FATE OF HEXAZINONE AND PICLORAM AFTER HERBICIDE SITE PREPARATION IN A CUTOVER NORTHERN HARDWOOD FOREST

D.G. Neary, J.L. Michael, and M.J.M. Wells[1]

ABSTRACT. Herbicides show promise to improve the efficiency and economics of forest stand conversion and regeneration. However, the impacts of herbicides on forest ecosystems and the ultimate fate of these chemicals are not completely understood. A major problem in pine regeneration in northern mixed hardwood forests is competition from fast-growing and easily sprouting species like red maple, northern red oak, aspen, and white birch. Three commonly used forest herbicides were applied to a cutover stand in Baraga County, Michigan, to study the ecological consequences of stand conversion and the movement and dissipation of herbicides in sandy-textured spodosols. A mixture of hexazinone (1.7 kg/ha), 2,4-D (1.1 kg/ha), and picloram (0.3 kg/ha) was aerially sprayed in July 1982. Picloram and hexazinone residues were analyzed in soil solution and streamflow samples collected over a 4-month period after herbicide application. Both chemicals are widely used in forestry, are low in toxicity to fauna, and have soil as well as foliar phytotoxic activity. Picloram and hexazinone are highly soluble and thus have the potential to move offsite. Picloram is more persistent in the environment than hexazinone or 2,4-D, the other herbicide used. Picloram moving through the soil profile peaked 2 weeks after application (40 µg/L) and hexazinone peaked (102 µg/L) 2 weeks later. Presence of an Oe horizon was instrumental in reducing herbicide residue movement deep into the soil by factors of 4 to 40. Streamflow contained only traces of hexazinone during the day of the application. Samples over the next 4-month period did not contain detectable residues. Picloram was never detected in streamflow. Water quality of streams adjacent to herbicide application areas was not affected.

---

[1] Authors are, soil scientist, USDA Forest Service, Southeastern Forest Experiment Station and Soil Science Department, University of Florida, Gainesville, FL 32611; and research forester and chemist, USDA Forest Service, Southern Forest Experiment Station, Auburn University, AL 36849, respectively.

INTRODUCTION

National concern for producing additional fiber and energy has stimulated interest in converting poor-quality northern hardwoods stands into productive conifer species. Forest type conversion involves initial site preparation to remove undesirable plant species prior to planting crop trees. Herbicides, in combination with salvage logging or minimal mechanical treatment, appear to be the most efficient silvicultural tool for accomplishing this task (Stewart and Row 1981). Since the ecological consequences of northern hardwood conversion are not fully understood, concurrent research with operational-scale conversions is still necessary.

Herbicides are being used more frequently in modern forest management because they can effectively and economically control herbaceous and woody weeds (Haines 1981). In addition, use of herbicides can minimize the soil displacement and erosion losses which are prime factors in adversely affecting site productivity and water quality (Neary et al., in press (b)). Herbicides used in forest management must also be safe as well as effective and economical. Safety concerns not only the user's and other human exposure, but also the biodegradability of the chemical, movement in the environment, impacts on water quality, toxicity to wildlife, target species selectivity, and effects on crop trees.

Public concerns about herbicide use, safety, and the long-term health risks of exposure to these chemicals have resulted in herbicide use being the most regulated of all forest management practices (Norris 1981). The national framework for herbicide regulation is provided by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), but state and local governments can also regulate herbicides. As part of the herbicide registration procedure (and the ongoing re-registration process), the U.S. Environmental Protection Agency (EPA) reviews data on the environmental fate and transport of herbicides. For many compounds, the current environmental data consist of laboratory studies or limited field evaluations. Very few herbicides have extensive data bases on environmental fate in a variety of forest ecosystems. Consequently, a number of research efforts are currently in progress to evaluate the environmental fate of many current forestry herbicides. Most of these efforts are using operational case studies to provide realistic data.

This paper will briefly review current information and understanding of the environmental fate of three commonly-used forestry herbicides and present some recent data on their fate in northern hardwood spodosols. Our intent is to update forestry professionals in the Lake States and provide sources of more-detailed information.

HERBICIDES

Our focus will be on three herbicides which have been widely used in the past 5 years and constitute the bulk of herbicide use: hexazinone, picloram, and 2,4-D. Several new chemicals and many of the older herbicides are covered in a recent and extensive review (USDA Forest Service 1984).

Hexazinone

This herbicide is a recently developed triazine herbicide that controls many annual and perennial weeds (Table 1). It is a very useful forestry herbicide that can be used at rates that provide effective weed control but at rates which many conifers can tolerate. Hexazinone has been registered as either a release or site preparation herbicide (Hamilton 1979, Gonzalez 1980, Michael 1980, Neary et al. 1981, DuPont 1984). Three granular formulations (5, 10, and 20% active ingredient) and three liquid formulations (0.48%, 0.5%, and 25% active ingredient) are available.

Hexazinone is considered to be practically nontoxic to aquatic invertebrates, fish, and birds since established LC50 and LD50 concentrations are not experienced in the actual use environment (Table 1). This herbicide is mildly toxic to mammals by oral, dermal, and inhalation exposure, but is not a carcinogenic, mutagenic, or a teratogenic agent (Table 1).

Since it dissolves easily in water, hexazinone is susceptible to offsite movement in leaching and storm runoff. In the soil, hexazinone is dissipated by photodegradation and microbial degradation (Rhodes 1980). It does not volatize to any appreciable extent due to its low vapor pressure (Table 1). The half-life of hexazinone is generally 1-2 months, but can be as short as 2 weeks and as long as 6 months. Lateral and vertical movement in the soil is controlled by soil water movement, cation exchange capacity, and the presence of organic matter. Metabolites produced in the soil by microbial degradation of the parent compound are phytotoxic but are short-lived.

Hexazinone residues in streamflow have been studied under operational-use conditions in several southern forest watersheds. Miller and Bace (1980) reported high hexazinone concentrations (up to 2,400 µg/L) from direct fall of pellets into a perennial forest stream. The hexazinone pellets were dropped when a helicopter overflew a streamside buffer zone. Concentrations fell to 110 µg/L within 24 hours, and to less than 20 µg/L after 10 days. In another aerial application in Tennessee, hexazinone pellets were applied to 18% of a 440-ha watershed at a rate of 1.68 kg/ha active ingredient, but no streams were overflown (Neary 1983). Consequently, no hexazinone residues were detected in streamflow during a 7-month period following the application.

Table 1. Name, chemical, physical and biological characteristics of hexazinone.

Characteristic	Value
1. Chemical name:	(3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine 2,4(1H,3H)-dione)
2. Trade name	Velpar L, Pronone 106, Pronone 56, Velpar Weed Killer
3. Formulation:	Liquid (25%), granular (5 and 10%), soluble powder (90%)
4. Vapor pressure:	2×10^{-7} mm of hg at 25°C
5. Solubility:	33,000 mg/L at 25°C (moderately soluble)
6. Photodegradation:	60% in 6 weeks
7. Microbial degradation	45-75% in 90 days
8. Half-life:	1 to 6 months
9. Volatilization:	Negligible
10. Activity:	Inhibits photosynthesis by inactivating photolysis of water in Photosystem II
11. LD50:	1,690 mg/kg of body weight (slightly toxic)
12. LC50:	320,000 to 240,000 µg/L (96 hr for rainbow trout)
13. Carcinogenic:	No
Teratogenic	No
Mutagenic	No
Oncogenic	No

[1] LD50 = dose in mg/kg needed to kill 50% of organisms (usually mammals) by oral, dermal, or inhalation exposure.

[2] LC50 = concentration in water needed to kill 50% of exposed organisms (24, 48, or 96 hr exposure).

[3] Carcinogenic = cancer causing
Teratogenic = causing birth defects
Mutagenic = causing genetic changes
Oncogenic = causing tumors

In a more detailed study in the upper Piedmont of Georgia, four small (1 ha) forested watersheds were treated with hexazinone pellets at a rate of 1.68 kg/ha (Neary et al., 1983). For the next year, 26 storms were sampled to determine hexazinone and metabolite concentrations in surface storm runoff. Resides peaked in the first storm after application (average of 442 µg/L) and declined with subsequent storms. Loss of hexazinone in storm runoff averaged 0.53% of the applied herbicide with two storms accounting for 59% of the chemical lost in runoff. One of these storms had the highest concentration but had a low volume. The other had a low herbicide residue level but very large stormflow. Hexazinone was the predominant compound in the runoff of all 26 storms. Subsurface movement of hexazinone appeared 3 to 4 months after application in stream baseflow (concentrations less than 24 µg/L).

Hexazinone was applied to a 11.5-ha watershed in Arkansas to determine the mobility and persistence of herbicide residues (Bouchard et al., 1985). The application rate was slightly higher than in the Georgia study (2.0 kg/ha) and the herbicide was not applied to intermittent stream channels. Consequently, the maximum hexazinone concentration did not exceed 14 µg/L. However, low-level residues persisted in streamflow for a year after application. The amount of herbicide transported out of the watershed amounted to 2-3% of the applied herbicide.

Picloram

This herbicide is an older picolinic acid chemical which functions similar to the phenoxyacetic acid herbicides (2,4,5-T, 2,4-D, dicamba, etc.) in mimicking plant growth hormones. It is a very effective herbicide on many hard-to-kill woody weeds (Foy 1975, NRCC 1974, Neary et al., 1979). Picloram is registered as a site preparation chemical and is used in forestry most often in combinations with 2,4-D (Table 2). There are two granular formulations (10% and 2% acid equivalent), two liquid formulations (20.8% and 21.1% acid equivalent), and three liquid mixtures with 2,4-D (5.4%, 2.8%, and 10.1% acid equivalent).

Picloram and its salts are relatively nontoxic to most nontarget organisms including soil microorganisms, fish, birds, and mammals (Table 2). This herbicide is not absorbed through the skin, has a very low oral toxicity, and causes only minor eye irritation. Long-term studies have shown that it is not teratogenic, mutagenic, or carcinogenic (USDA Forest Service 1984).

Picloram formulated as either the potassium or amine salts has a high water solubility (Table 2). A major environmental concern with the use of picloram in forestry is possible contamination of surface or groundwater used for irrigation. Crops such as alfalfa, beets, soybeans, tomatoes, and cotton are very sensitive to low concentrations of picloram (Baur et al., 1972; Davis et al., 1968). Misapplication of picloram herbicides to surface waters or overuse in humid regions where leaching is a potential problem could lead to significant adverse nontarget impacts.

Table 2. Name, chemical, physical and biological characteristics of picloram.

Characteristic	Value
1. Chemical name:	(4-amino-3,5,6-trichloropicolinic acid)
2. Trade name	Tordon 101 (25% 2,4-D and 5.7% picloram); Tordon 101R; Tordon 10K; Tordon RTV; Tordon 2K; Tordon 22K
3. Formulation:	Liquid, potassium and amine salts; granular, potassium salt (2 and 10%)
4. Vapor pressure:	6.16×10^{-7} mm of hg at 35°C
5. Solubility:	430,000 µg/L at 25°C (highly soluble)
6. Photodegradation:	In water and on soil surfaces
7. Microbial degradation	Slow; more rapid in warm, humid conditions
8. Half-life:	1 to 6 months
9. Volatilization:	Negligible
10. Activity:	Readily accelerates and distorts meristem activity to produce phloem and xylem blockage
11. LD50:	8,200 mg/kg of body weight (almost not toxic)
12. LC50:	34,000 µg/L (96 hr for rainbow trout)
13. Carcinogenic:	No
Teratogenic	No
Mutagenic	No
Oncogenic	No

[1] LD50 = dose in mg/kg needed to kill 50% of organisms (usually mammals) by oral, dermal, or inhalation exposure.

[2] LC50 = concentration in water needed to kill 50% of exposed organisms (24, 48, or 96 hr exposure).

[3] Carcinogenic = cancer causing
Teratogenic = causing birth defects
Mutagenic = causing genetic changes
Oncogenic = causing tumors

Picloram losses by volatilization are negligible because of its low vapor pressure (Table 2). Photodegradation occurs only when picloram is exposed directly to sunlight in water or on soil surfaces (Merkle et al., 1967). Leaching of picloram through the soil is similar to nitrate and chloride, and is a function of its high solubility and low, reversible adsorption potential. Sorption is controlled primarily by organic carbon, but also increases with decreasing pH and increased iron and aluminum oxide contents. Half-life in the soil can be as short as 4 weeks, but is more commonly longer (up to 6 months in arid or cold regions)(NRCC 1974).

Concentrations of picloram detected in streamflow or surface runoff have been studied in many different ecosystems. Applications of sprays (1.1 kg/ha acid equivalent) to cropland and rangeland in the South have produced peak concentrations of 90 to 2,170 µg/L (Baur et al., 1972). In the Pacific Northwest, aerial applications of 2.2 kg/ha picloram to a mixture of forests, right-of-ways, and pastures resulted in short-term maximum streamflow concentrations of 20-78 µg/L picloram (Norris 1969). Hand applications of picloram pellets to riparian vegetation in Arizona on 4.5% of a forested watershed produced stormflow picloram concentrations of 52-370 µg/L for a period of 2 months (Davis et al., 1968). Direct application of picloram to streams in Arizona and Texas produced concentrations as high as 13,720 µg/L which were diluted down to less than 5 µg/L over 6 km of stream distance. Drainage from a forest in Ontario sprayed with 0.9 kg/ha acid equivalent picloram contained herbicide residue levels of 38 µg/L 1 day after application and still carried trace amounts 1 year later (Suffling et al., 1974).

In a recent study, Neary et al. (in press (a)) applied picloram pellets to portions of a steep forested watershed in North Carolina. The herbicide was applied manually at a rate of 5.0 kg/ha acid equivalent to 14% of a mixed oak watershed in a high rainfall zone of the Southern Appalachian Mountains. Picloram residues in mineral soil had a half-life of about 4 weeks and were below detection limits after 7 months. Soil water contained a peak concentration of 350 µg/L in the upper 0.6 m of soil, but did not exceed 25 µg/L at a depth of 1.2 m. Intensive sampling of springs below the treated area detected trace amounts of picloram for a period of 18 days. Only sporadic, low-level (less than 10 µg/L) picloram residues were detected in streamflow during a 17-month monitoring period after the herbicide application. Use of high rates of picloram to small portions of a steep forested watershed thus did not adversely affect water quality.

2,4-D

This herbicide is one of the phenoxy herbicides that function as plant growth regulators (2,4-D; 2,4,5-T; 2,4-DP; MCPA; dicamba, etc.). Since its introduction into forestry use in the late 1940s, it has become the most widely used and intensively studied forest

herbicide still in use (Norris et al., 1983). A large variety of ester or amine formulations are available commercially (USDA Forest Service, 1984) (Table 3). Salt formulations of 2,4-D are readily absorbed through the roots of weeds, while ester formulations are most easily absorbed through foliage. While the mode of action of 2,4-D is not clearly understood, it interferes with normal meristem activity and ultimately impairs plant physiological processes.

Toxicological studies indicate that most formulations are mildly toxic to mammals and birds (Table 3). Ester formulations are toxic to highly toxic to aquatic invertebrates, while salt and acid formulations (used most frequently in forestry) are only slightly toxic to the same organisms. Oral and dermal toxicity usually results in a variety of symptoms. Inhalation toxicity is rare. And 2,4-D is not considered to be a teratogen, mutagen, or carcinogen. It also does not bioaccumulate to any appreciable extent.

Highly soluble in water, 2,4-D is thus potentially transportable anywhere in the environment. It is translocated and metabolized readily within plants. However, the persistence of 2,4-D in forest soils is rather short (less than 4 weeks) as it is degraded by microbes, translocated into plants, and photodegraded to a limited extent (Norris 1981). Volatilization is dependent on formulation but 2,4-D is more prone to volatilization losses than most other forest herbicides. Transport losses from forest soils to water are mediated by adsorption to organic matter, reduced surface runoff, and greater microbiological activity (Norris et al. 1983). Even with heavy applications of 2,4-D to streambanks, concentrations seldom exceed 10 µg/L (Schultz and Whitney 1974). Applications of 4 and 6 kg/ha of 2,4-D as the triisopropanol amine salt to brush fields in Oregon produced peak stormflow concentrations of 22 µg/L (Norris et al., 1982). Application of 3 kg/ha of 2,4-D to an entire watershed in the Southern Appalachians (except for a 3-m-wide buffer strip) did not produce any detectable residues in streamflow (Douglass et al. 1969).

BARAGA COUNTY (MICHIGAN) STUDY

An investigation of the environmental consequences of converting poor-quality hardwood stands to red pine was started by Michigan Technological University and the USDA Forest Service in 1981. As part of that effort, an additional study was begun to look at the movement of hexazinone, picloram, and 2,4-D in sandy-textured spodosols typical of many northern hardwood sites. The main objective of the herbicide fate study was to determine if these herbicides would have any impact on water quality. Considerable research has been conducted on herbicide effectiveness in northern hardwood and mixed conifer ecosystems, but very little work has been done on the environmental fate of these forest management chemicals. Analysis of 2,4-D fate was not included in the study since this herbicide is not considered to have much potential for impacting water quality.

Table 3. Name, chemical, physical and biological characteristics of 2,4-D.

Characteristic	Value
1. Chemical name:	(2,4-dichlorophenoxy) acetic acid
2. Trade name	Tordon 101 (25% 2,4-D); Tordon 101R; Tordon RTU; DMA-4; Weedar 64; Amine 4D; Weed Rhap A4D
3. Formulation:	Liquid, amine salt; oil soluble amine salt; inorganic salt; high and low volatile esters, etc.
4. Vapor pressure:	6.2×10^{-7} mm of hg at 25°C
5. Solubility:	3,000,000,000 µg/L at 25°C (extremely soluble)
6. Photodegradation:	Minor loss
7. Microbial degradation	Rapid
8. Half-life:	1 to 7 days
9. Volatilization:	Low
10. Activity:	Same as picloram
11. LD50:	300-1,000 mg/kg of body weight (moderately toxic)
12. LC50:	250,000 µg/L (24 hr for Rainbow trout)
13. Carcinogenic:	No
Teratogenic	No
Mutagenic	No
Oncogenic	No

[1] LD50 = dose in mg/kg needed to kill 50% of organisms (usually mammals) by oral, dermal, or inhalation exposure.

[2] LC50 = concentration in water needed to kill 50% of exposed organisms (24, 48, or 96 hr exposure).

[3] Carcinogenic = cancer causing
Teratogenic = causing birth defects
Mutagenic = causing genetic changes
Oncogenic = causing tumors

A mixture of Tordon 101[1/] and Velpar L was aerially applied to cut-over hardwood stands in portions of Sections 10 and 17, T50N, R34W, Baraga County, Michigan. The herbicides were applied by helicopter on 30 July 1982 in 40 L/ha of water carrier. The rates were 1.7 kg/ha active ingredient of hexazinone, 1.1 kg/ha acid equivalent of 2,4-D, and 0.3 kg/ha acid equivalent of picloram. This herbicidal combination produced good control of red maple, northern red oak, aspen, birch, as well as remaining understory vegetation (see other papers in this volume).

Water moving through Entic Haplorthod (Table 4) and Alfic Fragiorthod (Table 5) soils on the Section 10 site was sampled at a depth of 1.0 m using porous cup tension lysimeters (Hansen and Harris 1975, Neary et al., in press (a)). Samples were collected periodically, frozen, and shipped for analysis. Herbicide residues were quantified by standard chromatographic techniques at the G.W. Andrews Forestry Sciences Laboratory, Auburn University, Alabama (Holt 1981).

During the aerial application in July, a portion of Six Mile Creek was sampled to determine if residues were entering the stream. Six Mile Creek drains a watershed of about 4,400 ha. It originates in the Baraga State Forest, 11 km southwest of L'Anse, and flows northeast into L'Anse Bay of Lake Superior. Sampling continued periodically until late November 1982.

RESULTS AND DISCUSSION

Picloram and hexazinone residues determined in soil water at a depth of 1 m showed a pattern which relates to application rates, herbicide properties, and soil conditions. Concentrations plotted in Figure 1 were averaged for five to seven individual samples (as indicated) for each of seven sampling dates from 26 July to 20 October 1982.

Hexazinone, which was applied at the highest rate, had the highest average concentration of 102 µg/L (Figure 1). It peaked in concentration 4 weeks after the application. The single highest concentration was 242 µg/L. These concentrations were well within the range of data collected in a variety of Ultisols in the South. Hexazinone, with a lower solubility than picloram, took an additional month to return to baseline, nondetectable levels. Picloram peaked 2 weeks earlier than hexazinone since it is 10 times more soluble in water than hexazinone, but it was much lower at the peak (average of 26 µg/L) as a result of lower application rate. Individual soil water samples contained as much as 60 µg/L picloram.

---

[1] Use of trade and corporation names is provided for the information and convenience of the reader and does not constitute endorsement or approval of any product or company by USDA.

Table 4. Soil profile description: sandy over loamy, mixed, frigid Entic Haplorthod, Baraga County, Michigan, herbicide fate study, 1982.

Horizon	Depth	Thickness	Description
	----- cm -----		
O_i	+ 7-5	0-2	Organic litter composed primarily or leaves; discontinuous; abrupt broken boundary
O_e	+ 5-0	2-5	Partially decomposed organic matter; many roots, abrupt wavy boundary
A	0-2	0-2	Very dark gray (7.5 yr 3/0) sand; weak fine granular structure; many fine and few medium roots; discontinuous; very strongly acid; clear wavy boundary
E	2-13	4-11	Light gray (5 yr 7/1) sand; weak fine subangular blocky structure; very friable; common fine roots, few medium and coarse roots; very strongly acid; clear smooth boundary
B_{s1}	13-30	18-23	Strong brown (7.5 yr 4/6) sand; moderate fine subangular blocky structure; friable; common fine and medium roots; some Bhs tongues; strongly acid; clear wavy boundary
B_{s2}	30-45	10-18	Strong brown (7.5 yr 5/6) sand; moderate fine subangular blocky structure; friable; few fine roots, common medium roots; some Bhs tongues; strongly acid; clear wavy boundary
BC	45-67	22-29	Reddish yellow (7.5 yr 6/6) sand; weak fine subangular blocky structure; friable; few fine roots; some Bhs tongues; strongly acid; granular wavy boundary
C1	67-130	44-56	Reddish yellow (7.5 yr 6/4) sand; stratified with reddish thin clay bands; weak medium subangular blocky structure; friable; strongly acid; layer of coarse sand at bottom; clear smooth boundary
C_2, C_3, C_4	130-318		Reddish brown sands and sandy loam

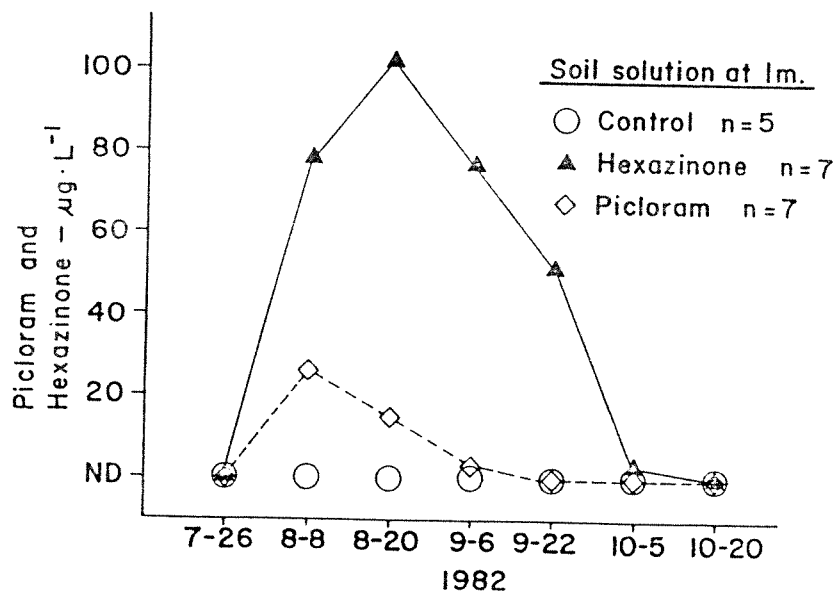

Figure 1. Picloram and hexazinone in soil solution at 1 m averaged across all samples, Baraga County, Michigan, 26 July to 20 October 1982.

Table 5. Soil profile description: coarse-loamy, mixed, frigid Alfic Fragiorthod; Baraga County, Michigan, herbicide fate study, 1982

Horizon	Depth	Thickness	Description
	----- cm -----		
O_i	+ 3-0	0-3	Organic litter comprised of leaves and grasses; abrupt broken boundary
A	0-6	0-6	Black (5 yr 2.5/1) sandy loam; weak fine granular structure; friable; many fine roots; strongly acid; discontinuous; abrupt brown boundary; some charcoal
E	6-15	9-18	Pinkish gray (5 yr 6/2) sandy loam; moderate medium subangular blocky structure; friable; common fine and medium roots; very strong acid; abrupt wavy boundary
Bw	15-27	7-16	Strong brown (7.5 yr 4/6) sandy loam; moderate medium subangular blocky structure; friable; common fine roots; few medium and coarse roots; very strongly acid; clear smooth boundary
E'	27-44	10-19	Reddish brown (5 yr 5/4) sandy loam; moderate medium subangular blocky structure; friable; common fine and medium roots; strongly acid; abrupt wavy boundary
B_{tx}/E	44-75	21-35	Weak red (2.5 yr 5/2) sandy loam (B) and red (2.5 yr 4/4) loamy sand (E); B material 60% of horizon; red clay flows on red faces; in root channels and pores; weak coarse subangular blocky structure parting to strong fine subangular blocky structure; very firm; weakly to strongly cemented; few fine and medium roots; clay flows continuous at lower boundary; 2% coarse fragments; strongly acid; abrupt smooth boundary
B_t/E	75-190		Reddish gray (5 yr 5/2) loam (E) surrounding peds of reddish brown (2.5 yr 4/4) sandy loam (B); E material 75% of the horizon; red clay flows on peds and pore spaces; weak coarse subangular blocky structure parting to weak fine subangular blocky; firm; few fine roots; 2% coarse fragments; strongly acid; many fine pores; clay flows on bottom of rocks

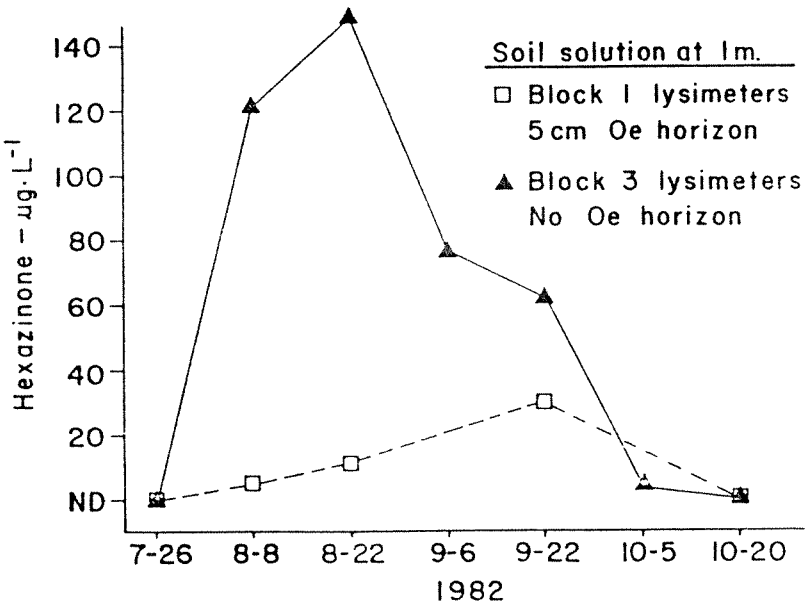

Figure 2. Hexazinone in soil solution at 1 m in soils with and without an Oe horizon, Baraga County, Michigan, 26 July to 20 October 1982.

Organic matter in soils is extremely important in holding herbicide residues in the mineral soil. Herbicides adsorbed onto organic exchange sites are not immediately available for leaching. Most soluble herbicides are reversibly adsorbed onto organic matter. However, the adsorption process provides a longer period of time for root uptake and microbial degradation. Thus, residues moving deeper into the soil profile with draining water should be lower in concentration where adequate organic matter-rich horizons exist.

An apparent block effect related to differences between the Alfic Fragiorthod and Entic Haplorthod soils was noted. The former does not contain an organic Oe horizon while the latter does (Table 4 and 5). Replotting the data with only Block 1 (Entic Haplorthod soil) and Block 3 (Alfic Fragiorthod soil), lysimeter data shows a considerable contrast. The peak hexazinone concentration without an Oe horizon was higher by 46 µg/L (Figure 2). The presence of the Oe horizon delayed the pulse of hexazinone moving down the soil profile by 1 month and reduced the peak concentration to only 30 µg/L. A similar pattern existed in the picloram residue data (Figure 3). Without the Oe horizon, picloram peaked at an average of 40 µg/L. Soil water moving through a profile with an Oe horizon carried detectable picloram residues only on 8 August (1.5 µg/L). The pattern of the residue pulse was not changed.

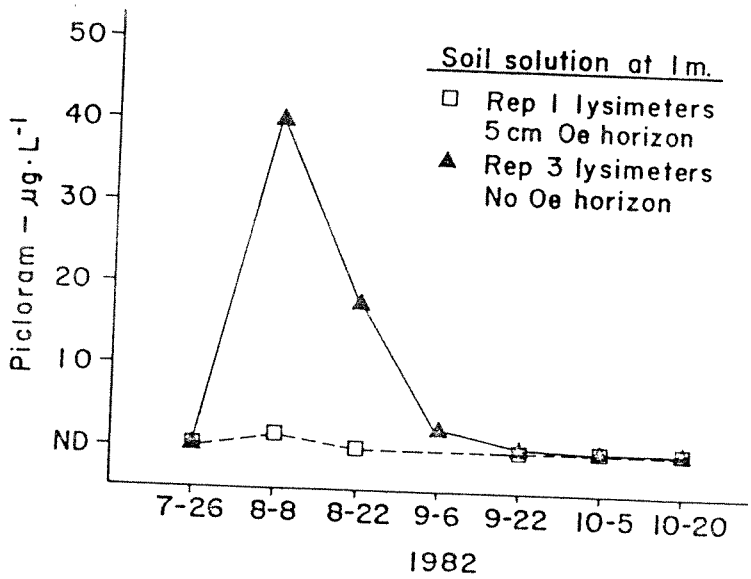

Figure 3. Picloram in soil solution at 1 m in soils with and without an Oe horizon, Baraga County, Michigan, 26 July to 20 October 1982.

Water samples were not analyzed for 2,4-D since this herbicide has a short residence time in most forest soils. Although as soluble as the other two herbicides, it is readily degraded by most naturally occurring soil microorganisms.

The herbicide concentrations measured in soil water indicated that hexazinone and picloram could move into surface groundwater tables and hence, streamflow. However, concentrations were so low and short-lived as to have no potentially adverse impact on water quality. In most managed forests only small portions would be treated in any 1 year. Thus, the dilutions from untreated areas within forested watersheds of the Upper Peninsula (and elsewhere in the upper Great Lakes region) would be more than enough to reduce herbicide residues below detection levels. Peak picloram concentrations were well below the 100 µg/L standard set for 2,4-D for municipal water supplies and the 1,000 µg/L standard suggested for picloram by the National Academy of Sciences. No standards exist for hexazinone in this country because of its short persistence, low toxicity, and recent use. In Australia, a water quality standard of 600 µg/L has been set for drinking water (Leitch and Flinn 1983). Concentrations of hexazinone measured by the Baraga County study were well below the Australian standard and 10 times lower than concentrations needed to impact the most sensitive aquatic species (Mayack et al., 1982; Fowler 1977).

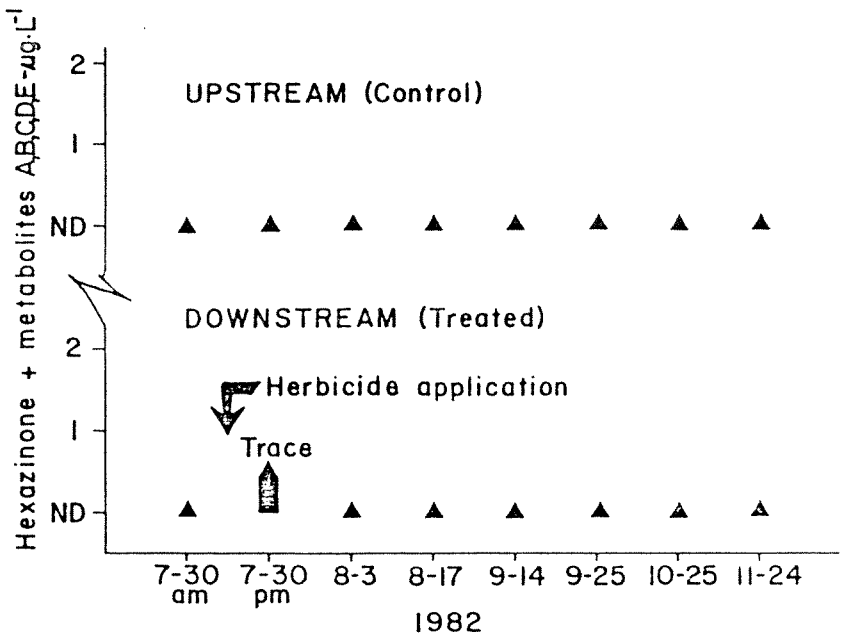

Figure 4. Hexazinone in streamflow of Six Mile Creek, Baraga County, Michigan, 30 July to 24 November 1982.

Streamflow

Water samples were taken from Six Mile Creek adjacent to and downstream of the aerially-sprayed area in Section 17. Only trace levels (less than 1 µg/L) of hexazinone and picloram were detected. This was on the afternoon of the herbicide application and probably represents drift directly into the stream. All other samples collected up to the end of November were free of detectable residues.

Even if hexazinone and picloram residues measured in soil water had reached Six Mile Creek in subsurface flow without groundwater dilution, detection of residues would have been impossible. The flow of Six Mile Creek from the untreated portion of the watershed was sufficiently large enough to dilute down the maximum soil solution concentration below detection levels. Thus, no water quality problems would exist adjacent to the sprayed areas or downstream in L'Anse Bay.

CONCLUSIONS

Hexazinone, picloram, and 2,4-D are effective and safe forestry herbicide that are part of the modern vegetation management toolkit. However, like all chemicals, they need to be used with care and respect. When used according to label instructions and at registered rates, they should not pose any adverse hazard to water quality in the northern forest ecosystems. Before using any herbicides, remember to

1. always read and follow label instructions on any herbicide container;

2. provide proper training, control, and guidance for applicators on any vegetation management product, and

3. seek additional information or assistance from manufacturers' representatives, state herbicide regulatory personnel, or cooperative extension agent.

ACKNOWLEDGMENT

The authors would like to thank Gary Lenz, Janet Pace, and Sue Wannersee for their help in the field portion of the study.

CAUTION: Use herbicides selectively and carefully. Follow recommended practices for the disposal of surplus chemicals and their containers. Some states may have restrictions on the use of certain herbicides. Check with your local state regulations. Furthermore, because registration is under constant review by the EPA, consult your state forestry agent, county agent, or state extension agent to be sure the intended use is still registered.

LITERATURE CITED

Baur, J.R., R.W. Bovey, and M.G. Merkle. 1972. Concentration of picloram in runoff water. Weed Sci. 20:309-313.

Bouchard, D.C., T.L. Lavy, and E.R. Lawson. 1985. Mobility and persistence of hexazinone in a forested watershed. J. Environ. Qual. 14:229-233.

Douglass, J.E., D.R. Cochrane, G.W. Bailey, J.I. Teasley, and D.W. Hill. 1969. Low herbicide concentration found in stormflow after a grass cover is killed. U.S. For. Serv. Southeast. For. Exp. Stn. Res. Note SE-94. 15 p.

DuPont Nemours, Inc. 1984. Velpar herbicide. Technical Information Factsheet. 10 pp.

Davis, E.A., P.A. Ingebo, and P.C. Page. 1968. Effect of a watershed treatment with picloram on water quality. U.S. For. Serv. Rocky Mt. For. Range Exp. Stn. Res. Note RM-100. 4 pp.

Fowler, M.C. 1977. Laboratory trials of the new triazine herbicide (DPX 3674) on various aquatic species of macrophytes and algae. Weed Res. 17:191-195.

Foy, C.L. 1975. Picloram and related compounds. Pp. 777-814 In: P.C. Kearney and D.D. Kaufman (ed.) Herbicides, Chemistry, Degradation and Mode of Action, Vol. 2. Marcel Deker, Inc. New York, NY.

Gonzalez, F.E. 1980. The development of Velpar "Gridball" Brushkiller-- hexazinone pellets-- for forestry. Proc. South. Weed Sci. Soc. 33:132-138.

Hamilton, R.A. 1979. A chemical method to reduce hardwood competition on pine stands. Proc. South. Weed Sci. Soc. 32:207-211.

Haines, L.W. 1981. Integrated pest management and competing forest vegetation. Pp 1-9 In: Proceedings Weed Control in Forest Management, H.A. Holt and B.C. Fisher (ed). 1981 Purdue University, Department of Forestry and Natural Resources. 305 pp.

Hansen, E.A., and A.R. Harris. 1975. Validity of soil-water samples collected with porous ceramic cups. Soil Sci. Soc. Am. Proc. 39:358-363.

Holt, R.H. 1981. Determination of hexazinone and metabolite residues using nitrogen selective gas chromatography. J. Agric. Food Chem. 29:165-172.

Leitch, C.J., and D.W. Flinn. 1983. Residues of hexazinone in streamwater after aerial application to an experimental catchment planted with radiata pine. Australian For. 46:126-131.

Mayack, D.T., P.B. Bush, D.G. Neary, and J.E. Douglass. 1982. Impact of hexazinone on invertebrates after application to forested watersheds. Arch. Environ. Contam. Toxicol. (In press).

Merkle, M.G., R.W. Bovey, and F.S. Davis. 1967. Factors affecting the persistence of picloram in soil. Agron. J. 59:413-415.

Michael, J.L. 1980. Formulation, rate, and season of application effects of hexazinone (Velpar) Gridball on oak topkill. Proc. South. Weed Sci. Soc. 33:110-113.

Miller, J.H., and A.C. Bace. 1980. Streamwater contamination after aerial application of pelletized herbicide. U.S. For. Ser. South. For. Exp. Stn. Res. Note SO-255. 4 pp.

National Research Council of Canada (NRCC). 1974. Picloram: The effects of its use as a herbicide on environmental quality. Publ. 13684, p. 128.

Neary, D.G. 1983. Monitoring herbicide residues in springflow after an aerial application of hexazinone. South. J. Appl. For. 7: 217-223.

Neary, D.G., P.B. Bush, J.E. Douglass, and R.L. Todd. In press (a). Picloram movement in an Appalachian hardwood forest watershed. J. Environ. Qual.

Neary, D.G., P.B. Bush, and J.E. Douglass. 1983. Off-site movement of hexazinone in stormflow and baseflow from forest watersheds. Weed Sci. 31:543-551.

Neary, D.G., P.B. Bush, and J.E. Douglass. 1981. 2-, 4-, and 14-month efficacy of hexazinone for site preparation. Proc. South. Weed Sci. Soc. 34:181-191.

Neary, D.G., P.B. Bush, and M.K. Grant. In press (b). Water quality of ephemeral forest streams after site preparation with hexazinone. J. Environ. Qual.

Neary, D.G., J.E. Douglass, and W. Fox. 1979. Low picloram concentrations in streamflow resulting from forest application of Tordon 10K. Proc. South. Weed Sci. Soc. 32:182-197.

Norris, L.A. 1981. Behavior of herbicides in the forest environment and risk assessment. Pp. 192-215 In: H.A. Holt and B.C. Fischer, ed. Weed Control in Forest Management. Proc. 1981 John S. Wright For. Conf., Dept. For. and Natl. Res., Purdue Univ., West Lafayette, IN.

Norris, L.A. 1969. Herbicide runoff from forested lands sprayed in summer. Research Program Report, West. Soc. Weed Sci., Las Vegas, NV. pp. 24-26.

Norris, L.A., H.W. Lorz, and S.V. Gregory. 1983. Influence of forest and rangeland management on anadromous fish habitat in western North American--forest chemicals. USDA For. Serv. Gen. Tech. Rep. PNW-149. 30 pp.

Norris, L.A., M.L. Montgomery, L.E. Warren, and W.D. Mosher. 1982. Brush control with herbicides on hill pasture sites in southern Oregon. J. Range Manage. 35:75-80.

Rhodes, R.C. 1980. Soil studies with C14 labeled hexazinone. J. Agric. Food Chem. 28:311-315.

Schultz, D.P., and E.W. Whitney. 1974. Monitoring 2,4-D residues at Loxahatchee Wildlife Refuge, Pesticide Monit. J. 7:146-152.

Stewart, R.E., and C. Row. 1981. Assessing the economic benefits of weed control in forest management. Pp. 26-53 In: Proceedings Weed Control in Forest Management, H.A. Holt and B.C. Fischer (ed). Purdue University, Department of Forestry and Natural Resources. 305 pp.

Suffling, R., D.W. Smith, and G. Sirons. 1974. Lateral loss of picloram and 2,4-D from a forest podsol during rainstorms. Weed Res. 14:301-304.