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HEXAZINONE APPLICATION TO RED PINE PLANTATIONS: EVALUATION OF EFFICACY, MOVEMENT THROUGH THE SOIL, AND GROUNDWATER CONTAMINATION

presented by

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HEXAZINONE APPLICATION TO RED PINE PLANTATIONS: EVALUATION OF EFFICACY, MOVEMENT THROUGH THE SOIL, AND GROUNDWATER CONTAMINATION

By

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ABSTRACT

HEXAZINONE APPLICATION TO RED PINE PLANTATIONS: EVALUATION OF EFFICACY, MOVEMENT THROUGH THE SOIL, AND GROUNDWATER CONTAMINATION

By

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A comprehensive study relating the effectiveness of Velpar L herbicide for releasing red pine seedlings to the groundwater contamination potential of its active ingredient, hexazinone, was conducted during 1988 and 1989. Compared to the control, the banded and dripline applications significantly reduced weed coverage by about 30 percent. The released red pine responded with greater groundline diameter growth. Height growth was not significantly affected by either treatment. The upper soil layers, high in organic matter, sorbed the hexazinone and released it slowly over the first year. Hexazinone leached into the groundwater to a maximum of 2.6 ppb at 120 days after treatment and declined thereafter. Groundwater concentrations were 80 times lower than the EPA health advisory and no build-up occurred, suggesting that continued use of Velpar L in red pine plantations is environmentally acceptable.

To my mother, father, and sister

for challenging me to attain the standards that
they themselves set so high

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LIST OF ABBREVIATIONS

Abbreviation	Definition
cm	Centimeter
CEC	Cation Exchange Capacity
DAT	Days After Treatment
DBCP	Dibromochloropropane
DNR	Michigan Department of Natural Resources
EPA	U.S. Environmental Protection Agency
ha	Hectare
hg	Mercury
kg	Kilogram
l	Liter
LD_{50}	Lethal Dose that will kill 50 percent of a population
meq	Milliequivalents
mg	Milligram
ml	Milliliters
mm	Millimeters
mμ	Millimicrons
nm	Nanometers
ppm	Parts per million (mg/l)
ppb	Parts per billion (μg/l)
SCS	Soil Conservation Service

Abbreviation	Definition
μg	Micrograms
μl	Microliters
USGS	U.S. Geological Survey
USDA	U.S. Department of Agriculture

CHAPTER I

BACKGROUND AND OBJECTIVES

THE IMPORTANCE OF PESTICIDES

Since the remarkable success of DDT and especially since WWII, society has continuously become more dependent on pesticides for everyday life. We depend on a variety of chemicals to combat everything from Gypsy moths to malaria to vegetation competing with desirable crops. This increasing dependence has lead to about 455 million kg of pesticides being used in the United States each year. Of this amount, 341 million kg are used in agriculture, 55 million kg by government and industry, 55 million kg in and around homes and about 4 million kg on forests as shown in Figure 1 (Pimental and Levitan 1986).

The reasons for the heavy use of these pesticides are really quite simple. First, in economic terms, the annual $3 billion invested in pesticidal control yields $12 billion in increased crop harvests (U.S. Department of Agriculture 1971; Pimental et al. 1978). This clearly represents an excellent return on investment especially in short term crops such as corn, soybeans, or even Christmas trees. Though long term crops such as timber products will yield a lower return on investment, the economics still favor pesticide application and use.

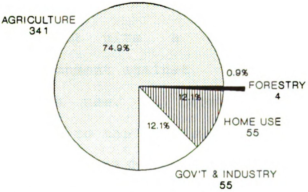


Figure 1. Amount of pesticide used in the U.S. in millions of kg and percent.

Though economics alone seems to justify pesticide use, the fact that they are effective also promotes their use. For the homeowner whose house is infested with termites, economics has little to do with calling a pest control agent. Before the lumber was used to build the house, a forest manager may have decided to use an herbicide to release seedlings from surrounding vegetation and promote good growth. Both choices have been made mainly from an effectiveness standpoint.

Even though pesticides have a positive effect on human welfare, large amounts of the applied chemicals often do not reach the pest population. In fact, Pimental and Levitan (1986) maintain that often less than 0.1 percent of the pesticides applied to crops reaches the target pest. The excess pesticide moves throughout the environment, possibly affecting non-target organisms in the soil, surface water, groundwater, and air.

This simple fact pits a concern for a clean, unadulterated environment against the many beneficial aspects of pesticide use. A benefit/cost ratio is often used as a solution to the problem. Do the benefits of applying pesticides outweigh the costs? Though ideally this ratio needs to be greater than one, the benefits and costs are not easily quantified.

With these considerations in mind, the Michigan Department of Natural Resources (DNR) has, for several years, chosen to apply Velpar L herbicide to red pine (Pinus resinosa) plantations. Velpar applied to the soil at a rate of 9.3 liters per ha (2.2 kg active ingredient per ha) can effectively control several grass species, several perennial weeds, low growing shrubs, and undesirable trees such as aspen (Populus spp.), birch (Betula spp.), and maple (Acer spp.). In addition to its wide spectrum of activity, Velpar is relatively easy to apply. A John Deere 740 skidder with a V plow attached to the front first cuts the roots of competing vegetation and prepares the bed for the planting of red pine seedlings. Attached to the rear of the skidder is a pump which dispenses a dripline of Velpar into the prepared tree row. In the same operation, a tree planter is pulled behind the skidder with the trees planted immediately after the Velpar application. Planting and herbicide application in this manner is very low in cost, operationally simple, and removes competing vegetation while keeping erosion at a minimum.

Though Velpar has been shown to be an inexpensive and efficient means to release red pine (Ware 1983; Michael 1985), some studies indicate that the active ingredient, hexazinone, and its degradation products could be leaching into deeper soil horizons and even the groundwater. The time required for 50 percent loss of hexazinone on silt loams in Delaware, Illinois, and Mississippi was 3-4 months, 6-7 months, and 10-12 months, respectively (Rhodes and Jewell 1980). However, Bouchard, Lavy, and Lawson (1985) found that the dissipation rate of hexazinone in the top 10 cm of soil was greater than could be accounted for solely by degradation; thus, hexazinone and its degradation products likely leached into lower soil horizons and possibly the groundwater.

THE IMPORTANCE OF GROUNDWATER

The importance of groundwater in the United States and Michigan cannot be overemphasized. Groundwater constitutes 22.2 percent of the earth's fresh water and over 97.0 percent of the earth's liquid fresh water (Lee 1980). Nationwide, 333 billion liters of groundwater are withdrawn per day to provide drinking water to 51 percent of the population and 97 percent of rural residents. However, not only is groundwater used for drinking purposes, it also provides 40 percent of all agricultural irrigation water, 26 percent of all industrial withdrawals, and nourishes and maintains many ecosystems (Lee 1980).

The numbers are similar in Michigan. Two billion liters of groundwater are withdrawn daily to supply drinking water to 43 percent of the population and 100 percent of the rural residents. Though agricultural irrigation approaches the 40 percent nationwide average, only 3 percent of industrial withdrawals come from the groundwater resource (Cheremisinoff, Gigliello, and O'Neill 1984; Groundwater Protection 1987).

Clearly, there is a strong dependence on groundwater in many facets of everyday life, but groundwater contamination is being discovered in a growing number of areas (The Library of Congress 1989). This is in stark contrast to reports as late as 1980 that serious pesticide contamination is rare (Lee 1980). The protection of this very finite resource is difficult to say the least. The existence of large and stable governmental programs to protect other environmental media complicates efforts to make groundwater protection a priority and to develop an integrated environmental management strategy. Furthermore, the relative inaccessibility of groundwater makes measurement of its characteristics and dynamics difficult (Groundwater Quality Protection, State and Local Strategies 1986).

FEDERAL AND STATE GROUNDWATER PROTECTION PROGRAMS

Despite these difficulties, federal and state governments are beginning to take action and protect America's groundwater. While no single federal agency is assigned lead responsibility for groundwater protection, the U.S. Department of Agriculture (USDA), the U.S. Geologic Survey (USGS), and the U.S. Environmental Protection Agency (EPA) are charged with the prevention, detection, and correction of groundwater contamination. Several pieces of legislation such as the Safe Drinking Water Act (P.L. 93-523), the Clean Water Act (P.L. 92-500), and the Federal Insecticide, Fungicide, and Rodenticide Act (P.L. 92-516) guide these agencies in protecting the nation's groundwater.

More specifically, the USDA has several agencies which are addressing groundwater concerns including the Soil Conservation Service, the Agricultural Research Service, the Cooperative State Research Service, and the Extension Service. These agencies have two primary responsibilities: 1) education and technical assistance and 2) research (The Library of Congress 1989). For instance, the Soil Conservation Service provides assistance to landowners to maintain conservation practices which manage pesticides, nutrients, and control groundwater withdrawal. On the other side, the Agricultural Research Service provides funds for basic and applied research on groundwater topics such as control and monitoring technologies.

The USGS, on the other hand, assesses both the quantity and quality of the nation's water resources and provides hydrologic information. While the work done by the USGS does not apply specifically to groundwater contamination, they provide necessary background and technical data for assessing existing contamination and potential problems (The Library of Congress 1989).

Finally, the EPA's groundwater protection strategy is based on the principle that states have primary responsibility for groundwater management. Thus, assistance to other federal and state agencies is their primary objective. A more aggressive strategy that the EPA has begun is the National Pesticide Survey. Scheduled to be completed in 1990, the survey is expected to be a statistically representative description of pesticide contamination of the nation's groundwater while also assessing patterns of agricultural chemical usage in relation to groundwater contamination (The Library of Congress 1989).

Currently no single federal program addresses all aspects of groundwater protection. The problem is afterall, one of astounding complexity since virtually all activities of society affect the groundwater resource. In fact, groundwater issues and conditions vary greatly from state to state and reflect differences in the states' physical, social, and political makeup (Groundwater Quality Protection 1986). Therefore, groundwater protection might best be handled at the state level. In Michigan, groundwater protection is administered by the DNR using a variety of federal and state statutes. Though no comprehensive state program has yet been instituted, the DNR has groundwater protection responsibilities ranging from prevention to remedial activities. In addition to the DNR, the Michigan Department of Health has a Public Water Supply Program which investigates and monitors groundwater throughout the state.

VELPAR L STUDY IN RED PINE PLANTATIONS

Regardless of the differences of opinion on how to handle groundwater protection, one point is agreed upon; there is a serious lack of basic, comprehensive knowledge about the current and potential extent of groundwater contamination. Therefore, in anticipation of increasing public concerns, comprehensive research on the use of Velpar for red pine establishment has been conducted and will be continued into the future.

The Department of Forestry and the Pesticide Research Center in conjunction with the Michigan Department of Natural Resources established a project in the Upper Peninsula of Michigan to examine the efficacy and fate of hexazinone in red pine plantations. The purpose of the project is to examine hexazinone efficacy and movement through the soil under actual field conditions. From this data, an assessment will be made concerning the actual vulnerability of groundwater to hexazinone contamination under red pine plantations.

Three objectives outlined the course of action for the project:

1) Efficacy of Velpar for Red Pine Establishment: Red pine seedling height and diameter growth and weed populations will be measured in treated plots and compared to untreated plots over a two year time frame.

2) Hexazinone Residues and Movement in Soil: Hexazinone movement through the soil will be followed by measuring concentrations of the chemical in consecutive 10 cm increments to a depth of 40 cm.

3) Hexazinone Contamination of Groundwater: Groundwater contamination will be measured through the establishment of fifteen well clusters arranged in grid fashion. This arrangement allows careful tracking of hexazinone concentrations and possible build-up or off-site movement.

The project was conducted over two growing seasons and involved studies at two sites in the Upper Peninsula of Michigan as shown in Figure 2. The efficacy study was established at the Cedarville site with initial measurements taken in the spring of 1988, first year growth measurements taken in the fall of 1988, and final measurements taken in the fall of 1989. The hexazinone soil residue and groundwater contamination study took place on the Stutts Creek site with samples taken periodically from the spring of 1988 to the spring of 1989. Since funding for the project continues until July, 1990, additional efficacy measurement and groundwater sample analysis will continue until that time. Further, the sites will remain under observation should additional research be deemed necessary.

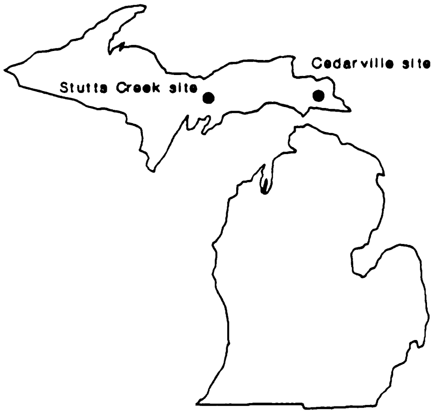


Figure 2. Location of the Stutts Creek site and Cedarville site in the Upper Peninsula of Michigan.

CHAPTER II

REVIEW OF LITERATURE

VELPAR TECHNICAL INFORMATION

Velpar L Weed Killer is a miscible liquid containing 25 percent hexazinone and 75 percent inert ingredients. The molecular formula of hexazinone, a triazine herbicide, is $C_{12}H_{20}N_4O_2$ and appears structurally as shown in Figure 3 (Herbicide Handbook 1983).

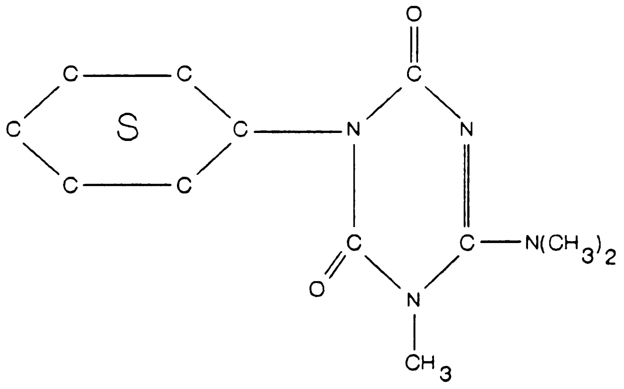


Figure 3. Structure of hexazinone.

Velpar L has contact properties and can be readily absorbed through the roots where translocation occurs primarily upward through the xylem. Though its mode of action is not clearly established, it appears to act as a photosynthetic inhibitor causing interveinal chlorosis and desiccation of green tissues. The selectivity of the herbicide, as with most triazines, is based on differential detoxification involving chemical transformations (i.e. hydroxylation) and formation of chemical complexes (i.e. conjugation with glutathione). This selectivity, though limited, allows Velpar to be used in many non-cropland areas including Christmas tree plantations and pine site preparation and release (Herbicide Handbook 1983). Water is the usual carrier of Velpar L due to its high solubility in the solvent, up to 3.3 grams per 100 grams at 25°C or 33,000 ppm. This property, while making application more convenient and efficient, greatly contributes to hexazinone's potential as a groundwater contaminant. Additionally, the soil thin-layer chromatography R_f value of hexazinone places the compound in Class 4 of the mobility classification scheme of Helling and Turner, making it highly mobile (Helling and Turner 1968; Rhodes and Jewell 1980).

Microbial degradation contributes to the decomposition of hexazinone in soil by breaking the triazine ring. The major microbial processes involved in hexazinone decomposition are demethylation and hydroxylation of the four position of the cyclohexyl ring liberating CO_2 (Rhodes 1980). Using ^{14}C labeled material in biometer flask studies to determine microbial degradation in the dark, 45 to 75 percent of the ^{14}C was given off as $^{14}CO_2$ after 90 day incubations. Though volatilization losses are negligible, photodegradation plays a part in hexazinone decomposition with 60 percent of applied ^{14}C material degraded during a six week exposure to ultraviolet light.

Despite Velpar's wide spectrum of activity on plants, its general toxicity to humans, wildlife, and fish is low. The Oral LD_{50} in rats is 1690 mg/kg and Dermal LD_{50} in rabbits is greater than 5278 mg/kg. In fact, no evidence was found of cumulative toxicity when administered orally to rats at a repeated dose of 300 mg/kg per day over a two week period (Herbicide Handbook 1983). Further, as part of the National Pesticide Survey, the EPA has issued a "Lifetime Health Advisory Value" for pesticides not proven to cause cancer in laboratory studies. This value represents the concentration of a chemical in water that the EPA believes to be an acceptable level for drinking every day during a person's lifetime without posing health problems. Hexazinone is non-cancer causing and has a "Lifetime Health Advisory Value" of 210 ppb (U.S. EPA 1988a). Hexazinone's technical information is summarized in Table 1.

EFFICACY

Three principal factors contribute to the effectiveness of herbicide performance in pine plantations. The chosen herbicide must control the target weed population, selectively permit adequate survival of the pine, and the

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 306, Velpar Weed Killer
3. Formulation:	Liquid (25% a.i.), granular (5 & 10%), soluble powder (90%)
4. Vapor Pressure:	2 x 10^{-7} mm of hg at 25°C
5. Water Solubility:	33,000 mg/L at 25°C
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. Mode of Action:	Possible photosynthetic inhibitor
11. Activity:	Contact and soil
12. LD_{50}	1690 mg/kg
13. Carcinogenic: Teratogenic: Mutagenic: Oncogenic:	Negative Negative Negative Negative
14. Lifetime Health Advisory Value:	210 ppb

Adapted from Herbicide Handbook 1983; Neary, Michael, and Wells 1985; Olsen 1989.

pine must be able to respond to the release treatment. Both weed control and survival are essentially inherent abilities of the herbicide to perform. Pine growth, on the other hand, is an inherent characteristic of the tree itself that needs to be considered to accurately determine the efficacy of an herbicide. Increased tree growth (height, diameter, quality, etc.) is the bottomline measure of herbicide release and if the inherent ability of a tree to respond to release is poor, the efficacy should also be considered poor.

WEED CONTROL

Before any pine response will occur, weeds need to be controlled sufficiently to allow the pine to capture environmental resources that were previously utilized by the weed species. Velpar has been on the market since the early 1970's and several studies indicate that, in its various forms, hexazinone can greatly reduce many forms of weed competition on varied sites. In the United Kingdom, 90 percent control was achieved on various broadleaf species at 4.5 kg active ingredient per ha (Allison and Joyce 1974). In Georgia, hexazinone was used to control oak and hawthorne with 80 to 95 percent defoliation recorded at 1.5 kg active ingredient per ha (Newbold 1977). Hexazinone control of grasses and forbs in Oregon and Washington state showed promise for the release of ponderosa pine and Douglas fir as shown in Table 2.

Table 2. Two-year weed control at TNT Gulch, Oregon and four-year weed control at Entiat River, Washington.

	Preplant	Postplant
	% Control	
Oregon		
First Year	92	82
Second Year	73	65
Washington		
First Year	45	54
Second Year	83	86
Third Year	72	87
Fourth Year	48	49

Adapted from Dimock, Beebe, and Collard 1983.

As these studies clearly illustrate, weed control with hexazinone is quite effective. However, weed control effectiveness depends on a variety of factors including formulation, degradation and movement, climate, method of application, amounts used, and amounts reaching pests (White-Stevens 1977).

Hexazinone to control weeds in pine plantations is available in several formulations (miscible liquid, pellets, soluble powder, and wettable powder). Velpar L, used by the DNR to release red pine in the Upper Peninsula of Michigan, is diluted in water and because of its high solubility eliminates the need for agitation to maintain a uniform distribution. This uniform distribution also fosters good application coverage onto plant surfaces; therefore, no surfactant is needed to break the surface tension of water to encourage the herbicide to adhere to the plant.

In terms of its soil activity, degradation and movement have a clear connection to efficacy. Both processes essentially remove the herbicide from the sphere of influence of the weed populations and weed control is decreased. To sufficiently control weed populations, neither process should occur too rapidly. Though photodecomposition and chemical transformations are essentially uncontrollable, microbial decomposition can be delayed by making applications during cool moist periods when microbial activity is at a minimum (White-Stevens 1977).

Climate can also directly and indirectly affect herbicide performance by affecting the growth of a plant. Though all aspects of climate affect weed control, rainfall, temperature, and humidity are the main determinants of how an herbicide will perform. In terms of the contact properties of hexazinone, rainfall is often a villain as it washes the chemical from the leaves of the target weed population. High humidity and moisture however, encourage plant growth which increases herbicide effectiveness. Likewise, temperature should be in the range where plant growth is optimum. A small amount of rainfall is needed to activate hexazinone applied to the soil but too much can cause it to leach out of the root zone. Humidity has little effect in the soil but once again, temperature should promote active growth of the target species.

Several methods of application exist that exploit the different characteristics of the different herbicides. For instance, glyphosate is generally applied aerially due to its contact properties and complete lack of soil activity. Other compounds such as simazine rely on soil activity. Therefore, simazine is generally applied by means of boom attachments to tractors, sprayed directly onto the soil, and possibly incorporated. Since hexazinone has both contact and soil activity, a method of application that exploits this fact will prove to be the most effective (Herbicide Handbook 1983; Ross and Lembi 1985). The varied terrain and slash of pine plantations limit the options for application. Incorporation of hexazinone into the soil, which would favorably disperse the compound, is not a viable option on difficult terrain. Therefore, the options most frequently used are a directed application and a banded application.

The amount of pesticide applied and the amount that reaches the target population have been under debate for many years. The amounts applied are restricted by federal and state regulations as described on the label and are often further restricted on sandy sites that are generally used for pine plantations. Of the amount applied, not all of it reaches its target. Though no study has yet addressed hexazinone specifically, Pimental and Levitan (1986) claim that less than 0.1 percent of the amounts applied reaches the target pest. Achieving 100 percent application effectiveness is unrealistic, though using the adequate rates, the proper method, and applying at the correct time can greatly overcome this problem and increase weed control.

SURVIVAL BASED ON SELECTIVITY

Another component of efficacy is survival of the species being released based on the selectivity of the herbicide. For pine species, mycorrhizae are regarded as essential for establishment, growth, and survival. While some studies have implicated certain pesticides in the elimination of mycorrhizae, in vitro studies with hexazinone have found that mycorrhizal fungi are not adversely affected by hexazinone at concentrations lower than 10 ppm (Chakravarty and Sidhu 1987a). Further studies by Chakravarty and Sidhu (1987b) have indicated that at 1 kg active ingredient per ha, survival of white spruce (Picea glauca) and lodgepole pine (Pinus contorta) was not affected and recovery of the roots occurred within six months of application. At 2 and 4 kg active ingredient per ha severe mortality occurred initially but was significantly reduced after four to six months.

Field studies with hexazinone in white pine (Pinus strobus), loblolly pine (Pinus taeda), slash pine (Pinus elliottii), and ponderosa pine (Pinus ponderosa) have generally showed excellent survival. Survival of white pine was 100 percent in a West Virginia study except with trees that had been previously overtopped; survival here was 90 percent (U.S. Department of Agriculture 1987). D'Anieri (1985) reported that there were no significant effects on slash pine survival due to treatment but survival for loblolly pine ranged from 57 to 84 percent. In a study on ponderosa pine injury in Oregon, trees exposed to hexazinone treatment exhibited minor to no damage at rates of 2.2 kg active ingredient per ha (Cole, Newton, and White 1987). Another study on ponderosa pine and Douglas fir (Pseudotsuga menziesii) showed survival to be about 80 percent and 90 percent respectively at 2.2 kg active ingredient per ha (Dimock, Beebe, and Collard 1983).

Survival data on hexazinone-released red pine has not been reported in the literature. However, based on the very favorable results on the variety of species discussed and their close relationship to red pine, its survival should also be favorable. This conclusion is supported by verbal reports from operational applications (Farnsworth 1988, pers. comm.).

TREE RESPONSE TO HEXAZINONE RELEASE

Like the data on survival, red pine growth in response to release with hexazinone is not available. However, there is a wealth of information on species such as loblolly pine, white pine, and Douglas fir.

Release trials in pine plantations often concentrate on height growth since weed control is no longer needed once the trees are above the surrounding vegetation. In essence, the pine, with a little help from a forest manager, has won the battle for the light resource. The pine can then continue to grow deeper in the soil for additional nutritive resources and also taller for more light. However, groundline diameter is also a useful measure since it indicates the general sturdiness of the seedling and the volume potential once mature.

Loblolly pine height growth in response to hexazinone application is generally moderate after just 2 to 4 years. For instance, while weed control was successful in an Alabama and Kentucky study, there were no significant treatment effects on loblolly pine height growth; in this same study, slash pine showed significant height growth increases (D'Anieri 1985). Another study in South Carolina showed significant diameter and height increases over two growing seasons of loblolly pine (Michael 1985). White pine in Pennsylvania and ponderosa pine in the Pacific Northwest showed little response to release with hexazinone (Dimock, Beebe, and Collard 1983; U.S. Department of Agriculture 1987). Douglas fir however, showed a significant height growth response to a release treatment of hexazinone. This data is summarized in Table 3.

Michael (1985) has stated that herbaceous weed control can increase growth of young planted loblolly pine on high site index lands following single applications at effective rates. This statement can be broadened to include several tree species and is especially true with improved varieties. The situation is similar with agricultural crops. Quite often, corn released by herbicides is an improved variety

Table 3. Comparison of height and groundline diameter growth of several species in several states after release with hexazinone. Percent response is listed in parentheses.

	Height Growth (cm)	Groundline Diameter Growth (cm)
Washington--3 yrs		
Ponderosa Pine	24.6 (23%)	N/A
Control	20.0	N/A
Douglas Fir	28.8 (49%)	N/A
Control	19.3	N/A
Pennsylvania--1 yr		
White Pine	18.3 (20%)	N/A
Control	15.2	N/A
S. Carolina--2 yrs		
Loblolly Pine	182.9 (28%)	3.6 (50%)
Control	143.3	2.4
Alabama--2 yrs		
Loblolly Pine	109.7 (16%)	N/A
Control	94.5	N/A
Kentucky--2 yrs		
Loblolly Pine	24.4 (15%)	N/A
Control	21.3	N/A
Georgia--2 yrs		
Loblolly Pine	106.7 (35%)	N/A
Control	79.2	N/A

Adapted from Dimock, Beebe, and Collard 1983; D'Anieri 1985; Michael 1985; U.S. Department of Agriculture 1987.

and is grown on nutrient rich soils. Further, these lands are then fertilized to improve yields. With the much longer rotations of tree plantations, it might behoove forest managers to release only the best trees on the best sites.

PESTICIDE FATE IN THE SOIL ENVIRONMENT

Pesticide fate in the soil environment is a direct function of the sorptive potential of the soil, the capacity of the pesticide to be sorbed, movement, and degradation. Certain pesticides such as paraquat have only contact properties and are deactivated by soil sorption once they contact the soil. Others such as hexazinone exhibit soil activity and are not sorbed to soil particles as strongly as other pesticides (Herbicide Handbook 1983).

SOIL SORPTION

Sorption is a generic term which refers to the uptake of a solute or vapor by soil without reference to a specific mechanism (Boyd 1988). Three types of sorption exist--absorption, adsorption, and partitioning. Absorption describes a process whereby a compound is literally taken inside another structure or engulfed wholly. Adsorption is a quite different process where a solute condenses on the surface or interior pores of a solid. Finally, partitioning describes a model in which the sorbed material is dissolved in an organic phase by forces common to solution. The latter two processes characterize what occurs in the soil environment to inhibit pesticide movement. Soil is essentially viewed as a dual sorbent where the mineral constituent behaves as a conventional adsorbent and soil organic matter behaves as a partitioning medium (Boyd 1988).

PARTITIONING

The partitioning process in soil organic matter was first described by Chiou, Peters, and Freed (1979). Though the subject is still open to debate, data showing no indication of isotherm curvature continue to reinforce their claims of nonionic organic compounds partitioning into soil organic matter. Essentially, organic materials are taken up evenly since there is no competition for adsorptive binding sites; this manifests itself in sorption isotherms which are linear to the point of maximum solubility. An important point concerning partitioning in soil organic matter is the relationship of water solubility to partitioning coefficients. A linear inverse relationship between the log of the octanol-water partitioning coefficient and the log of water solubility exists for a wide range of chemical classes (Chiou 1989). This indicates that as the water solubility of a compound decreases, the potential for organic compounds (pesticides) partitioning into soil organic matter increases.

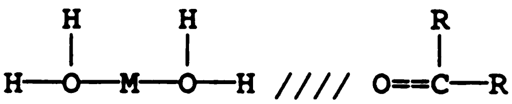
However, the amount of pesticide partitioned into the soil organic matter is also largely dependent on the amount of organic matter in the soil. This amount varies widely but in sandy soils such as those used for red pine plantations, the surface layers have high organic matter contents due to the forest floor. However, in underlying layers, organic matter decreases markedly. The importance of organic matter for inhibiting pesticide movement in soil cannot be overemphasized. The organic matter component of soil is almost singly responsible for the movement or adhesion of organic compounds (Boyd 1988). Chiou goes on to say that the sorption of nonionic organic compounds by soil in aqueous systems is controlled mainly by the organic matter of the soil. Note here that the saturation water content of soil is defined by the soil's moisture content in equilibrium with water vapors at 100 percent humidity (Chiou 1989). In saturated soils, water competes for the binding sites on the mineral surfaces and organic matter dominates. On the other hand, in dry systems, there is little water to compete with the organic compounds and adsorption on mineral surfaces dominates.

ADSORPTION

Pesticide adsorption to mineral surfaces is essentially the result of attractive forces contained in the pesticide molecule that find a binding site on a soil particle. While partitioning is a single process of dissolving organic materials, adsorption acts in several different ways depending on the nature of the pesticide. The different mechanisms of adsorption between pesticides and soil particles include Van der Waals attractions, hydrogen bonding, charge transfer, ion exchange, and ligand exchange. Other forces, such as hydrophobic bonding, have been described in the past (as late as 1980) but are probably better understood using Chiou's theory of partitioning.

Van der Waals forces result from short, weak dipole interactions. Due to the additive nature of these dipole interactions, a strong attractive force may result between a large molecule, such as a pesticide, and a soil particle. The extent of the attraction depends on how close the pesticide molecule is allowed to approach the clay surface due to other forces and its own molecular configuration (Khan 1980; Dinauer 1974).

Hydrogen bonding is another dipole interaction where the hydrogen atom serves as a bridge between electronegative atoms. The hydrogen atom is held by a covalent bond on one side and by electrostatic forces on the other, yielding a partial charge transfer. Similar to the Van der Waals forces, hydrogen bonds are weak as a single force but in combination can be very powerful (Khan 1980; Boyd 1988). A hydrogen bond is shown here:



$$H-\overset{H}{\overset{|}{O}}-M-\overset{H}{\overset{|}{O}}-H \;////\; O{=}\overset{R}{\overset{|}{C}}-R$$

In these examples, the letters represent their respective elements except M which represents a metal and R which represents a functional group.

The partial charge transfer of a hydrogen bond can be taken one step further to a total charge transfer. Essentially, a force is evolved when electrons are transferred from an electron rich donor to an electron deficient acceptor. The accepting molecule is then attracted to the soil particle as shown here:

$$R - NH_2 + H^{+}\text{- clay} \text{ ----> } RNH_3^{+}\text{- clay}$$

Adsorption of triazines such as hexazinone onto clay can be partially explained by charge transfer (Khan 1980; Boyd 1988).

Pesticides that exist as cations or that have become protonated can be adsorbed to soil by ion exchange. Basically, a cationic molecule displaces another cationic molecule that had been sorbed to the soil particle. The reaction can be seen thus:

$$RNH_3^{+} + M^{+}\text{- clay} \text{ <----> } RNH_3^{+}\text{- clay} + M^{+}$$

Ligand exchange is a fifth type of adsorption mechanism which involves replacing a ligand by an adsorbent molecule, namely a pesticide. The necessary condition for ligand exchange is that the adsorbent molecule be a stronger chelating agent than the replaced ligand (Khan 1980). One scenario might have the pesticide molecule displacing water with a partially chelated transition metal serving as an adsorptive site as shown here:

$$\text{Ethylene Glycol} + M(H_2O)_x{}^{+}\text{- clay} \text{ ----> } M(\text{Ethylene Glycol})_x{}^{+}\text{- clay} + H_2O$$

Though partitioning and adsorption are two entirely separate and different processes that operate under different conditions, they both result in inhibited pesticide movement. Additionally, since partitioning is a phenomenon that occurs in areas where organic matter dominates, the forest floor and upper soil horizons tend to have a significant impact on pesticide sorption. Likewise, adsorption is greatly affected by the number of available binding sites in the mineral portion of the soil and thus clay content is also significant.

DEGRADATION

While the sorption process in soil is occurring, other transformations and degradation of the parent compound are also taking place. The degradation that occurs ultimately has an effect on the fate of the pesticide and the amount that is later available to leach into deeper soil horizons. Two broad categories of degradation processes, biological and non-biological, exist but affect compounds in different ways depending on the chemical's nature and a variety of environmental factors.

BIOLOGICAL DEGRADATION

The population densities and varieties of microorganisms in the soil can approach astounding numbers (10^9 bacteria per gram) but generally occupy less than 0.1 percent of the soil volume (Torstensson 1980; Tiedje 1988). This vast array of microorganisms operates on the unwritten, yet generally accepted, principle of microbial infallibility that suggests any compound introduced into the environment can be degraded by microbial activity (Tiedje 1988).

Microbial activity is carried on by enzymatic reactions which are based on the fact that microbial metabolic activities (like all metabolic activities) require energy. While most organic materials can serve as an energy source, the fact remains that certain compounds are less degradable than others. For instance, degradation of polychlorinated biphenyls (PCB's) in the Hudson River was reported to be extremely slow (Tiedje 1988) while degradation of hexazinone is relatively rapid (Herbicide Handbook 1983). The reason for these differing rates of degradation is based on another attribute of microbial metabolism, adaptation. Microbes, due to induction, mutation, and high reproductive rates, can adapt to an enormous amount of chemicals, both natural and synthetic (Torstensson 1980; Tiedje 1988).

Certain synthetic organic compounds that are introduced into the environment closely resemble products that naturally occur. Therefore, the capacity or ability of a microbe to shift its energy (food) source from the natural product to the synthetic one is relatively easy. On the other hand, completely foreign entities require a greater and likewise slower change to the new energy source.

This fact can be seen in a process called plasmid assisted molecular breeding. Plasmids are extra-chromosomal elements in microbes that confer the ability to biodegrade compounds that are not common substrates for the cell. One study took several microbes and provided their normal substrates and a small amount of 2,4,5-T. As the diet was then slowly switched to 2,4,5-T, an adaptation occurred and the 2,4,5-T was degraded in larger and larger amounts. As greater amounts of the synthetic or unknown compound become available, its use as an energy source becomes more feasible and degradation occurs (Tiedje 1988). Similar studies have shown this for 2,4-D, chlorpropham, endothal, dalapon, chloridazon, and others (Torstensson 1980).

Another way that pesticides may be broken down is through a process called co-metabolism (Horvath and Alexander 1970; Bolag 1974). The process occurs when a pesticide closely resembles another compound which microbes commonly utilize as a food source. The pesticide is degraded accidentally and the process itself yields little energy for the microbe. Compounds that closely resemble natural products are more likely to be metabolized or degraded as a consequence of metabolic activity.

NON-BIOLOGICAL DEGRADATION

Non-biological degradation, as defined here, is any breakdown process that does not involve microbial actions. In general, non-biological degradation involves chemical reactions such as oxidation, reduction, elimination, substitution, isomerization, and hydrolysis (Lichtenstein 1977). The manners in which these reactions are triggered are numerous but generally involve sunlight, the correct environmental conditions, and/or water functioning as a reaction medium, a reactant, or both (Khan 1980).

Photolysis is essentially the splitting or degradation of a molecule by light, usually ultraviolet light (Ware 1983). Because the atmosphere of the earth effectively eliminates much shortwave ultraviolet radiation, no wavelength shorter than 290 $m\mu$ reaches the earth's surface (Matsumura 1973; Lichtenstein 1977). An important factor affecting photolysis is the presence of photosensitizers, chemicals that cause increased sensitivity to light by transferring the energy of light into the receptor chemicals (Matsumura 1973; Ware 1983). This then triggers the chemical reactions.

Of the chemical reactions listed above, oxidation and hydrolysis are quite common with the latter especially common with triazines such as atrazine, simazine, and hexazinone. The other reactions are important for specific compounds (Khan 1980).

PESTICIDE MOVEMENT--LEACHING

Given the fact that sorption and degradation seldom account for 100 percent of a chemical's fate, another process must also be at work. The pesticide can move through the environment in the form of the parent compound by leaching. Leaching losses by different chemicals vary incredibly and are essentially a function of the compound's sorption, water solubility, and available precipitation.

Herbicides like diquat are sorbed to the soil very strongly and leaching losses are therefore minimized. However, since diquat's water solubility is virtually infinite, some leaching of the compound should be expected (Herbicide Handbook 1983). These two opposing factors are mediated by the effects of climate, particularly the amount and timing of precipitation.

While partitioning into organic matter is a noncompetitive process, adsorption to soil involves a competition for available binding sites. In pine plantations where sandy soils generally dominate, clay content, and likewise binding sites, are limited. Therefore, once the pesticide makes its way past the organic rich upper layers, adsorption to the mineral fraction is minimal. Triazine herbicides, however, while showing some capacity to leach, do bind to both the organic and mineral portions of the soil (Weber, Weed, and Ward 1969; Gilmore and Coleman 1971; Carringer, Weber, and Monaco 1975; Hermosin et al. 1982; Wehtje et al. 1984).

For large amounts of precipitation, the water will compete for binding sites and the pesticide will likely leach deeper into the soil with the excess moisture. Likewise, precipitation soon after an application does not allow sufficient time for a pesticide to bind to the soil, be taken up by plants, or be degraded. Thus, the potential for pesticides to leach deeper into the soil and possibly the groundwater exists, particularly for highly water soluble compounds such as hexazinone.

HEXAZINONE FATE IN THE SOIL ENVIRONMENT

Like any pesticide, hexazinone's fate in the soil is affected by the processes of sorption, degradation, and leaching. However, the chemical nature and specific characteristics of hexazinone define its own behavior in the soil.

The processes of partitioning and adsorption, as discussed previously, have been shown to bind triazine herbicides to the mineral and organic matter fractions of soil (Weber, Weed, and Ward 1969; Gilmore and Coleman 1971; Carringer, Weber, and Monaco 1975; Hermosin et al. 1982; Wehtje et al. 1984). Hexazinone partitioned into the organic matter fraction is not immediately available for leaching and since this process is reversible, degradation can occur (Neary, Michael, and Wells 1985). However, many of the sandy clearcut sites typical of red pine plantations have significant amounts of organic matter in a thin forest floor layer and few mineral binding sites available in the underlying layers.

Hexazinone was used to convert a northern hardwood forest to a red pine plantation in Baraga County, Michigan (Neary, Michael, and Wells 1985). The concentrations of hexazinone in the soil solution at 1 meter depth are shown in Figure 4. Hexazinone concentrations moved quickly through the soil and reached a peak at 1 meter in less than one month after application. Additionally, when compared to other more water soluble compounds (2,4-D and picloram), hexazinone takes about one month longer to return to nondetectable levels (Neary, Michael, and Wells 1985). This study seems to indicate that with a higher water solubility,

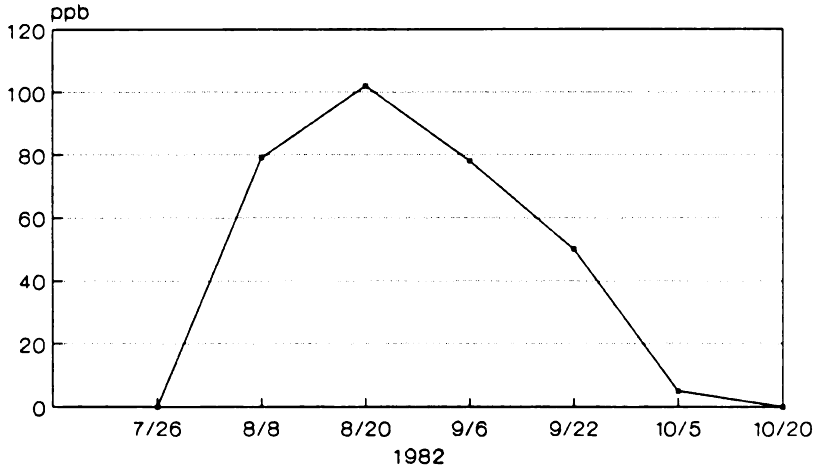


Figure 4. Hexazinone in soil solution at 1 m in Baraga County MI (Adapted from Neary, Michael, and Wells, 1985).

a compound will reach nondetectable levels faster. This decrease in hexazinone concentrations then can be attributed not only to degradation but also to leaching of the compound. Other studies have shown that the dissipation rate of hexazinone in the top 10 cm of soil was greater than could be accounted for solely by degradation (Bouchard, Lavy, and Lawson 1985). Further, in Georgia, subsurface movement of hexazinone on a small watershed was evident with concentrations as high as 23 ppb measured in a first order perennial stream (Neary, Bush, and Douglass 1983). These studies clearly illustrate that hexazinone is mobile in soil with sandy soils particularly vulnerable to hexazinone movement.

The movement of hexazinone through the soil is not so much a function of the compound's lack of degradability. On the contrary, Rhodes (1980) found that the time for 50 percent loss of ^{14}C residues of hexazinone is 3 to 12 months depending on the soil type. The major routes of degradation involve demethylation and hydroxylation of the 4 position of the cyclohexyl ring. Adding hexazinone to soils at a rate of 10 ppm did not significantly reduce the distribution of soil populations of fungi and bacteria in agricultural soils (Rhodes, Krause, and Williams 1979). In fact, the population of fungi and bacteria was slightly higher than the control at 2 and 4 weeks respectively, after application. Since hexazinone does not greatly affect microbial populations, the potential for degradation in soil is great. However, as hexazinone leaches deeper into the soil, oxygen becomes limited and microbes are less likely to degrade the compound.

Photodegradation is another process that contributes to the breakdown of hexazinone. The process can degrade up to 60 percent of the hexazinone in 6 weeks under ideal conditions (Herbicide Handbook 1983). Once the compound is activated by precipitation and moves into the soil surface, photodegradation is virtually nonexistent.

PESTICIDE CONTAMINATION OF GROUNDWATER

Since 1979, when aldicarb was first detected in 96 wells on Long Island and DBCP was detected in 2000 wells in California (1979-1982), the list of states reporting pesticide contamination of groundwater has continued to grow. In fact, 74 pesticides have now been found in wells in 38 states (U.S. EPA 1988b). In Michigan, for instance, atrazine and simazine have been found in the groundwater according to the November, 1988 EPA report.

According to the EPA (1988b), hexazinone has been found in wells in two states--Hawaii and Maine. Subsequently, a pilot groundwater monitoring program was conducted by the Michigan Department of Agriculture in 1989. The intent of the project was to assess the potential groundwater contamination problems across the state by examining high risk areas. Fifty high risk sites were located in the lower peninsula of Michigan based on the extent of pesticide use, the soil type, and the depth to groundwater. In nine of the 50 wells, hexazinone (2.5 ppb), atrazine (0.5-23.0 ppb), metolachlor 4.0 ppb), dicamba (15.0 ppb), and propazine (0.5 ppb) were detected (Olsen 1989). Based on the fact that triazine herbicides such as hexazinone, atrazine, and propazine were found in a study of such limited scope, hexazinone is a likely contaminant in other areas also.

Many individual, localized groundwater monitoring studies have been conducted across the country, but these studies have often been designed for very specific purposes. For instance, the hexazinone study described in this thesis is just that, a study to determine contamination by hexazinone alone. Should other contaminants be present, they will not be detected. In response to this, the EPA has published a 1988 Interim report compiling the results of this vast array of individual studies that have been conducted. While the report is by no means exhaustive, it provides a data base and in conjunction with the National Pesticide Survey, should prove useful in defining groundwater contamination problems.

Since groundwater contamination has only been a public issue in the 1980's (the problem itself dates back several decades), the problem has not been totally identified nor is it thoroughly understood (Cheremisinoff, Gigliello, and O'Neill 1984). However, groundwater contamination is a direct result of the vulnerability of the water table to quantifiable leaching losses.

The vulnerability of groundwater can be assessed by considering the depth to the groundwater, the amount of clay, and the amount of organic matter above the water table. The depth to groundwater is obviously a physical distance barrier that allows the chemical to filter through the soil before reaching the groundwater. The deeper the groundwater, the less chance for contamination and the greater the chance for degradation and/or sorption. The amount of clay and organic matter should be high to promote sorption of the pesticide. Triazine herbicides such as hexazinone have been shown to sorb to the mineral and organic matter fractions of soil to a certain extent (Weber, Weed, and Ward 1969; Gilmore and Coleman 1971; Carringer, Weber, and Monaco 1975; Hermosin et al. 1982; and Wehtje et al. 1984). However, over-application of pesticides, precipitation, or any number of factors can adversely affect pesticide sorption and cause leaching.

The EPA has stated that hexazinone potential to contaminate groundwater is a concern:

> Hexazinone belongs to the triazine family of pesticides. Some of these pesticides have been found in groundwater. Because hexazinone has been identified as being persistent in water and mobile in soils, there is concern for groundwater contamination. Data are required to address this concern (U.S. EPA 1988a).

The EPA (1988b) has reported that two states detected hexazinone at a maximum concentration of 9 ppb and a median concentration of 8 ppb. While these concentrations are well below the 210 ppb health advisory level, hexazinone's high water solubility promotes leaching of the herbicide into lower soil horizons and eventually the groundwater. Additionally, red pine sites frequently have high water tables and sandy soils with large amounts of organic matter in the upper horizons that decrease with depth. Therefore, especially in these instances, hexazinone has the potential to leach into the groundwater.

CHAPTER III

STUDY SITE CHARACTERIZATION

While labeled for use in red pine plantations, the effects of field applied hexazinone have not yet been studied in a comprehensive manner. Therefore, the main objective of this study is to examine the groundwater contamination potential of hexazinone in relation to its efficacy. In this way, the environmental costs of releasing red pine can be weighed against the benefits. Two similar sites were chosen so that control treatments in the efficacy study would not unduly affect the results of the groundwater contamination study. Thus, the Cedarville site was established for the efficacy study and the Stutts Creek site for the groundwater contamination study.

To be able to compare soil characteristics at both sites, the soils were sampled in 10 cm increments to a depth of 40 cm. Mechanical analysis was completed using the hydrometer method developed by Bouyoucos (1927). The other soil characteristics were determined at the Michigan State University soils laboratory with procedures published by the North Dakota Agricultural Experiment Station, 1988. The percent organic matter was determined using a modified Walkley-Black method involving the heat of dilution since this test gives the least variability among samples. Since determination of actual cation exchange capacity (CEC) is time consuming, an acceptable estimate was determined by the summation of exchangable potassium, calcium, magnesium, and neutralizable acidity. The procedure for determining pH was described by McLean (1982) and involves a potentiometrically determined pH in a slurry system using an electronic pH meter.

CEDARVILLE SITE

LOCATION AND SOILS

The efficacy study was established about 5 km north of Lake Huron and 10 km northwest of Cedarville, Michigan in Mackinac County as shown in Figure 5. The site occupies 2.02 ha and is located on a south facing toe slope. While not yet mapped by the Soil Conservation Service, the mineral soil is primarily structureless sand containing three distinct horizons below a thin forest floor layer. The A horizon averages 8 cm thick and is a very dark gray (10 YR 3/1). The E horizon is 15 cm thick and is a gray color (10 YR 6/1). The B horizon is a yellowish brown (10 YR 5/8) that extends to the parent material which is of glacial outwash origin. A water table exists at roughly 4.5 meters below the surface.

The soil characteristics at the Cedarville site are summarized in Table 4. The pH of the soil becomes slightly more alkaline with depth. However, the overall pH is

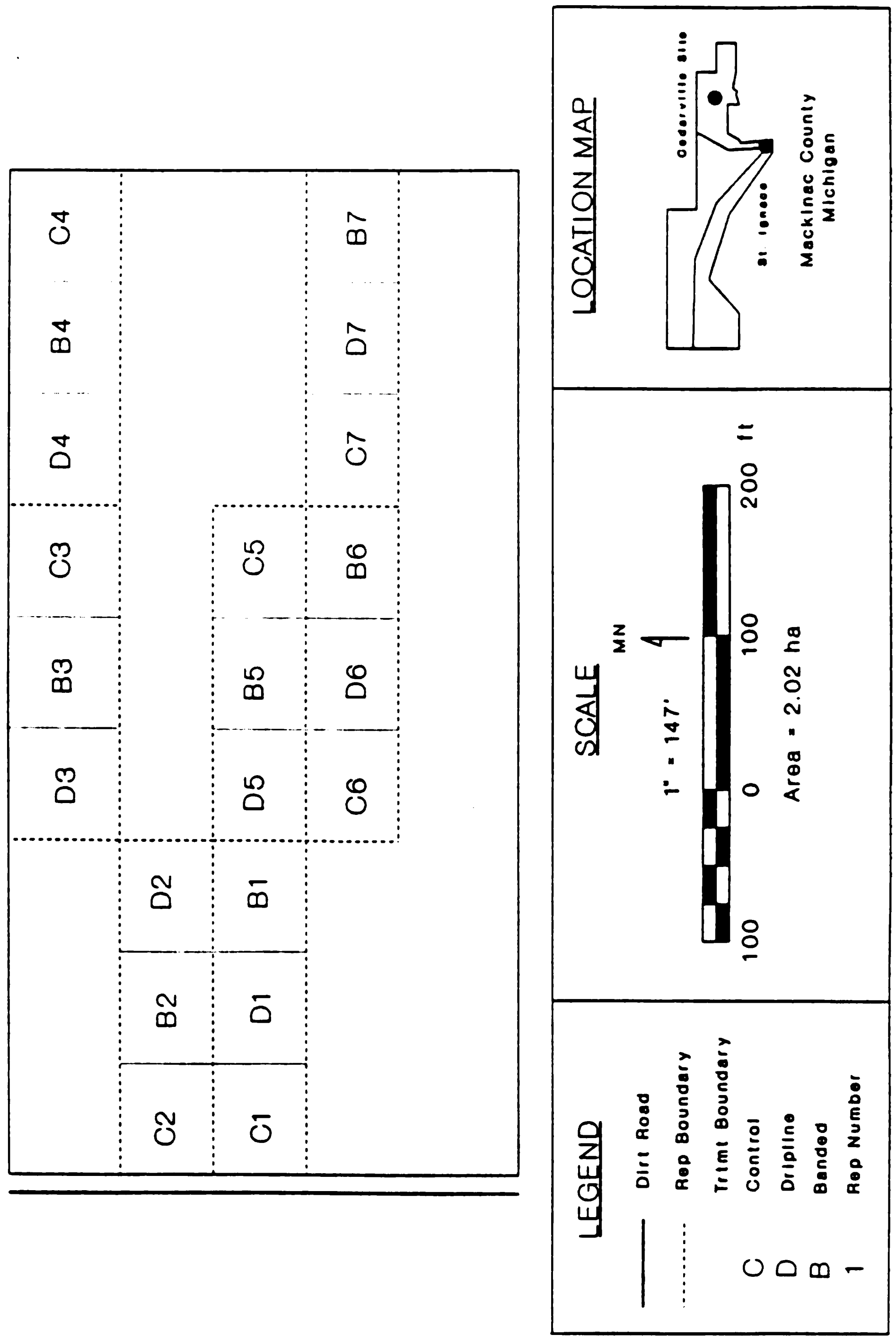


Figure 5. Base map for the Cedarville site. Mackinac County, Michigan

Table 4. Soil characteristics at the Cedarville site.

	Texture	% Organic Matter	pH	CEC (meq)
0-10	Sand	3.6	4.6	3.9
10-20	Sand	1.1	4.7	1.7
20-30	Sand	1.7	5.0	3.5
30-40	Sand	1.2	5.2	2.6

moderately acidic at 4.85. The percent organic matter decreases with depth from a maximum of 3.6 percent in the 0-10 cm layer to 1.22 percent in the 30-40 cm layer. The cation exchange capacity is low due to the sandy textures, averaging 2.9 meq.

VEGETATION

The native vegetation on the site before the clearcut was a pine stand (jack, red, and white) with some northern hardwoods. Surrounding the clearcut are extensive stands of northern hardwoods that had begun to colonize the clearcut prior to the Velpar L application. The clearcut was established in 1986 with the red pine planted during that spring. However, no Velpar L application was made at that time. A complete list of the site's vegetation is listed in Table 5 but the main competition was quaking aspen, red maple, and bracken fern.

Table 5. Species found on the Cedarville and Stutts Creek sites before Velpar L application (Spring, 1988).

Scientific Name	Common Name	Location
Acer rubrum	Red maple	C,S
Aridia spp.		C
Bromus tectorum	Downy Brome	C
Carex spp.	Sedge	C,S
Cladina rangiferina	Reindeer moss	S
Cornus Canadensis	Bunchberry	C
Diervilla Lonicera	Bush honeysuckle	C,S
Epigaea repens	Trailing arbutus	S
Fagaria vesca	Wood strawberry	S
Gaultheria procumbens	Wintergreen	C
Hieracum aurantiacum	Orange hawkweed	C,S
Hypericum spathulatum	Shrubby St. Johnswort	S
Lycopodium obsurum	Creeping Jenny	C
Picea spp.	Spruce	S
Pinus banksiana	Jack pine	S
Pinus resinosa	Red pine	C,S
Pinus strobus	White pine	C,S
Polyctrichum spp.	Moss	S
Populus tremuloides	Quaking aspen	C,S
Prunus serotina	Black cherry	C
Pteridium aquilinum	Bracken	C,S
Quercus rubrum	Northern red oak	C
Rubus spp.	Brambles	C,S
Rumex acetosella	Red sorrel	C,S
Salix discolor	Pussy willow	S
Solidago altissima	Tall goldenrod	S
Sonchus oleraceus	Annual sowthistle	S
Vaccinium angustifolium	Late low-bush blueberry	C
Vaccinium mertiloides	Velvetleaf blueberry	C

C = Cedarville site; S = Stutts Creek site.

CLIMATE

The climate in the area is moderated by the effects of the Great Lakes and has been described as quasimarine and essentially marine (National Oceanic and Atmospheric Administration 1985; Ruffner and Bair 1985). The growing season ranges from 98 to 170 days and the mean annual temperature is 4.3°C. The mean annual maximum temperature is 9.4°C and mean annual minimum is -0.8°C. The mean total yearly precipitation is 85.04 cm with 374.09 cm of snow cover. Permanent snow cover generally begins on November 21st and melts around April 7th.

STUTTS CREEK SITE

LOCATION AND SOILS

The Stutts Creek site is a 4.15 ha clearcut located 17 km north of Lake Michigan in Schoolcraft County, Michigan as shown in Figure 6. The site has negligible slope except for the presence of small mounds and knolls of sand that give much of the land a hummocky appearance. The only available soil survey was completed in 1939 by the U.S. Department of Agriculture and has not been updated since. The soil series is a Saugatuck sand containing poorly drained sandy soils with low fertility. These soils occur on flat sandy plains and have a dark coffee brown cemented sand layer that is known today as an ortstein layer (U.S. Department of Agriculture 1939). The soils here are quite similar to the

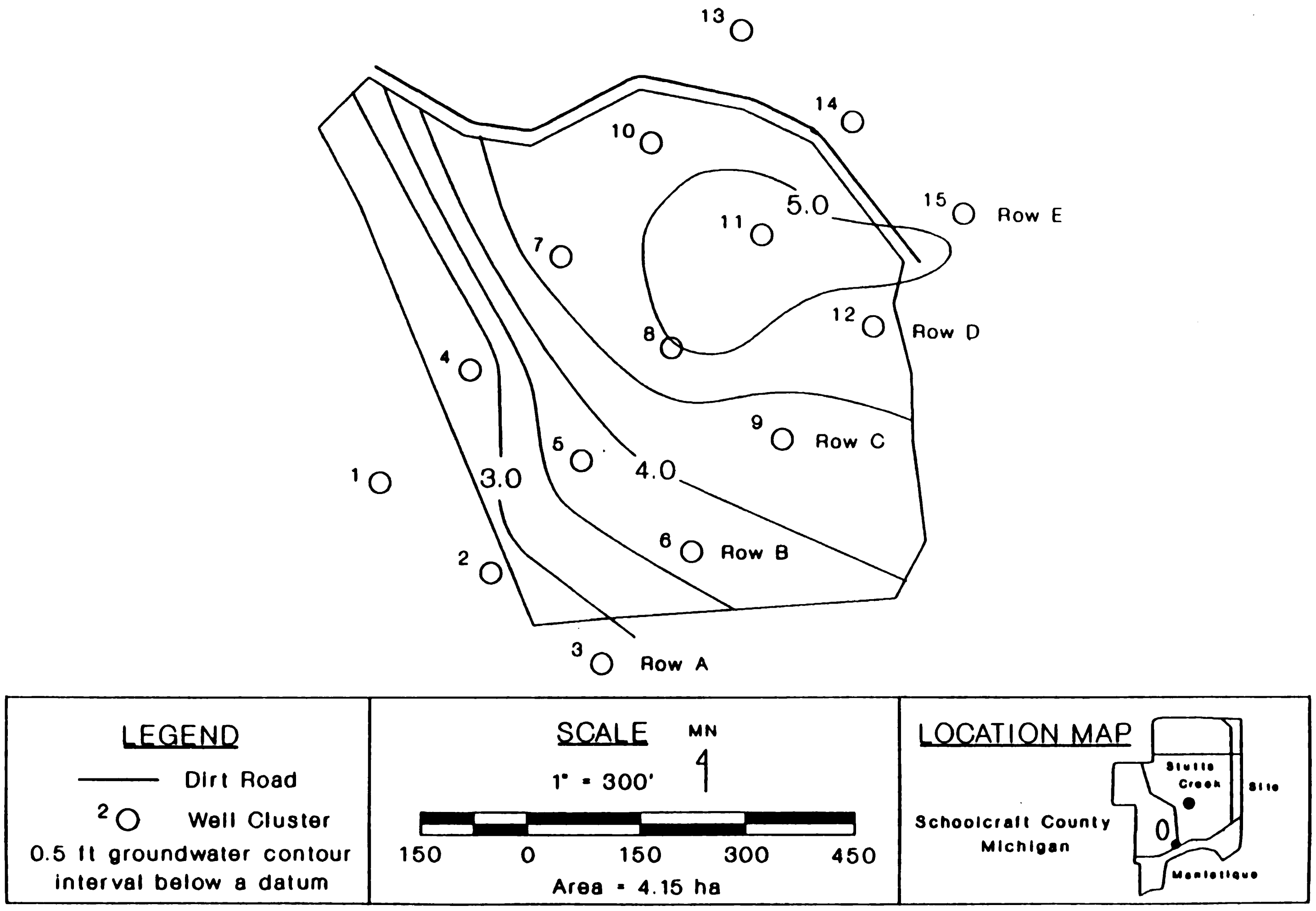


Figure 6. Base Map for Stutts Creek Site.
Schoolcraft County, Michigan

soils at the Cedarville site, except for the influence of a high water table. Below a thin forest floor layer, less than 2 cm thick, lie sandy structureless A, E, and Bs layers. The A horizon averages 10 cm in thickness and has a black color (7.5 YR 2/0). The E horizon is 17 cm thick and has a pinkish gray color (7.5 YR 7/2). The B horizon extends to the parent material which is of glacial outwash origin.

The soils data for the Stutts Creek site are summarized in Table 6 and are similar to the Cedarville site. The soil becomes more alkaline with depth, ranging from a pH of 4.5 in the 0-10 cm layer to a pH of 5.4 in the 30-40 cm layer. As would be expected, percent organic matter decreases with depth but is low throughout the soil with an average of 1.13 percent. The CEC is likewise low at an average of 2.3 meq.

Table 6. Soil characteristics at the Stutts Creek site.

	Texture	% Organic Matter	pH	CEC (meq)
0-10	Sand	1.9	4.7	2.6
10-20	Sand	1.2	4.9	1.9
20-30	Sand	0.7	5.3	2.1
30-40	Sand	0.7	5.4	2.6

GROUNDWATER CHARACTERISTICS

The water table on a typical Saugatuck sand ranges from several centimeters to 1 meter deep which leads to standing water on the site in the spring (U.S. Department of Agriculture 1939). In the spring of 1988, estimated high water tables ranged from 0.64 meters to 2.04 meters below the surface as shown in Table B1. In the spring of 1989 after significant amounts of groundwater recharge, the water tables were roughly 0.30 meters higher than the estimated high water tables in the spring of 1988. The differences in pressure head potential cause the groundwater to flow from the southwest to the northeast end of the site as shown in Figure 6.

VEGETATION

The site is a typical clearcut with a minimal amount of low lying slash. In addition to several 3 to 6 inch diameter at breast height (DBH) red pines left standing, the site has small amounts of naturally regenerated red pine, spruce, jack pine, and white pine. The vegetational composition of the Stutts Creek site is summarized in Table 5. While the species composition of the site is similar to that on the Cedarville site, the distribution is much more intermittent and spotty.

CLIMATE

The climate at the Stutts Creek site is quite similar to the Cedarville site. However, since the Stutts Creek site is located further inland, the temperature and precipitation are not moderated quite as much by the Great Lakes. Mean annual temperature is 4.8°C with a mean annual maximum of 10.1°C and a mean annual minimum of -0.4°C. Annual precipitation amounts to 83.7 cm with an annual snowfall of 268.7 cm (National Oceanic and Atmospheric Administration 1985; Ruffner and Bair 1985).

Climatic data collected during the study is shown in Figure 7. The data was collected at Seney National Wildlife Refuge, which is adjacent to the Stutts Creek site. The summer of 1988 was a period of major drought in the

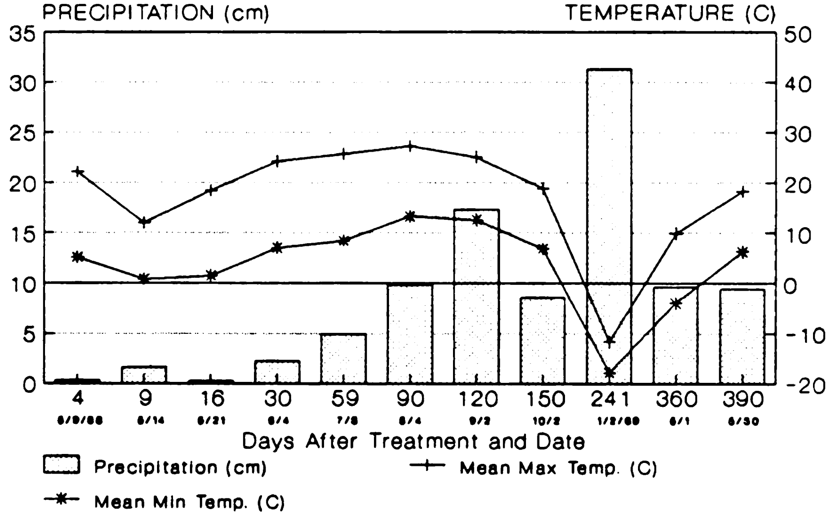


Figure 7. Climatic data for the Stutts Creek Site.

Midwest corn belt with the Upper Peninsula feeling only minor effects. Temperature was about 5 degrees higher than normal and precipitation was nearly average for 1988.

CHAPTER IV

VELPAR L EFFICACY STUDY

STUDY DESIGN AND SAMPLE COLLECTION

The efficacy study consisting of seven replications of three treatments--a dripline application, a banded application, and a control as shown in Figure 5--was established in the spring of 1988. The banded application involved applying Velpar L to both sides of the tree row with a backpack sprayer at roughly three feet above the ground. This method took advantage of both the foliar and residual properties of hexazinone. The dripline application involved applying Velpar L directly into the tree row at the ground level. Therefore, only the residual properties of hexazinone were utilized. The control was left untreated.

The treatments were established in plots of three rows by six tree positions with two row buffer strips on every side of the application. This amounts to roughly a 30 by 21 meter plot encompassing 0.4 ha per treatment and containing 18 planting positions. In the banded areas, 5.3 liters of Velpar L was applied amounting to 13.2 liters per ha (3.2 kg active ingredient per ha). In the dripline areas, 9.8 liters were applied, amounting to 24.6 liters per ha (5.9 kg acitve ingredient per ha).

The red pine was planted in the spring of 1986 by a mechanical tree planter two years prior to study initiation. A John Deere 740 skidder with a V plow attached to the front scarified the soil and chopped the roots of sprouts along the tree line. A tree planter pulled behind the skidder planted the red pine and packed the soil in the tree row. Because the trees were planted two years earlier and tree planting is not an exact science, some red pine had succumbed to mortality and others had simply not been planted. Therefore, the number of red pine measured within treatment plots was not equal and ranged from 3 to 15 seedlings.

Within the 21 treatment plots, (potentially 378 total red pine) seedlings were recorded as present, missing, or dead; survival was then calculated based on the initial living trees representing 100 percent stocking. The height and groundline diameter of the live seedlings were measured. In addition, number of sprouts, percent sprout cover, percent broadleaf cover, and percent grass cover were recorded within a 0.5 meter diameter circle around each tree. Sprouts include any woody plant (aspen, maple, etc.) while broadleaves include any non-woody plant (bracken, blueberry, etc.) excluding grasses that competes for the red pine's resources. The percent weed cover was estimated at 0, 10, 30, 50, 70, or 90 percent. Initial measurements were taken during the spring of 1988. Subsequent measurements occurred after the first growing season in the fall of 1988 and after the second growing season in the fall of 1989.

STATISTICAL ANALYSIS

The statistical analysis on the results was completed using the Statistical Analysis System (SAS). The efficacy study was established as a randomized complete block design with three treatments, seven replications, and potentially 18 tree subsamples. Since the initial heights and groundline diameters of the seedlings in each treatment were not significantly different, growth over each growing season was able to be used without the initial measurements influencing the data. The treatment plot averages from the growth data were then used because of unequal numbers of seedlings measured. Therefore, this established a straightforward randomized complete block analysis of variance with 3 treatments and 7 replications. The workable data is shown in Tables A1 to A9.

The variances for survival, height, diameter, and percent broadleaf cover were found to be homogeneous according to the F_{max}-test. Since they were homogeneous by a wide margin, Bartlett's test of homogeneity was not used to confirm the results. The variances for percent sprout cover and percent grass cover were borderline over the second growing season due to outlying values. Without the outlying values, the variances were homogeneous and no further tests or data transformations were performed (Steel and Torrie 1980).

Tukey's multiple range test was used at a significance level of 0.10 to determine differences in treatment effects. This test was chosen since it makes Type II error (as opposed to Type I error) which tends to accept the null hypothesis when it is in fact false. The Tukey test is generally used in instances where the results will not make a critical impact on society and Type II error is therefore more acceptable than Type I error. A significance level of 0.10 was chosen since it has been used in previous studies for testing differences in relatively variable ecosystem measurements (Steel and Torrie 1980).

RESULTS AND DISCUSSION

The results of the study proved to be similar to the results of the studies cited previously. Weed competition was significantly reduced with applications of Velpar L over the 1988, 1989, and both growing seasons compared to the control as shown in Tables 7, 8, and 9. Change in total

Table 7. Average change in percent sprout cover, percent broadleaf cover, and percent grass cover over the 1988 growing season.

	Sprout Cover (%)	Broadleaf Cover (%)	Grass Cover (%)
Dripline	-22.6 A	-17.0 A	-1.0 A
Banded	-25.4 A	-15.0 A	-3.5 A
Control	-2.6 B	20.7 B	3.4 B

Means followed by the same letter in the same column are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

Table 8. Average change in percent sprout cover, percent broadleaf cover, and percent grass cover over the 1989 growing season.

	Sprout Cover (%)	Broadleaf Cover (%)	Grass Cover (%)
Dripline	0.9 A	10.4 A	3.8 A
Banded	1.7 A	6.1 A	0.1 A
Control	9.4 A	9.6 A	3.2 A

Means followed by the same letter in the same column are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

Table 9. Average change in percent sprout cover, percent broadleaf cover, and percent grass cover over the 1988 and 1989 growing seasons.

	Sprout Cover (%)	Broadleaf Cover (%)	Grass Cover (%)
Dripline	-21.0 A	-8.4 A	2.6 AB
Banded	-23.2 A	-9.3 A	-3.3 B
Control	7.0 B	28.7 B	6.4 A

Means followed by the same letter in the same column are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

weed cover is illustrated in Figure 8. Notice, however, that between the dripline and banded application no significant differences were measured in any of the weed populations. Apparently, the residual properties of hexazinone are strong enough to overcome the lack of contact activity in the dripline application.

One measure of weed cover, number of live sprouts in the 0.5 meter diameter circle around each tree, did not

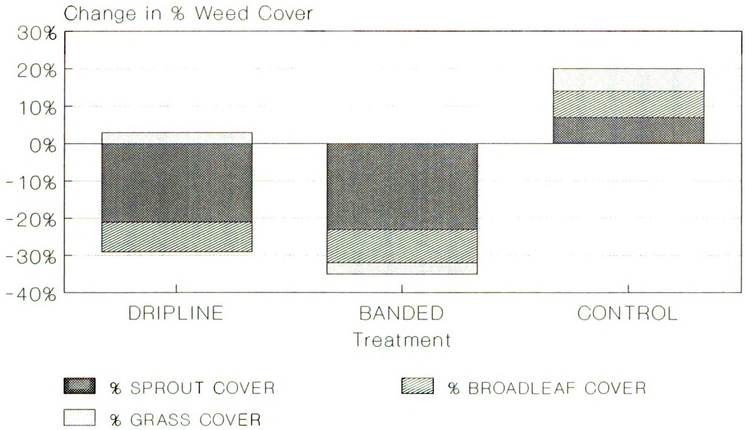


Figure 8. Average change in percent weed cover by treatment over two growing seasons at the Stutts Creek site.

prove to be a useful number. While densely populating the site, the sprouts were not so close together that large numbers of them were found growing inside the circle. This is due primarily to the fact that the V plow used in scarifying the soil essentially broke the sprouts' roots along the tree row. Additionally, sprouts outside the circle influenced red pine growth as much as the few sprouts found growing inside the circle. Average percent weed cover was therefore a better measure of the competition faced by the red pine seedlings on the Cedarville site.

In response to the approximately 30 percent decrease in weed cover, over the 1988 growing season, 1989 growing season, and both growing seasons, height growth was not significantly different from the control as shown in Figure 9. Limited height growth response after only two years of release has been documented in many studies (Dimock, Beebe, and Collard 1983; D'Anieri 1985; Michael 1985; U.S. Department of Agriculture 1987). However, after 4 or more years of growth, trees that have been released tend to show a significant height growth mainly because unreleased trees remain overtopped by weedy species that utilize the light, nutrient, and water resources (Dimock, Beebe, and Collard 1983). On a richer, more productive site, height growth likely would have far surpassed that measured on the Cedarville site; this trend has been shown in other studies by Michael (1985).

Note the tendency of greater height growth by the red

Figure 9. Average height growth by treatment at the Cedarville site. Means of adjacent bars with the same letter are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

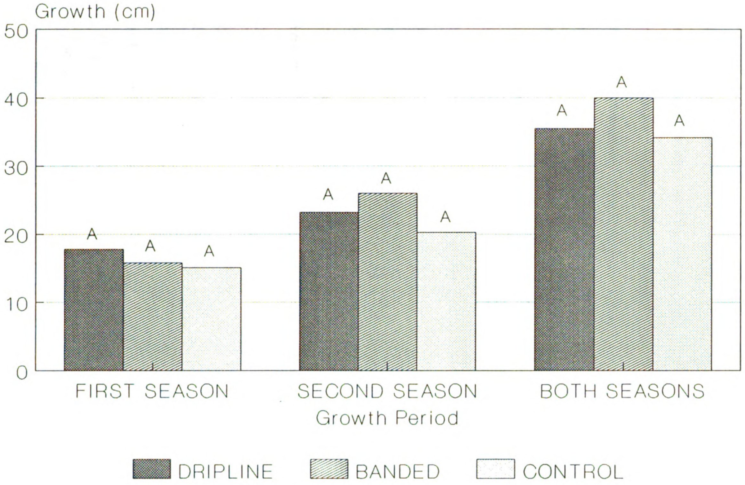

Growth (cm)
50
40
30
20
10
0
A
A
A
A
A
A
A
A
A
FIRST SEASON
SECOND SEASON
BOTH SEASONS
Growth Period
DRIPLINE
BANDED
CONTROL

Figure 9.

pine in the banded application versus both the dripline application and the control. While the difference was not significant, height growth should continue to respond to the release treatments and maintain a growth advantage over the long term. These long term benefits have been shown in studies by Wittenkamp and Wilde (1964), Wilde, Shaw, and Fedkenheuer (1968) and Stone (1976). The banded application is more effective since it takes advantage of both the contact and residual properties of Velpar L while the dripline application utilizes only the residual properties. In addition, the dripline application used almost twice as much Velpar L as the banded areas, 9.8 liters to 5.3 liters, which effectively increased the cost for a potentially less effective treatment.

Groundline diameter growth over each growing season was significantly larger than the control as shown in Figure 10. Since groundline diameter growth is a density dependent variable, the decrease in weed cover was expressed much more effectively in this measurement than in height growth. After the 1989 growing season, the banded and dripline treatments had groundline diameters of 0.32 cm and 0.22 cm larger than the control, respectively. This larger groundline diameter will result in more volume in a sturdier, healthier adult tree.

Over both growing seasons, the groundline diameter of the red pine in the banded application was significantly greater than the control but the dripline treatment was not.

Figure 10. Average groundline diameter growth by treatment at the Cedarville site. Means of adjacent bars with the same letter are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

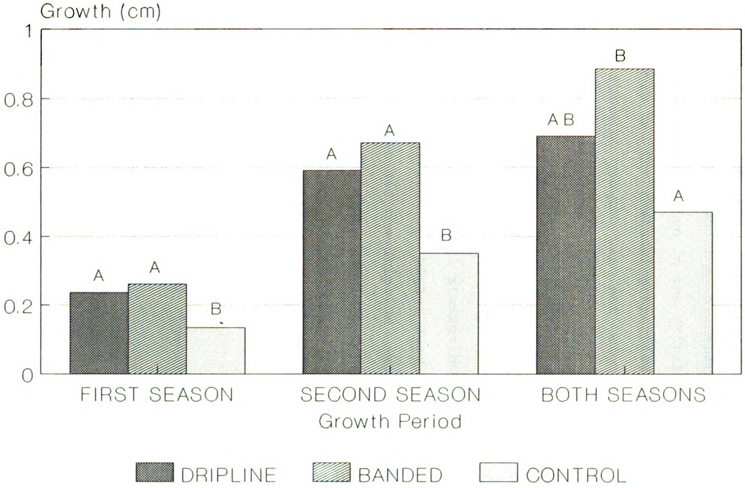

Growth (cm)
1
0.8
0.6
0.4
0.2
0
A
A
B
A
A
B
A B
B
A
FIRST SEASON
SECOND SEASON
BOTH SEASONS
Growth Period
DRIPLINE
BANDED
CONTROL

Figure 10.

By taking advantage of the contact and residual properties of hexazinone, the banded application contributed to significantly greater groundline diameter growth over 2 years. The weed competition in the dripline application was sensitive only to the residual properties of hexazinone and groundline diameter growth was not significantly greater over both growing seasons.

Survival for all the treatments was excellent, approaching 100 percent. Due to the low variability of the survival data, any small change will be registered as significant from a statistical standpoint. Therefore, the control had a significantly higher survival rate over both growing seasons than did the dripline application as shown in Table 10. However, since survival rates were more than acceptable (greater than 93 percent) for all treatments, Velpar L did not effectively inhibit survival. In fact, a few seedlings presumed dead sprouted and survival actually increased.

Table 10. Percent survival over the 1988, 1989, and both growing seasons.

Treatment	1988 Season	1989 Season	Both Seasons
Dripline	95 a	97 a	93 a
Banded	100+ a	95 a	98 ab
Control	100 a	100+ a	100 b

Means followed by the same letter in the same column are not significantly different at the 0.10 significance level according to Tukey's Multiple Range Test.

Though damage by factors not related to Velpar application was not quantitatively measured, an interesting trend seemed to be developing. Deer browse on red pine in the control plots was visually more extensive than on either of the treated plots. Most studies, as reported by Morrison and Meslow (1983), have found that preferred browse species can be increased if herbicide application is carefully planned, though the effects can be of short duration. In fact, the DNR has used Velpar to improve wildlife habitat in certain areas. However, Blake and Hurst (1983) reported findings in Mississippi where broadcast and banded hexazinone application areas had less deer forage than the control plots. Apparently, the amount of deer forage varies by type of herbicide used, application method, and forage type. In this study, the thick cover of aspen sprouts in the control plots provided good cover for the deer to bed down during the winter. In the spring, the new growth of the red pine in the control plots provided excellent forage for the deer. Hexazinone appears to indirectly decrease browsing by effectively reducing deer cover. This results in increased height growth, increased diameter growth, and maintains survival rates of the red pine seedlings.

CHAPTER V

HEXAZINONE MOVEMENT IN THE SOIL AND GROUNDWATER CONTAMINATION

STUDY DESIGN AND SAMPLE COLLECTION: HEXAZINONE MOVEMENT IN THE SOIL STUDY

On the Stutts Creek site, 42.8 liters (2.5 kg of active ingredient per ha) of Velpar L were applied to the soil on May 5, 1988 in a dripline along the tree row. Due to the difficult terrain, the Velpar was literally thrown to both sides of the tree row during application. Because of this, Velpar application was considered to be uniform across the site despite a definite concentration of hexazinone in and around the tree row. The assumption is that the herbicide is initially most effective nearest the tree row and will then move horizontally across the site.

To trace the movement of hexazinone through the soil, 12.2 by 16.5 meter plots (40 by 54 feet) were established around the nine well clusters on the Stutts Creek site. A random location was chosen along the 12.2 meter east border of the plot and a 16.5 meter transect was run across the plot. Along the transect, 12 randomly chosen soil cores were taken and combined by layer--forest floor, 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm. Information about each soil core was recorded including distance from the nearest tree row, surface condition, and horizon depths within each core.

Hexazinone concentrations in the soil prior to application were assumed to be zero. Subsequent soil samples were taken at 4, 9, 16, 30, 60, 90, 120, 150, 360, and 390 days after treatment (DAT) to trace hexazinone residues over time.

Field samples were placed in ziploc bags and labeled by well number, layer, and date. The samples were then transported to the laboratory, transferred to glass bottles, and stored in a freezer until the laboratory analysis could be completed. Laboratory analysis was completed using a high-performance liquid chromatography (HPLC) method developed by Bouchard and Lavy (1983). This HPLC method allows rapid analysis of large numbers of soil and water samples with the same or greater accuracy as other methods.

Twenty five grams of field moist soil were weighed and 25 ml of 20:80 acetone:water solution were added. The samples were then shaken in an Erlenmeyer flask for 30 minutes on a wrist action shaker. Because the forest floor layer absorbs the acetone:water, 50 ml of the solution were added to forest floor samples to achieve sufficient recoveries. The resultant slurries were then filtered through glass wool, washed once with 10 ml of the acetone:water mixture, and vacuum filtered through Whatman No. 42 filter paper. The filtrates were transferred to a separatory funnel and extracted twice with 25 ml of chloroform. The chloroform extracts were blown down to dryness and 5 ml of acetonitrile were added.

One hundred μl volumes of the acetonitrile mixture were injected into the HPLC. An ultraviolet detector was used at 254 nm, 0.1 range, and an attenuation of 64. The minimum detectable quantity was 0.01 ppm. However, since the soil samples had been concentrated from 25 g to 5 ml, the effective detectable quantity in the soil was 0.002 ppm. Figure D1 shows a typical chromatogram of hexazinone in a soil layer. Confirmation of hexazinone was made by comparing the mass spectra of a sample with the hexazinone standard. In recovery trials, 86.4 percent of the hexazinone residues could be extracted from the soil. The corrected data are shown in Table C1.

STATISTICAL ANALYSIS: HEXAZINONE MOVEMENT IN THE SOIL STUDY

The soil study was established as a split plot design with days after treatment as the whole plot in randomized complete blocks and soil layers as the split plot. The analysis includes 10 levels of the whole plot and 5 levels of the split plot replicated 9 times around the well clusters.

Heterogeneous variances within sample dates were found using Bartlett's test. This was mainly due to the large concentration differences between the forest floor and the lower soil layers. A logarithm and a square root transformation analysis of variance table was constructed along with the original data. The results were similar and the analysis of variance table using the original data was used (Steel and Torrie 1980).

Duncan's multiple range test was employed to determine the significance of concentration differences between layers and between days after treatment at a significance level of 0.05. As opposed to the Tukey test, Duncan's test is more conservative, tending to make Type I error and reject the null hypothesis when it is in fact true. The 0.05 significance level adds another level of conservatism to avoid wrongly testing the residues to be significantly different (Steel and Torrie 1980).

STUDY DESIGN AND SAMPLE COLLECTION: GROUNDWATER CONTAMINATION STUDY

The groundwater study was established by locating 15 well clusters on the Stutts Creek site (Figure 6) prior to Velpar L application. Well installation closely followed the procedure described by the U.S. Environmental Protection Agency (1988c). Each well cluster consists of three wells with a shallow well intercepting water in the top 1.5 meters of the aquifer, a medium well monitoring the 1.5 to 3.0 meter zone, and a deep well collecting water in the 3.0 to 4.5 meter zone. This setup is illustrated in Figure 11.

Initially, this cluster arrangement served two purposes: 1) to verify the vertical gradient of hexazinone and 2) to guard against significant changes in the water table. Unfortunately, the sandy nature of the aquifer did

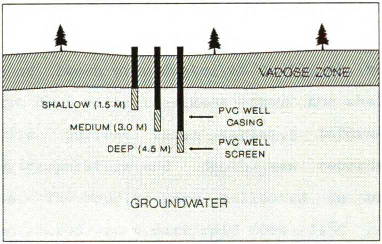


Figure 11. Well design at the Stutts Creek site.

not allow the medium and deep wells to be installed with well points. The pressure head potential of the aquifer caused the sand to refill the wells from the bottom. Consequently, collecting water from the medium and deep wells was not possible at all well clusters. Several of the medium wells were funtional and groundwater was retrieved from them when the water table had dropped below the shallow well. This drop in the water table did not occur uniformly across the site; therefore, only the medium wells at well clusters number 7, 10, and 11 were utilized, primarily in the late summer months.

The well clusters were arranged in grid fashion with three clusters in five rows perpendicular to the groundwater flow as shown in Figure 6. This arrangement allows careful tracking of hexazinone concentrations and possible build-up or off-site movement. Before sampling the groundwater, the stale water was removed from the well by bailing and fresh water was allowed to flow in. A baler was used to collect one gallon of fresh groundwater at 0, 30, 60, 90, 120, 150, 360, and 390 days after treatment from the shallowest well possible (i.e. current water table). Information about groundwater temperature and depth was recorded at each sample date. The samples were collected in brown gallon bottles and stored in a dark cold room (34°C to 38°C) to prevent degradation of the hexazinone. The groundwater extraction and analysis procedure developed by Bouchard and Lavy (1983) was used and is very similar to the soil analysis.

First, 900 ml of groundwater sample were measured and vacuum filtered through Whatman No. 42 filter paper. The filtrates were then transferred to separatory funnels and extracted twice with 25 ml of chloroform. The chloroform extracts were taken to dryness and 5 ml of acetonitrile were added. The HPLC was used with an ultraviolet detector at 254 nm and a minimum detectable quantity of 0.01 ppm. Since the groundwater samples had been concentrated from 900 ml to 5 ml, the effective detectable quantity was 0.06 ppb. Recovery trials showed the procedure to be 93.2 percent efficient. The corrected data are shown in Table C1. Figure D2 shows a typical chromatogram of hexazinone in the groundwater.

STATISTICAL ANALYSIS: GROUNDWATER CONTAMINATION STUDY

The groundwater study was statistically analyzed as a 5 by 7 factorial design replicated 3 times in randomized complete blocks. The factors included the well row as factor A, days after treatment as factor B, and each well cluster within the row as a replication.

Bartlett's test of homogeneity of variance was run on the groundwater data. Since large numbers of non-detectable levels of hexazinone confounded the test, Bartlett's test was completed without these zero values and heterogeneous variances were detected. An analysis of variance table was run using the original data, a logarithm transformation, and a square root transformation. The results were nearly identical and therefore, the analysis of variance using the original data was used (Steel and Torrie 1980).

As with the soil samples, Duncan's multiple range test was used to minimize Type II error. A significance level of 0.05 was used to conservatively measure concentration differences between rows and sample dates (Steel and Torrie 1980).

RESULTS AND DISCUSSION

The highest concentrations of hexazinone in the soil were detected at 9 days after treatment. At 4 days after treatment, virtually no precipitation had fallen to force the hexazinone into the forest floor and mineral soil layers. However, sufficient amounts of precipitation fell (1.6 cm) between May 9 (4 DAT) and May 14, 1988 (9 DAT) to move the hexazinone into the upper soil layers and activate it. Using the maximum concentration of hexazinone at 9 days after treatment, its half-life in the top 40 cm of soil was less than two months.

One trend that is clear is the ability of the organic matter to sorb hexazinone as shown in Figure 12a and 12b. At 9 days after treatment, a concentration of 1.066 ppm was detected in the forest floor with the amount slowly being dissipated over time. Looking at the deeper soil layers, hexazinone tends to move through the layers quickly with even small amounts of precipitation. Between June 4 (30 DAT) and July 3, 1988 (59 DAT), about 5 cm of precipitation fell and leached all but the smallest amounts from the 0-40 cm layers. However, larger amounts remained in the forest floor layer during this period. Some researchers, particularly Boyd and Chiou, consider organic matter to be almost solely responsible for the sorption of organic molecules. This is apparently true on the Stutts Creek site where there is a significant forest floor layer and minimal binding sites in the mineral horizons.

While the forest floor layer did tend to bind the hexazinone on the Stutts Creek site, there was a distinct lack of weed control on the site. Immediately after Velpar

Figure 12a. Hexazinone concentrations in the different soil layers from 4 to 59 days after treatment (DAT) at the Stutts Creek site. Means with the same letter at the same DAT are not significantly different at the 0.05 significance level according to Duncan's Multiple Range Test.

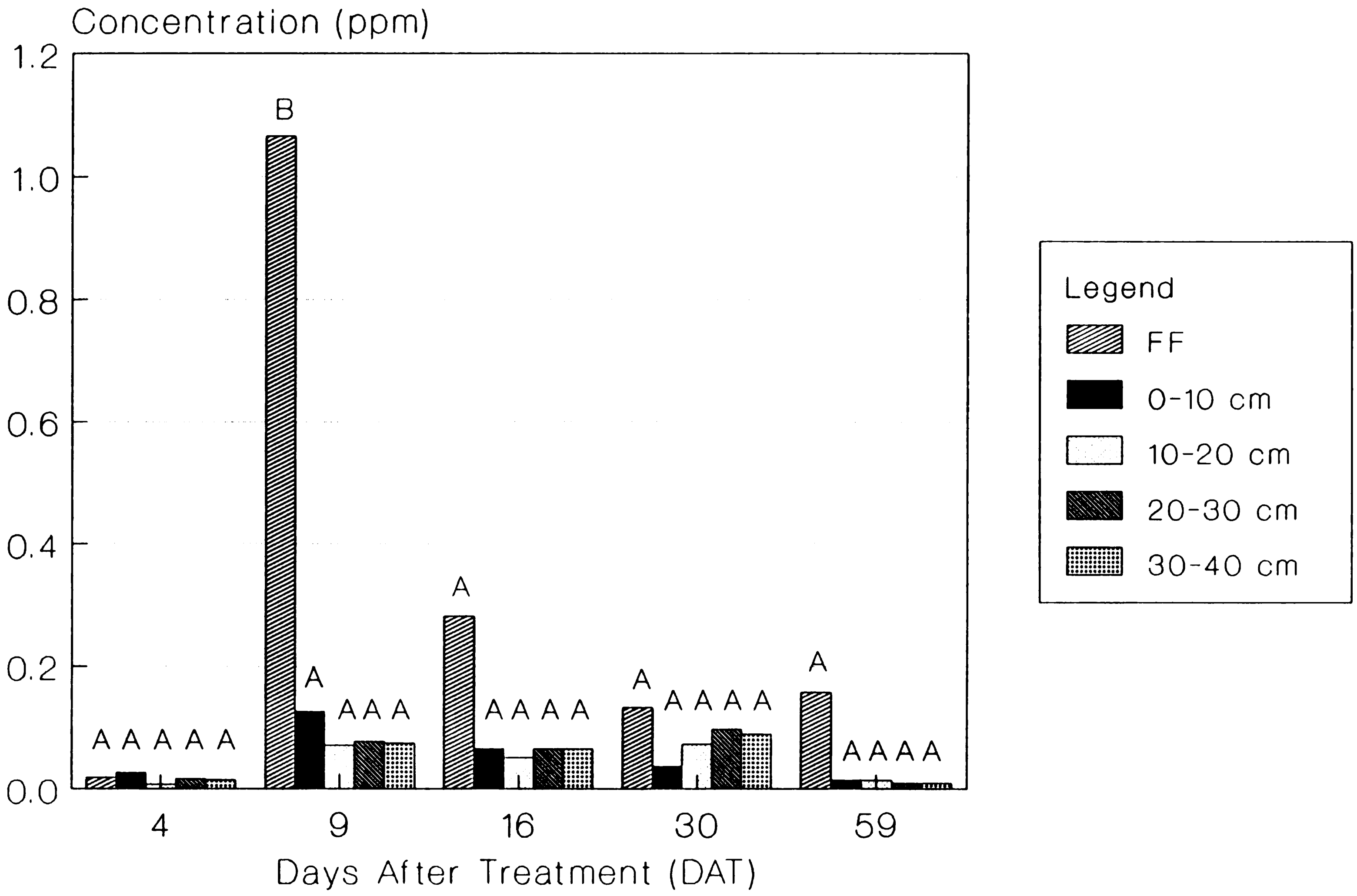

Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
B
A
A A A
A
A A A A
A A A A A
A
A A A A
A
A A A A
4
9
16
30
59
Days After Treatment (DAT)
Legend
▨ FF
■ 0-10 cm
□ 10-20 cm
▩ 20-30 cm
▦ 30-40 cm

Figure 12a.

Figure 12b. Hexazinone concentrations in the different soil layers from 91 to 390 days after treatment (DAT) at the Stutts Creek site. Means with the same letter at the same DAT are not significantly different at the 0.05 significance level according to Duncan's Multiple Range Test.

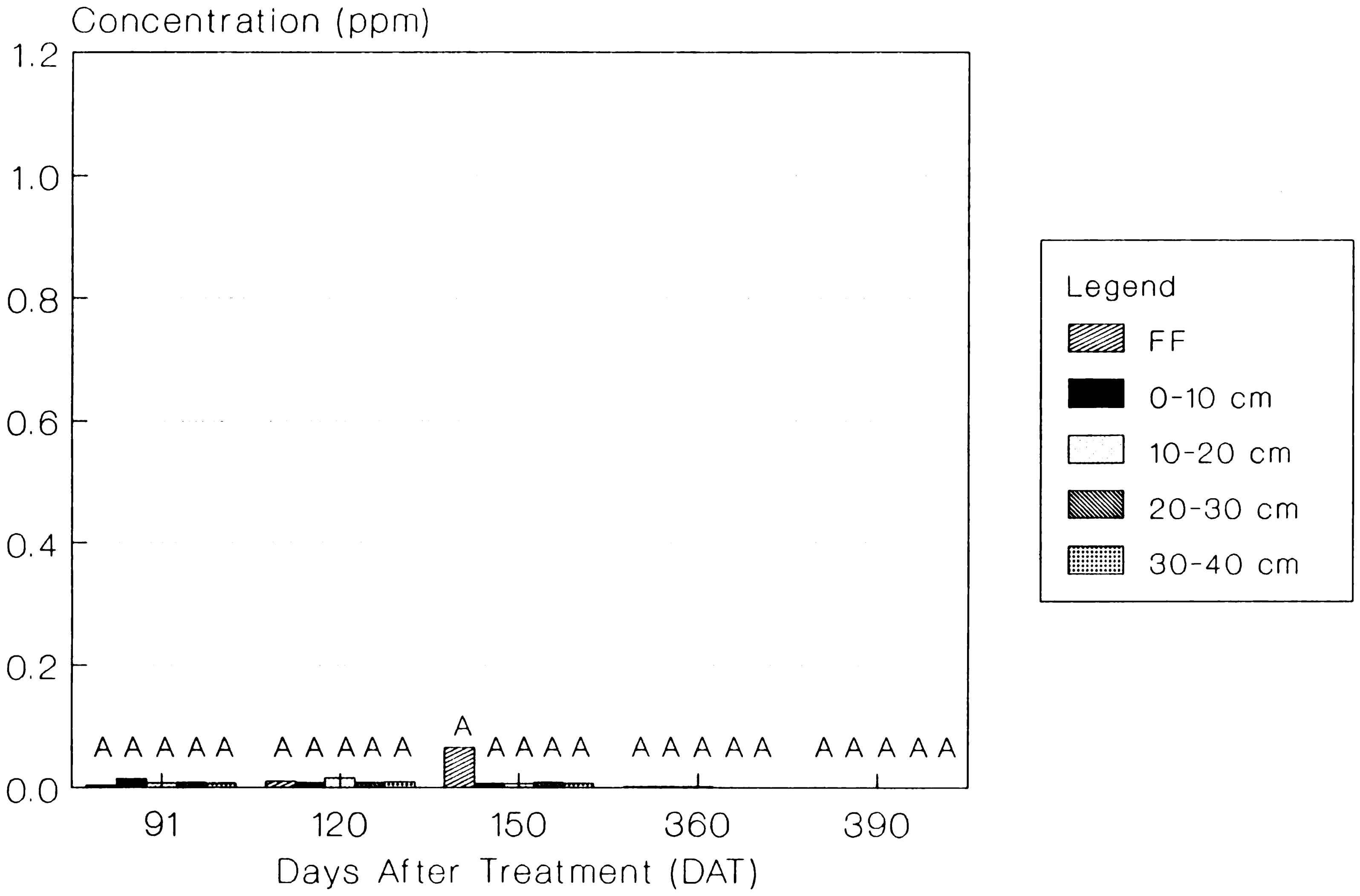

Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A A A A A
A A A A A
A
A A A A
A A A A A
A A A A A
91
120
150
360
390
Days After Treatment (DAT)
Legend
▨ FF
■ 0-10 cm
□ 10-20 cm
▧ 20-30 cm
▩ 30-40 cm

Figure 12b.

application, the populations of bracken and quaking aspen decreased and appeared to have died. However, over the course of the 1988 summer and into the next spring, the population of weeds rebounded and, at least visually, colonized the entire site. This seems to be a direct result of the rapid leaching of hexazinone through the soil. Only concentrations of less than 0.05 ppm remained in the upper mineral soil layers after just 59 days and residual control of weeds was lacking.

Precipitation, combined with hexazinone's high water solubility, is the driving force behind its leaching potential. Relatively little hexazinone had leached from the top 40 cm until significant rainfall had occurred during the first 59 days after treatment. As shown in Figure 13a and 13b, hexazinone was retained in the forest floor and 0-10 cm layer and released with increasing amounts of precipitation. In the 10-20 cm, 20-30 cm, and 30-40 cm segments, hexazinone concentrations decreased slightly at 16 days after treatment, apparently in response to a lack of rainfall. Due to a lack of rainfall, the hexazinone bound in the top layers failed to move into the underlying layers. The concentrations then rebounded at 30 days after treatment with about 3 cm of rainfall. A strong relationship between the amount and timing of precipitation and hexazinone movement through the soil exists. Small amounts of precipitation, less than 2 cm over the first month after application, are sufficient quantities to activate the

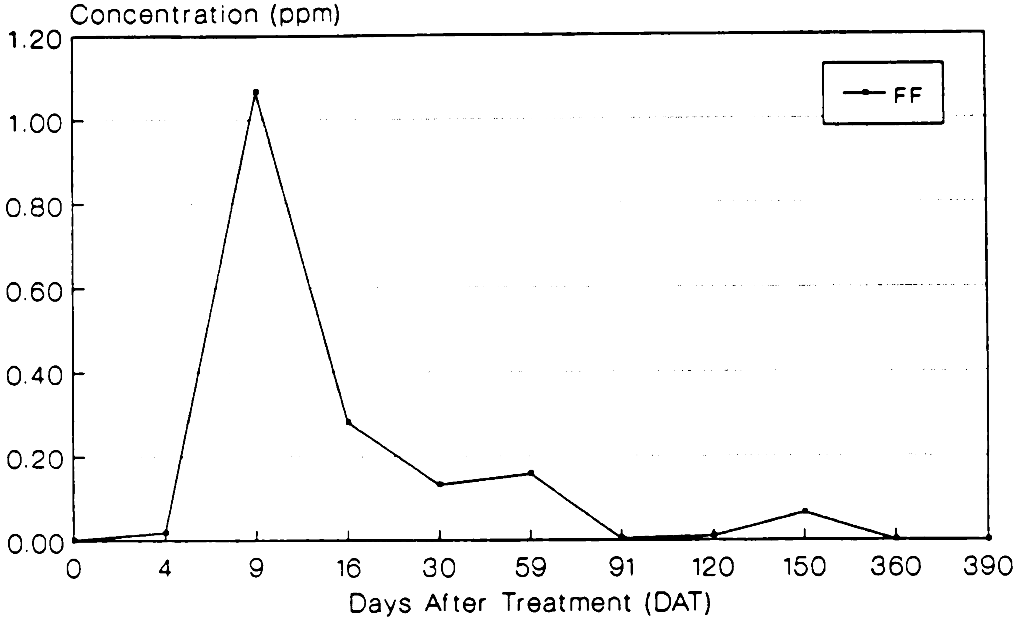


Figure 13a. Hexazinone concentrations in the forest floor layer over time.

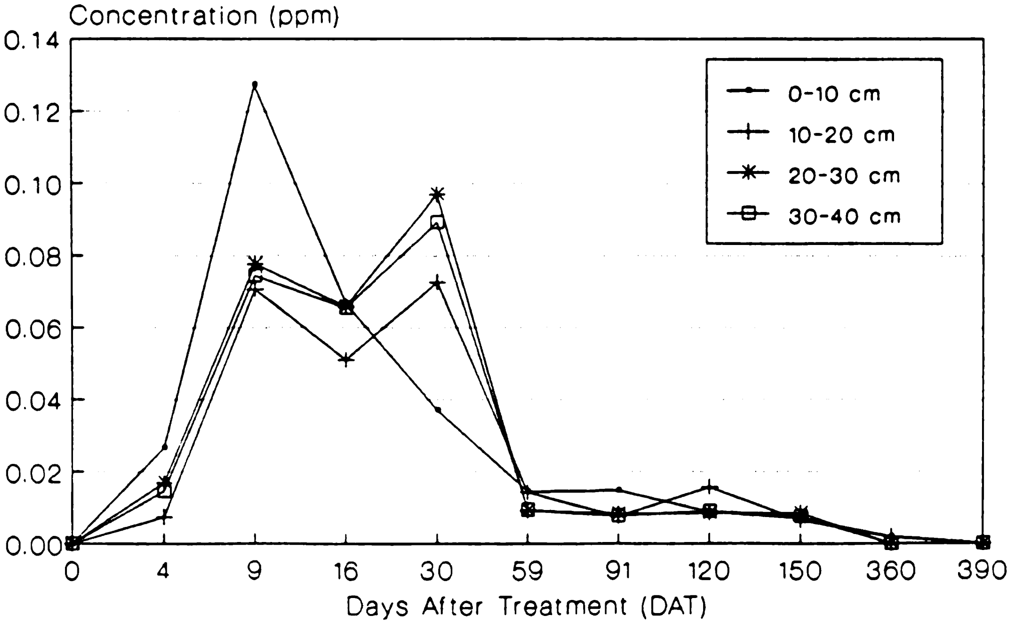


Figure 13b. Hexazinone concentrations in the mineral soil layers over time.

Velpar. More rainfall than this can foster leaching losses. This could reduce weed control and cause groundwater contamination since an average of 84 cm of precipitation falls annually in the Upper Peninsula, distributed relatively evenly in each month.

Further, these leaching losses can tend to mask the half-life of a chemical. While a half-life of less than two months is not unusual for hexazinone, this loss cannot be attributed solely to degradation. It is also moving out of the upper soil layers and essentially being diluted as it moves deeper into the soil. Bouchard, Lavy, and Lawson (1985) also claim that the dissipation rate is greater than can be accounted for by degradation alone. Therefore, the potential for hexazinone to contaminate groundwater is great.

Figure 14 shows the concentration of hexazinone found in the groundwater at the Stutts Creek site. Once again, relatively larger amounts of hexazinone detected in the groundwater coincide with significant rainfall events. By 120 days after treatment, over 16 cm of rain had fallen and hexazinone concentrations in groundwater had increased significantly, up to about 2.6 ppb. While the increase is significant, the actual concentration levels are still minute, not nearly approaching the 210 ppb advisory limit set by the EPA.

Small amounts (less than 0.1 ppb) of hexazinone had

Figure 14. Hexazinone concentrations in the groundwater over time at the Stutts Creek site. Means with the same letter in the same row are not significantly different at the 0.05 significance level according to Duncan's Multiple Range Test.

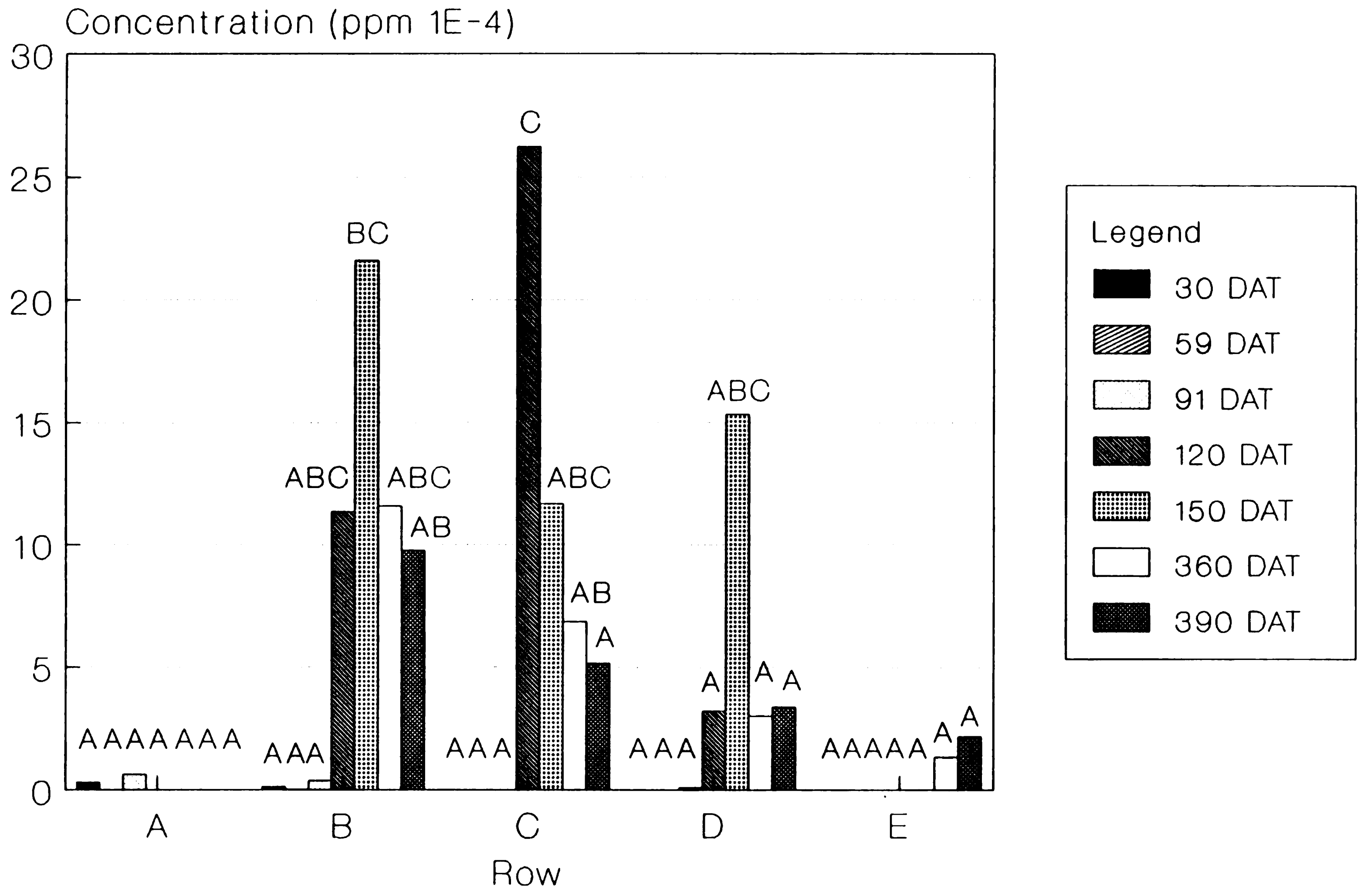

Concentration (ppm 1E-4)
30
25
20
15
10
5
0
A A A A A A A
A A A
ABC
BC
ABC
AB
A A A
C
ABC
AB
A
A A A
A
ABC
A
A
A A A A A
A
A
A
B
C
D
E
Row
Legend
■ 30 DAT
▨ 59 DAT
□ 91 DAT
▨ 120 DAT
▦ 150 DAT
□ 360 DAT
■ 390 DAT

Figure 14.

actually moved up the groundwater flow gradient and appeared in row A above the site. Differences in pressure head potential are slight across the entire site and a groundwater flow reversal is possible, if not likely.

Examining the trend of hexazinone concentrations in the groundwater shows results similar to that in lower soil layers. The concentration gradually increases, peaks, and then falls off. However, this decrease in hexazinone concentrations is primarily due to a dilution of the compound. As precipitation recharges the groundwater, especially after spring runoff, the concentrations decrease markedly. This fact, combined with decreased degradation in an anaerobic environment, suggests that hexazinone is decreasing essentially only in concentration and not in actual quantity. However, a build-up of hexazinone is unlikely since herbicide applications generally occur only once during a 50 year rotation. Less frequently, two applications may occur--first as a site preparation treatment and second as a release treatment.

Since the groundwater flows from row A to row E, a concentration of hexazinone in the down-gradient rows was expected. Though this did not occur to a significant extent, hexazinone does appear to be moving off-site to row E in small quantities (less than 0.5 ppb). Additionally, the concentrations appear to be increasing, though not significantly, between May 1 (360 DAT) and May 30, 1989 (390 DAT).

While precipitation is a significant factor in causing hexazinone to leach, the method of application may have also contributed. As mentioned, the dripline application directs the hexazinone in and around the tree line. As precipitation falls then, large amounts of hexazinone are forced into the soil along essentially one specific area. This tends to overload the few binding sites available in a sandy soil; thus, leaching into deeper soil layers and eventually the groundwater occurs. A banded application, while more effectively releasing the red pine, appears to have the added benefit of reducing the leaching and groundwater contamination potential of hexazinone.

CHAPTER VI

CONCLUSIONS AND FUTURE RESEARCH

The leaching of hexazinone through soils beneath red pine plantations and into the groundwater was evident on the Stutts Creek site. However, the maximum groundwater concentrations approached only 2.6 ppb, 80 times less than the health advisory limit set by the EPA. Also, the Stutts Creek site was very vulnerable to groundwater contamination since the high water table was within 2.04 meters and the soils had a sandy texture.

The research concerning groundwater contamination should continue for several years into the future, with samples taken once a year after the spring runoff. Research on red pine growth response to hexazinone release should continue for up to five years. Furthermore, long term studies over the course of an entire rotation are needed to determine if red pine reaches maturation significantly faster due to a release treatment (herbicide or mechanical). Short term studies indicate faster initial growth due to a lack of competition. However, the question remains whether this growth response continues or if growth levels off at some point with the released trees reaching maturity at the same time as the unreleased trees as shown in Figure 15. Based on this and other studies, this growth curve is possible on poor sites while good sites will likely enable the red pine to reach maturity at an earlier age.

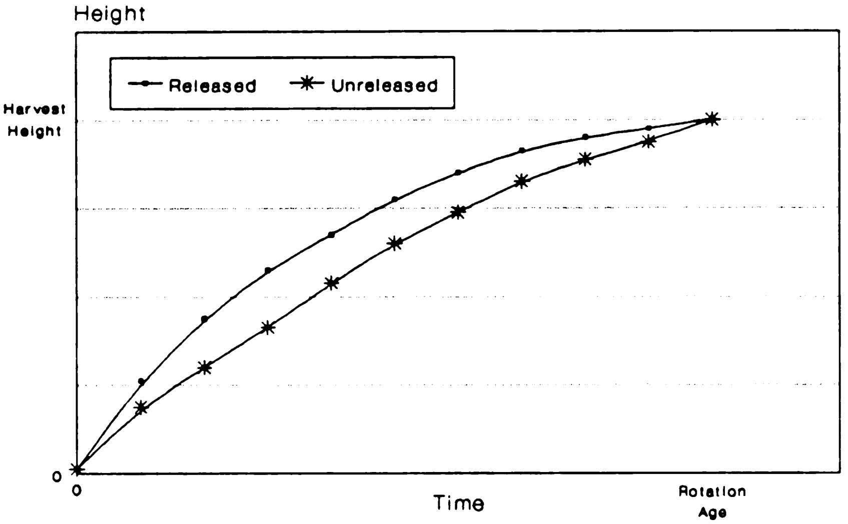


Figure 15. Theoretical height of red pine over a full rotation.

The question then is, do the benefits (increased red pine growth) of hexazinone outweigh the costs (groundwater contamination)? Consider the results derived from both sites:

1) Hexazinone significantly reduced all types of weed competition at the Cedarville site.

2) Red pine, when released with a banded application of hexazinone, did not significantly exceed the height growth of either the dripline application or the control. However, future growth appears promising.

3) The groundline diameter growth of red pine, when released by hexazinone, did significantly exceed the groundline diameter growth in the control plots.

4) Hexazinone contaminated the groundwater to a maximum of 2.6 ppb and has decreased significantly since that peak.

5) No build-up of hexazinone appeared in the down-gradient wells, though the compound began to move off-site.

6) For forestry use, hexazinone is generally applied only once per rotation (50 years) of red pine. Thus, build-up of hexazinone in the groundwater by repeat applications is highly unlikely.

The results suggest that continued use of hexazinone in releasing red pine from competing vegetation is environmentally acceptable. However, future applications should be banded along the tree row. This will foster excellent weed control, better growth response, and minimize groundwater contamination.

APPENDICES

APPENDIX A

RED PINE MEASUREMENTS AND WEED COVER

APPENDIX A

RED PINE MEASUREMENTS AND WEED COVER

Table A1. Mean change in red pine measurements and weed cover over the 1988 growing season at the Cedarville site in the dripline application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	20.9	0.227	-2	-23%	-4%	0%
Replication #2	19.7	0.229	-1	-13%	-21%	-1%
Replication #3	19.8	0.151	-2	-32%	-40%	-9%
Replication #4	14.2	0.225	-2	-46%	-21%	0%
Replication #5	12.3	0.158	-1	-21%	-4%	-1%
Replication #6	18.3	0.356	-1	-12%	-1%	7%
Replication #7	19.3	0.314	-1	-11%	-28%	-2%
Mean	17.8	0.237	-1	-23%	-17%	-1%

Table A2. Mean change in red pine measurements and weed cover over the 1988 growing season at the Cedarville site in the banded application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	16.6	0.245	-3	-50%	-10%	-6%
Replication #2	15.0	0.194	-1	-16%	-8%	-1%
Replication #3	21.2	0.352	-1	-18%	-15%	-8%
Replication #4	10.4	0.187	-2	-35%	-22%	-2%
Replication #5	14.9	0.231	-1	-13%	-9%	-1%
Replication #6	16.2	0.323	-2	-9%	-18%	-4%
Replication #7	16.5	0.294	-1	-37%	-24%	-2%
Mean	15.8	0.261	-2	-25%	-15%	-3%

Table A3. Mean change in red pine measurements and weed cover over the 1988 growing season at the Cedarville site in the control.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	15.8	0.020	-2	-13%	27%	7%
Replication #2	10.8	0.048	-0	21%	19%	3%
Replication #3	17.2	0.172	-1	-16%	12%	1%
Replication #4	10.8	0.051	-1	-6%	7%	1%
Replication #5	16.6	0.227	-0	4%	20%	0%
Replication #6	18.1	0.204	-0	0%	27%	2%
Replication #7	16.5	0.217	0	-8%	33%	10%
Mean	15.1	0.134	-1	-3%	21%	3%

Table A4. Mean change in red pine measurements and weed cover over the 1989 growing season at the Cedarville site in the dripline application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	23.7	0.617	0	4%	-2%	2%
Replication #2	26.9	0.646	0	-3%	17%	0%
Replication #3	19.4	0.650	0	3%	7%	0%
Replication #4	18.9	0.463	1	4%	8%	0%
Replication #5	19.4	0.365	0	-2%	34%	17%
Replication #6	29.0	0.779	0	1%	11%	0%
Replication #7	25.0	0.620	0	0%	-3%	8%
Mean	23.2	0.592	0	9%	10%	4%

Table A5. Mean change in red pine measurements and weed cover over the 1989 growing season at the Cedarville site in the banded application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	23.7	0.588	0	6%	3%	0%
Replication #2	23.2	0.534	0	3%	4%	0%
Replication #3	30.5	0.822	0	3%	6%	0%
Replication #4	22.8	0.513	0	1%	3%	0%
Replication #5	30.1	0.889	0	0%	10%	0%
Replication #6	27.2	0.665	0	-1%	15%	1%
Replication #7	24.9	0.694	0	1%	2%	0%
Mean	26.0	0.672	0	2%	6%	0%

Table A6. Mean change in red pine measurements and weed cover over the 1989 growing season at the Cedarville site in the control.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	13.0	0.217	-1	13%	7%	-0%
Replication #2	10.0	0.156	-1	-22%	16%	1%
Replication #3	18.1	0.328	0	13%	16%	8%
Replication #4	21.8	0.336	0	26%	19%	-1%
Replication #5	33.1	0.535	0	6%	-10%	1%
Replication #6	23.9	0.460	-0	3%	20%	11%
Replication #7	22.0	0.421	0	27%	-1%	1%
Mean	20.3	0.351	0	9%	10%	3%

Table A7. Mean change in red pine measurements and weed cover over the 1988 and 1989 growing seasons at the Cedarville site in the dripline application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	42.7	0.824	-1	-17%	-5%	2%
Replication #2	38.5	0.691	-1	-15%	-11%	-1%
Replication #3	28.5	0.477	-2	-30%	-34%	-9%
Replication #4	24.6	0.499	-2	-39%	-12%	0%
Replication #5	28.7	0.451	-1	-24%	26%	14%
Replication #6	41.0	0.960	-1	-11%	9%	7%
Replication #7	44.3	0.934	-1	-11%	-31%	6%
Mean	35.5	0.691	-1	-21%	-8%	3%

Table A8. Mean change in red pine measurements and weed cover over the 1988 and 1989 growing seasons at the Cedarville site in the banded application.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	39.2	0.818	-2	-41%	-7%	-6%
Replication #2	38.2	0.728	-1	-13%	-3%	-1%
Replication #3	47.7	1.057	-1	-15%	-9%	-8%
Replication #4	29.9	0.619	-2	-35%	-20%	-2%
Replication #5	45.0	1.120	-1	-13%	1%	-1%
Replication #6	38.7	0.862	-2	-9%	-5%	-4%
Replication #7	41.4	0.988	-1	-37%	-22%	-2%
Mean	40.0	0.885	-1	-23%	-9%	-3%

Table A9. Mean change in red pine measurements and weed cover over the 1988 and 1989 growing seasons at the Cedarville site in the control.

	TREE HEIGHT (CM)	TREE DIAMETER (CM)	NUMBER OF SPROUTS	PERCENT SPROUT COVER	PERCENT BROADLEAF COVER	PERCENT GRASS COVER
Replication #1	28.8	0.237	-3	0%	33%	7%
Replication #2	16.6	0.141	-1	-2%	30%	4%
Replication #3	33.8	0.486	-0	-3%	27%	9%
Replication #4	31.9	0.383	-1	21%	26%	0%
Replication #5	49.7	0.762	-0	10%	10%	1%
Replication #6	42.0	0.664	-0	3%	47%	13%
Replication #7	36.7	0.614	0	20%	28%	10%
Mean	34.2	0.470	-1	7%	29%	6%

APPENDIX B

WELL LOG FOR THE STUTTS CREEK SITE

APPENDIX B

Table B1. Well log for the Stutts Creek site.

	WELL CLUSTER #1			WELL CLUSTER #2		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	05/01/88	05/01/88	05/02/88	05/01/88	05/01/88	08/02/88
TIME	10:30	10:30		12:00	12:00	
SOIL INFORMATION						
Depth of A horizon	0.3	0.3	0.3	0.4	0.4	0.4
Depth of B horizon	2.3	2.3	2.3	2.3	2.3	2.3
Depth of C horizon	3.5	7.5	11.5	4.0	8.0	12.0
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	2.1	6.1	10.1	2.7	6.7	10.7
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	6.1	10.1	14.1	6.7	10.7	14.7
WATER TABLE INFORMATION						
Water table depth (ft)	2.1	2.1	2.1	2.7	2.7	2.7
High water table estimate (ft)	2.1	2.1	2.1	2.7	2.7	2.7
Level height above well (ft)	5.5	5.5	5.5	5.0	5.0	5.0
Level height above well cap (ft)	4.4	4.3	4.4	4.3	4.4	4.5
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-2.7	-2.7	-2.7	-2.8	-2.8	-2.8
COMMENTS	Clay lens at 2.0'					

Table B1 (cont'd.).

	WELL CLUSTER #3			WELL CLUSTER #4		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	05/01/88	05/01/88	05/02/88	05/01/88	05/01/88	05/03/88
TIME	01:30	01:30		08:30	08:30	
SOIL INFORMATION						
Depth of A horizon	0.5	0.5	0.5	0.4	0.4	0.4
Depth of B horizon	1.6	1.6	1.6	2.2	2.2	2.2
Depth of C horizon	4.0	8.0	12.0	4.0	8.0	12.0
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	2.1	6.1	10.1	2.6	6.6	10.6
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	6.1	10.1	14.1	6.6	10.6	14.6
WATER TABLE INFORMATION						
Water table depth (ft)	2.1	2.1	2.1	2.6	2.6	2.6
High water table estimate (ft)	2.1	2.1	2.1	2.6	2.6	2.6
Level height above well (ft)	5.4	5.4	5.4	5.0	5.0	5.0
Level height above well cap (ft)	4.9	5.0	4.9	4.5	4.6	4.6
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-2.5	-2.5	-2.5	-2.7	-2.7	-2.7
COMMENTS				Clay lens at 2 '		

Table B1 (cont'd.).

	WELL CLUSTER #5			WELL CLUSTER #6		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	04/30/88	04/30/88	05/03/88	04/30/88	04/30/88	05/03/88
TIME	12:00	12:00		11:00	11:00	
SOIL INFORMATION						
Depth of A horizon	0.3	0.3	0.3	0.9	0.9	0.9
Depth of B horizon	4.2	4.2	4.2	2.1	2.1	2.1
Depth of C horizon	4.0	8.0	12.0	3.9	7.9	11.9
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	4.5	8.5	12.5	2.9	6.9	10.9
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	8.5	12.5	16.5	6.9	10.9	14.9
WATER TABLE INFORMATION						
Water table depth (ft)	4.5	4.5	4.5	2.9	2.9	2.9
High water table estimate (ft)	4.5	4.5	4.5	2.9	2.9	2.9
Level height above well (ft)	4.3	4.3	4.3	5.8	5.8	5.8
Level height above well cap (ft)	3.7	3.8	3.8	5.3	5.7	5.0
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-3.9	-3.9	-3.9	-3.8	-3.8	-3.8
COMMENTS	Clay lens at 3'					

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Table B1 (cont'd.).

	WELL CLUSTER #7			WELL CLUSTER #8		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	04/30/88	04/30/88	05/02/88	04/30/88	04/30/88	05/02/88
TIME	02:30	02:30		01:30	01:30	
SOIL INFORMATION						
Depth of A horizon	0.7	0.7	0.7	0.5	0.5	0.5
Depth of B horizon	3.8	3.8	3.8	3.1	3.1	3.1
Depth of C horizon	4.0	8.0	12.0	4.0	8.0	12.0
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	4.5	8.5	12.5	3.6	7.6	11.6
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	8.5	12.5	16.5	7.6	11.6	15.6
WATER TABLE INFORMATION						
Water table depth (ft)	5.0	5.0	5.0	3.6	3.6	3.6
High water table estimate (ft)	4.5	4.5	4.5	3.6	3.6	3.6
Level height above well (ft)	4.8	4.8	4.8	6.4	6.4	6.4
Level height above well cap (ft)	4.3	4.4	4.6	6.1	6.0	5.9
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-4.9	-4.9	-4.9	-5.0	-5.0	-5.0
COMMENTS						

Table B1 (cont'd.).

	WELL CLUSTER #9			WELL CLUSTER #10		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW	P.C., SALAH			P.C., SALAH		
DATE	04/30/88	04/30/88	05/02/88	04/29/88	04/29/88	05/02/88
TIME	09:45	09:45		11:00	11:00	
SOIL INFORMATION						
Depth of A horizon	0.8	0.8	0.8	0.8	0.8	0.8
Depth of B horizon	3.2	3.2	3.2	3.2	3.2	3.2
Depth of C horizon	4.1	8.0	12.0	4.0	8.0	12.0
WELL INFORMATION						
Bore hole diameter (in)	3.2 5	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	4.0	8.0	12.0	4.0	8.0	12.0
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	8.0	12.0	16.0	8.0	12.0	16.0
WATER TABLE INFORMATION						
Water table depth (ft)	4.0	4.0	4.0	4.0	4.0	4.0
High water table estimate (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Level height above well (ft)	5.3	5.3	5.3	5.8	5.8	5.8
Level height above well cap (ft)	5.0	5.1	4.9	5.3	5.2	5.2
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-4.4	-4.4	-4.4	-4.9	-4.9	-4.9
COMMENTS				Clay lens at 2.8'		

Table B1 (cont'd.).

	WELL CLUSTER #11			WELL CLUSTER #12		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	04/29/88	04/29/88	05/02/88	04/29/88	04/29/88	05/02/88
TIME	02:30	02:30		04:15	04:15	
SOIL INFORMATION						
Depth of A horizon	0.9	0.9	0.9	0.9	0.9	0.9
Depth of B horizon	1.9	1.9	1.9	2.4	2.4	2.4
Depth of C horizon	4.5	8.5	12.5	4.0	8.0	12.0
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	3.3	7.3	11.3	3.3	7.3	11.3
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	7.3	11.3	15.3	7.3	11.3	15.3
WATER TABLE INFORMATION						
Water table depth (ft)	3.3	3.3	3.3	3.3	3.3	3.3
High water table estimate (ft)	3.3	3.3	3.3	3.3	3.3	3.3
Level height above well (ft)	6.7	6.7	6.7	6.3	6.3	6.3
Level height above well cap (ft)	6.5	6.4	6.3	5.9	6.1	6.0
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-5.1	-5.1	-5.1	-4.7	-4.7	-4.7
COMMENTS						

Table B1 (cont'd.).

	WELL CLUSTER #13			WELL CLUSTER #14		
	SHALLOW	MEDIUM	DEEP	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH			P.C., SALAH	
DATE	05/01/88	05/01/88	05/03/88	05/01/88	05/01/88	05/03/88
TIME	06:15	06:15		05:10	05:10	
SOIL INFORMATION						
Depth of A horizon	0.6	0.6	0.6	0.4	0.4	0.4
Depth of B horizon	2.6	2.6	2.6	5.4	5.4	5.4
Depth of C horizon	4.0	8.0	12.0	4.1	8.1	12.1
WELL INFORMATION						
Bore hole diameter (in)	3.25	3.25	3.25	3.25	3.25	3.25
Screen slot size	7	7	7	7	7	7
PVC casing material (ft)	3.2	7.2	11.2	5.9	9.9	13.9
PVC screen material (ft)	4.0	4.0	4.0	4.0	4.0	4.0
Total well depth (ft)	7.2	11.2	15.2	9.9	13.9	17.9
WATER TABLE INFORMATION						
Water table depth (ft)	3.2	3.2	3.2	5.9	5.9	5.9
High water table estimate (ft)	3.2	3.2	3.2	5.9	5.9	5.9
Level height above well (ft)	6.4	6.4	6.4	3.8	3.8	3.8
Level height above well cap (ft)	6.0	6.2	5.8	3.2	3.4	3.2
Instrument height (ft)	4.9	4.9	4.9	4.9	4.9	4.9
Water depth from datum (feet)	-4.6	-4.6	-4.6	-4.8	-4.8	-4.8
COMMENTS						

Table B1 (cont'd.).

	WELL CLUSTER #15		
	SHALLOW	MEDIUM	DEEP
CREW		P.C., SALAH	
DATE	05/01/88	05/01/88	05/03/88
TIME	04:15	04:15	
SOIL INFORMATION			
Depth of A horizon	0.5	0.5	0.5
Depth of B horizon	6.2	6.2	6.2
Depth of C horizon	4.0	8.0	12.0
WELL INFORMATION			
Bore hole diameter (in)	3.25	3.25	3.25
Screen slot size	7	7	7
PVC casing material (ft)	6.7	10.7	14.7
PVC screen material (ft)	4.0	4.0	4.0
Total well depth (ft)	10.7	14.7	18.7
WATER TABLE INFORMATION			
Water table depth (ft)	6.7	6.7	6.7
High water table estimate (ft)	6.7	6.7	6.7
Level height above well (ft)	3.3	3.3	3.3
Level height above well cap (ft)	2.9	2.7	2.7
Instrument height (ft)	4.9	4.9	4.9
Water depth from datum (feet)	-5.1	-5.1	-5.1
COMMENTS			

APPENDIX C

HEXAZINONE CONCENTRATIONS IN THE SOIL LAYERS AND GROUNDWATER AT THE STUTTS CREEK SITE

APPENDIX C

Table C1. Hexazinone concentrations in the soil layers and groundwater at the Stutts Creek site.

	5/9/88 4 DAT (ppm)	5/14/88 9 DAT (ppm)	5/21/88 16 DAT (ppm)	6/4/88 30 DAT (ppm)	7/3/88 59 DAT (ppm)
ROW A					
WELL #1				NOT DETECTED	NOT DETECTED
WELL #2				9.903E-005	NOT DETECTED
WELL #3				NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE				3.301E-005	NOT DETECTED
ROW B					
WELL #4				4.426E-005	7.218E-006
FF	NOT DETECTED	6.291E-002	5.747E-001	1.205E-001	8.796E-001
0-10	5.861E-002	5.662E-002	4.721E-002	2.798E-002	4.352E-002
10-20	4.383E-003	5.711E-002	5.240E-002	5.528E-002	8.044E-002
20-30	5.581E-003	1.068E-001	6.055E-002	8.060E-002	6.062E-002
30-40	2.032E-003	1.060E-001	6.168E-002	4.668E-002	4.694E-002
WELL #5				NOT DETECTED	NOT DETECTED
FF	5.040E-003	1.443E+000	2.002E-001	1.069E-001	7.433E-002
0-10	7.757E-002	1.166E-001	5.652E-002	4.007E-002	6.429E-003
10-20	3.790E-003	1.378E-001	4.563E-002	4.811E-002	1.902E-002
20-30	6.181E-003	1.515E-001	8.353E-002	9.030E-002	NOT DETECTED
30-40	1.210E-002	1.781E-001	7.060E-002	9.543E-002	9.245E-003
WELL #6				NOT DETECTED	NOT DETECTED
FF	4.898E-003	9.722E-001	2.745E-001	5.759E-002	8.722E-002
0-10	1.039E-002	4.026E-002	3.982E-002	3.327E-002	6.442E-003
10-20	2.198E-002	7.306E-002	3.186E-002	5.525E-002	1.064E-002
20-30	2.432E-002	1.013E-001	4.462E-002	9.713E-002	9.953E-003
30-40	1.323E-002	9.550E-002	5.985E-002	1.076E-001	1.065E-002
GROUNDWATER AVERAGE				1.475E-005	2.406E-006
ROW C					
WELL #7				NOT DETECTED	NOT DETECTED
FF	1.353E-002	5.343E-002	7.755E-001	3.009E-001	5.977E-002
0-10	1.375E-002	1.312E-001	2.088E-001	4.126E-002	4.492E-002
10-20	6.015E-003	1.144E-002	8.061E-002	9.389E-002	3.635E-003
20-30	1.369E-002	6.679E-003	7.308E-002	1.196E-001	8.347E-004
30-40	1.154E-002	8.730E-003	9.430E-002	1.292E-001	3.642E-003

APPENDIX C

Table C1. Hexazinone concentrations in the soil layers and groundwater at the Stutts Creek site.

	5/9/88 4 DAT (ppm)	5/14/88 9 DAT (ppm)	5/21/88 16 DAT (ppm)	6/4/88 30 DAT (ppm)	7/3/88 59 DAT (ppm)
ROW A					
WELL #1				NOT DETECTED	NOT DETECTED
WELL #2				9.903E-005	NOT DETECTED
WELL #3				NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE				3.301E-005	NOT DETECTED
ROW B					
WELL #4				4.426E-005	7.218E-006
FF	NOT DETECTED	6.291E-002	5.747E-001	1.205E-001	8.796E-001
0-10	5.861E-002	5.662E-002	4.721E-002	2.798E-002	4.352E-002
10-20	4.383E-003	5.711E-002	5.240E-002	5.528E-002	8.044E-002
20-30	5.581E-003	1.068E-001	6.055E-002	8.060E-002	6.062E-002
30-40	2.032E-003	1.060E-001	6.168E-002	4.668E-002	4.694E-002
WELL #5				NOT DETECTED	NOT DETECTED
FF	5.040E-003	1.443E+000	2.002E-001	1.069E-001	7.433E-002
0-10	7.757E-002	1.166E-001	5.652E-002	4.007E-002	6.429E-003
10-20	3.790E-003	1.378E-001	4.563E-002	4.811E-002	1.902E-002
20-30	6.181E-003	1.515E-001	8.353E-002	9.030E-002	NOT DETECTED
30-40	1.210E-002	1.781E-001	7.060E-002	9.543E-002	9.245E-003
WELL #6				NOT DETECTED	NOT DETECTED
FF	4.898E-003	9.722E-001	2.745E-001	5.759E-002	8.722E-002
0-10	1.039E-002	4.026E-002	3.982E-002	3.327E-002	6.442E-003
10-20	2.198E-002	7.306E-002	3.186E-002	5.525E-002	1.064E-002
20-30	2.432E-002	1.013E-001	4.462E-002	9.713E-002	9.953E-003
30-40	1.323E-002	9.550E-002	5.985E-002	1.076E-001	1.065E-002
GROUNDWATER AVERAGE				1.475E-005	2.406E-006
ROW C					
WELL #7				NOT DETECTED	NOT DETECTED
FF	1.353E-002	5.343E-002	7.755E-001	3.009E-001	5.977E-002
0-10	1.375E-002	1.312E-001	2.088E-001	4.126E-002	4.492E-002
10-20	6.015E-003	1.144E-002	8.061E-002	9.389E-002	3.635E-003
20-30	1.369E-002	6.679E-003	7.308E-002	1.196E-001	8.347E-004
30-40	1.154E-002	8.730E-003	9.430E-002	1.292E-001	3.642E-003

Table C1 (cont'd.).

	5/9/88 4 DAT (ppm)	5/14/88 9 DAT (ppm)	5/21/88 16 DAT (ppm)	6/4/88 30 DAT (ppm)	7/3/88 59 DAT (ppm)
WELL #8				NOT DETECTED	NOT DETECTED
FF	5.349E-002	1.742E-002	1.766E-001	2.484E-001	5.470E-002
0-10	4.906E-003	7.737E-002	2.934E-002	3.973E-002	1.005E-002
10-20	3.786E-003	1.661E-001	4.526E-002	9.777E-002	4.016E-003
20-30	8.220E-003	1.808E-001	6.059E-002	1.204E-001	4.010E-003
30-40	1.375E-002	1.706E-001	6.111E-002	1.091E-001	NOT DETECTED
WELL #9				NOT DETECTED	NOT DETECTED
FF	2.540E-002	NOT DETECTED	2.201E-001	8.935E-002	1.612E-002
0-10	3.535E-002	3.333E-003	2.164E-002	4.292E-002	5.367E-003
10-20	8.788E-003	6.029E-003	5.217E-002	8.441E-002	4.692E-003
20-30	1.710E-002	6.050E-003	6.431E-002	1.074E-001	3.355E-003
30-40	8.788E-003	NOT DETECTED	3.496E-002	1.084E-001	4.701E-003
GROUNDWATER AVERAGE				NOT DETECTED	NOT DETECTED
ROW D					
WELL #10				NOT DETECTED	NOT DETECTED
FF	9.743E-003	1.232E+000	5.121E-002	1.926E-001	2.352E-001
0-10	1.815E-002	4.868E-002	9.781E-002	4.914E-002	3.292E-003
10-20	1.093E-002	1.430E-002	4.964E-002	8.284E-002	NOT DETECTED
20-30	2.059E-002	4.922E-003	5.090E-002	1.002E-001	1.200E-003
30-40	6.113E-002	3.864E-003	6.944E-002	9.982E-002	1.899E-003
WELL #11				NOT DETECTED	NOT DETECTED
FF	5.769E-002	NOT DETECTED	NOT DETECTED	NOT DETECTED	1.493E-002
0-10	2.006E-002	5.919E-001	7.175E-002	4.566E-002	1.894E-003
10-20	4.584E-003	1.639E-001	4.367E-002	5.822E-002	2.589E-003
20-30	5.406E-002	1.404E-001	7.081E-002	1.155E-001	1.896E-003
30-40	5.220E-003	1.065E-001	5.845E-002	3.445E-002	2.594E-003
WELL #12				NOT DETECTED	NOT DETECTED
FF	NOT DETECTED	5.813E+000	2.578E-001	7.220E-002	NOT DETECTED
0-10	1.975E-003	7.942E-002	2.653E-002	1.486E-002	8.838E-003
10-20	3.281E-003	5.355E-003	5.707E-002	7.639E-002	3.296E-003
20-30	3.932E-003	NOT DETECTED	8.335E-002	4.148E-002	1.899E-003
30-40	4.571E-003	NOT DETECTED	7.791E-002	7.233E-002	4.686E-003
GROUNDWATER AVERAGE				NOT DETECTED	NOT DETECTED
ROW E					
WELL #13				NOT DETECTED	NOT DETECTED
WELL #14				NOT DETECTED	NOT DETECTED
WELL #15				NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE				NOT DETECTED	NOT DETECTED

Table C1 (cont'd.).

	5/9/88 4 DAT (ppm)	5/14/88 9 DAT (ppm)	5/21/88 16 DAT (ppm)	6/4/88 30 DAT (ppm)	7/3/88 59 DAT (ppm)
OVERALL					
SOIL AVERAGES					
FF	1.887E-002	1.066E+000	2.812E-001	1.321E-001	1.580E-001
0-10	2.675E-002	1.273E-001	6.660E-002	3.721E-002	1.453E-002
10-20	7.504E-003	7.057E-002	5.092E-002	7.246E-002	1.426E-002
20-30	1.708E-002	7.761E-002	6.575E-002	9.695E-002	9.308E-003
30-40	1.471E-002	7.438E-002	6.537E-002	8.922E-002	9.373E-003

Table C1 (cont'd.).

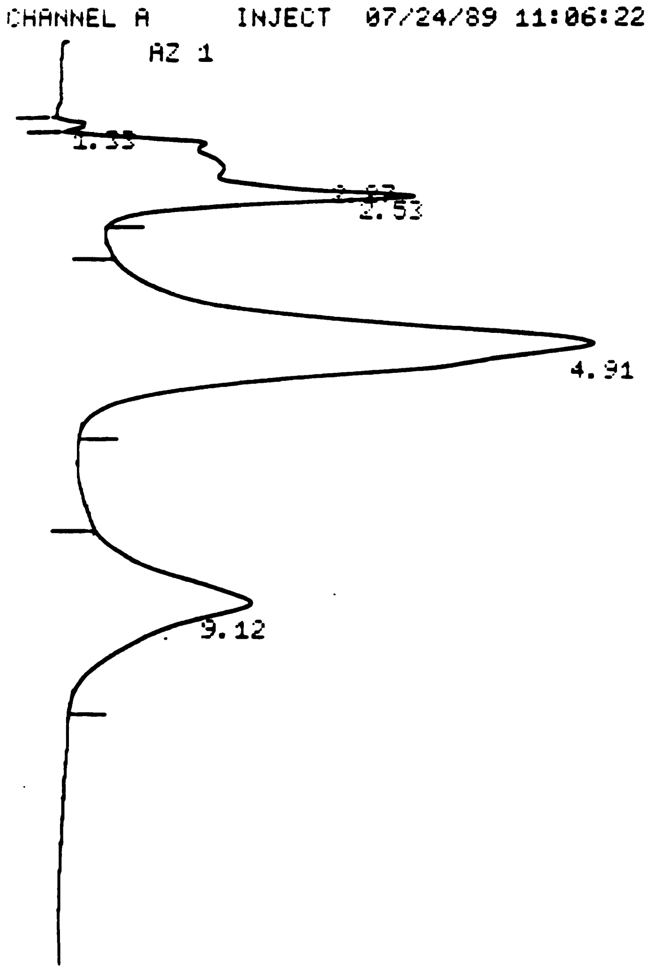
	8/4/88 91 DAT (ppm)	9/2/88 120 DAT (ppm)	10/2/88 150 DAT (ppm)	5/1/89 360 DAT (ppm)	5/31/89 390 DAT (ppm)
ROW A					
WELL #1	1.604E-004	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
WELL #2	2.784E-005	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
WELL #3	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECETED	NOT DETECTED
GROUNDWATER AVERAGE	6.275E-005	NOT DTECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
ROW B					
WELL #4	1.129E-004	1.425E-004	2.186E-003	1.689E-003	1.100E-003
FF	NOT DETECTED	NOT DETECTED	5.093E-001	NOT DETECTED	NOT DETECTED
0-10	3.834E-002	3.772E-002	5.255E-002	7.534E-004	NOT DETECTED
10-20	3.693E-002	7.723E-002	5.465E-002	NOT DETECTED	NOT DETECTED
20-30	5.707E-002	7.732E-002	7.720E-002	NOT DETECTED	NOT DETECTED
30-40	5.961E-002	8.138E-002	5.911E-002	NOT DETECTED	NOT DETECTED
WELL #5	NOT DETECTED	3.053E-004	2.546E-003	1.480E-003	1.627E-003
FF	NOT DETECTED	NOT DETECTED	8.858E-003	NOT DETECTED	NOT DETECTED
0-10	1.203E-003	NOT DETECTED	NOT DETECTED	2.132E-003	NOT DETECTED
10-20	NOT DETECTED	NOT DETECTED	1.287E-003	6.462E-005	NOT DETECTED
20-30	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
WELL #6	NOT DETECTED	2.960E-003	1.750E-003	3.053E-004	2.055E-004
FF	NOT DETECTED	NOT DETECTED	5.635E-003	NOT DETECTED	2.833E-003
0-10	1.301E-002	1.114E-002	3.838E-003	1.446E-003	NOT DETECTED
10-20	1.895E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
20-30	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE	3.763E-005	1.136E-003	2.161E-003	1.158E-003	9.773E-004
ROW C					
WELL #7	NOT DETECTED	7.016E-003	2.355E-003	1.431E-003	7.644E-004
FF	2.106E-002	NOT DETECTED	1.290E-002	NOT DETECTED	NOT DETECTED
0-10	3.181E-002	9.232E-003	NOT DETECTED	1.442E-003	NOT DETECTED
10-20	6.082E-003	4.092E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED
20-30	6.060E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	8.933E-003	NOT DETECTED	NOT DETECTED
WELL #8	NOT DETECTED	7.880E-004	5.724E-004	3.214E-004	4.291E-004
FF	NOT DETECTED	NOT DETECTED	3.122E-002	NOT DETECTED	NOT DETECTED
0-10	1.895E-003	4.083E-003	NOT DETECTED	2.131E-003	NOT DETECTED
10-20	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
20-30	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED

Table C1 (cont'd.).

	8/4/88 91 DAT (ppm)	9/2/88 120 DAT (ppm)	10/2/88 150 DAT (ppm)	5/1/89 360 DAT (ppm)	5/31/89 390 DAT (ppm)
WELL #9	NOT DETECTED	6.383E-005	5.724E-004	3.053E-004	3.491E-004
FF	8.478E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
0-10	NOT DETECTED	NOT DETECTED	3.206E-003	NOT DETECTED	1.468E-003
10-20	NOT DETECTED	1.372E-002	NOT DETECTED	NOT DETECTED	NOT DETECTED
20-30	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE	NOT DETECTED	2.623E-003	1.167E-003	6.860E-004	5.142E-004
ROW D					
WELL #10	NOT DETECTED	6.383E-005	NOT DETECTED	1.282E-004	4.450E-004
FF	8.158E-003	9.290E-002	1.581E-002	NOT DETECTED	NOT DETECTED
0-10	1.242E-002	1.115E-002	2.565E-003	6.454E-005	NOT DETECTED
10-20	7.940E-003	2.206E-002	2.563E-003	3.508E-003	NOT DETECTED
20-30	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
WELL #11	NOT DETECTED	8.363E-004	4.424E-003	6.109E-004	3.173E-004
FF	NOT DETECTED	NOT DETECTED	NOT DETECTED	3.054E-003	NOT DETECTED
0-10	6.016E-003	6.007E-003	2.564E-003	1.105E-002	NOT DETECTED
10-20	4.728E-003	2.402E-002	NOT DETECTED	1.718E-003	NOT DETECTED
20-30	4.732E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	4.724E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
WELL #12	3.164E-005	6.383E-005	1.746E-004	1.604E-004	2.534E-004
FF	NOT DETECTED	NOT DETECTED	NOT DETECTED	1.063E-002	NOT DETECTED
0-10	2.919E-002	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
10-20	1.116E-002	NOT DETECTED	NOT DETECTED	1.182E-002	NOT DETECTED
20-30	7.298E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
30-40	6.009E-003	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
GROUNDWATER AVERAGE	1.055E-005	3.213E-004	1.533E-003	2.999E-004	3.386E-004
ROW E					
WELL #13	NOT DETECTED	NOT DETECTED	NOT DETECTED	1.121E-004	4.579E-005
WELL #14	NOT DETECTED	NOT DETECTED	NOT DETECTED	2.248E-004	5.089E-004
WELL #15	NOT DETECTED	NOT DETECTED	NOT DETECTED	6.383E-005	9.370E-005
GROUNDWATER AVERAGE	NOT DETECTED	NOT DETECTED	NOT DETECTED	1.336E-004	2.161E-004
OVERALL SOIL AVERAGES					
FF	4.188E-003	1.032E-002	6.485E-002	1.521E-003	3.148E-004
0-10	1.488E-002	8.815E-003	7.192E-003	2.114E-003	1.631E-004
10-20	7.637E-003	1.568E-002	6.500E-003	1.902E-003	NOT DETECTED
20-30	8.351E-003	8.591E-003	8.577E-003	NOT DETECTED	NOT DETECTED
30-40	7.816E-003	9.042E-003	7.560E-003	NOT DETECTED	NOT DETECTED

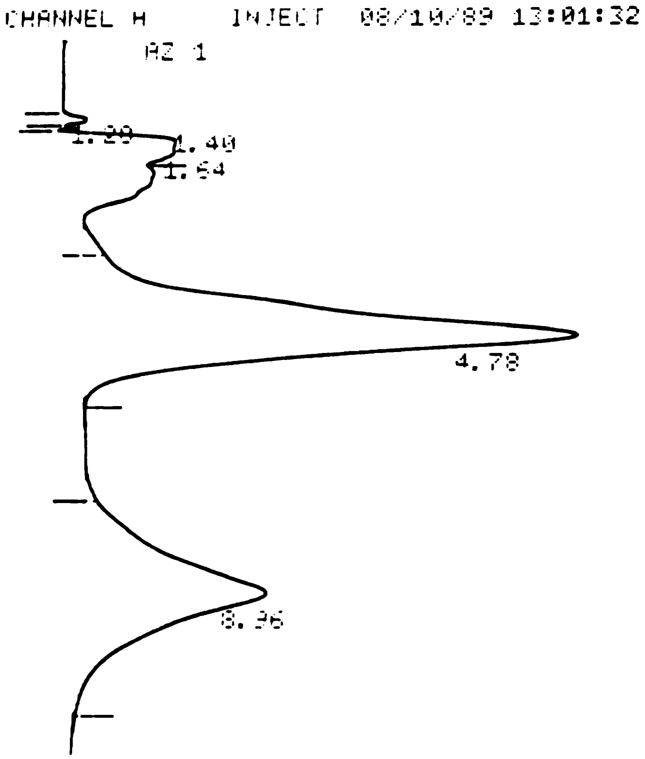
APPENDIX D

HPLC CHROMATOGRAMS AND MASS SPECTRA OF HEXAZINONE



```
PETE                -            07/24/89 11:06:22      CH= "A"   PS=  1.

FILE  2.      METHOD  0.      RUN 370      INDEX 370

PEAK#        HT%         RT       PK HT BC

    1         2.219      1.33      1488 02
    2        13.031      2.27      8740 02
    3        27.515      2.53     18455 03
    4        42.592      4.91     28567 01
    5        14.644      9.12      9822 01

TOTAL      100.                   67071
```

Figure D1. Typical chromatogram of hexazinone in a soil layer.



```
PETE                          08/10/89 13:01:32     CH= "A"  PS=  1.

FILE  2.      METHOD  0.      RUN 886      INDEX 886

PEAK#      AREA%       RT       AREA BC

    1       0.469     1.28     19806 02
    2       0.113     1.4       4759 02
    3       4.7       1.64    198499 03
    4      60.724     4.78   2564852 01
    5      33.994     8.96   1435838 01

TOTAL     100.                4223754
```

Figure D2. Typical chromatogram of hexazinone in the groundwater.

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