Off-Site Movement of Hexazinone in Stormflow and Baseflow from Forest Watersheds[1]

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Abstract. Four forest watersheds (1 ha each) in the upper piedmont of Georgia were treated with hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] pellets[3] at a rate of 1.68 kg ai/ha. From the end of April, 1979, until May, 1980, 26 storms were monitored to determine movement of hexazinone and two of 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] in runoff water. Residues in runoff peaked in the first storm after application (mean concentration of 442 ± 53 ppbw), and declined with subsequent storms in a power curve function: Conc. (ppbw) = $405 \times$ rate $\times (1 + 0.44 \times$ days$)^{-1.1}$. Loss of hexazinone in storm runoff averaged 0.53% of the applied herbicide, with Storms 1 and 17 accounting for 59.3% of the chemical exported. Storm 1 had high residue concentrations and low runoff volume, while Storm 17 contained only low residue levels but a very large stormflow. Hexazinone was the predominant compound in the runoff of all 26 storms. Metabolites A and B occurred in runoff in low-to-trace concentrations (<23 ppbw) for up to 7 months after application. Subsurface movement of hexazinone appeared in streamflow 3 to 4 months after application and produced an additional loss of 0.05%. A second-order perennial stream below the treated watersheds periodically contained hexazinone residues of <44 ppbw.
Additional index words. Residue, herbicide, ecosystem model, runoff.

INTRODUCTION

Development of new herbicides for agricultural and forestry uses has focused on two primary topics, efficacy and safety (17). Safety concerns not only applicator and other human exposure, but also biodegradability, movement in the environment, impacts on wildlife, target species selectivity, and effects on the protected crop. Clearly, the ideal herbicide is one which is effective, is applied in an easy-to-handle formulation, is biodegradable, has a low toxicity to animals, and does not move off-site. The first four characteristics can be adequately assessed under controlled laboratory conditions. The fifth feature can be approximated with laboratory microcosms and models. The validity of any model predicting herbicide movement in ecosystems however, must be verified with systematic field evaluations.

The considerable body of information on herbicide and insecticide residues leaving agricultural fields has been reviewed by Wauchope (29). He noted several interesting generalizations which applied to 22 studies involving 32 chemicals. Pesticide runoff events were classified into critical (1 cm of rain within 2 weeks of application producing the bulk of runoff losses), catastrophic (a storm event removing >2% of the applied chemical), and high-low (high pesticide concentration but low runoff volume). Most pesticides lost were in the solution phase and, excluding wettable powders and persistent compounds, total loss of pesticides from fields was generally 0.5% or less.

Over the past 10 yr there has been a fairly intense effort to model pesticide loss from agricultural areas (1, 4, 5, 7, 8, 12, 18, 30). All of the models function on an edge-of-the-field basis. Until recently, little research has been directed towards modeling the downstream fate of pesticides. Most models have application to forest pesticide use, but none have been developed specifically for the edaphic and hydrologic conditions of forest ecosystems. In addition, the literature contains few references to replicated data sets on pesticide movement in storm runoff from forest ecosystems (6, 9, 23, 24, 25, 26, 27). In most reported instances, maximum concentrations and total amounts lost in runoff under forested conditions were less than those reported for agricultural land (29).

Hexazinone is a recently-developed, symmetrical triazine herbicide which is effective in controlling a broad spectrum of annual and perennial weeds at herbicide rates tolerated by many conifers. The 10% ai pellet formulation (2 and 0.5 cm^3 sizes) and the 20% ai formulation (1 cm^3 size) were recently registered for non-crop and reforestation areas, and have considerable potential as cost-effective tools in pine silviculture (2, 11, 13, 20, 22). In addition, the pellet formulation and low toxicity reduce potential nontarget organism impacts (10, 16).

High water solubility (33 000 ppmw at 25 C) makes hexazinone susceptible to off-site movement in storm runoff and leaching[4]. Lateral or vertical movement in soil is slowed by high organic matter or clay cation exchange capacity. Hexazinone is subject to microbial degradation but resists photodegradation. Miller and Bace (21) reported high hexazinone concentrations (up to 2400 ppbw) from direct fall of pellets into a forest stream during an aerial application

in Alabama. Concentrations fell to 110 ppbw within 24 h and to <20 ppbw after 10 days.

This study was established to determine: a) the off-site movement of hexazinone in storm runoff from small forest watersheds; and b) the extent of dilution of the chemical downstream from the treated areas.

MATERIALS AND METHODS

Site description. The study site is located in the Chatta-hoochee National Forest, 10 km southeast of Clarksville in northeast Georgia. It lies within the drainage of Moonshine Creek, a tributary of the Broad River. The site consists of a series of well-defined, ephemeral drainages at the 400- to 450-m elevation. Ridge tops are broad and show evidence of extensive erosion induced by past agriculture. The drainages are typically broad, bowl-shaped in their upper reaches, deeply eroded at their midpoints, and broad-bottomed in their lower reaches. Maximum relief from ridgetop to peren-nial stream averages 50 m. The original stream bottoms are buried under fine-textured alluvial deposits which reach 2 m in depth. Moonshine Creek alternates from low gradient sections with sandy bottoms to steep ones with rocky riffles, pools, and waterfalls.

The soils on the ridges are sandy loams of the Cecil series (Typic Hapludults). These well-drained soils have formed from mica-rich gneiss and schist of the pre-Cambrian Tallulah Falls formation. Upper ridges contain eroded phases of the Cecil series with a remnant A horizon (0 to 10-cm thick) overlying a massive B 2t horizon. The A horizon increases in thickness on the slope toe. Bottomlands surrounding the headwater ephemeral and perennial streams are colluvial in nature.

The 60- to 80-yr-old mixed pine-hardwood overstory is characterized by scattered shortleaf pine (*Pinus echinata* Mill.), chestnut oak (*Quercus prinus* L.), white oak (*Q. alba* L.), black oak (*Q. velutina* Lam.), flowering dogwood (*Cornus florida* L.), sourwood [*Oxydendrum arboreum* (L.) DC.], pignut hickory [*Carya glabra* (Mill.) Sweet], and various other species (22). Hardwood growth is poor on the ridges and good in the stream bottoms. The sparse understory consists of overstory hardwood species and various herbaceous plants.

Instrumentation. Five watersheds (designated WS 1 to WS 5), 0.85 to 1.09 ha in area, were selected and surveyed in early March, 1979 (Figure 1). These watersheds produce flow only during storm events. They were instrumented in April, 1979, with 30-cm H-flumes, Coshocton wheel flow-proportional samplers, analog water level recorders[5], and sample collection systems (3). The flow-proportional

samplers were designed to collect approximately 0.5% of the total flow through the H-flumes. Runoff samples were routed by pipe to two 100-L polypropylene storage con-tainers. The water level recorders produced a continuous trace of water head in the H-flume which was translated into total discharge using a standard rating equation and processing program (15). Storage and recording rain gauges[6] were installed in a clearing on a ridge north of watershed WS[5].

Watersheds WS 1 through WS 4 were selected for herbi-cide treatment because storm runoff from these watersheds converges into the same drainage (Stream A, Figure 1). Over much of its length, this stream alternates from open-channel flow to subsurface flow in recent alluvium. Stream A was instrumented, below the point of convergence of drainage from watershed WS 4 and Stream A, with a cutoff wall, H-flume, and water level recorder, but no flow proportional sampler (No. 87). This monitoring station (No. 87, Figure 1) was established to determine if hexazinone or its metabolites would leach deep into the soil, bypass the H-flumes, and then move downstream. Water sample collection began in May, 1979, and flow measurements were started in June.

In April, 1979, a sampling and stream gauging station (No. 88, Figure 1) was established on Moonshine Creek about 30 m downstream of its confluence with Stream A.
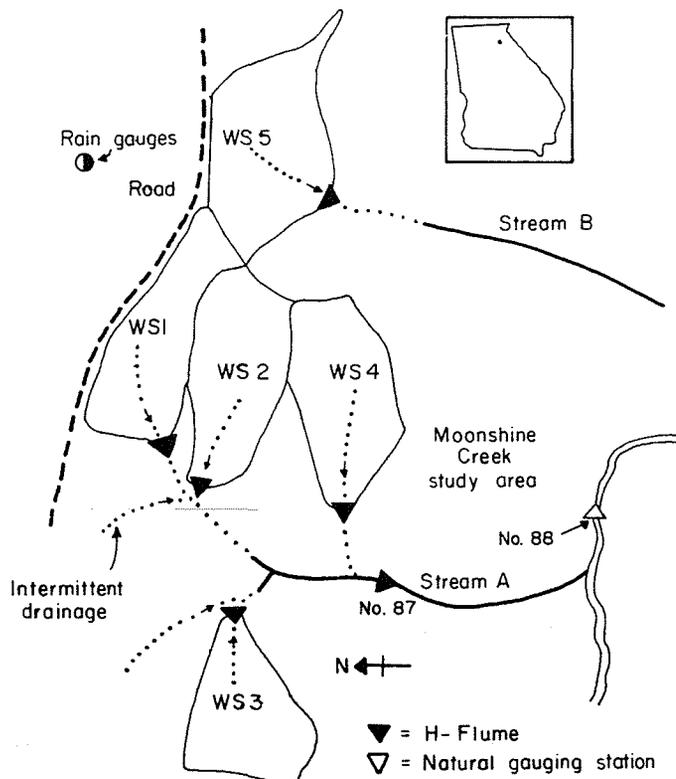

Figure 1. H-flume locations and stream gauging stations, Moon-shine Creek study area (watersheds WS 1 through WS 4 received 1.68 kg ai/ha hexazinone, WS 5 served as control).

A solid rock-bottomed channel, suitable for rating water discharge, was instrumented with an analog water level recorder and automatic water sampler. A staff gauge was installed in the stream, and a rating developed from stream-velocity measurements taken weekly and during selected storms.

Treatment. Watersheds WS 1 through WS 4, plus some surrounding areas, were treated with 1.68 kg ai/ha of hexazinone (10% ai pellets) on April 23, 1979. Pellets were spread at a spacing of 1.8 by 1.2 m to achieve the desired application rate. Wire flags were used to mark pellets for later sampling of mineral soil, and to tally pellets which fell into the ephemeral drainage channels.

Water and sediment sampling. Runoff water samples were collected with the flow-proportional Coshocton wheels during each of 26 storms between April 26, 1979, and May 27, 1980. Several long-duration storms were repeatedly sampled and some exceeded the storage system capacity. Water samples collected at the No. 87 flume on Stream A were all discrete, manually-collected samples taken under baseflow conditions rather than during storm runoff (28). Water samples collected at No. 88, from Moonshine Creek, were either discrete or bulk samples depending on the type of sampler in operation.

Water samples were removed from the sampling systems immediately after storms and put into 1-L washed and methanol-rinsed glass jars. The samples were stored at 4 C and transported in insulated, ice-packed containers to the University of Georgia where they were stored at 4 C prior to herbicide extraction and analysis. Duplicate samples retained for residue cross-check analysis were frozen in 1-L polypropylene bottles. Bedload sediment, which accumulated during several severe storms, was collected to determine total sediment mass and herbicide-residue content.

Soil samples. Litter and mineral-soil samples were collected 3, 14, 30, 60, and 90 days after the first rain following herbicide application. During the hexazinone pellet spreading, the location of individual pellets was marked with flagging to locate future sampling points. Litter and mineral-soil samples were obtained from three positions, 60 cm in distance from pellets marked for the given sampling date, and composited. Samples were also separated by topographic position (ridge, mid-slope, and toe) on each of the four treated watersheds. Litter was collected first, and then mineral soil cores were removed in 10-cm increments to a depth of 30 cm. Soil and litter material were frozen prior to residue analyses.

Hexazinone residue analyses. Water, soil, and litter samples were extracted with chloroform and ethyl acetate, and the amounts of hexazinone and its metabolites were determined by nitrogen-selective gas chromatography after reaction

of metabolites with trifluoroacetic anhydride (16). The derivatives were analyzed on the same day as derivatization[7]. The gas chromatograph was operated under the following conditions: inlet temperature 230 C; detector temperature 280 C; helium carrier gas flow 35 cc/min. The column was temperature-programed from 230 to 280 C at a rate of 10 degrees/min, and was held at the final temperature for about 8 min. Hexazinone and metabolite levels were determined by comparison of peak heights with those of known analytical standards[8]. A reagent blank and sample of known hexazinone and metabolite content was included in each set of analyses, and results were corrected for percent recovery. The detection limit for hexazinone and both metabolites was normally 1 ppbw for water and 0.1 ppmw for soil and litter.

RESULTS AND DISCUSSION

Precipitation and storm runoff. Rainfall 3 days after the hexazinone pellet application produced the first of 26 runoff events. Mean storm discharge for watersheds WS 1 through WS 4 ranged from a low of 0.05 m^3 for Storm 11 to a high of over 172 m^3 for Storm 17 (Table 1). By contrast, flow from the untreated control watershed (WS 5) ranged from none for Storms 1 and 2, to nearly 81.5 m^3

Table 1. Rainfall and mean storm runoff for 26 storm events in four upper-piedmont watersheds, April 26, 1979, to May 21, 1980.

Date of storm	Storm no.	Amount of rain	Mean storm runoff	
			Area-depth	Volume
		(mm)		(m³)
1979				
April 26	1	50	0.6	5.67 ± 3.43
May 10	2	47	0.2	2.24 ± 1.72
May 21	3	55	0.8	7.23 ± 2.23
May 31	4	34	0.4	3.42 ± 2.43
July 8	5	72	0.1	1.23 ± 1.83
July 12	6	13	<0.1	0.81 ± 1.17
July 23	7	38	<0.1	0.20 ± 0.20
July 26	8	55	0.3	3.20 ± 3.31
Aug. 25	9	70	0.2	1.70 ± 0.43
Sep. 3	10	70	0.6	5.47 ± 3.79
Sep. 18	11	11	<0.1	0.05 ± 0.00[a]
Sep. 21	12	55	2.0	18.87 ± 4.55
Sep. 28	13	43	0.2	1.45 ± 2.62
Oct. 4	14	25	<0.1	0.50 ± 0.88
Oct. 23	15	11	<0.1	0.10 ± 0.06
Oct. 30	16	44	0.4	4.27 ± 3.28
Nov. 2	17	94	18.2	172.38 ± 55.15
Nov. 10	18	35	0.2	1.52 ± 1.45
Nov. 25	19	93	5.1	48.79 ± 7.68
1980				
Jan. 18	20	92	5.5	52.49 ± 16.50
March 7	21	107	11.4	107.84 ± 14.63
March 17	22	128	12.0	114.13 ± 14.51
March 20	23	111	16.8	159.43 ± 30.72
March 28	24	62	6.7	63.61 ± 9.17
April 12	25	87	10.1	95.65 ± 18.90
May 21	26	82	4.4	41.48 ± 8.78

[a]Estimated storm runoff due to equipment failure.

for Storm 17. Total flow for the control watershed for the period April 26, 1979, through May 27, 1980, was 37% of the mean for the treated watersheds. Some of this difference was due to inherent variability of these small watersheds, and the remainder due to increased runoff on the treated watersheds after elimination of the hardwoods.

Storm 17 in early November produced 94 mm of rain in 13 h. A storm of this size is expected to occur once every 2 to 5 yr in north Georgia (14). This storm included a downpour of about 25 mm in 1 h and accounted for 75% of the mean discharge from the treated watersheds over the duration of the first 17 storms. The probability of this size storm occurring during the hexazinone application months of April and May is relatively high (p = 0.015 to 0.02 compared to P<0.01 in the month it actually happened (14).

Rainfall during 1979 set new records in north Georgia, with an excess of 30% recorded at some stations. Annual rainfall in the area is usually 1300 to 1400 mm. The yr 1980 remained wet through May with precipitation 31% above average due to record rainfall in March (441 mm, 162% of average). Three storms during this unusually wet month accounted for 41.4% of the total runoff recorded during the course of the study.

Hexazinone and metabolite concentrations. The mean concentration of hexazinone in storm runoff followed a typical residue decay curve. The peak concentration for the four treated watersheds averaged 442 ± 53 ppbw and occurred with Storm 1, three days after the herbicide application (Table 2). The maximum concentration, 514 ppbw, occurred in runoff from watershed WS 3. Hexazinone concentrations declined sharply in Storm 2 runoff 2 weeks later, dropped even further in Storm 3, climbed again in runoff 40 days after application (Storm 4), and thereafter stayed below 34 ppbw. Except for Storms 1 and 4, the coefficient of variation (CV) in hexazinone concentrations between watersheds often exceeded 50% of the mean. As time progressed and hexazinone concentrations dropped, the CV increased because one watershed in the four frequently had nondetectable residue levels in runoff.

During Storm 8 (July 26, 1979) runoff carried low hexazinone concentrations from all four watersheds (20 to 45 ppbw) (Table 2). In the next significant event, Storm 10 in early September, hexazinone levels varied more. The lack of residues in watershed WS 2 stormflow reduced the mean concentration. Storm 12 produced the largest flow of the first 5 months after herbicide application, but hexazinone concentrations continued to be in the same range. Runoff from watershed WS 4 did not carry detectable levels of hexazinone during this storm. A month later, in Storm 16, hexazinone appeared in runoff from all four watersheds but at lower concentrations (1 to 15 ppbw). Storm 17 (November 2, 1979) produced the most runoff of all 26 events, but hexazinone concentrations were low. During the next two storms, watersheds WS 1 through WS 3 did not carry hexazinone residues in either runoff events. Storm 20, which occurred in mid-January, 1980, after a dry period of nearly 54 days, contained the last hexazinone residues of any size. The next three storms produced 41.4% of the

total runoff during the study but the runoff contained no detectable hexazinone residues. Runoff from watershed WS 4 during Storm 24 contained the last measurable amount of hexazinone (15 ppbw).

Metabolite A did not appear consistently in runoff until Storms 5 through 7 when it was detected in trace quantities (Table 2). It peaked in concentration in Storm 8, but then was present in detectable amounts in only one other runoff event (Storm 10). The highest metabolite A concentration was 54 ppbw in runoff from watershed WS 3 during Storm 10.

Metabolite B concentration means oscillated from nondetectable to trace levels during the first 12 storms (Table 2). Except for Storm 17, metabolite B was not detected in runoff after September, nearly 7 months following hexazinone application. The highest concentration in runoff from any one watershed was 15 ppbw (WS 3 following Storm 10).

Except for one water sample with a trace level (3 ppbw) of herbicide, residues of hexazinone and metabolites A and B were not detected in storm runoff from the untreated

Table 2. Mean content of dissolved hexazinone and metabolites A and B in storm runoff from four herbicide-treated upper piedmont watersheds.

Date of storm	Storm no.	Herbicide residues[a]			Total residue runoff
		Hexazinone	Metabolites		
			A	B	
		————(ppbw)————			(g/ha)
1979					
April 26	1	442 ± 53	ND ± 0	ND ± 1	2.54 ± 1.25
May 10	2	105 ± 73	T(2) ± 2	T(3) ± 3	0.36 ± 0.44
May 21	3	39 ± 76	ND ± 0	ND ± 1	0.39 ± 0.74
May 31	4	107 ± 23	ND ± 0	T(6) ± 3	0.43 ± 0.32
July 8	5	11 ± 5	T(5) ± 6	ND ± 1	0.03 ± 0.05
July 12	6	T(4) ± 2	T(2) ± 4	T(1) ± 1	<0.01 ± <0.01
July 23	7	T(4) ± 5	T(2) ± 4	ND ± 0	<0.01 ± <0.01
July 26	8	34 ± 10	23 ± 18	T(2) ± 5	0.20 ± 0.20
Aug. 25	9	6 ± 12	ND ± 0	ND ± 0	0.01 ± 0.03
Sep. 3	10	30 ± 35	14 ± 27	T(4) ± 8	0.32 ± 0.35
Sep. 18	11	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Sep. 21	12	17 ± 19	ND ± 0	T(3) ± 6	0.46 ± 0.62
Sep. 28	13	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 4	14	T(2) ± 4	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 23	15	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
Oct. 30	16	7 ± 6	ND ± 0	ND ± 0	0.04 ± 0.02
Nov. 2	17	18 ± 10	ND ± 0	T(1) ± 2	3.02 ± 1.32
Nov. 10	18	T(4) ± 5	ND ± 0	ND ± 0	0.01 ± 0.01
Nov. 25	19	T(4) ± 4	ND ± 0	ND ± 0	0.44 ± 0.66
1980					
Jan. 18	20	14 ± 11	ND ± 0	ND ± 0	0.88 ± 0.27
March 7	21	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 17	22	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 20	23	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
March 28	24	T(4) ± 0	ND ± 0	ND ± 0	0.24 ± 0.48
April 12	25	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
May 21	26	ND ± 0	ND ± 0	ND ± 0	0.00 ± 0.00
				Σ = 9.39	

[a]ND = <1 ppbw, and T = 1 to 10 ppbw with actual values in parentheses.

watershed WS 5. The sample with a trace level involved low flow and may have been contaminated during sample handling or analytical preparation. It did not represent a transfer of herbicide into the control watershed as subsequent samples were all negative.

Concentration models. Hexazinone and metabolite concentrations were summed by watershed for each storm and fitted to two non-linear models:

I. Power Curve:

Concentration = a T^b,

where   T = time in days from rainfall activation, and

a,b = regression coefficients.

II. Maximum Concentration Estimation (30):

Concentration = AR $(1 + 0.44\ T)^{-1.6}$,

where   A = availability for runoff index (3000 hexazinone),

R = application rate (kg ai/ha), and

T = time in days since the first significant rainfall after application.

The power curve model produced a significant fit to the observed data (a = 550.0; b = −1.0; F = 211.72: significance = 0.001), but overestimated the mean concentration in runoff following Storm 1 by 108 ppbw. This model also underestimated the concentrations in runoff from the next three storms. For Storm 4 onward there was reasonable agreement between observed and predicted data. Because this model reaches the non-detectable concentration levels (1 ppbw) fairly rapidly, it does not simulate the intermittent spikes and near-baseline concentrations observed 70 to 220 days after rainfall activation of the hexazinone-containing pellets.

The maximum concentration estimation model (MCE) was tested against the hexazinone residue concentrations using the 3000 availability index suggested by Wauchope and Leonard (30). The MCE prediction for peak concentration was 2812 ppbw, six-times greater than the measured value. This was somewhat higher than the four-fold overestimation proposed by Wauchope and Leonard as typical of the MCE. A non-linear regression analysis of the concentration data produced a much lower availability index (482.0) for the MCE model, but did not fit as closely as the power curve. Although it produced a better estimate of the initial storm concentration, it still suffered from the same tendency to underestimate concentrations immediately after Storm 1.

The MCE model was modified to the form:

$$\text{Concentration} = AR\ (1 + 0.44)^{-1.1}$$

Using this model the prediction of hexazinone residues was further improved (F = 790.32; significance = 0.001). This was especially true for data following Storms 5 through 19 in the 20- to 220-day range (Figure 2). Residue pulses were still not accounted for and concentrations in Storms 2 through 4 were again underestimated. The availability factor from the original MCE model fell to 405 with the modified model.

The residue pulses, particularly following Storms 4 and 8, which were underestimated by these models, could be due to a phenomenon discussed in greater detail in the section on soil residues. Extensive defoliation of the hardwood over-
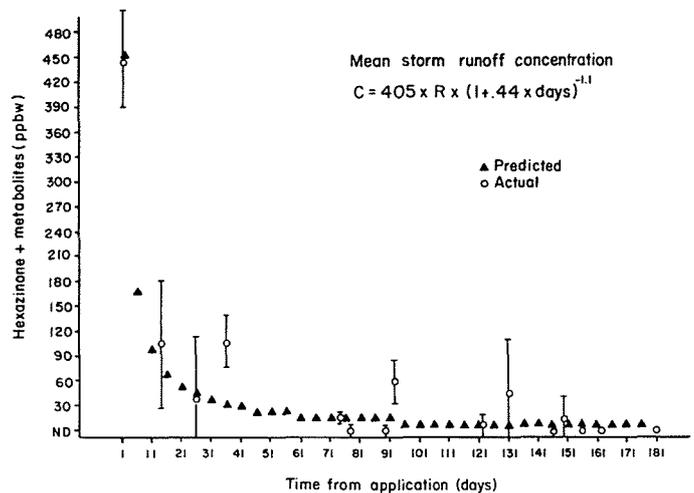

Figure 2. Modified Maximum Concentration Estimation (MCE) equation for the prediction of mean hexazinone residue concentrations in storm runoff.

story starting in late May returned significant quantities of hexazinone and its metabolites to the forest floor. This recycling could account for several of the higher-than-predicted concentrations in runoff water.

Residue outputs. Concentrations of hexazinone and both metabolites in storm runoff from each watershed were summed and multiplied by the volume of water discharge to produce a total output for each storm (Table 2). The cumulative output of dissolved herbicide residues was dominated by Storms 1 and 17 (Figure 3), which accounted for about 71% of the total herbicide loss in runoff. Storm 1 was characterized by low runoff but a high residue concentration. Storm 17 produced a very high runoff discharge, but the runoff contained only a low concentration of herbicide. By the end of Storm 26 in May, 1980, the mean output of residue in storm runoff had accumulated to 9.39 g/ha.

The source of this residue output was probably hexazinone pellets which fell in the ephemeral drainage channels. These channels, which were the source areas for storm runoff, contained 1.5% of the applied herbicide pellets. This figure was determined by flagging and counting hexazinone pellets lying in the drainage channels after application. Over the 397-day study period, the amount of hexazinone and metabolite residues lost in storm runoff was only 34.9% of that which fell into the channels, and only 0.53% of the herbicide applied on each 1-ha watershed.

The only storm which deposited any coarse sediment in the H-flumes was Storm 3. Sediment collected in the flume approaches averaged less than 400 g per watershed. The mean concentration of hexazinone plus metabolites A and B in the sediment was rather high at 250 ppbw oven-dry weight (ODW). But this amounted to an additional output of 5×10^{-5} g/ha of herbicide residue, an insignificant amount compared to that lost in the dissolved phase in the first three storms. Some organic debris, which accumulated through
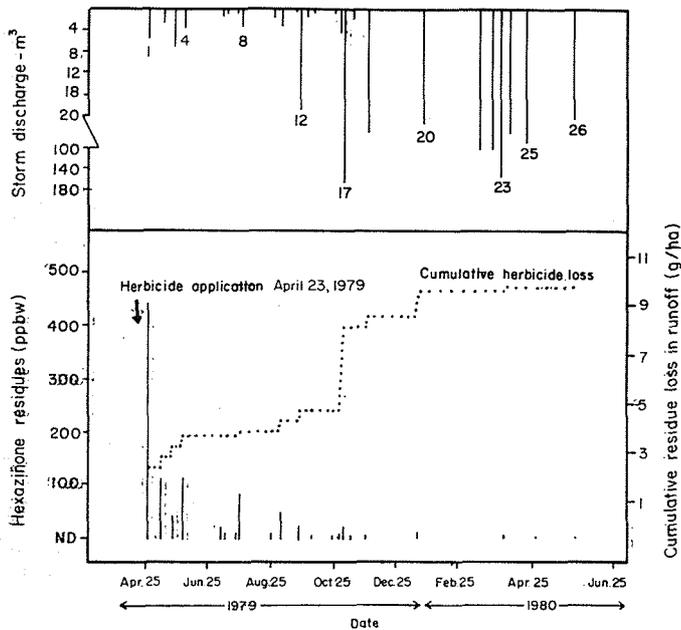
Figure 3. Mean hexazinone residues (hexazinone plus metabolites A and B) in storm runoff (vertical bars), cumulative output of residues (dots), and runoff volume (Storms 1 to 26), April 23, 1979, to May 27, 1980.

Table 3. Mean concentration of hexazinone and metabolites A and B in litter and the upper 30 cm of mineral soil of watersheds treated with hexazinone April 23, 1979.

| Sampling date | Time from first rain | Type of sample | Herbicide residue | | |
| | | | Hexazinone | Metabolites | |
				A	B[a]
			— (ppmw oven dry weight) —		
April 30, 1979	3	Litter	0.177	0.100	ND
		Soil	0.108	0.102	0.122
May 10, 1979	14	Litter	0.007	ND	ND
		Soil	0.043	ND	0.016
May 24, 1979	30	Litter	ND	0.103	ND
		Soil	0.063	0.015	ND
June 25, 1979	60	Litter	0.060	ND	ND
		Soil	0.015	ND	0.027
July 25, 1979	90	Litter	3.42	0.046	ND
		Soil	ND	0.025	0.023

[a]Detection limit for individual samples was <0.01 ppm. Values listed are means of nine individual samples.

the first three storms, contained varying amounts of hexazinone (90 to 620 ppbw ODW) and metabolite A (non-detectable levels to 600 ppbw), but no detectable amounts of metabolite B. The amount of organic debris was small and was not measured.

One interesting question arises from these analyses of hexazinone and metabolite output. What would have been the impact of the largest storm (Storm 17, Figure 3) if it had occurred at the time of Storm 1? If we assume a worst-case is one in which a hypothetical Storm 1 removes the amount of herbicide Wauchope (29) classed as constituting a catastrophic loss (2%), then 160 g of hexazinone would be diluted into 172.383 m³ of runoff. This would produce a vastly greater output of hexazinone than was actually measured in the first storm. The mean concentration of runoff from this hypothetical Storm 1 (926 ppbw) would, however, be insufficient to affect aquatic algae, invertebrates, or fish (10, 19).

Soil and litter residues. Residues of hexazinone in the mineral soil, irrespective of slope position, exhibited a regular decrease over time (Table 3). The amount of metabolite residues was erratic in both litter and mineral soil. This trend paralleled that of residue concentrations in storm runoff. The half-life of hexazinone in mineral soil was in the order of 10 to 30 days. The exact half-life is difficult to determine due to the increase in concentration on May 24, 1979, relative to the previous sampling date. The mean hexazinone concentration present over the month of May would indicate a half-life of 20 days.

The increase in litter hexazinone residue measured towards

the end of June probably reflects the defoliation of the hardwood overstory. By the end of May, 1979, hexazinone had caused almost complete necrosis of the hardwood crowns (22). Leaf fall increased in June and was extensive by July. This process apparently returned considerable amounts of herbicide to the forest floor. Data from a 1980 treatment (Figure 4) indicates that the hexazinone content of the first leaves shed by treated trees was less than 3.0 ppmw ODW. Concentrations increased to 6.0 ppmw ODW during the
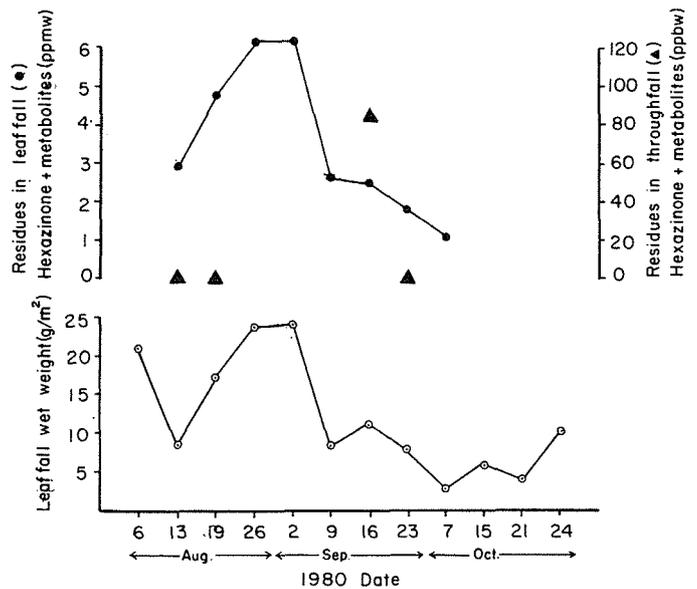

Figure 4. Hexazinone residues returned to the forest floor by litter fall and leaching after application of 1.68 kg ai/ha, 1980.

3rd month after application, which coincided with the greatest rate of leaf deposition (240 kg/ha/week ODW). Litter data from 1979 (Table 3) indicates that hexazinone was probably the predominant residue (71 to 76%) in the 1980 leaf fall. Small amounts (12 to 157 ppbw) of hexazinone and metabolite residues were measured in 1980 in rain throughfall and litter collection gauges. These residues apparently leached out of hexazinone-affected hardwood leaves in the tree crowns and on the forest floor. Residue fluxes from affected foliage could have some effect on mineral-soil residues, but they could potentially affect herbicide concentrations in storm runoff to a greater degree. This may explain in part the elevated residue concentration following Storm 8, about 90 days after hexazinone application (Table 2). Recycling of hexazinone is consistent with the chemical properties of this herbicide, and would account for delayed herbicide activity on small hardwood stems (22). Small-diameter hardwoods, not immediately affected by the application of hexazinone pellets, did not show much herbicidal activity until the overstory crowns began to defoliate. Distribution of herbicide to these small stems may have been enhanced by return of hexazinone residues to the soil via leaf fall and subsequent leaching.

An interesting slope position-depth-time trend can be noted in the 0- to 10-cm soil residue data. Hydrologically, this is the most important depth layer in piedmont soils. It encompasses the existing A horizon developed under forested conditions and the Ap horizon remnant of past agriculture. Since the well-structured, well-drained A horizon usually overlies a massive, somewhat impervious B 2t horizon, a large proportion of subsurface water flow occurs as interflow downslope along the A-B 2t horizon boundary.

Samples from the 0- to 10-cm soil depth indicated that a pulse of hexazinone residues moved downslope during the 90 days after herbicide application (Figure 5). Residues of hexazinone and metabolites A and B peaked on the upper slopes (ridge) 3 days after the first rain, and then dropped below detection limits after 2 weeks. At the midslope position, residues also peaked on day 3 but took 30 days to drop below detection limits. At the slope toe, hexazinone and metabolite concentrations climbed steadily, peaking 60 days after the first rainfall, and dropping below detection by day 90. Further evidence to support the possibility of a downslope concentration wave moving with subsurface interflow is contained in baseflow residue data from monitoring Station No. 87.

Baseflow residues. Baseflow from the 10.4-ha watershed above the No. 87 Station averaged 0.002 m^3/s during the sampling. Storm discharge reached a maximum in Storm 17 when the H-flume was overtopped by 15 cm. The discharge at maximum for the 30-cm H-flume is 0.056 m^3/s. Storms 8, 10, 12, 17, and 19 through 26 produced peakflows greater than 0.011 m^3/s. Except for Storms 1 through 4, which were not gauged, the remaining storms had peakflows between 0.0004 and 0.011 m^3/s.

Herbicide residues were not detected in baseflow until late July, 1979 (Figure 5). The set of four residue pulses which occurred during the dry period from July 27, 1979,
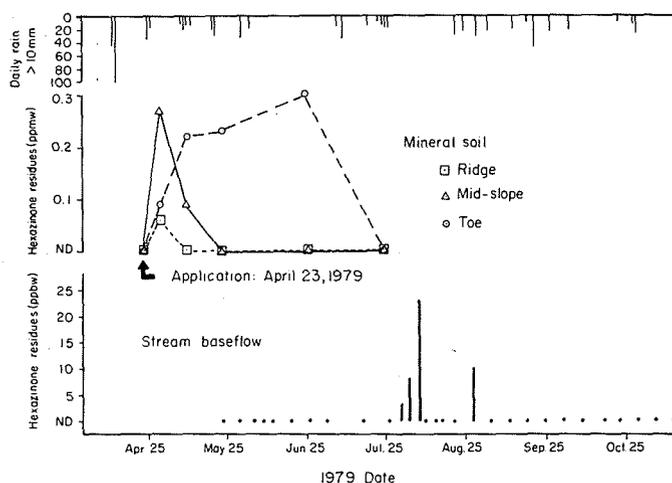

Figure 5. Hexazinone residues (hexazinone plus metabolite A and B) in the 0 to 10-cm soil depth and in baseflow in Stream A below the herbicide-treated watershed area, 1979.

to August 12, 1979, corroborate the previously discussed soil residue dynamics. These apparent pulses of herbicide residue in baseflow followed the drop in soil residue concentrations below the detection limit. The first and largest pulse peaked at 23 ppbw on August 7, 1979, but may have been higher since samples collected at Station No. 87 were instantaneous values. The second pulse is represented by a peak at about 10 ppbw. Although the sample was collected during non-storm conditions, it may have been influenced by Storm 9 on August 25, 1979. Hexazinone made up almost 49% of the first pulse and 100% of the second pulse. Metabolite A accounted for the remainder of the first pulse, but was not detected again. Metabolite B was found only in the beginning of the first residue pulse.

Samples collected manually at weekly intervals from September 4, 1979, through October 29, 1980, were generally free of herbicide residues. Individual samples on January 15, 1980, and June 24, 1980, contained trace amounts of hexazinone.

Mainstream residues. At Station No. 88, where Moonshine Creek drains a 104-ha watershed, baseflow ranged from 0.014 to 0.042 m^3/s. The highest discharge was estimated at 1.7 to 2.8 m^3/s.

Residues of hexazinone plus metabolites A and B in stormflow at Station No. 88 were less than 44 ppbw (Figure 6). Hexazinone was the primary residue, and metabolite B was never detected. During Storm 1, which produced the highest residue concentration in runoff from the small watersheds (442 ppbw), a trace level (2 ppbw) of hexazinone was detected in a composite sample collected automatically over a 7-day period. No residues of either metabolite were detected in this sample. Following Storms 2 and 3, no hexazinone nor metabolites were detected. A trace amount (5 ppbw) of hexazinone was detected in a 24-h composite sample after Storm 4, but again metabolites A and B were not detected.
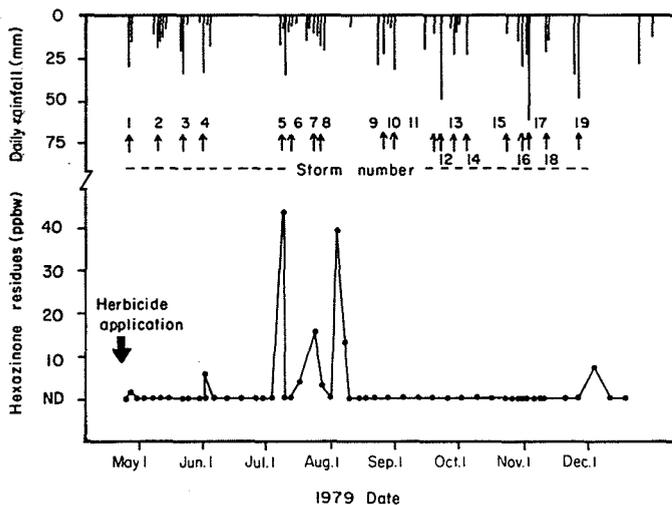
Figure 6. Hexazinone residues (hexazinone plus metabolites A and B) in solution at Moonshine Creek No. 88 gauging station, 1979.

Storm 5 in the beginning of July, 1979, was small in size (Table 1) but produced the first herbicide residue pulse of any size in Moonshine Creek (Figure 6). A manually-collected sample on July 9, 1979, contained 22 ppbw hexazinone and 21 ppbw metabolite A. Another sample taken 24 h later was free of herbicide residues. A trace amount (4 ppbw) hexazinone was detected in samples taken from Moonshine Creek between Storms 6 and 7, but neither metabolite was present. During Storm 7 which lasted from July 19 to July 24, 1979, another pulse of herbicide residue (only hexazinone) was detected in streamflow. This was followed by another trace concentration (3 ppbw of hexazinone) after Storm 8.

During the period of July 31 through August 10, 1979, another pulse of herbicide residues in streamflow occurred. The peak concentration of 40 ppbw (25 ppbw hexazinone and 15 ppbw metabolite A) occurred in a composite sample collected automatically between July 31 and August 3, 1979. The residue level fell to 13 ppbw (all hexazinone) during the next 4 days, and then returned to the non-detectable level over the next 3 days. This pulse of hexazinone residues occurred during a dry period (Figure 6) and corresponded with the pulse of residues observed in baseflow at monitoring Station No. 87.

One additional sample from Moonshine Creek in late November, 1979, contained a low level (7 ppbw) of hexazinone.

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[9] This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed have been registered. All pesticides must be registered by appropriate state and/or federal agencies before they can be used. CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife — if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

Water samples collected manually at weekly intervals from December, 1979, through October, 1980, were free of residues.

The low and intermittent concentrations of hexazinone and its metabolites in Moonshine Creek did not expose aquatic organisms to toxic herbicide levels. This conclusion was confirmed by a concurrent study of benthic organisms in Moonshine Creek (19). Aquatic invertebrates and macrophytes did not accumulate hexazinone residues, and no species composition nor diversity shifts were noted.

The application of hexazinone to forest ecosystems according to maximum recommended rates and following label instructions should not produce any adverse environmental effects on water quality or aquatic ecosystems[9].

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