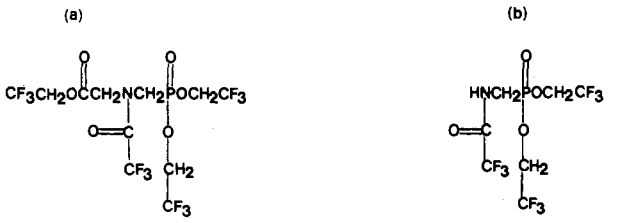

Figure 3. Structures of derivatized (a) glyphosate and (b) AMPA.

limits of detection for GLYPH and its metabolite AMPA were 0.05 and 0.01 μg/g, respectively. At present this method is being utilized to analyze GLYPH and AMPA in different substrates, and the results will be presented in subsequent communications.

Overall this method is very economical and less laborious than existing methods.

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Registry No. GLYPH, 1071-83-6; AMPA, 1066-51-9.

LITERATURE CITED

Bardalaye, P. C.; Wheeler, W. B.; Moye, H. A. Analytical Techniques of Glyphosate Residue Analysis. In *The Herbicide Glyphosate*; Grossbard, E., Atkinson, D., Eds.; Butterworths: London, 1984; pp 263–285.

Deyrup, C. L.; Chang, S. M.; Weintraub, R. A.; Moye, H. A. Simultaneous Esterification and Acylation of Pesticides for Analysis by Gas Chromatography. 1. Derivatization of Glyphosate and (Aminomethyl)phosphonic Acid with Fluorinated Alcohols—Perfluorinated Anhydrides. *J. Agric. Food Chem.* **1985**, *33*, 944–947.

Glass, R. L. Liquid Chromatographic Determination of Glyphosate in Fortified Soil and Water Samples. *J. Agric. Food Chem.* **1983**, *31*, 280–282.

Jotcham, J. Environmental Properties of Triclopyr. M.Sc. Dissertation, University of Guelph, 1985.

Lundgren, L. N. A New Method for the Determination of Glyphosate and (Aminomethyl)phosphonic Acid Residues in Soils. *J. Agric. Food Chem.* **1986**, *34*, 535–538.

Moye, H. A.; St. John, P. A. A Critical Comparison of Pre-column and Post-column Fluorogenic Labeling for the HPLC Analysis of Pesticide Residues. In *Pesticide Analytical Methodology*; Harvey, J., Jr., Zweig, G., Eds.; ACS Symposium Series 136; American Chemical Society: Washington, DC, 1980; pp 89–102.

Moye, H. A.; Miles, C. J.; Scherer, S. J. A Simplified High-Performance Liquid Chromatographic Procedure for the Determination of Glyphosate Herbicide and (Aminomethyl)-phosphonic Acid in Fruits and Vegetables Employing Post-column Fluorogenic Labeling. *J. Agric. Food Chem.* **1983**, *31*, 69–72.

Pesticide Analytical Manual; FDA: Washington, DC, 1977.

Sprankle, P.; Meggitt, W. F.; Penner, D. Adsorption, Mobility, and Microbial Degradation of Glyphosate in the Soil. *Weed Sci.* **1975**, *23*, 229–234.

Sprankle, P.; Sandberg, C.; Meggitt, W. F.; Penner, D. Separation of Glyphosate and Possible Metabolites by Thin-Layer Chromatography. *Weed Sci.* **1978**, *26*, 673–674.

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Determination of Persistence, Movement, and Degradation of Hexazinone in Selected Canadian Boreal Forest Soils

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One flat and one slope site for each type of soil (sand, clay) were chosen near Matheson, Ontario, to study the persistence, movement, and degradation of hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] after spraying at a rate of 4 kg of active ingredient (AI)/ha. Soils at three depths were collected and analyzed for residues of hexazinone and its metabolites A [3-(4-hydroxycyclohexyl)-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] and B [3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione]. The time required for hexazinone residues to remain consistently below 50% of the highest amount recovered was 43 days in both clay and sand soils. Results indicated that hexazinone had very limited potential to leach vertically through the soil column. The mobility study showed that there was no evidence of lateral movement of the herbicide either in runoff water or through subsurface flow. Metabolites A and B were found within a range of 0–32% and 0–50% of hexazinone concentration.

The ongoing search for herbicides with the desired characteristics of short half-life, little or no toxicity to humans and wildlife, and low environmental impact possessing a broad range of activity has resulted in the introduction of a group of triazine-based herbicides to the market. Hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] (Figure 1) is the active ingredient of Du Pont's Velpar (formerly DPX-3674) and conforms to the above criteria. It has a potential for use in site preparation, conifer release, and nursery stock production in the boreal forest regions of Canada. The operational use of Velpar in these regions will be extremely important as this is an area of major economic significance

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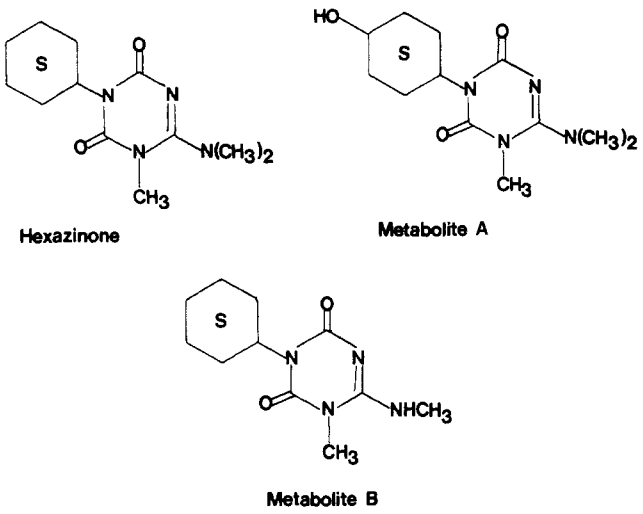

Figure 1. Structures of hexazinone and its metabolites A and B.

in forestry.

Studies on the behavior of hexazinone in or on soil have also been reported ((Rhodes, 1980; *Weed Science Society of America Herbicide Handbook*, 1983; Sung et al., 1985; Feng, 1987). However, data on the persistence, mobility, and degradation of hexazinone in boreal forest soils are still inadequate for its registration in Canada, and hence this study was undertaken.

EXPERIMENTAL SECTION

Reagents. Analytical standards of hexazinone (99%), metabolite A (90%), metabolite B (90%), and Velpar L containing 24% hexazinone (AI) were supplied by Du Pont, Wilmington, DE. Stock solutions of hexazinone (100 μg/mL), metabolite A (100 μg/mL), and metabolite B (50 μg/mL) were prepared separately in ethyl acetate. Anhydrous Na_2SO_4 was heated at 140 °C overnight prior to use. All organic solvents used were pesticide grade (Caledon Laboratories Ltd., Georgetown, Ontario, Canada).

Site Selection. One flat site for persistence and leaching studies and one sloping (7–8°) site for a mobility study for each type of soil (clay and sand) were selected. The clay sites were in an open cutover covered by weeds and the occasional remnant of the original forest namely white birch, black spruce, and poplar. The sand sites were part of a recently planted jack pine plantation that also contained the occasional blueberry plants. The clay and sand sites were located in Lamplugh (48°35′ N, 79° W) and Harker (48°30′ N, 79° W) townships, respectively, about 40 km east of Matheson in the district of Cochrane, Ontario.

Experimental Site Design. Each site (20 m × 20 m) was divided into five replicate chemical application strips separated by buffer zones (1 m × 20 m). Each strip (2 m × 20 m) was further subdivided into 10 squares (2 m × 2 m) as sampling plots.

Site Preparation. The sites were cleared of slash and logs by hand with a minimal disturbance of the humus layer (5–10 cm in depth). For the mobility study, dead wood and other matter thought to have potential for runoff channeling was removed from the sites, and an application strip at the top of each slope was cleared as above. A back-hoe was used to prepare a trench at the bottom of each slope for the collection of runoff water. Each trench was 25 m long, 1 m wide, and 1 m deep, unlined and open.

Soil Characteristics. Prespray soil samples were collected at random from each site and analyzed for pH, cation-exchange capacity, moisture content, organic matter, field capacity, and particle size distribution (Table I).

Table I. Characteristics of the Study Soils[a]

		clay[b]		sand[b]	
	soil[c] fraction	persistence site	mobility site	persistence site	mobility site
pH	O	4.13	4.48	3.50	3.46
	M	4.56	4.43	3.73	4.72
% clay	O	0.00	0.00	0.00	0.00
	M	85.60	87.60	5.60	7.60
% silt	O	0.00	0.00	0.00	0.00
	M	14.40	12.40	14.00	10.00
% sand	O	0.00	0.00	0.00	0.00
	M	0.00	0.00	80.40	82.40
% organic matter	O	29.47	29.47	39.70	5.43
	M	1.52	0.00	0.76	0.34
CEC, mequiv/100 g	O	17.00	21.40	18.50	4.10
	M	18.10	3.80	5.30	2.50
% moisture content	O	7.27	8.26	7.71	1.28
	M	2.36	0.85	0.56	0.55
field capacity	O	131.57	137.43	24.47	26.22
	M	34.55	38.94	9.24	7.92

[a] Soil classification (Jotcham, 1985): clay of the Ryland Series Orthic Humic Gleysol type; sand of the Abitibi series Orthic Humo-Ferric Podzol type. [b] Soil texture. [c] Key: O = organic (5–10 cm); M = mineral (20–25 cm in depth of the total 30-cm soil core).

Table II. Chemical Application to the Clay Sites

rep	vol appl, mL	rate appl, kg/ha	rate appl from deposit sheets,[a] kg/ha
		Persistence Site	
A	1500	4.59	4.65
B	1200	3.69	3.71
C	1350	4.02	4.47
D	1300	3.87	3.55
E	1410	4.20	2.71
av	1352	4.07	3.88
		Mobility Site	
spray strip	1530	4.62	3.49

[a] An average of the three replicate deposit sheets per application zone.

Table III. Chemical Application to the Sand Sites

rep	vol appl, mL	rate appl, kg/ha	rate appl from deposit sheets,[a] kg/ha
		Persistence Site	
A	1250	3.72	3.68
B	1450	4.32	3.95
C	1310	3.90	3.56
D	1410	4.20	3.89
E	1350	4.02	3.20
av	1354	4.03	3.65
		Mobility Site	
spray strip	1245	3.70	3.38

[a] An average of three replicate deposit sheets per application zone.

Chemical Application. Chemical applications were made on June 20, 1984, to replicate strips in each of the flat sites and to the zone of chemical application for the slope sites. Hexazinone was applied as an aqueous solution of Velpar L (24% AI) with a Pestex backpack sprayer (boom length 2 m, number of nozzles 4, nozzle type Tee Jet AL 8004) using compressed air (200 kPa) as a propellant. An application rate of 4 kg/ha was targetted, and actual application rates were determined by the use of deposit sheets and also by the reservoir volumes before and after spraying (Tables II and III). Deposit sheets prepared from 20 cm × 20 cm glass plates wrapped in aluminum foil were placed in each application strip. Immediately after application, the foil sheets were unwrapped (thereby quantitatively trapping the deposit), labeled, and frozen until analyzed.

Table IV. Monthly Rainfall and Temperature Data for the Period 1975 (May–September) to 1984 (May–September)

month	1984	1983	1982	1981	1980	1979	1978	1977	1976	1975
					Rainfall, mm					
May	54.8	118.4	46.5	46.6	41.0	80.5	55.9	19.9	69.4	101.6
June	128.5	70.4	69.5	94.1	49.4	151.0	143.2	118.2	71.3	83.9
July	93.7	55.2	71.7	46.3	44.8	96.4	141.8	54.1	95.8	49.0
Aug	88.5	64.0	68.5	64.2	79.8	94.1	103.0	71.9	40.2	50.3
Sep	41.0	38.3	85.0	79.0	111.2	92.0	62.1	58.8	156.4	103.9
					Temperature, °C					
May	10.1	10.1	17.7	12.1	14.9	14.4	19.6	17.0	12.1	17.6
June	17.4	19.3	16.0	18.0	16.1	19.0	16.6	16.9	22.2	16.1
July	21.0	21.5	20.9	23.4	21.7	21.6	20.2	21.1	20.2	22.0
Aug	20.4	20.9	15.0	21.0	20.9	17.3	19.0	17.3	20.5	20.5
Sep	13.6	15.9	12.4	11.7	11.8	13.7	12.6	13.7	12.8	11.0

Sampling. Samples were collected from sampling plots with use of a random number table. For the mobility sites, samples were also collected at 3, 6, 9, and 12 m downslope from the chemical application zone. Cores were taken with a soil auger (length 54 cm, diameter 10 cm) driven to a depth of 32 cm with a sledge hammer. The bottom 2 cm of the cores was discarded and the adjacent 15 cm of mineral soil (M2, 15–30 cm) collected. The remainder of the core was divided into organic and mineral (M1, organic to 15 cm) layers and collected separately. The sections were bagged, weighed, and stored at −20 °C. The sampling schedule was 0, 2, 7, 14, 28, 43, 78, 125, 365, 721, and 792 days postspray.

Water samples (1 L) were collected from the trench and stored at −20 °C.

Weather. Field weather stations were placed at each experimental site to monitor rainfall and temperature. On examination of the rainfall data produced from these it was discovered that they had intermittently malfunctioned, and as a result these data were discarded. However, weather data were obtained from Minstry of Natural Resources (MNR) district weather station in Kirkland Lake, Ontario, which is approximately 40 km southwest from the study sites. It was felt that these data were the second best source to provide a reasonable approximation of the climatic conditions during the experimental period. These weather data were used to indicate that the year 1984 was climatically normal compared to past years (Table IV).

Soil Preparation. The frozen samples were allowed to thaw at 25 °C, with any large clumps crushed with a large spatula so as to increase drying efficiency. The time required to reduce the moisture content to approximately 10% was 48 h. A moisture content of 5–7% was obtained after an additional 2–4 days. The air-dried soil was then homogenized in a heavy-duty stainless steel blender and sieved through a 10-mm-mesh brass sieve (Feng and Klassen, 1986).

Extraction and Cleanup. The method of Holt (1981) was used for the analysis of hexazinone and its metabolites A and B but modified to the extent that no derivatization was performed, thereby increasing the stability of the samples from 8 h to 30 days at 5 °C. An aliquot of 25 g of homogenized air-dried soil was extracted with 75 mL of an acetone–water solution (80:20, v/v) in a 250-mL capped Nalgene bottle, shaken manually for 2 min, and centrifuged for 10 min at 2000 rpm. The supernatant liquid was decanted through a small cotton plug and collected. The extraction was repeated two more times each with 75 mL of 80% aqueous acetone, and the extracts were combined. The acetone was evaporated in a vacuum rotary evaporator at 60 °C, and the resulting aqueous solution (40 mL) was washed three times each with 50 mL of *n*-hexane, discarding the hexane fractions. The aqueous fraction was extracted three times each with 75 mL of chloroform. The extracts were combined, dried over anhydrous sodium sulfate, and concentrated to dryness in a vacuum rotary evaporator at 60 °C. The residue was dissolved in acetonitrile and washed two times each with 50 mL of *n*-hexane. The acetonitrile fraction was concentrated to 2 mL in a vacuum rotary evaporator at 60 °C, and transferred quantitatively to a vial with small volumes of chloroform as rinse. The sample was evaporated in a water bath (60 °C) under a stream of nitrogen, and the residue was dissolved in an appropriate volume of ethyl acetate and injected into the gas chromatograph.

Runoff water samples were allowed to thaw at 4 °C. They were then evaporated to 40 mL and extracted according to the method described above. The deposit sheets were also thawed at 4 °C and the contents eluted with water, which was concentrated to 40 mL and extracted as described above.

Gas Chromatographic Analysis. The gas chromatographic analysis was conducted on a Shimadzu GC-9A gas chromatograph (Shimadzu Corp., Kyoto, Japan) equipped with a nitrogen–phosphorus detector. The chromatographic column (60-cm glass, 3-mm i.d.) was 10% SP 2250 on 100/120-mesh Supelcoport (Supelco, Inc.). Acid-treated glass wool was used in the column ends. The operating parameters were as follows: detector temperature, 300 °C; injector temperature, 300 °C; column temperature program, 260 °C for 3 min, then 10 °C/min to 300 °C, hold for 5 min; gas flow rate, nitrogen (ultra high purity) 30 mL/min, hydrogen 4 mL/min, air 175 mL/min.

Samples were sandwiched between two injections of the same standard. A detector fluctuation of ±10% was considered acceptable, and a linear range between 50% and 200% of the average of standards was used in the quantification. Residue concentrations were quantified by the comparison of peak heights to average peak height of standards run before and after each sample. A Shimadzu C-R3A data processor was used for quantification.

Fortification. Prespray field samples were fortified with hexazinone, metabolite A, and metabolite B at three concentrations. Soil samples were placed in a 250-mL Nalgene bottle and fortified by the addition of appropriate volumes of previously prepared stock solutions of the above. The bottles were capped, manually shaken to ensure thorough mixing, and stored at −20 °C for 24 h to simulate residue sample storage conditions.

The fortification of water was performed in the same manner. Levels of fortification were as follows: hexazinone, 2.0, 0.2, and 0.05 ppm (μg/g); metabolite A, 10.0, 1.0, and 0.1 ppm (μg/g); metabolite B, 5.0, 0.5, and 0.1 ppm (μg/g).

RESULTS AND DISCUSSION

Recovery Efficiency. The recovery efficiency for the analytical method is shown in Table V. An average of

Table V. Recovery Efficiencies for Hexazinone (H), Metabolite A (A), and Metabolite B (B) from Soil, Organic Matter, and Water

substrate	fortification, ppm (μg/g)			% recovery ± SD		
	H	A	B	H	A	B
organic	2.00	10.00	5.00	98.9 ± 2.46	96.5 ± 5.97	106.4 ± 4.55
	0.20	1.00	0.50	100.5 ± 2.69	99.0 ± 4.95	104.1 ± 4.37
	0.05	0.10	0.10	92.3 ± 2.65	85.5 ± 4.85	88.9 ± 2.82
clay	2.00	10.00	5.00	96.2 ± 5.44	92.2 ± 1.63	100.1 ± 6.72
	0.20	1.00	0.50	97.7 ± 1.20	92.6 ± 1.20	99.4 ± 5.87
	0.05	0.10	0.10	88.2 ± 2.72	82.2 ± 3.42	86.2 ± 3.86
sand	2.00	10.00	5.00	98.6 ± 2.47	95.0 ± 5.66	101.9 ± 7.14
	0.20	1.00	0.50	100.1 ± 4.45	96.0 ± 5.66	101.4 ± 5.65
	0.05	0.10	0.10	90.1 ± 3.38	82.9 ± 2.91	88.3 ± 3.30
water	2.00	10.00	5.00	99.3 ± 0.99	98.4 ± 6.36	99.2 ± 1.13
	0.20	1.00	0.50	97.7 ± 2.80	100.4 ± 3.32	102.6 ± 3.01
	0.05	0.10	0.10	96.2 ± 2.41	101.4 ± 3.71	100.2 ± 2.44

Table VI. Hexazinone Residue Values (μg) from Clay Persistence Site

days postspray	soil layer[a]	hexazinone	metabolite A	metabolite B
0	O	699.4 ± 364.8	ND[d]	ND
	M1	ND	ND	ND
	M2	ND	ND	ND
2	O	610.1 ± 349.0	ND	ND
	M1	ND	ND	ND
	M2	ND	ND	ND
7	O	1208.1 ± 492.8	(29.1)[b]	(25.2, 26.7)
	M1	51.8 ± 6.2	ND	ND
	M2	ND	ND	ND
14	O	1491.8 ± 848.1	146.0 ± 146.6	33.3 ± 30.7
	M1	262.2 ± 157.6	(138.3, 24.6)	(101.7)
	M2	ND	ND	ND
28	O	1161.6 ± 274.4	(41.7, 31.3)	58.9 ± 19.9
	M1	197.8 ± 50.4	ND	40.5 ± 9.9
	M2	57.1 ± 4.7	ND	ND
43	O	716.4 ± 400.4	143.1 ± 91.3	72.0 ± 42.3
	M1	64.3 ± 39.7	(36.9)	ND
	M2	ND	(101.3)	ND
78	O	324.4 ± 133.7	68.1 ± 50.1	91.6 ± 28.9
	M1	70.7 ± 37.3	34.1 ± 25.5	41.3 ± 9.0
	M2	55.3 ± 69.2	135.6 ± 35.7	181.3 ± 67.2
125[c]	O	202.8	(22.0)	ND
	M1	29.3	ND	ND
	M2	ND	ND	ND
365	O	171.7 ± 87.1	21.2 ± 19.4	57.8 ± 63.2
	M1	68.5 ± 27.6	87.5 ± 83.3	69.4 ± 52.2
	M2	ND	ND	ND
721	O	86.7 ± 8.7	(9.3)	30.1 ± 3.4
	M1	8.5 ± 14.7	ND	ND
	M2	ND	ND	ND
792	O	61.7 ± 24.6	ND	ND
	M1	ND	ND	ND
	M2	ND	ND	ND

[a] Key: O = organic; M1 = organic to 15 cm; M2 = 15–30 cm. [b] Values in parentheses indicate less then three detectable values. [c] Single data point. [d] ND = not detectable; limits of detection 0.025, 0.05, and 0.05 μg/g for hexazinone, metabolite A, and metabolite B, respectively.

Table VII. Hexazinone Residue Values (μg) from Sand Persistence Site

days postspray	soil layer[a]	hexazinone	metabolite A	metabolite B
0	O	1430.2 ± 955.1	ND[d]	ND
	M1	ND	ND	ND
	M2	ND	ND	ND
2	O	1559.4 ± 302.1	ND	ND
	M1	ND	ND	ND
	M2	ND	ND	ND
7	O	646.2 ± 50.0	(13.2)[b]	(67.9)
	M1	90.0 ± 64.6	ND	(29.9)
	M2	ND	ND	ND
14	O	546.6 ± 121.9	ND	(35.5)
	M1	ND	ND	ND
	M2	ND	ND	ND
28	O	422.1 ± 190.5	(8.64, 14.9)	(38.2, 48.7)
	M1	31.9 ± 15.5	(36.9, 54.1)	(47.0, 68.1)
	M2	ND	(185.6, 309.5)	(234.7, 220.7)
43	O	662.6 ± 8.6	ND	(37.7, 52.7)
	M1	28.4 ± 15.2	ND	(47.1, 64.4)
	M2	63.6 ± 16.5	ND	(68.1)
78	O	384.6 ± 196.2	14.3 ± 12.3	57.5 ± 7.6
	M1	48.9 ± 34.6	57.9 ± 54.4	68.1 ± 74.7
	M2	29.1 ± 20.5	(108.9)	(110.9)
125[c]	O	131.9	(12.2)	(165.9)
	M1	47.2	ND	(12.9)
	M2	ND	ND	ND
365	O	105.2 ± 104.0	(43.9)	39.8 ± 25.2
	M1	5.6 ± 12.4	19.1 ± 18.8	ND
	M2	ND	(102.5, 68.1)	ND
721	O	65.3 ± 12.6	ND	33.4 ± 16.7
	M1	8.2 ± 14.2	ND	ND
	M2	ND	ND	ND
792	O	46.0 ± 16.9	ND	25.1 ± 3.54
	M1	ND	ND	ND
	M2	ND	ND	ND

[a] Key: O = organic; M1 = organic to 15 cm; M2 = 15–30 cm. [b] Values in parentheses indicate less than three detectable values. [c] Single data point. [d] ND = not detectable; limits of detection 0.025, 0.05, and 0.05 μg/g for hexazinone, metabolite A, and metabolite B, respectively.

96.3% of hexazinone was recovered from all fortified samples. For metabolites A and B average values were 93.5% and 98.2%. The limits of detection for the hexazinone and its metabolites were as follows: hexazinone, 0.025 μg/g; metabolite A, 0.05 μg/g; metabolite B, 0.05 μg/g.

Persistence. In both clay and sand sites, the time required for hexazinone residues to remain consistently below 50% of the highest residue values observed was 43 days (Tables VI and VII). After 365 days postspray, these residue values were reduced to 13.5% for the clay site and 8.5% for the sand site based on the highest residue values observed. The gradual decrease in hexazinone residue values was observed, thereafter, 365 days postspray for both the sites. Hence, this study indicated that hexazinone is relatively nonpersistent in both clay and sand soils of boreal forests under climatically normal summer condition.

Recovery of hexazinone for the first few days postspray was lower than expected. This could be due to the fact that immediately after spraying the chemical reaching the ground was of unilayer in thickness and that sufficient time had not been allowed for its translocation within the soil. In this situation the collection of soil cores could have resulted in a loss of the herbicide via sorption to plastic bags or instruments used. Alternately, this type of poor recovery in the initial postspray days could be explained by the fact that certain vegetation cover still remaining on the ground prevented the total spray from reaching the ground and that the spray gradually washed down as a result of heavy mist or dew. The variability was observed

Table VIII. Hexazinone Residue Values (μg) from Clay Mobility Site[a]

days postspray	distance, m 0	3	6	9	12
0	758.7	ND	ND	ND	ND
2	703.1	ND	ND	ND	ND
7	1405.9	ND	ND	ND	ND
14	2419.1	ND	ND	ND	ND
28	889.7	ND	ND	ND	ND
43	758.6	ND	ND	ND	ND
78	385.0	ND	ND	ND	ND
125	NA	ND	ND	ND	ND
365	283.3	ND	ND	ND	ND
721	89.5	ND	ND	ND	ND
792	ND	ND	ND	ND	ND

[a] Only the top strip was sprayed. Key: ND = not detectable; NA = not available. Limit of detection 0.025 ppm (μg/g).

Table IX. Hexazinone Residue Values (μg/g) from Sand Mobility Sites[a]

days postspray	distance, m 0	3	6	9	12
0	425.7	ND	ND	ND	ND
2	–	ND	ND	ND	ND
7	700.0	ND	ND	ND	ND
14	551.9	ND	ND	ND	ND
28	1266.3	ND	ND	ND	ND
43	NA	ND	ND	ND	ND
78	728.0	ND	ND	ND	ND
125	NA	ND	ND	ND	ND
365	229.8	ND	ND	ND	ND
721	86.3	ND	ND	ND	ND
792	ND	ND	ND	ND	ND

[a] Only the top strip wasy sprayed. Key: ND = not detectable; – = sample lost; NA = not available. Limit of detection 0.025 ppm (μg/g).

on both sites, but the effect was more pronounced on clay as this site was more covered with herbaceous vegetation than the sand site.

Leaching. From the analysis of individual soil core layers (organic, organic to 15 cm, and 15–30 cm) it was evident that hexazinone had a very limited potential to leach vertically through the soil column under the conditions of this study. In fact results showed that, considering all the sampling times together, an average of 88% or more of the hexazinone was found in the upper organic layer at both clay and sand sites. A yield of 98% or more was recovered within 15 cm from the top of the soil surface. Therefore, it is obvious that hexazinone resides mainly in the organic layer and that leaching is retarded in the mineral layers.

Mobility. On the basis of results of this study at both clay and sand slope sites, there was no evidence of lateral movement of the hexazinone down the 7–8° slopes either in runoff water or through subsurface flow. Hexazinone in the quantifiable range (0.05 ppm) could not be detected either at a distance 3 m from the top of the application zone or in the runoff water collected in the trench (Tables VIII and IX).

Metabolites A and B. The overall formation of metabolites A and B was low. The maximum amounts of metabolite A and B were 240 and 310 μg and 200 and 220 μg for clay and sand soil, respectively. Within the observation period, as hexazinone concentration decreased, concentrations of both metabolites A and B increased and then decreased, indicating that these are relatively nonpersistent metabolites (Tables VI and VII).

It is interesting to note that metabolite B was found in a comparatively higher percentage (up to 50% of hexazinone concentration) than metabolite A (up to 32%) in both clay and sand soils. Thus, it is apparent that demethylation rather than hydroxylation was favored under the conditions of this experiment. Studies on the degradation of hexazinone in forest silt loam soil (Feng, 1987) however indicated the predominance of metabolite A over B. Thus, it is suggested that soil type and climatic conditions could be the key factors in controlling the predominance of one metabolite over the other. Sung et al. (1985) reported that metabolite B is the only phytotoxic compound among the metabolites of hexazinone. Our results showed that, in all cases, the concentration of metabolite B was well below its phytotoxic threshold value (1 mg/kg). Although there is some variability observed in the persistence, movement, and degradation behavior of hexazinone, this is not uncommon for forest soils as similar variability has also been reported by other research workers (Miller and Bace, 1980; Harrington et al., 1982; Baerring and Torstensson, 1983; Neary et al., 1983; Feng, 1987).

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Registry No. Hexazinone, 51235-04-2; metabolite A, 72576-13-7; metabolite B, 56611-54-2.

LITERATURE CITED

Baerring, U.; Torstensson, L. An Example of the Mobility of Hexazinone on a slope. *24th Swedish Weed Conference* **1983**, *24*, 311–325.

Feng, J. C. Persistence, Mobility, and Degradation of Hexazinone in Forest Loam Soils. *J. Environ. Sci. Health, Part B* **1987**, *B22*(2), 221–233.

Feng, J. C.; Klassen, H. D. Forestry field and laboratory manual for herbicide residue sampling, sample processing and reporting. FPMI Information Report FPM-X-72; Canadian Forestry Service: Victoria, BC, 1986.

Harrington, K. C.; Rolston, M. P.; Ivens, G. W. Movement of Hexazinone Spots Applied to Hill Slopes. *Proc. 35th N.Z. Weed Pest Control Conf.* **1982**, 162–165.

Holt, R. F. Determination of Hexazinone and Metabolite Residues Using Nitrogen-Selective Gas Chromatography. *J. Agric. Food Chem.* **1981**, *29*, 165–172.

Jotcham, J. Environmental Properties of Triclopyr. M.Sc. Dissertation, University of Guelph, 1985.

Miller, J. H.; Bace, A. C. Streamwater Contamination After Aerial Application of Pelletized Herbicide. USDA Forestry Service Southern Forestry Experimental Station Research Note SO-255; GPO: Washington, DC, 1980.

Neary, D. G.; Bush, P. B.; Douglass, J. E. Off-Site Movement of Hexazinone in Stormflow and Baseflow from Forest Watersheds. *Weed Sci.* **1983**, *31*, 543–551.

Rhodes, R. C. Soil Studies with ^{14}C-Labeled Hexazinone. *J. Agric. Food Chem.* **1980**, *28*, 311–315.

Sung, S. S.; South, D. B.; Gjerstad, D. H. Bioassay Indicates a Metabolite of Hexazinone Affects Photosynthesis of Lablolly Pine (*Pinus taeda*). *Weed Sci.* **1985**, *33*, 440–442.

Weed Science Society of America Herbicide Handbook, 5th ed.; Weed Science Society of America: Champaign, IL, 1983.

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