Specific Persistence and Fate of a Soil Active Herbicide-Hexazinone and Implications for Management

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Introduction

Federal pesticide regulation began officially in 1947 with the promulgation of P.L. 80-104, also known as the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). This early version was administered by the U.S. Department of Agriculture. Responsibility for administration of FIFRA was transferred to the U.S. Environmental Protection Agency (EPA) when it was created in 1970. Subsequently FIFRA was completely revised in 1972 to form the basis for our current Federal pesticide regulation policy. FIFRA, 1972 (7 USC 136 et seq.) required the registration of all pesticides marketed in the U.S. FIFRA was again amended in 1988 to require re-registration of all active ingredients with outstanding data gaps registered before 1984. The Food Quality Protection Act of 1996 (P.L. 104- 170) further amended FIFRA by facilitating the registration of minor use pesticides and required FIFRA coordination with activities of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 321 et seq.). It is under this backdrop of regulation that all pesticides are registered and regulated in the United States.

Hexazinone, the active ingredient in Velpar herbicides, was first registered in 1975 for general weed control in non-cropland areas. Since the initial registration, EPA has allowed registration for additional uses that now include forestry, drainage systems, Christmas tree plantations, industrial areas, rights-of-way, fencerows, hedgerows, recreational areas, alfalfa, grass forage/fodder/hay, pastures, rangelands, pineapple, sugarcane, and blueberries.

In 1982 the EPA issued a Registration Standard for hexazinone that identified some data gaps for the active ingredient, which was then registered for non-cropland uses and for culture of sugarcane and alfalfa. In 1988, a second Registration Standard was issued requiring additional information on chemistry, toxicology, ecological effects, and environmental fate data. Much of the environmental fate data are required under the current version of FIFRA in the context of the forest dissipation study, which was conducted in 1990-1992 and reported by Michael et al. (1999). This paper presents a summary of the Michael et al. (1999) paper, some of the unpublished original study data, and implications for management. For specific details, the reader is referred to the original paper or the author.

Methods

Three contiguous watersheds ranging from 72 to 122 ha each and with the same aspect and topographical relief were selected in Coosa County for study. The watersheds were clear-cut in 1988-89 prior to the site preparation treatment in April 1990. Two of the watersheds were randomly selected to receive 6.72 kg ai ha^{-1} (6 lbs ai ac^{-1}) aerially applied as either Velpar L or Velpar ULW. This treatment rate was three times (3X) the prescription rate for the site

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under study. Application rates were validated using measurements at the ground surface. The third watershed was maintained as an untreated control. The watersheds were intensively monitored during the application and for the following year.

Visual observations indicate the treatments were very effective, but the Velpar ULW treatment resulted in more vegetation kill than the Velpar L treatment. Even difficult to control species and species which are usually not controlled by this treatment were affected.

During the course of the study, water samples were collected at H-flume gaging stations on each site and soil, litter and vegetation were also sampled periodically from randomly located ridge, mid-slope, and toe-slope positions. All samples were frozen at the time of collection. Water samples were frozen in high density polyethylene bottles. All other samples were frozen in their respective collection containers.

Freezer storage stability studies were conducted for each analyte in water, soil, and vegetation. Samples of water, soil, and vegetation collected from each site prior to treatment with herbicide were fortified with known amounts of hexazinone and its metabolites and stored frozen. These samples were periodically analyzed over the following 9 months. No significant concentration changes were observed in fortified samples over the period of freezer storage.

In addition to monitoring for the fate of hexazinone and its metabolites in water, soil, and vegetation, the impact of hexazinone treatment on benthic macroinvertebrates and fish was also assessed. Macroinvertebrates were qualitatively monitored in riffle and run habitats using D-frame nets (mesh size about 1 mm). Quantitative monitoring was accomplished by using two biologists (for replication) and the kick-net sampling method from available habitat in a 10 to 20 m reach of stream. Fish communities were sampled on a 100-m section of stream with a backpack electro-shocker. Captured fish were identified, weighed, measured and examined for physical abnormalities in the field. Most fish were released alive after sampling. Fish were further classified based on their tolerance to pollution and trophic level.

Results

Streamflow. Hexazinone was detected in stream samples from both treated watersheds. The highest concentration detected in streams was observed on the day of application at the flume on each treated watershed (Figure 1) and was the result of direct application to the streams. The highest post-application concentrations were of short duration, lasting for a few minutes to less than a few hours. In general the highest pulsed concentration and baseflow contributions were found on the Velpar ULW treated site. The maximum concentration observed on the Velpar L site (473 $\mu g\ L^{-1}$, ppb) was similar to the maximum on the Velpar ULW (422 ppb) treated watershed (Figure 1).

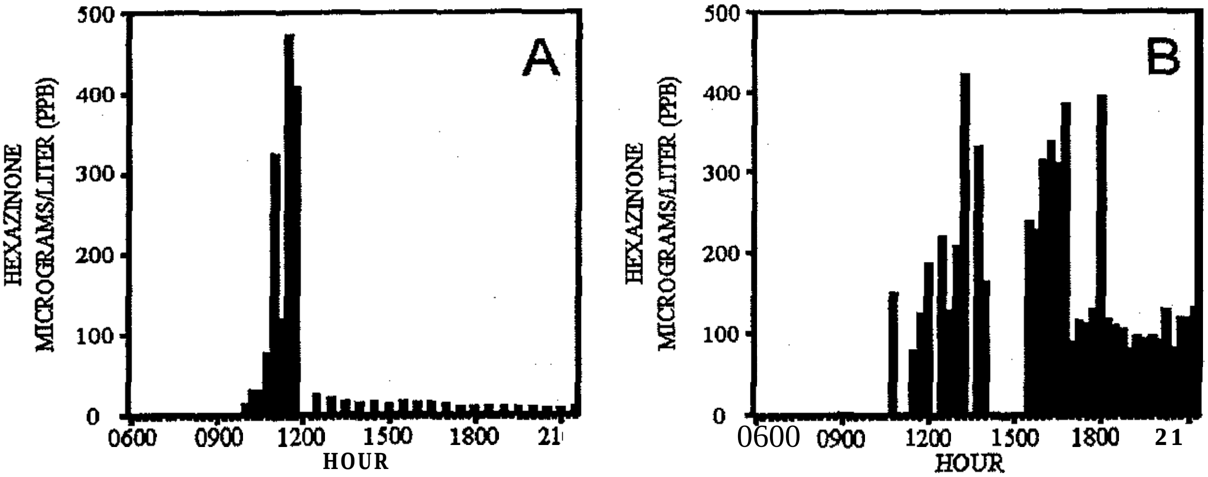

Figure 1. **Hexazinone** concentrations observed in streamflow from watersheds treated with three times the prescription rate of Velpar L (A) and Velpar ULW (B) on the day of application were the result of direct application into the streams.

Peak stormflow concentrations were measured for several precipitation events on each watershed. The maximum observed stormflow concentrations were less than those observed on the day of application, but were highest for the Velpar L treated site (Figure 2). The highest stormflow concentrations of hexazinone lasted 15-30 minutes and rapidly decreased to near detection limits, usually within 24 hours after peak discharge. Subsequent observations of same-time baseflow concentrations in the two streams, however, were 2 to 3 times higher in the ULW stream than in the Velpar L stream. Peak hexazinone concentrations decreased with each successive storm until little hexazinone was detected (approximately 2-3 months after application, Figure 3).

As hexazinone moved downstream from the treated sites, it was diluted by stormflow into the stream from non-treated areas. Hexazinone concentrations were measured in streamflow 1.6 km downstream and found to be 3-5 times lower than at the perimeter of the treated areas (Figure 3). When the area of the treated watersheds is compared to the larger watershed drained at the monitoring station downstream, one finds that the theoretical dilution factor is 4.3, which compares nicely to the observed 4.6 dilution factor. In other words, at least 93% of the change in concentration of hexazinone at 1.6 km downstream is explainable directly by dilution. The remainder is probably due to degradation and short-term sorption.

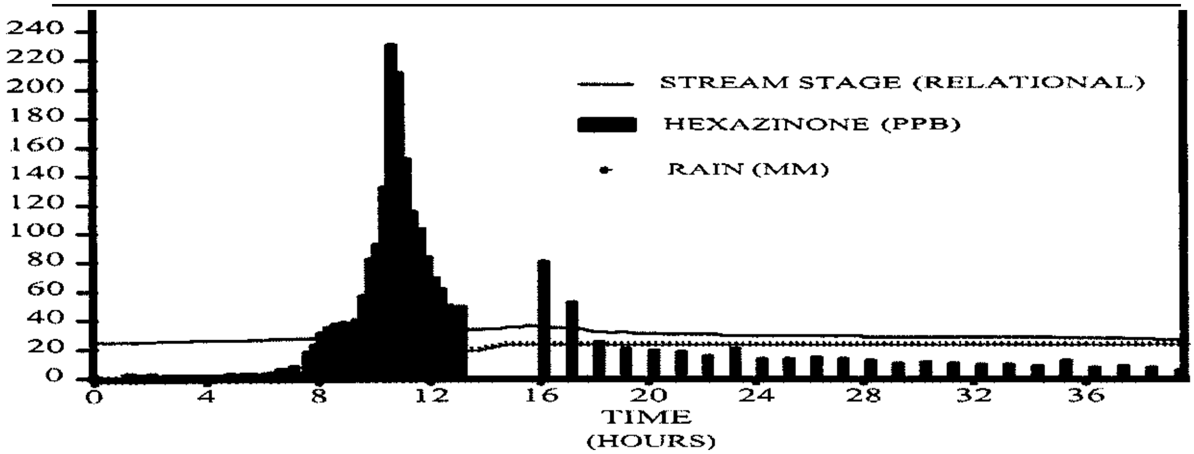

Figure 2. Hexazinone concentration observed at 15-minute intervals in stormflow for the first storm on the watershed treated with three times the prescription rate of Velpar L.

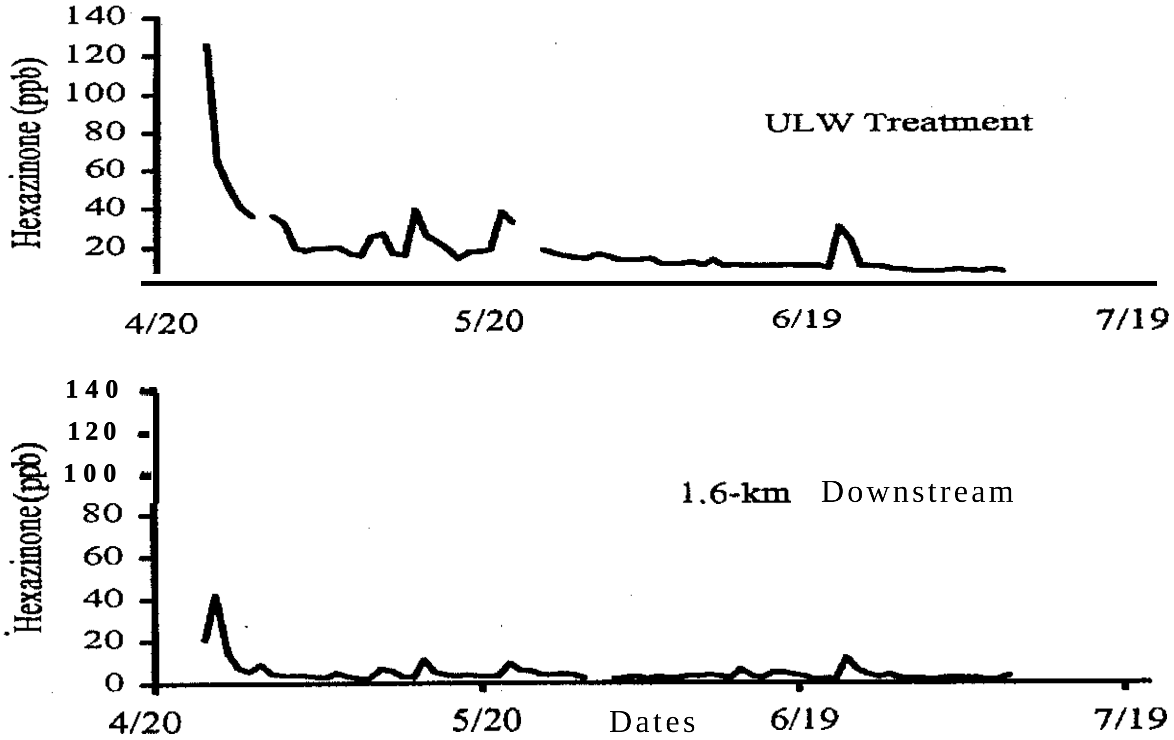

Figure 3. Mean daily hexazinone concentration in streamflow from watersheds treated with a 3X rate of Velpar was 3-5 times higher than observed 1.6 km downstream from the study site.

Soil. Hexazinone was detected in soil from bare ground and from under litter on both treated watersheds. Hexazinone residues decreased rapidly following application and approached background levels within 365 DAT for both watersheds. Metabolite B was frequently detected in soil samples from both treated watersheds and generally followed a dissipation pattern similar to hexazinone. Coeluting (with hexazinone) substances that interfered with the analysis for hexazinone were observed in soil from the control watershed and in soil collected from the test watersheds prior to treatment at concentrations up to 370 µg kg^{-1} (ppb). The average interference was estimated at 25 ± 9 ppb and appeared to approximate a normal distribution with the data point at 370 ppb possibly an outlier, i.e., 95% of all samples with values reported for hexazinone up to 43 ppb (mean + two standard deviations) should be considered interference and values up to 370 ppb may be interference. Hexazinone residues were infrequently observed at depths greater than 45 cm, and then usually below the concentration of coeluting interference, leading to the conclusion that hexazinone rarely moved below 45 cm in this study (Table 1). Hexazinone, a soil active herbicide, is often referred to as highly mobile in the soil, but in this study most remained *in* the upper 15 cm of soil throughout the study.

Table 1. Hexazinone concentration (µg kg^{-1}) in treated soil at various depths and times after treatment (DAT). The apparent hexazinone concentrations have not been corrected for coeluting compounds (background noise).

Days After Treatment	Bare Soil Treated With Velpar L Depth In Centimeters					Bare Soil Treated With Velpar ULW Depth In Centimeters				
	0-15	16-30	31-45	45-60	61-75	o-15	16-30	31-45	46-60	61-75
0	1600	10	NST*	NST	NST	1600	0.03	NST	NST	NST
1	1360	10	NST	NST	NST	3630	0.05	NST	NST	NST
3	1210	10	NST	NST	NST	3330	10	NST	NST	NST
7	1950	200	10	10	0	4290	180	10	10	10
14	750	420	10	0	0	3070	80	0	0	0
30	740	60	10	0	10	1500	160	190	110	0
60	250	50	30	30	0	620	60	30	10	0
120	140	40	20	30	90	450	80	10	10	20
269	50	0	0	0	10	160	30	20	10	10
365	80	10	10	0	0	130	10	0	0	0

*NST, No sample taken at this depth and date.

Vegetation and Litter. Hexazinone and Metabolites A, B, C, D, and E were detected in plant tissue from both sites. Treatment effectiveness precluded sampling vegetation on the ULW treated site after 178 DAT, but samples were collected on the Velpar L treated site even after the prescribed bum. Each of the species selected for monitoring in this study had its own set of coeluting compounds (CCs) that interfered with analysis of the parent compound and/or with one or more of its metabolites. Concentrations of the CCs was highly variable in all species with a coefficient of variation of from 80% to >200%.

Hexazinone residues were highest in the Velpar L treated plants. Concentrations in vegetation ranged from 196,000 to 95 1,000 ppb for Velpar L treated and from 60 to 34,000 ppb for ULW treated plants. Residue levels decreased rapidly, especially for the Velpar L treated plants, and were 99% dissipated within approximately 180 DAT except for dogwood on the Velpar ULW watershed which was 88% dissipated.

Metabolites A, B, D, and E followed the same general concentration pattern observed for hexazinone, but peak concentrations were much lower, and delayed 1-3 days past peak concentrations for hexazinone. Concentrations of metabolites were generally higher in Velpar L treated plants than in Velpar ULW treated plants. Mass spectrometry confirmed the presence of metabolites A, B, and D in vegetation at concentrations similar to those observed under HPLC conditions. Detection limits in this system for Metabolite E were too high to permit confirmation.

Relatively large amounts of CCs were detected in litter for hexazinone and its metabolites. Residues of hexazinone were approximately the same order of magnitude in both ULW and Velpar L treated litter, but concentrations remained higher longer in the Velpar L treated litter. The more dispersed liquid application also had the greater potential for absorption onto the organic matter in litter. Peak concentrations of hexazinone in litter were not observed until 1-7 DAT on the Velpar L site, presumably as some of the hexazinone intercepted by vegetation at application was washed off the foliage and into the litter layer.

Metabolites B and D were the most frequently observed in litter and both occurred in the highest concentrations in the Velpar L treated site. Metabolites A, C, and E were observed infrequently and at lower concentrations.

Half-life. Half-lives for vegetation, litter, and soil are presented in Table 2. Residues of hexazinone were dissipated to near background levels by 200 DAT for most components sampled. Except for the Velpar soil under litter, half-lives ranged from 18-77 days. Half-life for hexazinone in the soil under litter on the Velpar L site was 275 days. The litter on both sites acted as a reservoir supplying hexazinone to the soil through 365 DAT.

Table 2. Hexazinone half-life (in days) in vegetation, litter, and soil from a Piedmont site in Alabama treated with 3-times the prescription rate. Half-life for soil found in the published literature ranges from 24 to 365 days.

Matrix	Velpar L	Velpar ULW
Blueberry foliage	31.7	26.3
Dogwood foliage	18.9	58.5
Fern fronds	36.4	30.5
Grass foliage	31.2	30.2
Litter	55.6	55.2
Exposed soil	76.5	67.6
Soil under litter	275.1	74.3

Benthic Macroinvertebrates and Fish. A total of 162 macroinvertebrate taxa was collected from the tributaries during the study. The Chironomidae were the most diverse family of invertebrates and comprised 27% of the total number of taxa. Evaluations of the health of the macroinvertebrate community included taxa richness and the EPT index. The EPT index is the number of insect taxa in the orders Ephemeroptera (mayflies), Plecoptera (stoneflies) and Trichoptera (caddisflies). This index measures the diversity of insect groups consisting mostly of pollution-sensitive species (Barbour et al. 1992). The Hilsenhoff Biotic Index (HBI, Hilsenhoff 1987, Plafkin et al. 1989) and the Shannon-Weaver Diversity Index were also calculated. The diversity indices and taxa richness were analyzed statistically based on Duncan's Multiple Range test. There were no significant differences among the control and Velpar treated watershed streams with respect to benthic macroinvertebrate taxa richness, EPT richness, or Shannon-Weaver diversity. That is, no changes in richness or important shifts in community structure relative to the control condition were observed in this study even though the aquatic community was exposed to concentrations of hexazinone over a period of two to three months. HBI values were low throughout the study indicating stream quality was very good to excellent throughout the study.

Fish diversity was low as is typical of ephemeral to first-order streams in the South. A total of 5 species were collected in the streams, but numbers were low in all three streams. No changes in fish communities could be identified in the test streams when compared with the control streams.

Research Conclusions

Hexazinone, which was applied to individual watersheds at 6.72 kg ha^{-1}, three times the prescription rate, was observed in streams on the day of application and during precipitation producing storms. The hexazinone in the streams on the day of application was the result of direct application to running water and it was on the day of application that the highest concentrations of hexazinone were observed in the streams draining each watershed. Hexazinone observed in the streams during precipitation events was largely due to the phenomenon of overland flow as indicated by the occurrence of concentration peaks that coincided with peak stream discharge. At least some of the hexazinone observed in stormflow was due to the direct application of Velpar to ephemeral and intermittent drainage channels that were not protected by streamside management zones (SMZs) on the day of application. While SMZs as prescribed by most forestry best management practices were utilized in this study, additional protection of obvious drainage channels, even though they do not contain water at the time of application is warranted.

The application of three times the prescription rate of hexazinone in this study was for experimental purposes and is not recommended for general use. Application of the prescribed rate would obviously have resulted in much lower concentrations on the day of application and in stormflow than observed in this study. However, it should also be recognized that there is a considerable margin of safety for the aquatic ecosystem since no adverse impacts were observed for benthic macroinvertebrates or fish in this study.

Maximum observed concentration on day of application exceeded the adult lifetime Health Advisory Level (maximum allowable drinking water concentration that can be safely consumed daily over an adult lifetime, HAL) by only 73 ppb on the Velpar L watershed and 22 ppb on the Velpar ULW treated watershed and then for a period of less than 30 minutes. The IO-day Hal for a child (2000 ppb) was never exceeded.

Management Implications

Hexazinone is widely used in the United States and around the world. Approximately 8% of the hexazinone used in the US annually is applied to woodlands, 8-14% is applied to rangeland and 70-79% is used on alfalfa. The remainder is used on other permitted treatments including growth of blueberries, pineapple, sugarcane, etc. (U.S. EPA, 1994). When hexazinone is used in agriculture residues may be observed in some food commodities. EPA has determined these residue concentrations identified in food commodities are allowable under the Delaney Act (U.S. EPA, 1994) and has established maximum allowable food concentrations (U.S. EPA, 1994; CFR 40 Part 180.399) in many products (alfalfa hay, 8000 ppb; blueberries, 200 ppb; cattle meat, 100 ppb; goat meat, 100 ppb; hog meat, 100 ppb; milk, 100 ppb; pineapple, 500 ppb; sugarcane, 200 ppb; sugarcane molasses, 5000 ppb). Similarly, EPA established the adult lifetime HAL of200 ppb (U.S. EPA, 1988). Following consideration of new toxicity data required under the Registration Standard issued in 1988, EPA increased the adult lifetime HAL to 400 ppb in 1996 (U.S. EPA, 1996). Clearly hexazinone is not very toxic to mammals, particularly humans and the same is true for most forestry herbicides (Table 3).

Table 3. No Observable Effect Level (NOEL) data for mammals and No Observable Effect Concentrations (NOEC) for aquatic organisms for the active ingredient of several common forestry herbicides.

Herbicide	Mammalian NOEL ($\mu g\ kg^{-1}$)	Aquatic NOEC ($\mu g\ L^{-1}$)
Fosamine (Krenite)	200000	15000
Glyphosate (Roundup, Rodeo)	10000-500000	25000-50000
Hexazinone (Velpar)	10000-250000	10000->80000
Imazapyr (Arsenal)	300000-10000000	240->100000
Triclopyr (Garlon)	2500-240000	NA*

*NA, Not available
Data in this table come from the National Pesticide Retrieval System (NPIRS), EPA's Integrated Risk Information System (IRIS), EPA's Reregistration Eligibility Decision (RED), and HAL documents.

Toxicity tests are normally conducted at static concentrations for long periods of time (i.e., 48 or 96 hours to more than a year in feeding studies) and on several different species of mammals and aquatic organisms. The values given in Table 3 are derived from such tests and where ranges are given emphasize that many species were tested. In the case of the hexazinone NOEC data, for example, the reported NOEC for fathead minnow is 17,000 $\mu g\ L^{-1}$, while the value for the daphnid, *Daphnia* magna, the value is 29,000 $\mu g\ L^{-1}$. Similarly hexazinone is practically non-toxic to rainbow trout and many other species. The NOEC values in Table 3 are 25 to 400 times greater than the streamflow concentrations observed in this study where hexazinone was applied at three times its prescribed rate.

Offsite movement of herbicides, especially hexazinone, has often been cited as an area of concern that causes many managers to refrain from herbicide use. However it has been demonstrated in this study and many others like it for a variety of herbicides, that offsite movement is principally a function of the method and formulation of application and the care with which the herbicide is applied. When application contaminates drainage channels, even those with no water in them at the time of application, offsite movement will occur when the first precipitation events till those same channels containing highly water soluble herbicides. The good news, however, is that with proper care this condition can be avoided and *even* when it occurs the contamination is well below toxicity levels for humans, other mammals and to most aquatic organisms. At least one study has indicated that offsite movement of hexazinone, imazapyr and triclopyr are very similar under the same set of conditions (Michael et al. 1996).

Most of the forestry herbicides have some soil activity and all exhibit foliar activity. There are three caveats to this statement. Fosamine and glyphosate do not appear to be soil active. They are very tightly sorbed onto soil particles and generally are not available for root uptake. Hexazinone does exhibit foliar activity, but because it is translocated acropetally only (is not translocated downward through the stem to the roots) foliar activity is generally limited to foliage actually sprayed and to a limited extent unsprayed foliage above sprayed leaves.

Herbicides are useful tools capable of controlling a wide variety of weeds in a manner more efficient that almost any other tool foresters have at their disposal They dissipate quickly from forest sites through degradation, although small amounts, usually less than 1-2% do move offsite in stormflow. While short-term contamination of surface waters has been shown to occur, the amounts that enter streams and other bodies of surface water do not exceed EPA established safe drinking water levels and they are practically nontoxic to aquatic organisms and have not been shown to adversely impact aquatic ecosystems when used according to label directions. In fact they can be used to protect water quality from the choking effects of sediment created by more intensive mechanical methods (Michael et al. 2000). They have not been shown to cause cancer and are generally classified by EPA as slightly toxic to practically nontoxic.

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