliminary GC analysis, the sample extract was diluted to near the concentration of the mix-standards and reanalyzed.

Gas Chromatography: Sample extracts in ethyl acetate were analyzed alternately with mix-standard solution containing 2.5, 5.0 and 10.0 ppm of hexazinone, metabolite-B and metabolite-A, respectively, on a Varian VISTA 6000 GC equipped with a thermionic specific detector (TSD) and a Varian data system (DS402). The specific gas chromatographic conditions were as follows:

Chromatographic column: 60 cm glass, 2 mm i.d., packed with 10% SP2250DA on 100/120 Supelcoport, and with acid-treated glass-wool plugs.

Temperatures: Injector - 260°C; Detector - 300°C; Column Temp Program - 240°C (2.5 min) - 10°C/min-280°C (3.5 min).

Gas Flow Rates: N_2 (UHP grade) - 33 mL/min; H_2 (prepurified) - 4.5 mL/min; air (zero gas grade) - 175 mL/min.

Retention times under these GC conditions were 2.6, 3.5 and 5.5 min for hexazinone, metabolite B and A, respectively.

Peak heights were used for the calculation of residue concentrations. When a sample injected showed more than 5 ppm of hexazinone, the sample was diluted to near 2.5 ppm with ethyl acetate and reanalyzed. The average of two peak heights, obtained from a mix-standard solution analyzed immediately prior to and after sample analysis, was used proportionally in calculating the residue concentration in the sample.

When the difference between the average value (i.e., hexazinone) and either one of the standard peak heights (hexazinone) was greater than 10% of the average value, the sample analysis was rejected. Alternate analysis of the standard solution and the sample was repeated sequentially at least 3-4 times until the standard peak height stabilized.

RESULTS AND DISCUSSION

Percent recoveries of hexazinone and metabolites B and A from soils when spiked at 1, 2 and 4 µg/g were 100.3%, 105.8% and 92.2%, respectively, with a 3% coefficient of variation (% CV or % SD); when spiked at 0.1, 0.2 and 0.4 µg/g were 88.9%, 93.0% and 60.3%, respectively, with a 10% CV (Table 1). Air drying procedures involved in soil

Table 1. Percent recovery of hexazinone and its metabolites A and B from soil.

Date of Analysis	Percent Recovery		
	Hexazinone	Metabolite-B	Metabolite-A
Spiked Conc.	(1 µg/g)	(2 µg/g)	(4 µg/g)
27/7	103.7	108.8	94.2
30/7	100.4	104.2	91.6
31/7	96.3	101.8	88.9
1/8	100.7	108.4	93.9
Mean ± SD	100.3 ± 3.0	105.8 ± 3.4	92.2 ± 2.5
Spiked Conc:	(0.1 µg/g)	(0.2 µg/g)	(0.4 µg/g)
27/7	101.6	102.7	55.6
30/7	82.8	87.1	72.4
31/7	-	-	-
1/8	82.4	89.2	52.9
Mean ± SD	88.9 ± 11.0	93.0 ± 8.5	60.3 ± 10.6

* Sample lost during cleanup.

preparation did not modify soil properties nor the adsorption capacity of soils (Dao *et al.* 1982). The rapid loss of 70% of the total moisture content during the first day of drying greatly reduced the possibility of microbial degradation of hexazinone in the soil samples. Overall consistency of the subsampling, extraction, cleanup and gas chromatography was examined with 50 replicated subsamples from one homogenized air dried field sample. Results showed reproducibility, with a mean hexazinone residue value of 0.84 µg/g, a 6.9% CV and a range of 0.66-0.95 µg/g (Table 2). The modified Holt's (1981) method used in this study was improved in simplicity and reproducibility.

Field samples collected at 0 and 70 days after application were lost during transit from the field to the FPMI analytical laboratory. Results of residues of hexazinone and its metabolites A and B in treated soils, 9 to 104 days after application are shown in Table 3, and those from the run-off sites, 20 m and 40 m outside the treated plot are shown in Tables 4 and 5, respectively. In the treated soils (Table 3), hexazinone degraded from the initial (9 days postspray) concentration of 7.12 µg/g to 2.09 µg/g (104 days postspray), indicating a degradation of approximately 70% 3 months after application. Metabolite A, a hydroxylation product of hexazinone, found 9 days after treatment and consistently throughout the rest of the sampling periods, was 30-50% of the concentration of hexazinone found in the same sample. This result suggests the initial high soil moisture content (near field capacity) and continuous rain falls (12 rain events) within the 104 day period might have enhanced the hydroxylation of hexazinone. Lower amounts (0-10% that of hexazinone) of the phytotoxic metabolite B (Sung *et al.* 1985)

Table 2. Consistency of hexazinone subsampling, extraction and analysis from homogenized air-dry soils collected in a field trial.

Replications	ppm (µg/g)	Replications	ppm (µg/g)
1	0.823	26	0.856
2	0.834	27	0.831
3	0.831	28	0.859
4	0.862	29	0.854
5	0.833	30	0.878
6	0.868	31	0.758
7	0.830	32	0.804
8	0.887	33	0.844
9	0.738	34	0.835
10	0.814	35	0.784
11	0.834	36	0.658
12	0.873	37	0.731
13	0.918	38	0.769
14	0.818	39	0.790
15	0.947	40	0.806
16	0.935	41	0.806
17	0.792	42	0.820
18	0.788	43	0.953
19	0.896	44	0.838
20	0.823	45	0.815
21	0.851	46	0.834
22	0.910	47	0.931
23	0.796	48	0.901
24	0.779	49	0.913
25	0.840	50	0.887

Mean ± SD (% CV) = 0.838 ± 0.058 (6.9%) (n = 50)
Range: 0.658 - 0.953

Table 3. Residues of hexazinone and its metabolites A and B found in Velpar L (4.3 kg ai/ha) treated clay loam soils, Stewart Lake area, British Columbia.

Days Postspray	Soil Layer	Residues, ppm (µg/g) Hexazinone	Metabolite A	Metabolite B
9	organic	6.82,7.14,7.20 7.09,7.14,7.34	2.12,2.15 2.09	0.262,0.254 0.200,0.233
		x = 7.12 ± 0.17	x = 2.12 ± 0.03	x = 0.237 ± 0.028
	mineral (0-15 cm)	ND, ND	ND, ND	ND, ND
23	organic	2.85,2.78,2.98	1.60,0.96	0.149,0.139
		x = 2.87 ± 0.10	x = 1.28	x = 0.144
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND
55	organic	1.37,1.49	0.353,0.706	Trace
		x = 1.43	x = 0.530	
	mineral (0-15 cm)	0.196,0.214	0.084,0.125	ND,ND
		x = 0.205	x = 0.105	
	(15-30 cm)	ND	ND	ND
104	organic	2.01,2.09,2.02 2.08,2.23,2.07 2.10	1.076,0.982,0.758 0.826,0.811,0.786 0.772	0.226,0.228,0.256 0.220,0.295,0.238 0.285
		x = 2.09 ± 0.07	x = 0.859 ± 0.122	x = 0.250 ± 0.030
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND

ND: Less than 0.03, 0.06, 0.06 ppm (µg/g) for hexazinone, metabolites A and B, respectively.

Trace: Metabolite B, less than 0.4 ppm (µg/g).

Table 4. Residues of hexazinone and its metabolites A and B found in clay loam soils, 20 m outside treated plot (Velpar L, 4.3 kg ai/ha), Stewart Lake area, British Columbia.

Days Postspray	Soil Layers	Residues, ppm (μg/g)		
		Hexazinone	Metabolite A	Metabolite B
9	organic	Trace	ND	ND
	mineral (0-15 cm)	ND	ND	ND
23	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND
55	organic	ND,ND	ND	ND, ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND
104	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND

Trace: Hexazinone less than 0.1 ppm (μg/g)
ND: Less than 0.03, 0.06, 0.06 ppm (μg/g) for hexazinone, metabolites A and B, respectively.

Table 5. Residues of hexazinone and its metabolites A and B found in clay loam soils, 40 m outside treated plot (Velpar L, 4.3 kg ai/ha), Stewart Lake area, British Columbia.

Days Postspray	Soil Layers	Residues, ppm (μg/g)		
		Hexazinone	Metabolite A	Metabolite B
9	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
23	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND
55	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND
104	organic	ND	ND	ND
	mineral (0-15 cm)	ND	ND	ND
	(15-30 cm)	ND	ND	ND

ND: Less than 0.03, 0.06, 0.06 ppm (μg/g) for hexazinone, metabolites A and B, respectively.

found during the same period of time suggested low demethylation activity in this silt loam soil.

Leaching from the surface organics of the forest floor to the next 15 cm of mineral soil was only found in the 55-day postspray samples, which contained approximately 14% of the hexazinone and 20% of the metabolite A found in the organic layer above (Table 3). No metabolite B was detected in this 55-day sample. That no detectable residues were found in the 15-30 cm mineral layer suggest that the silt loam soil in this area may effectively prevent the vertical leaching of hexazinone from contaminating groundwater.

In the run-off studies, no residues were detected 20 m and 40 m outside and downslope (5-10% gradient) of the treated plot (Table 4 and 5) within the 104-day period. In studies elsewhere, hexazinone persistence, leaching and lateral mobility have been highly variable, dependent on soil types and climate (Harrington *et al.* 1982; Miller and Bace 1980; Roy pers. comm[2].; Barring and Torstensson 1983; Parker *et al.* - 1982; Rhodes 1980a; Neary 1984; Neary et al. 1983). Extended soil sampling for up to two or more growing seasons may be required for the study of persistence and mobility of hexazinone in the cooler, northern regions of Alberta and British Columbia. Bulk density data for individual soil layers should be obtained to provide transformation of residue data from a weight basis (μg/g) to an areal basis (kg/ha) to allow a

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[2] D.N. Roy. 1986. Persistence, movement and degradation of hexazinone (Velpar) in boreal forest soils. Faculty of Forestry. University of Toronto, pre-publication results.

direct comparison with the initial amount applied (kg/ha) (Feng and Campbell pers. comm.)[3].

ACKNOWLEDGMENTS

The research was financed by the Forest Pest Management Institute (FPMI) Canadian Forestry Service and E.I. Du Pont De Nemours & Company (Inc.), Delaware, USA. Field experimental design and soil sampling were conducted by K. Teskey and S. Masterson, Du Pont Canada Inc. and supported by P. Reynolds, FPMI. The authors also acknowledge the excellent technical support of B. Staznik, V. Squire, T. Buscarini, L. Belsito and D. Moore (FPMI) and professional advice of C. Feng (FPMI), C. McIntosh and T. Priester (E.I. Du Pont) and H. Klassen (V.A. Poulin & Assoc., Ltd.).

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