

# Monitoring Herbicide Residues in Springflow After an Operational Application of Hexazinone

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**ABSTRACT.** Parts of two forested watersheds (440 ac and 482 ac) in central Tennessee were aerially treated with 15 lb/ac of hexazinone pellets (10-percent active ingredient) to remove hardwood competition prior to establishing loblolly pine (*Pinus taeda* L.). Both treated watersheds and a control were monitored to determine if hexazinone residues were entering ground water and appearing in springflow. Seven months of monitoring included two intensively sampled periods during application and the first storm. No detectable residues of hexazinone or its two primary metabolites were measured in samples from a watershed in which hexazinone was applied up to 66 ft. from the monitoring point. Springflow samples from a watershed treated a year earlier (in 1980) were also clear of herbicide residues.

A major problem in regenerating southern yellow pine stands is competition from hardwoods and herbaceous weeds. Extensive use of mechanical site preparation for weed control in the past two decades has resulted in soil losses up to 4 tons/ac/yr (9 metric tons/ha/yr) during re-establishment (Douglass and Goodwin 1980). Not only does this loss of sediment pose water quality problems downstream, but it also depletes the site of vital nutrients, thereby impairing long-term site productivity (Nutter and Douglass 1978). In addition, the costs of mechanical site preparation have risen to the point where landowners are delaying or foregoing reforestation (Knight 1981).

Herbicides are a potentially useful site preparation alternative to mechanical methods. Hexazinone<sup>1</sup>, a recently registered, symmetrical

triazine herbicide, shows considerable promise to be a cost-effective tool in pine regeneration (Barber 1979; Gonzalez 1980; Hamilton 1979; Michael 1980, 1981; Neary et al. 1981). This chemical is highly active on competing hardwood species at levels producing only low toxicity (< 10 percent) to southern yellow pines. It can be applied easily from the air in pellet form with minimal drift potential, is low in toxicity to nontarget organisms, and is not persistent for long time periods.

Hexazinone is a white, odorless, crystalline solid in its pure state. It is not prone to volatilize into the air (vapor pressure of  $8 \times 10^{-9}$  in., or  $2 \times 10^{-7}$  mm, of Hg at 25°C), but it is highly soluble in water (33,000 ppm at 25°C). There are two primary metabolites (A and B) which form from the progressive breakdown of the hexazinone molecule (Holt 1981). The half-life of hexazinone in the soil ranges from 3 to 6 weeks (Neary et al. 1983; Sung et al. 1981, 1982).

The mammalian acute oral toxicity (LD<sub>50</sub>) for hexazinone is low (0.03 oz/lb — 1,690 mg/kg of body weight for rats), and both the inhalation and dermal toxicities are low. Laboratory determinations of toxic concentrations needed to kill 50 percent of target organisms (LC<sub>50</sub>) are high for most aquatic species. Hexazinone and metabolite levels need to reach 151,000 ppb to affect freshwater invertebrates such as *Daphnia* sp., but can inhibit common algae (*Cladophora* sp., *Rhizochonium* sp., and *Vaucheria* sp.) at lower concentrations (500 to 1,000 ppb) (Fowler 1977). Most fish species have LC<sub>50</sub> concentration thresholds in the 274,000 to 420,000 ppb range. Hexazinone concentrations in

<sup>1</sup> 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, EPA Reg. No. 352-387, manufactured by E. I. DuPont de Nemours and Co., Inc., Wilmington, Delaware, under the trade name "Velpar® Gridball® Brushkiller."

streamflow up to 45 ppb (Neary et al. 1983) did not affect aquatic invertebrate population diversity or abundance over a seven-month period (Mayack et al. 1982).

One major concern with the routine use of highly soluble chemicals in forest ecosystems is potential ground water and streamflow contamination. This is of particular interest with herbicides and insecticides, since many municipal and private water supplies originate from forested watersheds. An investigation by Neary et al. (1983) measured hexazinone losses in storm runoff and baseflow from small (<2.5 ac — < 1 ha) forest watersheds. Stormflow accounted for a loss of 0.5 percent of the applied chemical. Hexazinone residue concentrations in storm runoff never exceeded 600 ppb and attenuated to <10 ppb after seven months. Residues of hexazinone appeared in subsurface baseflows three to four months after application but were <24 ppb, very short lived, and only produced loss of another 0.05 percent of the applied chemical. Another study of hexazinone's impact on water quality reported high concentrations (2,400 ppb) after direct inputs into a perennial stream, but measured a quick decline in concentrations (to <20 ppb) within 10 days (Miller and Bace 1980).

The objective of the study reported here was to gather additional data on subsurface movement of hexazinone residues after operational applications to stands up to 124 ac (50 ha) in size. To contrast with the study by Neary et al (1983), the watersheds in this investigation occur in sedimentary geological areas rather than metamorphic, and require 247 to 494 ac (100 to 200 ha) to produce perennial streamflow instead of 2.5 to 25 ac (1 to 10 ha).

## METHODS

### Sites

Two sites were chosen for monitoring which would provide data from consecutive hexazinone pellet applications. The site previously treated with hexazinone in 1980 is in the upper reaches of the Lost Creek watershed, a tributary of the Buffalo River in central Tennessee. It lies about 15.8 mi (25.3 km) west of Centerville. The site treated in 1981 was selected in the Coleman Hollow watershed of Big Swan Creek, a tributary of the Duck River, about 17.8 mi (28.4 km) east of Lost Creek. The control watershed in Jenkins Hollow was selected because of its proximity to Coleman Hollow. All three sites are on land owned by Willamette Industries and are being converted to loblolly pine to provide a long fiber resource for paper production.

### Geomorphology

The geology of the Lost Creek, Coleman Hollow, and Jenkins Hollow watersheds consists of the Mississippian-aged Fort Payne formation on the upper channels and ridges and Silurian-aged Decatur limestone in the broad bottoms. The dominant Fort Payne formation is a calcareous siltstone and chert which weathers into a thick cherty rubble averaging 70 ft. (21.3 m) in depth. The impervious Chattanooga Black Shale is an aquaclude which separates the Fort Payne formation from the underlying Decatur limestone. Numerous springs originate at the interface between the Chattanooga shale and bottom of the Fort Payne. The Decatur formation contains mainly limestone with some shale. The main part of the Lost Creek upper stream bottom consists of wide, cherty, alluvial rubble with numerous small springs emerging at the slope base. One large spring was estimated to be flowing at a rate of 5 cfs (142 l/sec) when observed in April 1981. The Lost Creek watershed, westerly in aspect, ranges in elevation from 540 to 760 ft. (164.6 to 231.6 m). Slopes generally range from 15 to 35 percent but may approach 100 percent in some locations.

The Coleman Hollow watershed and its nearby control Jenkins Hollow contain the same geologic formations as Lost Creek. Perennial streamflow in both these watersheds originates at the base of chert ledges in the broad rubble-filled stream bottoms. The east-facing Coleman Hollow ranges in elevation from 620 to 900 ft. (189 to 274 m), with slopes averaging 2 percent in the hollow bottom and 40 to 60 percent on the steep sidewalls of the drainage. Jenkins Hollow is similar to Coleman Hollow except that its elevation range is narrower.

The majority of water movement out of all three watersheds is subsurface. This occurs as saturated flow within cherty rubble which fills the broad watershed bottoms, and within the surface Fort Payne Formation. Flow within the chert rubble emerges as surface perennial flow at the indicated springs. The origin of surface flow evidently migrates upstream during some large storm events as indicated by a scoured dry channel. This phenomenon was not observed during the monitoring. Droughts undoubtedly cause surface flow to start even farther downstream than the monitored springs.

### Soils

The soils in all three watersheds are part of the Boone-Baxter-Ennis Association. The broad bottoms of the watersheds are predominantly Minvale cherty loam (typic paleudult, fine loamy, siliceous, thermic family). Side slopes are Bodine cherty

loams (typic paleudult, loamy skeletal, siliceous, thermic family) with some pockets of Fullerton silt loam (typic paleudult, clayey, kaolinitic, thermic family). Ridge tops are dominated by Bodine cherty loam and Mountainview silt loam (typic paleudult, fine loamy, siliceous, thermic family). Depth to bedrock ranges from 2 to 4 ft. (.6 to 1.3 m). These soils are very droughty and low in natural fertility.

### Herbicide Treatment

Two sections of the Lost Creek watershed (hatched area on Figure 1) were treated with 15 lb/ac (16.8 kg/ha) of hexazinone pellets (10 percent a.i.) by helicopter in April 1980. Control of vegetation in April 1981 appeared to be greater than 90 percent. Little soil disturbance outside road areas was noted. The total hexazinone-treated area amounted to 35.1 percent of the monitored portion of Lost Creek watershed.

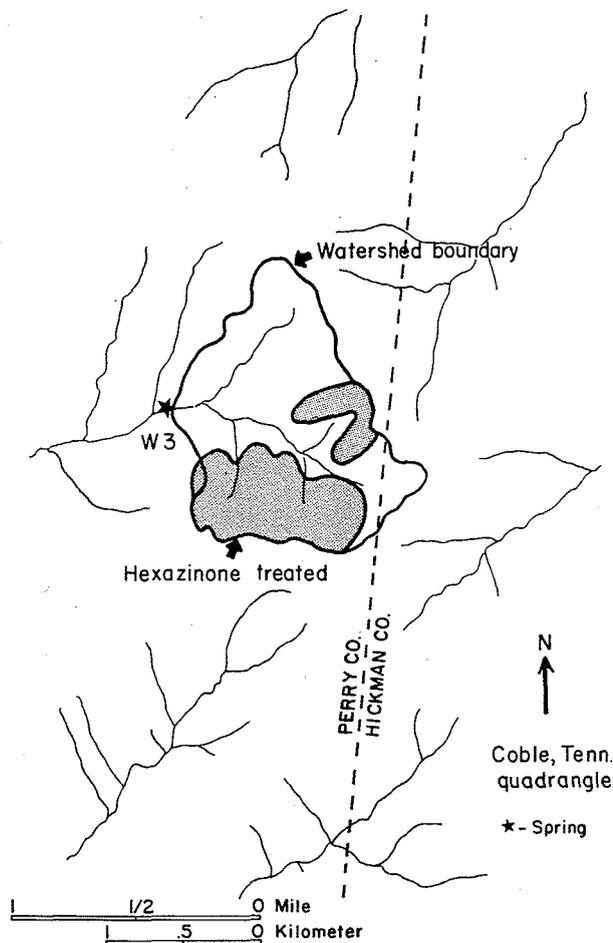


Figure 1. The 1980 hexazinone treatment areas, upper Lost Creek watershed (W 3), Perry and Hickman counties, Tennessee.

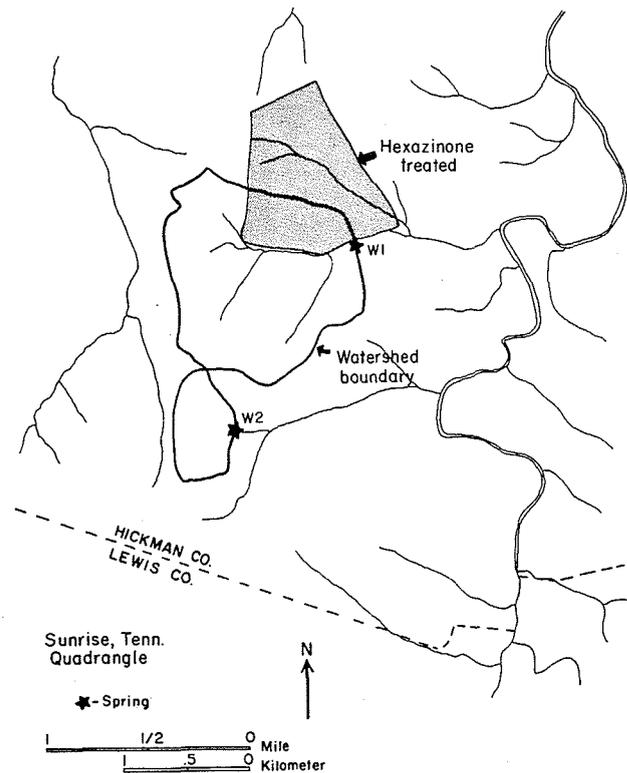


Figure 2. The 1981 hexazinone treatment area, Coleman Hollow (W 1) watershed and control area Jenkins Hollow (W 2) watershed, Hickman County, Tennessee.

The hexazinone application area in Coleman Hollow comprised about 86.9 ac (35.2 ha) or 18.1 percent of the monitored section of the watershed (Figure 2). The herbicide was applied in April 1981 at the same rate as at Lost Creek and also by helicopter. Even though this application was about half the relative size of the Lost Creek one, it had a greater potential to impact water quality. The Lost Creek application (Figure 1) did not approach the broad bottom of the watershed so that the closest hexazinone-treated area was 1,000 ft. (305 m) from the spring monitoring site. The Coleman Hollow application boundary (Figure 2) runs along the edge of the main ephemeral drainage channel for a distance of nearly 3,000 ft. (915 m). Also, the spring sampling site for Coleman Hollow lies only 66 ft. (20 m) from this boundary. Thus, the potential of hexazinone residues appearing in spring flow was much greater in the Coleman Hollow watershed because of the limited buffer strip. Potential residue concentrations in streams are a function of distance to residue sources as well as dilutions from untreated watershed subunits.

### Sampling Locations

**W1-1981 treatment:** The Coleman Hollow watershed perennial flow originates at a spring be-

neath a broad chert ledge. The sample collection point (W1) was selected about 45 ft. (14 m) downstream from the spring because of heavy slash deposits. This point in the stream was marked with a metal stake and flagged. Water samples were taken at this point in midstream using techniques described below.

A 10-ft. (3-m) long flow measurement section was also staked out. Standard measurements (stream width, depth at midpoint, and surface velocity) were taken to determine flow each time a sample was collected. Width and midstream depth were measured at a metal stake marking the flow section. Surface velocity was determined by timing the movement of a float along a 10-ft. measurement section. Flow on the initial sampling date (23 April 1981) was estimated to be 3.5 cfs (100 l/sec). The channel at this point is broadly triangular in shape with a steep gradient.

**W2- 1981 control:** In Jenkins Hollow, immediately south of Coleman Hollow, a water sample collection point (W2) was established in a spring similar to W1 but with a much smaller source watershed (83.6 ac - 34.1 ha), and hence less flow. The collection point, a pond area immediately below the spring face, was marked in a similar manner to W1, but a shorter 5-ft. (1.5 m) flow measurement section was used. The gradient at this location is low and the channel more rectangular in cross section.

**W3- 1980 treatment:** A third monitoring station was set up in the Lost Creek watershed to determine if any remaining hexazinone residues were detectable in springflow. The spring selected for monitoring (W3) was neither the largest nor the main source of flow for Lost Creek. However, the monitored spring originates from subsurface flow immediately below the main 1980 hexazinone-treated area. The water sampling point for Lost Creek was also marked with a metal stake at this small spring about 328 ft. (100 m) upstream of the main spring. Flow at this point consists of many

low volume seeps along a defined stream channel. The channel contains large amounts of coarse chert rubble and is mainly dry on the surface. The configuration of the channel is rectangular and the gradient is low. A 10-ft. (3 m) streamflow measuring station was marked out below the spring pool.

### Sampling Procedures

The sampling procedures used in this study generally follow water quality monitoring guidelines developed for operational use by the USDA Forest Service (Ponce 1980). The purpose of these guidelines is to ensure technically sound and systematic water quality monitoring. This approach is intended to provide useful information to forest managers to that adequate decisions related to water quality can be made.

Sampling at the Coleman Hollow and Jenkins Hollow springs started on 23 April 1981 on a weekly basis until the herbicide application. Beginning on the application date, samples were taken daily for seven days and then weekly until the first storm with precipitation greater than 2 in. (50 mm) in 24 hours (6 June 1981). Sampling returned to a daily frequency for seven days after this storm, and then reverted to a weekly basis until 18 September 1981. At this point sampling was changed to biweekly. Water sample collection at Lost Creek followed a biweekly schedule for the entire period.

At each sample collection date, duplicate 33.8 fl. oz. (1,000 ml) samples were collected in polypropylene plastic bottles. Samples were taken by grab sampling from the midchannel section at each point. Each bottle was rinsed once from the sampled stream before filling. During each collection, midchannel depth, stream width, and surface velocity data were recorded. Labeling information placed on each bottle included: (1) sample point; (2) duplicate; (3) time (4) date; and (5) sample

**Table 1. Hexazinone, metabolite A, and metabolite B recoveries from spiked water samples.<sup>1</sup>**

Spike level	No. of spikes	Detected			Recovery		
		Hexazinone	Metabolite A	Metabolite B	Hexazinone	Metabolite A	Metabolite B
ppb		ppb			Percent		
0	1	10 <sup>2</sup>	10	10	—	—	—
40	3	35 ± 3	37 ± 5	37 ± 4	89 ± 8	93 ± 13	94 ± 9
80	1	73	73	84	91	91	105
100	1	100	98	96	100	98	96
200	2	182 ± 4	192 ± 11	172 ± 4	92 ± 2	96 ± 5	88 ± 1
500	1	480	470	470	96	94	94
1,000	2	950 ± 14	935 ± 50	960 ± 57	95 ± 1	94 ± 5	96 ± 6

<sup>1</sup> Craven Laboratories, Inc., Austin, Texas.

<sup>2</sup> Detection limit 10 ppb.

description. The bottles were then transported in an insulated container to Centerville and frozen. Samples were periodically air-freighted to Craven Laboratories, Inc., Austin, Texas, and E. I. DuPont de Nemours and Co., Inc., Wilmington, Delaware, using dry-ice packed, insulated containers.

Residues of hexazinone, metabolite A, and metabolite B were determined by nitrogen-selective gas chromatography after extraction with chloroform and anhydride (Holt 1981). Percent recovery of spiked samples (40 to 1,000 ppb) averaged 93, 102, and 93 percent for hexazinone, metabolite A, and metabolite B, respectively (Table 1). The analytical detection limit for hexazinone and its two metabolites was 10 ppb.

## RESULTS AND DISCUSSION

### Spring Discharge

Flow from the Coleman Hollow spring (2.1 to 6.2 cfs— 60 to 175 *l*/sec) was generally 10 times greater than that of the Jenkins Hollow spring (< 0.1 to 1.2 cfs — < 1 to 35 *l*/sec) during the period

23 April to 16 December 1981 (Figure 3). The Lost Creek spring consistently had the lowest flow of the three—generally one-third of Jenkins Hollow. The peak flows during the 240-day monitoring period occurred one to two days after a particularly rainy period the first week in June. This period included the first storm producing rainfall greater than 2 in. (50 mm) in any given 24-hour period. A larger storm [2.24 in. (56 mm) on 16 August] did not produce much of a response in springflow in either the W1 or W2 springs.

### Hexazinone Residues

The herbicide residue data from only the independent Texas laboratory are presented. Only selected samples were analyzed by the manufacturer for quality control. Analysis of samples collected at all three sites through 16 December 1981 indicates that detectable residues of hexazinone, metabolite A, or metabolite B were generally not present (Figure 4). This period includes samples collected during a seven-day period after the first large storm [rain greater than 2 in (50 mm) in 24

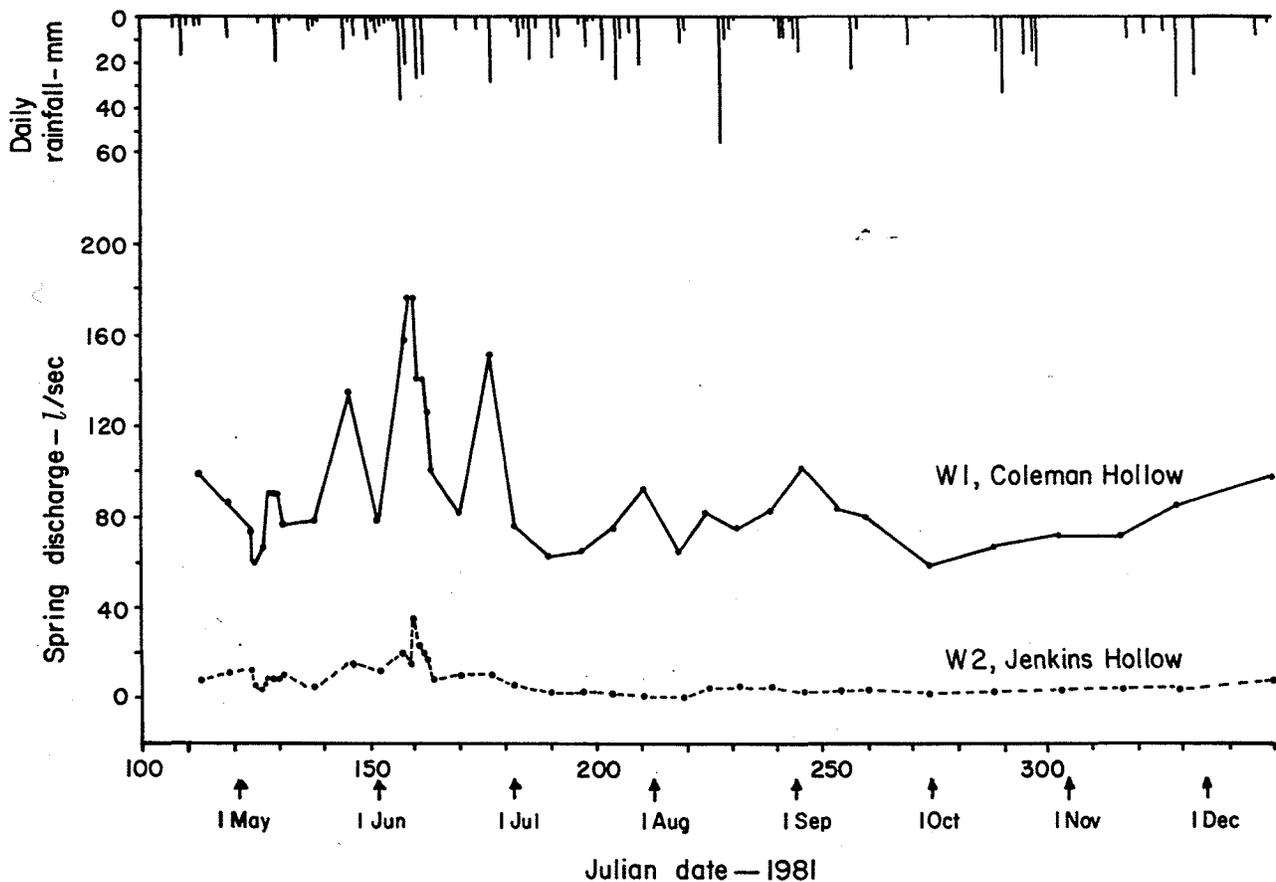


Figure 3. Springflow and precipitation at the 1981 hexazinone-treated (W 1) and control (W 2) monitoring springs, Coleman Hollow and Jenkins Hollow watersheds, Hickman County, Tennessee.

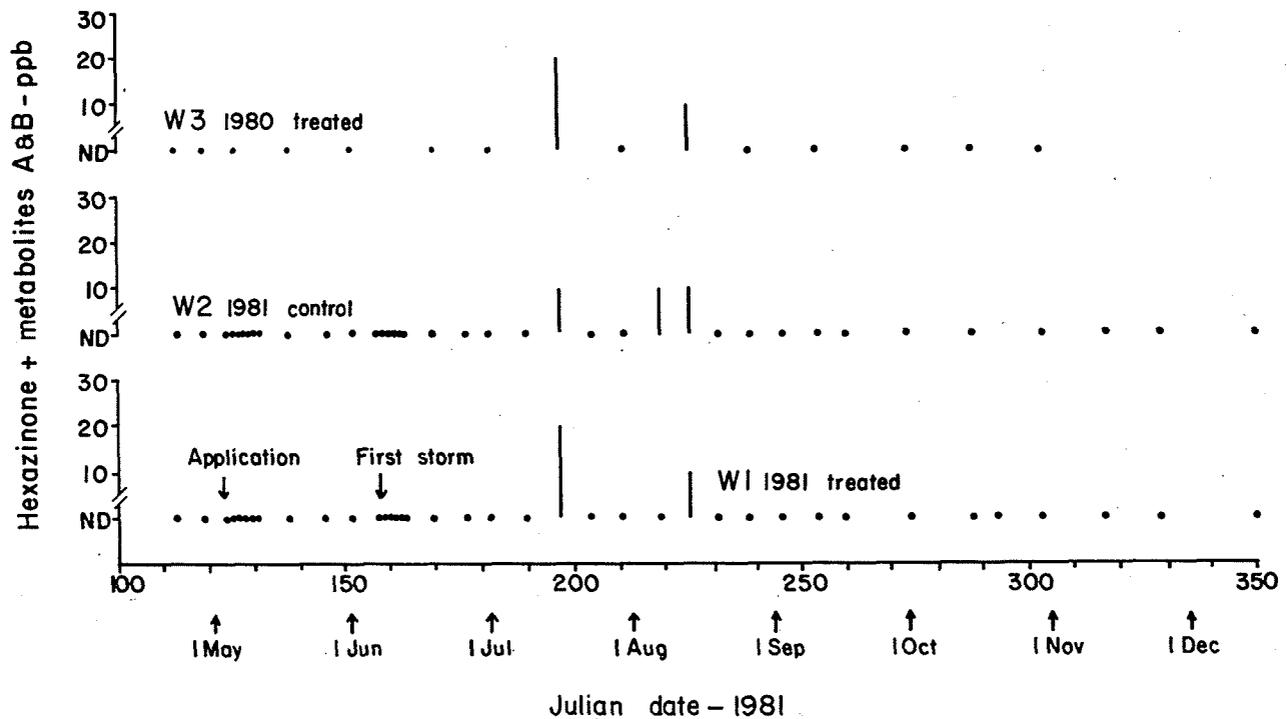


Figure 4. Hexazinone plus metabolite A and metabolite B residues in the W 1 (1981 hexazinone-treated), W 2 (untreated control), and W 3 (1980 hexazinone-treated) monitoring springs, 1981. (ND is less than 10 ppb, dots indicate negative samples, and bars indicate positive samples 10 ppb or above.)

hours]. While this was not the largest storm, it occurred during the wettest part of the eight-month monitoring period and resulted in the highest measured springflow volumes.

Seven of the 99 samples collected in the study were positive for hexazinone or metabolite residues, and these contained  $\leq 20$  ppb (0.02 ppm) of metabolite B. Because all samples taken on each of two days were positive, and three of these came from the untreated watershed, these samples appear to have been accidentally contaminated. Samples collected on 16 July 1981 from all three watersheds contained similar, low concentrations of 10 to 20 ppb (0.01 to 0.02 ppm). These samples were probably contaminated in the collection, handling, extraction, or analytical phases. It is unlikely that the sample from the Lost Creek Spring contained a "real" amount of residue because of the long time period since application and the lack of any other positive concentrations earlier in the sampling schedule. Intermediate samples on July 23 and 30, 1981, were free of detectable amounts of hexazinone and metabolite residues. On August 7, the control watershed (Jenkins Hollow) sample had 10 ppb (0.01 ppm) metabolite B again, but the corresponding 1981 treatment (Coleman Hollow) sample did not have detectable amounts. The following sample on August 13 showed the same

residue levels in all three samples. Again, this indicates a strong probability of low-level contamination of the samples rather than a flux of hexazinone residues in springflow. Subsequent samples from all three watersheds through December did not contain detectable residues. This "false" appearance of low levels of hexazinone residues indicates the utility and necessity of obtaining check samples from untreated (control) watersheds. The two salient features of the residue data are the lack of any significant hexazinone or metabolite residues in the area treated in 1980 and the lack of obvious residue pulses in flow from the 1981 treatment area during stormflow and baseflow conditions. Present knowledge of the behavior of hexazinone in ecosystems confirms what was observed in both treated areas—that residues of hexazinone or its metabolites should not be present in significant quantities in storm runoff or baseflow after seven months.

Using storm runoff data from a hexazinone movement study in Georgia (Neary et al. 1983) as a comparative basis for estimating residue movement in the Coleman Hollow watershed, the mean flow-weighted maximum concentration expected in surface storm runoff would be 80 ppb during the first storm. This amount is based on the peak concentration ( $442 \pm 53$  ppb) from the Georgia

study and the minimum area-dilution factor for the Coleman Hollow watershed (5.5). Observations from the early June storm on the 1981 treated site indicates that surface movement of hexazinone residues did not occur due to the absence of surface runoff during the storm. This contrasts sharply with results from the study in north Georgia where impermeable, metamorphic geologic strata are at shallow depths and surface movement during stormflow was the major pathway for off-site movement of hexazinone residues (Nearly et al. 1983).

The data indicate that a delayed subsurface movement of detectable amounts of hexazinone did not occur through the cherty loam soils of Coleman Hollow within the first seven months after application. Several samples from both treated and the control watersheds did contain positive, low levels of metabolite B. However, accidental contamination of these samples cannot be ruled out. Subsequent samples from this watershed did not contain detectable hexazinone or metabolite residues. If a discrete subsurface flux of hexazinone residues had occurred, then a water quality problem would not exist in this situation since the potential dilutions in either the 1980 or 1981 hexazinone-treated watersheds are large (Neary et al. 1983). Since hexazinone residues would have to migrate through deep, loamy soils and weathered parent material, the opportunities for adsorption of residues and storage of some residue-laden water would be large. Referencing observed concentrations of hexazinone residues in subsurface flow in Georgia (Neary et al. 1983), the maximum expected concentration in the Coleman Hollow watershed spring would be 4 ppb. This particular value is below the analytical detection limit used by the laboratory involved in this study. Thus, it is unlikely that residues of hexazinone or its metabolites could be detected in samples from the Coleman Hollow spring.

Hexazinone is normally applied only once or twice in a 30- to 40-year rotation of a forest and is relatively short lived. It is readily adsorbed in loam-textured soils and is low in toxicity to a broad range of animal species. Contamination of ground water aquifers would not be expected to be a problem under normal registered uses of hexazinone. Applicators should always ensure that water-soluble herbicides cannot enter water directly. In situations where hexazinone or other soluble herbicides are applied near sensitive water areas, operational monitoring of the types discussed by Ponce (1980) should be used. As indicated in this study, normal use of hexazinone adjacent to stream channels does not necessarily result in residues entering stream systems. This information can effectively assist forest managers in evaluating the environmental safety of their herbicide use in silvicultural operations.

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