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ATRAZINE, SIMAZINE, HEXAZINONE, AND NITRATE IN
GROUNDWATER UNDER CHRISTMAS TREE PLANTATIONS

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ATRAZINE, SIMAZINE, HEXAZINONE, AND NITRATE IN GROUNDWATER UNDER CHRISTMAS TREE PLANTATIONS

By

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ABSTRACT

ATRAZINE, SIMAZINE, HEXAZINONE, AND NITRATE IN GROUNDWATER UNDER CHRISTMAS TREE PLANTATIONS

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Regulatory agencies manage groundwater contamination from herbicides and nitrate using site-specific plans. Atrazine, simazine, hexazinone, and nitrate were measured in shallow groundwater at four dates to develop effective plans for Christmas tree production. Groundwater depths ranged from 90-620 cm for 38 Christmas tree fields on diverse soils across lower Michigan. Concentrations were compared to treatment rates, soil properties, water quality standards, and nearby deep drinking water wells. Deep wells had lower average levels than shallow wells for all chemicals. Logistic regression equations predicted probability of exceeding critical contaminant levels: maximum contaminant level (MCL), 1/3 MCL, and analytical detection limit. Probabilities of exceeding the 10 mg/L nitrate MCL were related to nitrogen application rates, clay in the top 150 cm of soil, groundwater depth, and A+B soil horizon thickness, with application rates most predictive. Only 4 of 147 shallow samples exceeded herbicide MCLs. Herbicides are not water quality problems as currently used for Christmas trees, while nitrate requires more study.

To my mother, father, and brother
for all of their support

and to my fiancé Bob Wachholder
for all of those weekends spent sampling wells

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LIST OF ABBREVIATIONS

Abbreviation	Definition
weights, measures, volumes, rates	
cm	centimeters
m	meters
mm	millimeters
nm	nanometers
µm	micrometers
ft	feet
ac	acre
g	grams
mL	milliliters
λ	wavelength
V	volume of well casing
TWD	total well depth, bottom of well to riser
DW	depth of water from top of well to water
r	radius of well
µg/L	micrograms per liter (parts per billion)
mg/L	milligrams per liter (parts per million)
kg/ha	kilograms per hectare
µs/cm	microsiemens per centimeter
soil textures	
C	clay
CL	clay loam
S	sand
SC	sandy clay
SCL	sandy clay loam
SI	silt
SIC	silty clay
SICL	silty clay loam
SIL	silty loam
SL	sandy loam
L	loam
LS	loamy sand
site variables	
CLY	clay loamy soil = SCL, CL, or SICL ≥ 30 cm
CY	clayey soil = SC, C, or SIC ≥ 30 cm
LY	loamy soil = SL, L, SIL, or SI ≥ 30 cm
SY	sandy soil = S or LS ≥ 30 cm
PD-SPD	poorly drained to semi-poorly drained soil
ABDEPcm	thickness of A + B soil horizons in centimeters
AvalTHcm	measure of organic matter in soil based on

C150cm	amount of clay in top 150 centimeters of soil
CVADcm	amount of clay in vadose zone
	color code of A horizon
GWDEPcm	depth to groundwater in centimeters
GWZcm	depth to groundwater zone in centimeters

treatment variables

A4	amount of atrazine applied from 1994-1997
A97	amount of atrazine applied in 1997
A96	amount of atrazine applied in 1996
H4	amount of hexazinone applied from 1994-1997
H97	amount of hexazinone applied in 1997
H96	amount of hexazinone applied in 1996
N4	amount of nitrogen applied from 1994-1997
N97	amount of nitrogen applied in 1997
N96	amount of nitrogen applied in 1996
S4	amount of simazine applied from 1994-1997
S97	amount of simazine applied in 1997
S96	amount of simazine applied in 1996

concentration variables

ADWppb	atrazine deep groundwater concentration in µg/L
Appb	atrazine shallow groundwater concentration in µg/L
HDWppb	hexazinone deep groundwater concentration in µg/L
Hppb	hexazinone shallow groundwater concentration in µg/L
NDWppm	nitrate deep groundwater concentration in mg/L
Nppm	nitrate shallow groundwater concentration in mg/L
SDWppb	simazine deep groundwater concentration in µg/L
Sppb	simazine shallow groundwater concentration in µg/L

other

ai	active ingredients
DEA	deethylatrazine
DIA	deisoproplyatrazine
EPA	U. S. Environmental Protection Agency
HPLC	high performance liquid chromatography
Koc	soil sorption coefficient
LPL	least permeable layer
MCL	maximum contaminant level
MDA	Michigan Department of Agriculture
n	number of samples
PVC	polyvinylchloride
QC	quality control
SPE	solid phase extraction

INTRODUCTION

Importance of Pesticides

Pesticides have been used since ancient Roman times, and society has grown very dependent on them. Today, crop production without the use of agricultural chemicals would result in increases in crop prices and health risks, and decreases in the food supply. A 1991 economic survey conducted in Canada estimated farming income losses due to weeds at $984 million (Swanton et al., 1993). Worldwide, over $30 billion is spent annually on pesticides. In the U.S., an estimated 545 million kilograms of pesticide active ingredients (ai) are used per year, with about 70 percent in production agriculture (Varshney et al., 1993). It has been estimated that less than 0.1 percent of applied pesticides actually reach target pests, with the excess affecting non-target organisms in soil, surface water, groundwater, and air (Pimentel and Levitan, 1986). Even with this threat of environmental injury, the benefits and economic advantages of pesticide use are great. The balance between chemical benefit and harm requires detailed examination and quantification for proper management.

Pesticides, Fertilizers, and Christmas Tree Production in Michigan

Effective weed control practices are important for producing uniform, high quality Christmas trees in a reasonable length of time. Weeds can reduce tree survival and growth by competing for nutrients, light, and water. Weeds can decrease tree quality due to loss of lower limbs and poor needle color (Khun, 1997). High weed growth can also favor the development of foliar diseases and danger from wildfires. Overgrown weeds can impede the shearing of the trees, interfere with insecticide and fungicide protection, and provide food and cover for rodents that can girdle the trees in winter (Lantange and Koelling, 1997). Before the development of effective herbicides, growers avoided high fertility soils because of the intense weed competition at these sites. Previously, 10-15 years were required to complete a production cycle, but with proper herbicide use and management, the more fertile sites can produce superior trees in 5-8 years. Finally, with the current trends toward "choose and cut" tree production, the appearance of fields where weeds are controlled is an important element for attracting and keeping customers. For these reasons, it is important to maintain the availability of herbicide use for Christmas tree production.

Christmas tree production is an important industry in Michigan. From a 1991 survey of Christmas tree growers, there were an estimated 2,153 growers with areas of less than 300 acres and 73 growers with areas of 300 acres or more (Snider, 1992). The estimated total acres of Christmas trees in Michigan was 122,000 acres. Twenty nine counties have more than 750 acres in Christmas trees (Table 1). This demonstrates that growers are located across many counties in Michigan, which accounts for the variety in growing conditions. The 1991 survey also collected information on fertilization of Christmas trees. Table 2 presents the number of trees planted and fertilized by species. Approximately 21-32 percent of the blue spruce and firs planted are fertilized each year. Many scotch pine are fertilized, although the percentage is only 6.5 percent. White pine was the only other pine that was frequently fertilized, but the number of trees is low. One can conclude that significant numbers of Christmas trees are being fertilized and where nitrogen is used, there is potential for nitrate leaching to shallow groundwater systems.

To maintain registration of pesticides for this industry, the Michigan Department of Agriculture (MDA) requires verification that these chemicals are not harming the environment. While most atrazine and simazine are used on corn, sorghum, alfalfa, fruit, berries, turf, and bean crops, these pesticides have significant use for Christmas tree production in Michigan. Hexazinone is another important herbicide commonly used for scotch pine production. MDA is interested in protecting the groundwater under production Christmas tree plantations, specifically nitrate, atrazine, simazine, and hexazinone.

Table 1. Estimated Acres and Proportions of a Total of 112,000 Acres Used for Christmas Tree Production in Counties with over 750 acres.

COUNTY	Percentage of 122 thousand ac		Acres of trees in county
	%	Accumulated %	
WEXFORD	4.9	4.9%	15,081
MONTCALM	4.6	9.5%	13,909
MANISTEE	3.3	12.8	10,146
NEWAYGO	2.5	15.3	7,597
MISSAUKEE	2.3	17.7	7,117
OCEANA	2.0	19.7	6,125
ALLEGAN	2.0	21.6	5,945
KALKASKA	1.9	23.5	5,660
CHEBOYGAN	1.3	24.8	4,048
OSCEOLA	1.3	26.1	4,086
OTTAWA	1.3	27.5	3,978
LAKE	1.2	28.7	3,748
BENZIE	1.0	29.7	2,989
MASON	0.9	30.6	2,889
ANTRIM	0.9	31.5	2,806
VAN BUREN	0.7	32.3	2,262
MENOMINEE	0.7	33.0	2,082
TUSCOLA	0.6	33.5	1,749
MUSKEGON	0.6	34.1	1,742
KENT	0.5	34.6	1,549
EMMET	0.4	35.0	1,342
OAKLAND	0.4	35.5	1,337
GTRAVERSE	0.3	35.8	1,057
IONIA	0.3	36.2	975
BARGA	0.3	36.5	900
MECOSTA	0.3	36.8	900
KALAMAZOO	0.3	37.1	832
DELTA	0.3	37.4	800
ISABELLA	0.2	37.6	757
GRAND TOTAL			122,000

Table 2. Number of Trees Planted and Fertilized by Species for Survey Respondents.

Species	Scotch pine	Douglas fir	Blue spruce	White spruce	Balsam fir	Frasier fir	Red pine	Austrian pine	White pine
Trees Planted (th)	13278	3336	2413	585	552	910	42	184	532
Trees Fertilized (th)	867	704	657	84	179	288	0	11	48
% of Trees Fertilized	6.5%	21.1%	27.2%	14.4%	32.4%	31.7%	0.1%	6.1%	9.1%

Importance of Groundwater

Groundwater occurs in the saturated zones beneath the soil surface. In contrast to the visible surface water in streams and lakes, groundwater comprises over 97 percent of the earth's liquid fresh water (Brooks et al., 1991). The importance of groundwater in providing drinking water and maintaining life is greater than most people are aware. In the United States, 333 billion liters of groundwater are withdrawn daily to provide drinking water from local wells to over 50 percent of the general population and 97 percent of the rural residents (Lichtenberg and Shapiro, 1997). Groundwater also provides 40 percent of all agricultural irrigation water and 26 percent of all industrial withdrawals (Lee, 1980). Clean groundwater is critical to our survival.

Since conventional drinking water treatments do not remove most agricultural chemicals, it is critical to protect groundwater from pesticide contamination. Water percolation of chemicals through the soil is the primary source of groundwater contamination, with more leaching through unconsolidated aquifers, than through bedrock aquifers (Burkart and Kolpin, 1993). Influx of soil runoff from spring flooding can also contribute to groundwater contamination. Many occurrences of surface water contamination have been reported due to runoff during the spring flush (Mills and Thurman, 1994; Squillace, and Thurman, 1992; Thurman et al., 1991). Since the interface of groundwater and surface water allows these waters to mix, there is potential for groundwater contamination from surface water runoff, and vice versa. In soils that are especially resistant to water infiltration and leaching, the groundwater contamination can be mostly attributed to runoff and surface water influx (Blanchard et al., 1994). Prevention of groundwater contamination in such settings depends on preventing high herbicide levels in surface runoff water.

Groundwater can also be a source of surface water contamination during the low water levels of mid-summer. Blanchard et al. (1994) found that the main source of atrazine contamination of surface waters during mid-summer was from groundwater. Squillace and Thurman (1992) found that in the Cedar River, IA, about 6 percent of the annual river load of atrazine was transported with the groundwater. They concluded that the groundwater discharged by the alluvial aquifer was the primary non-point source of atrazine and its metabolites in the

Cedar River during base flow conditions. Atrazine moves between groundwater and surface water fairly easily, and once in surface water, is very slow to degrade.

During the last 10 years, more research has gone into determining the amount of agricultural chemicals in groundwater. Once groundwater is contaminated, the remedial actions can be expensive, time consuming, and in some cases, not feasible. Therefore, prevention and early detection of contamination are critical to water safety and human health.

Most of the groundwater utilized for drinking and irrigation is withdrawn from depths of greater than 8 meters. This research project sampled groundwater from field wells less than 6 meters deep, as well as from privately-owned deeper wells. The quality of the shallow groundwater does not directly relate to drinking water standards, since the water at these depths would not normally be used for drinking. However, the shallow groundwater with time may percolate to greater depths, and carry contaminants to deep drinking water supplies. Information gathered from the shallow well research will be useful in managing water quality at the depths used for drinking wells.

Federal and State Protection of Groundwater

The American public demands that government agencies protect drinking water and human health by reducing the risks associated with the exposure to potentially dangerous chemicals such as pesticides. In response, water quality regulations have been passed at federal and state levels. No single federal agency is assigned sole responsibility for groundwater protection; the U.S. Department of Agriculture (USDA), U.S. Geological Survey (USGS), and U.S. Environmental Protection Agency (EPA) are all involved in the prevention, detection, and correction of groundwater contamination.

The regulations that protect the nation's drinking water include the Safe Drinking Water Act Amendment of 1986, the Clean Water Act, Amendments of 1987, and the Federal Insecticide, Fungicide, and Rodenticide Act, Amendment of 1988. The later act was amended by Congress to require a 1997 deadline for reregistration of 611 active ingredients, or about 44,000 pesticide products registered prior to 1984 (Lyon, et al., 1996). This is one example of federal government actions to protect society from pesticides.

Following a 1981 decision, EPA is acting to protect groundwater supplies from five widely used weed controling pesticides. The five pesticides all classified as potential human carcinogens based on animal studies, are atrazine, simazine, cyanazine, alachlor, and metalochlor. The EPA groundwater protection strategy gives primary responsibility for groundwater protection to the states. The goal is to govern sale and use of these five pesticides based on management plans developed and tailored by each state to prevent groundwater contamination under conditions of use in that particular state.

Michigan Department of Agriculture Project

In Michigan the state agency partnering with EPA is the Michigan Department of Agriculture (MDA). The federal-state partnership proposes state management plans based on the assessment of the potential for groundwater contamination. The pesticide product labels would be changed to restrict use in accordance with terms of the state MDA developed management plans, which would be approved by EPA. The plans, called Pesticide Specific Management Plans (PSMP), consider site types and application practices in determining use of pesticides for each crop. Information is needed to ensure that application rates do not result in degradation of drinking water supplies above acceptable water quality standards. MDA developed a Grants Program to obtain groundwater pollution information for commodities, including Christmas trees. This research responds to the program in cooperation with commodity groups and grower-funded organizations, particularly the Michigan Christmas Tree Association.

The overall research goal is to provide information for implementation of a groundwater quality management plan for Christmas trees production, and at the same time, maintain the availability of chemicals that are effective and safe. The MDA has little information on atrazine, simazine, or hexazinone pesticides in groundwater for management specific treatments by site-type. Lack of such information on management specific treatments and specific site conditions could result in MDA inability to implement EPA approved PSMPs for specific

Christmas tree production site-types. This could result in cancellation of pesticide registration, even if no contamination is in fact occurring. Alternative outcomes are (1) determine groundwater pollution problems do not occur with current pesticide use practices on managed sites and continue chemical labeling for Christmas trees, or (2) determine which specific soils, subsoil textural strata, groundwater depths and pesticide use practices result in groundwater pollution problems and use PSMP approaches and label modifications to control these problems by specific site conditions.

Research Objectives

The specific objectives for this research project are:

1. Determine herbicide and nitrate fertilizer application practices and specific soil characteristics for 38 shallow wells located in fields representing the range of sites used to grow Christmas trees in Michigan.

2. Determine the concentrations of agricultural chemical pollutants (atrazine, simazine, hexazinone, and nitrate) in shallow groundwater under the fields at four separate sampling dates.

3. Compare concentrations of the chemicals in shallow groundwater under fields used for Christmas tree production to nearby established deep aquifer wells (DW) used for drinking water supplies.

4. Compare the concentration of groundwater pollutants to state and federal groundwater contamination limits.

5. Determine which site characteristics (soil texture, soil depth, organic matter content, depth to groundwater) and treatment rates are related to shallow groundwater contamination at four sampling dates.

These objectives were addressed by conducting a literature review, installing field research wells, sampling at four dates, and analyzing the results. This thesis is organized to first summarize the known technical information on nitrate, hexazinone, simazine, and atrazine. Then, the methods and materials employed in the research are presented. Next, the results are presented and discussed. Lastly, results are summarized and conclusions drawn for the five objectives.

REVIEW OF LITERATURE

One purpose of the literature review was to review appropriate methodology for site evaluations, well installation, well purging prior to sampling, and statistical analysis. Specific methods employed are presented in the Methods and Materials section. Groundwater terms were set using the definitions for aquifer and aquiclude materials, and confined and unconfined aquifers found in standard hydrology books (Brooks et al., ed., 1991).

Most research on agrichemicals in groundwater utilize domestic drinking-water wells at depths greater than the 6 meter depth studied for this research. Two studies used comparable depths; Isensee and Sadeghi (1995) utilized sampling wells at depths of 5-7 meters, while Masse et al. (1994) utilized wells at 3 meters deep. Little detail was included on the exact method of site evaluation and well installation. Therefore well design and installation techniques were adapted from methods summarized by Wilson (1995, pp.2-7, 31-65).

Well purging is critical in obtaining representative groundwater samples. Purging strategies depend on the recovery times of the individual wells. For medium- to high-yielding shallow wells screened at or near the water table, such as the wells for this project, EPA recommends purging by placing the pump inlet at the surface of the groundwater table. Wilson (1995, p 116) reports several possible purging strategies available, varying from a specified number of bore volumes, to timed sampling, to field parameter stabilization. It is concluded that three to six bore volumes should produce representative samples, but this should be verified by testing field parameters. Gibb et al. (1981) suggested that monitoring pH while sampling is a useful check for assuring representative samples.

Options for statistical analysis of groundwater pollutant concentration data were evaluated from other studies. Most studies utilized nonparametric rank correlations to analyze concentrations, since their data were non-normally distributed and many of the concentrations were less than the detection limit (Hamilton and Helsel, 1995; Kolpin and Thurman, 1993). Nonparametric statistics are not overly affected by outliers because the ranks of the data are used in the analysis rather than the actual concentrations. These statistics effectively indicate trends in the data, being less useful for predictions. The use of logistic regression, though less common than nonparametric analyses, is becoming popular for formulation of predictive models. Druliner et al. (1996) used logistic regression analysis to predict the probability of the presence of a chemical at a specified detection limit. The binary variables used in logistic regression allow for analysis of concentration results below the detection limit. This proves very useful in analyses of groundwater chemical concentrations.

The other major purpose of reading the scientific literature was to review the nature and occurrence of agrichemicals in groundwater. The review focused on information about each herbicide, particularly characteristics that affect the movement of the chemical through the soil to the groundwater. A search for information on the target species, mode of action, persistence in the soil, degradation and environmental fate, leaching, occurrences in groundwater, and toxicity was included for each herbicide studied. This information gave general background for each chemical, helped determine factors pertinent to herbicide occurrences in groundwater, and was useful in understanding and discussing research results.

Nitrate Technical Information

Nitrogen is an essential nutrient for living plants and animals. In plants, it is part of the chlorophyll molecule, amino acids, proteins, and many other fundamental compounds. It takes large amounts of nitrogen to optimize growth in plants, with inadequate levels resulting in stunted growth, diminished water use efficiency, reduced crop quality, and low yields (Farm Chemicals Handbook, 1996). Nitrogen is also necessary for carbohydrate production, nutrient uptake, and protein synthesis. Deficiencies of nitrogen can cause chlorosis of the leaves, moving from the older leaves to the newer ones.

Fertile soils with adequate decomposable organic matter and large microbial populations are capable of storing enough nutrients for optimal plant growth. However, much agricultural land can not support the nitrogen demands of continuous cropping, and nitrogen fertilizers, like anhydrous ammonia, ammonium nitrate, ammonium sulfate, and urea, are commonly used to supplement the nitrogen supply. An estimated 6.3 million tons of nitrogen fertilizer were applied to cropland in the Mississippi River Basin in 1991 alone (Goolsby et al., 1994). Other inputs that are harder to determine include animal wastes, septic systems, domestic sewage, nitrate fixed by legumes, microbial mineralization of soil organic matter, and with less frequency, natural geological origins. Nitrogen fertilizers are the most frequently cited cause for groundwater contamination of nitrate, even though the other sources collectively can contribute hundreds of kilograms of nitrate per hectare each year (Power and Schepers, 1989).

Environmental Fate and Degradation

To understand the significance of nitrate (NO_3^-) in the environment, a short overview of the nitrogen cycle is in order, as summarized in Figure 1. Due to space constraints and the complexity of the nitrogen cycle, only the basics will be presented for a general background. Ninety percent of the

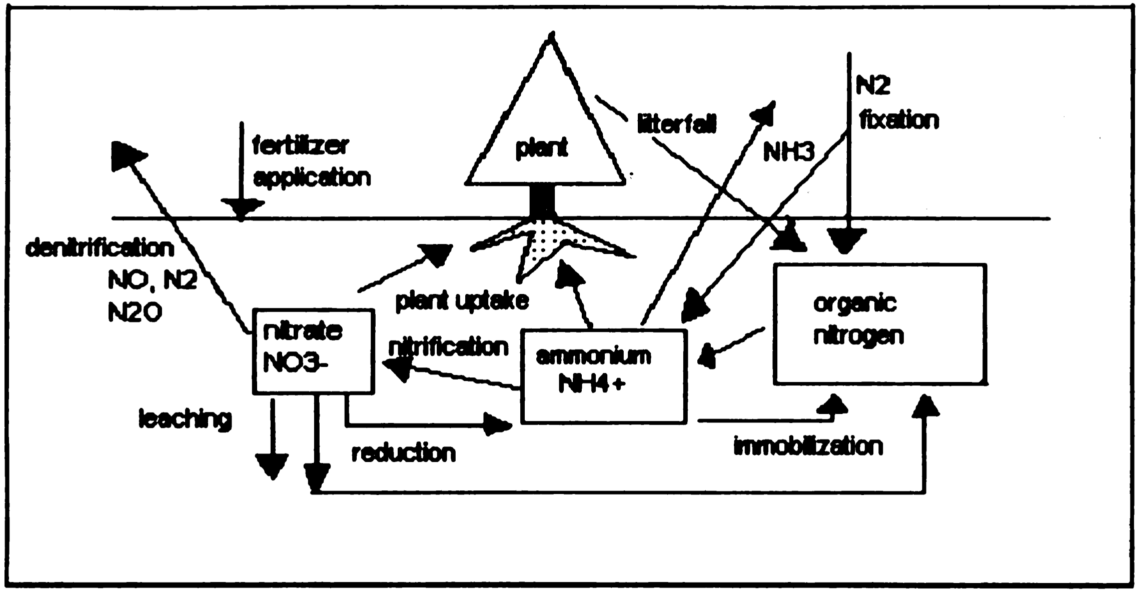

Figure 1. Nitrogen Cycle

nitrogen in the soil can be in organic forms due to the decaying of plant material and litter fall, and from atmospheric nitrogen (N_2) fixation (Ellis lecture, 1996). Nitrogen fixation occurs in legumes, and, to some extent, in other plants. Plants absorb nitrogen in inorganic forms, and nitrogen must be mineralized by soil bacteria into ammonium ions (NH_4^+) or nitrified from ammonium into nitrate prior to plant uptake. In the root zone, ammonium absorbed to soil particles or in the soil solution is available for plant uptake, or it can be volatilized as ammonia (NH_3) and released into the atmosphere. Nitrate formation from microbial nitrification of ammonium occurs under aerobic, low temperature conditions.

Nitrification: $2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 4H^+ + 2H_2O$
$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^-$

Nitrate is generally not significantly adsorbed to soil particles, allowing for leaching to occur (Vinten and Smith, 1993, p 51). The nitrite (NO_2^-) intermediate, though the greater health concern, is usually not stable enough during nitrification to leach out of the root zone, as in the case of nitrate. Once nitrate moves below the root zone, there are a number of possible fates. There can be soil retention, reduction into microbial biomass, dissimilatory reduction to ammonium, denitrification, and continued leaching to groundwater (Korom, 1992). Dissimilatory reduction to ammonium is the reverse of nitrification, while denitrification is the process of nitrate reduction to nitrogen oxides (NO, N_2O) or N_2

by soil bacteria under anaerobic conditions (Farm Chemicals Handbook, 1996; McFarland, 1995; Vinten and Smith, 1993).

Denitrification:

$$4\ NO_3^- + 5\ HCHO \rightarrow 2\ N_2 + 5\ CO_2 + 4\ OH^- + 3\ H_2O$$

(carbon source)

or in a more simple example:

$$2\ HNO_3 + 4\ H^+ \rightarrow 2\ HNO_2 + 2\ H_2O$$
$$2\ HNO_2 + 2\ H^+ \rightarrow 2\ NO + 2\ H_2O$$

Soil retention of nitrate and microbial degradation are less notable factors after nitrate moves below the root zone. Denitrification, on the other hand, can eliminate nitrogen from soil and groundwater. For example, in the groundwater and vadose zone below the root zone, nitrification of ammonium can form nitrate under aerobic conditions, while in the absence of dissolved oxygen, nitrate reduction to ammonium can occur (Lawrence, 1996). Ammonium is less likely to leach than nitrate since it adsorbs to soil. Therefore, reduction to ammonium only temporarily changes the state of the nitrogen and doesn't remove it from the system.

The four general requirements for denitrification are 1) nitrogen oxides as terminal electron acceptors, 2) bacteria capable of denitrifying, 3) electron donors, and 4) anaerobic conditions (Korom, 1992; Lawrence 1996). The most common electron donors are organic carbon, sulfides, and reduced manganese and iron. If the supply of nitrate exceeds the supply of organic carbon, denitrification can not continue without finding an alternative electron source. Surface water and vegetation often provide the additional carbon source. It is generally accepted that denitrification is optimal with increased temperature and water content and in the range of pH 7.0 to 8.0 in anaerobic soils within 305 cm (10 ft) of the soil surface (Bruggeman et al., 1995; Koskinen and Keeney, 1982; Goodroad and Keeney, 1984, Ellis lecture, 1996). Denitrification has been found to occur in water-logged, poorly aerated soils and aquifers with a shallow water table (Kolpin and Thurman, 1993; Spalding and Exner, 1993,). In the southeastern U.S., vegetative uptake and denitrification are responsible for natural remediation of nitrate in shallow aquifers. The warm, wet, carbon-rich environment in the south contributes to the denitrification occurring below the root zone (Spalding and Exner, 1993).

Leaching

Of the various forms of nitrogen present in soils, nitrate is the only form leached to groundwater in appreciable amounts (Vinten and Smith, 1993). The groundwater contamination is partially due to the high solubility and mobility of nitrate and the lack of substantial soil sorption (Wehtje et al., 1984; Chen, 1996). Precipitation appears to be the driving force that moves nitrate vertically, usually in identifiable zones (Bobier et al., 1993; Jones and Schwab, 1993; Southwick et al., 1995). Less nitrate movement has been seen in dryer years than in comparable years with average or above average rainfall

(Kalkhoff and Schaap, 1995). Dry periods may allow a nitrate build up in the soil that can leach in subsequent years having greater rainfall. For this research, nitrogen application data from several years is included to take into account variability in precipitation and delayed leaching.

For one study, a fine-textured soil had a vertical transport rate of 76 cm (30 inches) in a year, which corresponded with the annual rainfall of 66 cm (26 inches) (Bobier et al., 1993). Jones and Schwab (1993) found that nitrate could move 254-360 cm (100-142 inches) in a year through a fine-textured silty clay loam soil, depending on the amount of rainfall in that year. Under normal conditions, concentrations of nitrate can reach groundwater 4 to 12 months after application at a site with a water table at 152-457 cm (5-15 feet deep) (Delin et al., 1994). Through the use of bromide tracers, Chen (1996) estimated the rate of nitrate downward movement to be about 335 cm (132 inches) in one year through a heavier textured soil, allowing for groundwater contamination within 2 years in lowlands, and taking longer than 9 years in uplands. This suggests that nitrate applied in normal years might intercept the groundwater surface at depths of 122-620 cm (4-20 feet) within 4 months to 2 years after application.

A number of factors contribute to groundwater contamination from nitrate. Land use, especially farming, can affect groundwater nitrate levels. Nitrate levels are significantly higher in agricultural areas than in residential areas, due to irrigation and the application of fertilizers and manure in the agricultural areas (Fishel and Lietman, 1985; Hamilton and Hesel, 1995; MacLeod et al., 1994). If the nitrate levels in soil are higher than the amount required by the plants, leaching is more likely to occur. The increased pH associated with lime treatment has also been linked to an increase in nitrate leaching (Azevedo et al., 1996; Hamilton and Hesel, 1995). Permeable soils having low organic matter content, like sandy soils, may facilitate the leaching of nitrate to groundwater, especially under conditions of high rainfall seen in spring and early summer (Farm Chemicals Handbook, 1996; Hamilton and Helsel, 1995). The role of water in nitrate movement can also be seen in the higher incidence of nitrate contamination in irrigated farmland and lowland areas compared to observed occurrences in non-irrigated farmland and highlands (Chen, 1996).

Nitrate is carried in subsurface waters more often than herbicides, with concentrations at the highest during late fall, winter, and spring, and the lowest during summer (Kladivko et al., 1994). The lower summer nitrate concentrations found above are in part due to the correlation to the growing season, when plants can assimilate the available nitrate. Decreased water movement in the summer also contributes to less leaching from the soil into the groundwater (Goolsby et al. 1993). Once in groundwater, nitrate can persist under acidic, low temperature conditions. Groundwater can also be contaminated from the surface water interface (McFarland, 1994). Komor and Magner (1996) found that the groundwater nitrate concentrations increased with proximity to a stream due to mixing with nitrate-rich stream water.

There are a number of factors that lessen nitrate contamination. Highly organic, water-saturated riparian soils are effective at naturally removing nitrate from the groundwater (Schipper et al. 1993; Groffman et al., 1996). The organic matter may store the nitrate for plant uptake and anaerobic microbial degradation. The organic riparian soils provide greater water quality protection, with less nitrate reaching the groundwater, when compared to fertilized croplands. Also, the greater the depth to the water table, the less nitrate can leach to the groundwater (Hamilton and Helsel, 1995). Once nitrate reaches the groundwater, it tends to remain at the top of the saturated zone, with less contamination in the deeper groundwater (Chen, 1996; Kalkhoff and Schaap, 1995; Spalding and Exner, 1993). This may be due to the anaerobic conditions and the increased potential for denitrification at the greater depths.

Occurrences in Groundwater

Nitrate is the most ubiquitous chemical contaminant in the world's aquifers, with the occurrences of contamination increasing (Spalding and Exner, 1993). In the EPA's national survey of agrichemicals in drinking water wells from 1988 to 1990, nitrate was the most frequently detected compound in the 94,600 community water system wells and in more than 10.5

million rural domestic wells. Community water wells had detectable nitrate levels below the MCL of 10 mg/L in 50.9 percent of the wells, and above the MCL in 1.2 percent, while the rural wells had detectable levels below the MCL in 54.6 percent, and above the MCL in 2.4 percent (USEPA, 1990).

Other studies found similar groundwater concentrations. For 110 wells sampled in the Mississippi River Basin, over 70 percent of the groundwater samples had detectable levels of nitrate (Kolpin and Thurman, 1993). Burkart and Kolpin (1993) found detectable levels of nitrate in 59 percent of the 303 wells sampled, with 6 percent exceeding the MCL. For one study of nearly 35,000 wells that have been tested in the Midwest, 3.4 percent exceeded the drinking water standard for nitrate with 29 percent of the wells also testing positive for nitrate at levels below the MCL (Richards et al., 1996). The older and more shallow wells had more nitrate problems, with fewer than half of the less than 15 meter deep wells being free of nitrate. A key characteristic of nitrate detection for this study was that the very high nitrate levels accounted for only 1 percent of the samples, while the very low levels constituted about 50 percent. Chen (1996) found a nitrate detection of greater than 5 mg/L in 81 percent of the groundwater samples from 1991-1993 in a Nebraska study of agricultural areas. Groundwater under agricultural areas tend to have higher nitrate levels than under nonagricultural lands (McFarland, 1994; Spalding and Exner, 1993). This indicates that actions to manage health concerns for public drinking water supplies may differ depending on land use near the aquifer.

Toxicity

In order to comply with the Safe Drinking Water Act, drinking water is not allowed to exceed the nitrate maximum contaminant level (MCL) of 10 mg/L based on a single sample. This is unlike herbicides where the maximum contaminant level is based not on a single sample, but on an annual average. Nationwide data suggest that nitrate levels below 3 mg/L represent naturally occurring background levels in groundwater (Lawrence, 1996; Spalding and Exner, 1993). Many researchers group drinking water nitrate analysis results into degrees of contamination. Less than 3 mg/L is considered natural, 3-10 mg/L is termed nitrate-enriched, and 10 mg/L or greater is contaminated. Other researchers disagree and choose 1 ppm as the indicator of background nitrate levels (Lawrence, 1996; McFarland, 1994; MacLeod, et al., 1995). For this research, 3 mg/L will be the line between natural and anthropomorphic sources of nitrate. It will also be used as an indicator for potential health concerns in the interpretation of results.

There have been unconfirmed relationships between nitrate ingestion and a variety of ailments. Among these are hypertension, central nervous system birth defects, and certain cancers including stomach cancer and non-Hodgkin's lymphoma (Spalding and Exner, 1993). Though there had been only weak correlations between nitrate ingestion and these health problems, there is strong evidence of nitrate impairing the ability of blood to carry oxygen.

Nitrites can cause problems in young children and farm animals. Nitrites bind very strongly to hemoglobin, and can affect the blood's ability to carry and release oxygen. This serious medical condition, called methemoglobinemia, is found mostly in infants under six months of age or in newborn animals. Nitrates are ingested, through water or food, and nitrate-reducing bacteria in the infant's digestive tract convert the nitrates to nitrites. The nitrites find their way to the circulatory system, and bind very tightly with hemoglobin. These reactions change the healthy blood hemoglobin to an inactive methemoglobin form, hindering the delivery of oxygen to body tissue. Nitrite-bound hemoglobin is practically useless for oxygen transfer; causing shortness of breath, increased susceptibility to illness, heart attacks, and even death by asphyxiation in extreme cases. As children develop, stomach acidity increases, nitrate-reducing bacteria are killed, and the danger of nitrate to older children and adults is eliminated.

Hexazinone Technical Information

The molecular formula of hexazinone, a triazine herbicide, is $C_{12}H_{20}N_4O_2$. First described in 1975 by DuPont, hexazinone can be formulated as a water-soluble powder, granule, or water soluble liquid. Velpar L formulation is a water-dispersible liquid herbicide manufactured by DuPont that is mixed in water and applied as a spray for weed control in alfalfa, pineapple, sugarcane, Christmas trees, forestry site preparation and release areas, and industrial areas (Velpar L label, 1997). Hexazinone is an effective general herbicide that provides both contact and residual control of many established annual, biennial and perennial weeds and woody plants. Foliar activity is most effective under conditions of active plant growth, high temperature, high humidity, and good soil moisture. Moisture is required to activate hexazinone in the soil, with best results obtained upon application to moist soil and followed within two weeks by rainfall (Farm Chemicals Handbook, 1996; Extoxnet, 1993).

Mode of Action of Herbicide

The contact properties of hexazinone allow it to be readily absorbed through the roots. Once applied to the stems or contacting the roots, the triazines are absorbed, move upward through the xylem, and are carried in the transpiration stream to the leaves (Jachetta et al., 1986). Triazine herbicides, including hexazinone, simazine, and atrazine, are reported to block photosynthesis by binding to the D1 protein in the electron transport chain. This stops CO_2 fixation and production of ATP and $NADPH_2$, needed for plant growth (Herbicide Handbook, 1994). Others postulate that rather than causing damage by blocking carbohydrate production, there is a secondary phytotoxic substance produced. When the electron chain is blocked, energy builds up and can lead to the production of free radicals, such as singlet O_2 (Penner, 1994). The free radicals can bypass the protection from carotenoids and attack membranes, resulting in peroxidation of membrane lipids (Fuerst and Norman, 1991). This causes leaky membranes, leading to leaf desiccation and interveinal chlorosis, followed by necrosis, in the target plants. Hexazinone can be metabolized by *Pyrus melanocarpa* and *Rubus hispidus* into several demethylated or hydroxylated triazinone metabolites (Herbicide Handbook, 1994; Rhodes, 1980). Once metabolized, the plant is tolerant to the metabolite and will be protected from damage.

Persistency

With time, hexazinone will degrade in the soil. Reported values for the half life of hexazinone in soils range from less than 28 days to 180 days (Bouchard et al., 1985; Neary et al., 1983; Rhodes, 1980; Sung et al., 1981). For example, an alfalfa plot displayed no residue after two months, while hexazinone had a half-life of three months when applied to pineapples. Persistence of hexazinone in the soil is variable, depending on soil types, pH, and soil temperature (Weber et al., 1969; Extoxnet, 1993). This variability can be attributed to the processes of sorption, degradation, and leaching. For example, it was shown that hexazinone degradation is slower at

10 degrees C than at 30 degrees C in both gravely fine sandy loam and clay loam soil types (Bouchard et al., 1985). Weber et al. (1969) suggest that triazine herbicide persistency and adsorption to soil increase at lower pH, and with increased soil clay or organic matter content. Lateral or vertical movement in soil is slowed by high organic matter or clay levels, adding to the persistence in the soil (Neary et al., 1983). Sung et al. (1981) found that the half-life for hexazinone was 4-6 weeks in a clay soil, and only 4 weeks in loamy sand, while Rhodes (1980) found a half-life of less than 4 months in both silt loam and sandy loam soils. This demonstrates the subtle variability in persistence due to soil types, allowing for hexazinone residue to persist in the soil for between 1-6 months.

Environmental Fate and Degradation

Hexazinone that has adsorbed or partitioned into the organic matter of soil is not immediately available for leaching, and degradation can occur. Hexazinone can be degraded by both microbes and sunlight. The ring structure of hexazinone is broken by soil microbes, releasing carbon dioxide. The major microbial processes involved in hexazinone decomposition are demethylation and hydroxylation of the four position of the cyclohexyl ring (Rhodes, 1980). Using ^{14}C labeled material, microbial degradation reveals 45 to 75 percent of the ^{14}C is given off as $^{14}CO_2$ after 90 day incubations. Since hexazinone does not greatly effect microbial populations, the potential for degradation in the soil is great (Rhodes et al., 1980). However, as hexazinone leaches deeper into the soil, oxygen becomes limited and microbes are less likely to degrade the compound.

Sunlight can break down the compound through photodegradation. When dissolved in water under artificial sunlight, approximately 20 percent of the hexazinone photodegrades in 8 weeks, while in the dark, it remains stable for at least 8 weeks (Herbicide Handbook, 1994). In studies on thin soil surfaces, 60 percent of applied hexazinone was degraded during a 6 week exposure to UV light. Photodecomposition rates are about three times faster when small amounts of inorganic salts are present. Again, once hexazinone leaches deeper into the soil, photodegradation is nearly impossible. In the event hexazinone reaches stream water, it requires several years to degrade to even one-half of the original concentrations (Bouchard et al., 1985).

Leaching

Decreases in hexazinone can be attributed not only to degradation, but also to leaching. 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 et al., 1985). Hexazinone has been classified as mobile in the environment, even though it adsorbs to the organic matter and leaf litter layer of forest soils (Bouchard and Lavy, 1985; Rhodes, 1980). Due to its solubility, hexazinone is transported mainly in the aqueous phase, interacting mostly with nonpolar surfaces. This indicates that once it moves below the organic layer, it is weakly adsorbed by soil and the potential for movement and leaching increases, especially in sandy soils. If hexazinone leaches to the groundwater, both microbial degradation and photodegradation are negligible processes of dissipation of the compound.

Occurrences in Groundwater

Hexazinone has been detected in groundwater and water-supply systems in the United States due to agricultural uses. Though reported levels generally have been low, hexazinone has been detected in Minnesota, Arkansas, and Georgia (Hallberg, 1989). Not many research studies are looking for hexazinone in groundwater, especially when compared to atrazine and simazine. This may be due to the low human toxicity associated with hexazinone.

Toxicity

Despite hexazinone's effective toxicity to a number of plants, its general toxicity to humans, wildlife, and fish is low (Extoxnet, 1993; Herbicide Handbook, 1994). The oral LD_{50} in rats is 1690 mg/kg and the dermal LD_{50} in rabbits is greater than 6000 mg/kg. Two-year studies with dietary levels of up to 500 mg/kg in rats and mice revealed no evidence of cancer. Hexazinone is unlikely to be teratogenic to developing fetuses, based on rat and rabbit studies; nor mutagenic, based on a variety of bacteria and mammalian cell tests. Eye irritation in rabbits and humans is severe, and likely to cause irreversible eye damage. The potential for eye contact is limited to herbicide handlers, while ingestion from drinking water is the major route of exposure for the public. As part of the National Pesticide Survey, the EPA has issued a Lifetime Health Advisory Value of 200 µg/L for hexazinone. 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.

Simazine Technical Information

The molecular formula for the triazine herbicide simazine is $C_7H_{12}ClN_5$. Synthesis and testing of triazine compounds as herbicides began in 1952 in the Geigy laboratories in Basle, Switzerland. Simazine was first released for experimental evaluation in 1956, and became commercially available for use in corn in 1958 (Herbicide Handbook, 1994). Manufactured as Princep by Ciba-Geigy, simazine is formulated as a wetable powder, granule, water dispersible granule, or liquid. Simazine is a soil-applied herbicide used to control annual broadleaf and grass weeds for corn, berry fruits, turfgrass, ornamental trees, orchards, and vineyards. Before 1992, it was used to control algae and submerged weeds in ponds and cooling towers (Extoxnet, 1993). After application, moisture is needed to move simazine into the root zone for absorption by the plants (Princep DF label, 1993).

Mode of Action of Herbicide

Simazine, like hexazinone, is a systemic herbicide readily absorbed through roots after soil application. It is transported to the leaves via the apoplast and works by inhibiting photosynthesis by causing interveinal chlorosis and necrosis in susceptible plants (Herbicide Handbook, 1994). However, the chloro-s-triazine herbicides, such as simazine and atrazine, can be degraded in some higher plants by three major metabolic pathways: hydrolysis at the 2 position of the heterocyclic ring, N-dealkylation of the side chains, and conjugation with glutathione (Hatzios and Penner, 1982). Plant tolerance can be principally associated with the reactions at the 2-position site of the chlorine atom. Benzoxazinone-catalyzed hydrolysis, producing hydroxy simazine, occurs in the roots of some tolerant species such as corn and contributes extensively to the detoxification of soil-applied simazine (Herbicide Handbook, 1994; Hatzios and Penner, 1982). The other essential degradation mechanism is glutathione conjugation seen in highly-tolerant species, such as corn. N-dealkylation of the side chains occurs at moderate rates in most plant species, though it is not considered as a vital mechanism for detoxification. Rather, it is accepted that N-dealkylation contributes to the selectivity of tolerant plants (Hatzios and Penner, 1982). The ability of simazine to reduce weed growth is more closely correlated with the amount of organic matter in the soil than with the amount of simazine in the soil solution (Day et al., 1968). This can be indicative of the relationship between the effectiveness as an herbicide and the persistence in the soil.

Persistency

The soil sorption coefficient, Koc, for simazine is 138 mL/g. The Koc measures the tendency of the chemical to adsorb to soil particles. A Koc less than 500 mL/g indicates that the herbicide tends to be transported in the dissolved phase, rather than adsorbed to soil particles (Goolsby et al., 1993). Simazine is one of the most persistent herbicides in soil and groundwater, despite its weak adsorption to soil particles (Nearpass, 1965). Reported values for the half life of simazine range from 36 to 234 days on sandy loam soils, 85 to 178 days on loamy sand soils, and 55 to 186 days on loam soils (Extoxnet, 1993; Herbicide Handbook, 1994). The variability can be attributed to pH and temperature, as well as to the amount of clay and organic matter in the soil. Simazine more readily adsorbs to acidic, organic, or clay soils, than to neutral, low organic soils, or calcareous soils (Weber et al., 1969; Harris and Sheets, 1965). Also, as pH and temperature decrease, adsorption of simazine increases, contributing to the persistency in the soil (Harris and Warren, 1964). A longer half life can imply that the herbicide will be more available for plant uptake or to wash off in a storm. Due to such variability, residual activity in the soil can remain for 2 to 7 months. This should allow for wells in this study to detect simazine applied sometime within the last three years.

Environmental Fate and Degradation

Simazine that has adsorbed to the clay and organic matter in the soil is potentially available for chemical degradation. Simazine chemically decomposes more readily when adsorbed onto soil particles, especially in warmer acidic soils. Simazine is subject to photodegradation from sunlight when field applied. On a sandy loam soil at 25 °C, simazine has a half life of 21 days under natural light. Mono-N-deethylated metabolites and hydroxy simazine were produced 207 hours after herbicide application. Photodegradation can contribute more to the dissipation of simazine the longer it remains in surface soil, especially under prolonged lack of rainfall.

Microbial degradation is the major form of simazine dissipation in high pH soils, where hydrolysis rates are slow; while in low pH soils, biological degradation is less important due to the faster rate of non-microbial, chemical hydrolysis

(Herbicide Handbook, 1994; Whetje et al., 1984). The half-life for simazine was 91 days for aerobic microbial degradation and 77 days for anaerobic degradation in a sandy loam soil. Once simazine leaches below the Ap soil horizon, there is a higher risk of movement to the groundwater, especially in sandy soils, since adsorption in the lower depths is minimal.

Once simazine reaches surface water, it is relatively stable with little photodegradation and microbial degradation. This is because surface water contains much less organic matter and fewer microorganisms to degrade the herbicide (Goolsby et al, 1993). In surface water, the average half-life is 30 days, dependent upon the amount of algae and weeds present (Extoxnet, 1993; Herbicide Handbook, 1994). This made simazine a good treatment for controlling growth of algae in surface water.

Leaching

Since simazine is loosely sorbed to soil particles, the potential for leaching is assumed to be great. Chemicals with water solubilities less than 30 mg/L are less likely to wash off the soil during storms, though the potential for eventual leaching remains (Goolsby et al. 1993). Simazine has low water solubility (6.2 mg/L), but once it moves out of the top soil layer, slower degradation and less binding to soil can lead to an increase in leaching. For simazine and atrazine, leaching can be influenced by many factors, including pH, rainfall, and fertilization. At an acidic pH, simazine and atrazine would be bound to the soil via cationic bonds. Leaching can be increased with an increase in pH, such as seen with ammonia fertilizer. A soil pH increase from 5.7 to 9, due to the addition of ammonia, can increase the amount of triazine herbicide leached by up to 60% when compared to unfertilized soil (Clay and Harper, 1994). Studies have shown that many spring-applied herbicides are mainly detected in drainage water and groundwater less than 620 cm (20 ft) deep during the first month or two after application, with little or no pesticides detected during fall, winter, and early spring (Kladivko et al., 1991; Isensee and Sadeghi, 1995). The majority of this herbicide loss has been dependent on rainfall, especially the first large stormflow (Kladivko et al., 1991; Cullum, 1995; Fenster et al., 1969; Muir and Baker, 1976). The amount, intensity, and frequency of rainfall can all affect herbicide persistency in the soil, and consequently the amount of herbicide that can leach into the groundwater.

Occurrences in Groundwater

Simazine levels in groundwater have only recently been measured by the government and other researchers. According to the EPA's National Pesticide Survey in 1990, 1.1 percent of 94,600 community water system wells, and 0.2 percent of 10.5 million rural domestic wells had measurable levels of simazine (EPA, 1990). Many other studies found similar occurrences of simazine in the groundwater. Kolpin et al. (1996) detected simazine in 2.6 percent of the 303 wells, with a maximum concentration of 0.27 µg/L. Bukart and Kolpin (1993) found 1.0 percent of the 579 near-surface aquifer wells sampled contained simazine in the water. Kolpin and Thurman (1993) detected simazine in 1.8 percent of the 110 near-surface wells sampled after the Mississippi River flooding of 1993, with a maximum concentration of 0.7 µg/L. Even though these levels are all lower than the EPA's MCL of 4 µg/L, this still shows the potential for simazine contamination of the groundwater due to agricultural uses. Long-term modeling for atrazine, simazine, and alachlor indicate that for a well 8 meters deep located 200 meters from a pesticide application site in an alluvial sand soil, the probability of exceeding the maximum contaminant level for simazine is about 35 percent, while nearly zero for atrazine and alachlor (Varshney et al., 1993). Therefore, prudent use of simazine in very susceptible areas was recommended, and identification of these areas was considered crucial for the continued use of simazine.

Toxicity

The EPA has classified simazine as a possible human carcinogen because it may have caused cancer in test animals receiving high doses over the course of their lifetimes (Extoxnet, 1993). Dermal LD_{50} for simazine in rabbits is greater than 3100 mg/kg body weight, and chronic dietary studies show minimal effects in rats and dogs at levels greater than 100 mg/L (Herbicide Handbook, 1994). Since simazine in drinking water may possibly increase the risk of cancer in humans, the Lifetime Health Advisory value of 4 µg/L includes an additional safety factor. The EPA believes that consuming water at or below this level is acceptable for drinking every day over the course of a lifetime without posing health concerns. Simazine stimulates its own breakdown in the liver, but consuming levels much higher than the advised level has caused tremors, gene mutations, and damage to the kidneys, liver, and thyroid in laboratory animals. Despite these serious conditions in laboratory animals, ecological effects on birds and other animals have been insubstantial. Therefore, the greatest safety consideration for simazine is the potential health effects to humans from drinking water.

Atrazine Technical Information

The molecular formula of atrazine, a triazine herbicide, is $C_{12}H_{14}ClN_5$. Synthesis and testing of triazine compounds as herbicides began in 1952 in the Geigy laboratories in Basle, Switzerland. Atrazine was first released for experimental evaluation in 1957, and became commercially available for use in corn in 1958 (Herbicide Handbook, 1994). Manufactured by Ciba-Geigy as Aatrex, atrazine is formulated as a wetable powder, dry flowable, water dispersible granule, flowable liquid, or liquid. Atrazine is one of the most widely used herbicides in North America, though it is classified as a

Restricted Use Pesticide, due to groundwater concerns (Masse et al., 1994). Since 1993, Ciba labels have not listed atrazine use for noncrop total vegetation control and have required buffer areas between atrazine application sites and surface water (Herbicide Handbook, 1994). This is of particular concern since after application, moisture is needed to move atrazine into the root zone for absorption by the plants (Aatrex 4L label, 1994). Atrazine is a pre-emergent, soil-applied herbicide used to control annual broadleaf and grass weeds for corn, sorghum, turfgrass, Christmas trees, sugar cane, and pineapples. More than 80 percent of the atrazine used in the United States is applied to control broadleaf weeds in cornfields in the Midwest (Fausey, et al., 1994).

Mode of Action of Herbicide

Atrazine, like simazine and hexazinone, is a systemic herbicide that is readily absorbed through roots from soil application. It is transported to the leaves via the apoplast and works by inhibiting photosynthesis (Herbicide Handbook, 1994). Atrazine causes interveinal chlorosis and necrosis in susceptible plants, and can be degraded in some higher plants by the same three major metabolic pathways as simazine. Unlike simazine, glutathione conjugation is the vital mechanism for detoxification of atrazine in corn and sorghum and other plants with high levels of glutathione transferase. Benzoxazinone-catalyzed hydrolysis, producing hydroxy atrazine, occurs in the roots of some tolerant species such as corn, but not sorghum, to detoxify soil-applied atrazine (Herbicide Handbook, 1994; Hatzios and Penner, 1982). Removal of the ethyl group on atrazine results in a partially phytotoxic metabolite, while removal of both the ethyl and isopropyl groups leads to a completely inactive metabolite (Hatzios and Penner, 1982). N-dealkylation of the side chains occurs at moderate rates in most plant species, though it is not considered as a vital mechanism for detoxification. Rather, it is accepted that N-dealkylation contributes to the selectivity of tolerant plants.

Persistency

Atrazine has been found to persist in soils up to the next growing season. The soil sorption coefficient, Koc, for atrazine is 100 mL/g. Since the Koc is less than 500 mL/g, this indicates that the herbicide tends to be transported in the dissolved phase, rather than adsorbed to soil particles (Goolsby et al., 1993). Atrazine is one of the most detected herbicides in soil and groundwater, even though it adsorbs to soil particles. The average half-life of atrazine in the field is 60 days, though residues have been found to remain in a clay loam soil for up to 12 months (Sirons et al., 1973). The half-life can range from 20 days and up in a sandy soil, 39 to 119 days for sandy loam, and 35 to 261 days for loam soils (Extoxnet, 1993; Leonard and Hicks, 1994; Workman and Nokes, 1994). In laboratory experiments, the half-life of atrazine can extend from 50 days at the surface to 100 days at 107 cm (3.5 feet) below the surface (Leonard and Hicks, 1994). Typically, atrazine remains in the first 15 cm (6 in) of soil for long periods of time (Burnside et al., 1969; Leonard and Hicks, 1994; Fausey et al., 1994; Clay et al., 1994). This can vary, as with the other triazines, due to the pH, temperature, soil type, and amount of organic matter and clay in the soil. Atrazine more readily adsorbs to acidic, organic, or clay soils, than to neutral, low organic soils, or calcareous soils (Weber et al., 1969; Harris and Sheets, 1965; Harris, 1966). Atrazine and simazine are more easily desorbed from bentonite clay than from organic matter (Harris and Warren, 1964) The amount of atrazine bound to soil decreases at high pH (McGlamery and Slife, 1966). Ammonia fertilizers increase the pH to around 9, and can decrease the amount of atrazine bound to soil and increase movement through the soil by 30 to 60 percent (Clay and Harper, 1994).

Environmental Fate and Degradation

Atrazine, like simazine, can degrade in the soil environment due to microbes and chemical hydrolysis. Chemical hydrolysis rates are slow at high pH (pH 7.5-8), but hydrolysis becomes the major contributor to degradation at lower pH (pH 5.5-6.5), producing hydroxy atrazine (Herbicide Handbook, 1994). Hydrolysis rates can increase with the addition of organic material, regardless of pH. Microbial degradation plays a larger role than hydrolysis in the dissipation of atrazine in the soil. More atrazine is degraded in aerobic than anaerobic conditions. Atrazine uses oxygen as an electron acceptor, so without oxygen, the isopropyl side chain degrades very slowly. Microbial metabolism in a loam soil produced a half life of 146 days for aerobic conditions and 159 days for anaerobic conditions (Herbicide Handbook, 1994). Nair and Schooner (1992) concluded that under anaerobic conditions, 2 kg/ha would degrade in 4 years, while in aerobic conditions, it would only be 100 days, with the later comparable to literature values of 20-100 days. Atrazine is aerobically transformed into the dealkylated metabolites deethylatrazine (DEA) and deisopropylatrazine (DIA) by microorganisms and fungi (Adams and Thurman, 1991; Thurman et al., 1991; McMahon and Chapelle, 1992; Squillace et al., 1993). Atrazine is metabolized into DIA preferentially over DEA, which is more mobile than atrazine, moving rapidly through the soil (Behki and Khan, 1986; Muir and Baker, 1976).

Fausey and others reported that most atrazine remains near the soil surface where soil organisms can degrade it. Atrazine will remain longer on the surface of soils with high clay or organic matter content, as long as no heavy rainfall events occur (Workman and Nokes, 1994). If atrazine moves below the soil A horizon, limited available oxygen generally decreases the biotransformation rates (Burkart and Kolpin, 1993; Clay et al., 1994; Burnside et al., 1969). Degradation in subsoil layers can proceed at up to one-third of the rate in surface soil (Weihtje, 1984). Microbial populations decrease with soil depth, resulting in slower degradation, less soil binding, and increased leaching potential at greater soil depths (Clay et al., 1994). This can allow atrazine to persist for longer than a year in high pH soils with cooler, dry soil conditions, where microbial activity is at a minimum (Extoxnet, 1993).

Atrazine has a greater potential for surface run off during the first 45 to 60 days after application, or after the first large rainfall (Alberts et al., 1994). The first major rainfall event can account for greater that 90 percent of the herbicide losses due to surface runoff (Cullum, 1994). Most herbicide loss is in May through July, with less atrazine reaching drainage water during fall, with increases during the winter recharge (Alberts et al., 1994; Donald et al., 1994; Isensee and Sadeghi, 1995; Kladivko et al., 1994). Once atrazine reaches surface water, degradation is dependent on chemical hydrolysis rather than biological activity (Extoxnet, 1993). Hydrolysis rates in water, as in soils, can increase with extreme pH and with the addition of humic materials. Atrazine photolysis in surface water, however, is inhibited by dissolved organic matter, but enhanced by nitrate (Johnson et al., 1994).

Leaching

Sorenson et al. (1994) found that leaching potential is greatest in sandy loam for the first 2-3 months after treatment, while clay loam leaching continued for over a year after application. A delay of several days between application and rainfall can allow time for sorption and decrease its availability for leaching (Isensee and Sadeghi, 1995). Dissolved atrazine has been found in groundwater due to percolation of water through the soil (Adams et al., 1991).

Generalizations regarding pesticide leaching with respect to soil type have suggested that coarse-textured soils, like sands, have greater potential for pesticide leaching than fine-textured soils, like loams. However, field research has indicated that rapid water infiltration and short water residence time in coarse-textured soil may result in less pesticide being leached than in finer textured soils (Sorenson et al., 1994; Adams et al., 1991; Masse et al., 1994; Felding, 1992). Atrazine should be bound to the soils with more clay and organic matter, but leaching studies have found that due to a greater water-holding capacity and a slower infiltration rate in the fine-textured soils, the herbicide had more time to desorb and move with the water through the soil. Rapid water movement in the sandy loam did not allow sufficient time for residues to desorb from the soil, therefore it appears that the greatest leaching threat for sandy soils would occur shortly after application. Movement in clay loam, however, could continue for over a year after treatment because of the slower water movement and greater time available for desorption to occur (Sorenson et al., 1994). For this same study, more leaching occurred in the clay loam than in the sandy loam, with the initial leaching in the clay loam showing rapid macropore flow, similar to results in previous studies.

Adams et al. (1991) similarly evaluated the transport of atrazine and the metabolite DEA through two soil types. Soil cores from a clay loam site with 4 meters to groundwater and a silt loam site with 5 meters to groundwater were evaluated for atrazine and atrazine metabolite concentrations. Their results indicated that the atrazine and DEA were transported through the soil unsaturated zone into the shallow aquifer, with atrazine bound more strongly to the clay loam soil than to the silt loam soil. Despite this, atrazine transport was greater in the clay loam soil compared to the silt loam. The slower movement through the silt loam allowed for more metabolic dealkylation of atrazine. Masse, et al. (1994) found more atrazine and metabolite concentrations in the groundwater of a loam soil than in a sand soil. This was attributed to a restricting clay layer at shallow depths under the sand that stopped the herbicide movement down to the groundwater, though the greater water-holding capacity of the loam soil could also explain the results. The loam soil also had more sand content in the underlying clay layer, possibly favoring the presence of macropores allowing the downward movement of water.

Degradation of atrazine in groundwater can be practically nil with a possible 3 percent conversion to hydroxy atrazine every 90 days (Weihtje, 1984). Laboratory tests have found that atrazine, when in groundwater samples, did not biodegrade in 539 days of incubation (Klint and Jensen., 1993). While atrazine can be degraded by the aerobic microbes in the soil environment, once the herbicide reaches the groundwater, the anaerobic conditions and small microbe community retard the degradation (Adams and Thurman, 1991; Kolpin et al., 1996; Nair and Schooner, 1992). Even with the addition of nutrients and an increase in pH and temperature, the degradation of atrazine does not accelerate (Klint and Jenson, 1993). Atrazine travels to the aquifer because the degradation rates are slower than transport rates (McMahon and Chapelle, 1992).

Occurrences in Groundwater

Atrazine is considered mildly water soluble with a solubility of 30 mg/L. Even though atrazine is significantly correlated with organic carbon (r = 0.81) and suspended solids (r = 0.81), which would suggest transportation in the suspended phase, atrazine is estimated to be in the dissolved phase up to 99 percent of the time (Squillace and Thurman, 1992). Atrazine has been detected in wells and tile drainage water in various rural regions of the United States and Canada, ranging in concentration from 0.01 to 88 µg/L (Masse et al., 1994). According to the EPA's National Pesticide Survey in 1990, 1.7 percent of 94,600 community water system wells, and 0.7 percent of 10.5 million rural domestic wells reportedly had measurable levels of atrazine (EPA, 1990). Many other studies found similar occurrences of atrazine in the groundwater. Kolpin et al. (1996) tested near-surface aquifers (defined as having aquifer material within about 15 meters of the surface) under corn and soybean fields for pesticides and their metabolites. Atrazine was the most frequently detected parent compound (22 percent of 303 wells) with a maximum concentration of 0.27 µg/L. The metabolites DEA or DIA were detected in 33 percent of the wells. Bukart and Kolpin (1993) found 17.8 percent of the 579 near-surface aquifer wells sampled contained atrazine in the water. Kolpin and Thurman (1993) detected atrazine in 23.6% of the 110 near-surface wells sampled after the Mississippi River flooding of 1993, with a maximum concentration of 1.8 µg/L, and the metabolites DEA or DIA were detected in 37.2 percent of these wells. Even though these levels are all lower than the EPA's MCL of 3 µg/L, this still shows the potential for atrazine contamination of the groundwater due to agricultural uses. Since health effects have not been studied concerning the metabolites, the extensive occurrences of DEA and DIA could potentially add to the health concerns associated with atrazine.

Toxicity

The EPA has classified atrazine as a possible human carcinogen because it may have caused cancer in rats receiving high doses over the course of their lifetimes (Extoxnet, 1994). The oral LD_{50} for atrazine in rats ranges from 1075-3090 mg/kg body weight. Chronic dietary studies show little effect on dogs, and increased mammary tumors in rats at levels greater than 400 ppm (Herbicide Handbook, 1994). Since atrazine in drinking water may possibly increase the risk of cancer in humans, the Lifetime Health Advisory value of 3 µg/L includes an additional safety factor. The EPA believes that consuming water at or below this level is acceptable for drinking every day over the course of a lifetime without posing health concerns. Atrazine stimulates its own breakdown in the liver, but consuming levels much higher than the advised level has caused tremors and damage to the lungs, kidneys, liver, and heart in laboratory animals. Despite these serious conditions in laboratory animals, ecological effects on birds, bees, and other animals have been insubstantial. Ingested atrazine is readily adsorbed through the gastrointestinal tract. The greatest safety consideration for atrazine, then, is the potential health effects to humans from drinking water.

METHODS AND MATERIALS

Selection of Cooperators

The membership list of the Michigan Christmas Tree Growers Association was obtained and, with Dr. Melvin Koelling's assistance, approximately 80 potential cooperators were identified. The possible well sites were distributed throughout lower Michigan, excluding the upper peninsula. The potential cooperators were then selected in random order and grouped by areas that were named: Cheboygon, Montcalm, Flint, Port Huron, Cadillac, Traverse City, Hart, Monroe, Lansing, and Dowagiac. The areas were then randomly visited in the order listed above. As an area was visited, the randomly selected growers were interviewed and fields were selected to meet certain criteria of site characteristics and past and current chemical use, and to complete a stratified random sample. The design had 7 classification strata that were defined by variables groundwater depth and soil texture. The plan was to visit and select fields using a random process until a strata had 6 fields. An attempt was made to fill out all strata and avoid over sampling individual strata. As the sampling was completed, additional cooperators were identified in some areas to result in a balanced sample by strata, species, and treatment.

Selection of Fields for Shallow Well Locations

As growers were visited, they were asked to cooperate in identifying fields having groundwater within ~6 meters (20 feet) of the surface and applications of 2 of the 4 compounds (atrazine, simazine, hexazinone and N fertilizers) in at least 2 of the last 3 years for commercial Christmas tree production. The specific fields were also evaluated for species, sampling strata and associated treatments. The seven strata were based principally on 1) texture of the soil overlying the groundwater system, 2) the soil drainage class, and 3) the depth to groundwater table. Final choices of growers or fields were made based on a stratified random sample approach. This approach had the primary purposes of insuring that all sites had an equal chance of selection and a specified range of sites were sampled, balancing of sample size in each strata, and facilitating statistical analysis and summarization of the results. With grower assistance, 1-3 fields were evaluated for vegetation, soils, subsoil textural strata, and surface groundwater presence/depth within 6 meters of the surface. Dose-rate-time information was collected for atrazine, simazine, hexazinone and nitrogen fertilizer treatments for the selected fields.

Deep Well Location

As each field was selected, a nearby deep well was located at the growers home, place of business, or at a nearby residence. Some deep wells were in close proximity to more than one shallow well, allowing for a smaller number of deep wells needed for the comparison. At the time of well installation, owner permission was obtained to collect samples from the deep wells during the four sampling dates, at installation, September of 1996, November of 1996, and May of 1997.

Groundwater Zones and Sampling Depth Concepts

Groundwater concepts were defined for uniformity of site description. Water generally infiltrates the soil surface and percolates downward through permeable materials to a zone of saturation. Aquifer materials are porous and permeable, yielding significant amounts of groundwater. Aquiclude materials, on the other hand, have low macropore space and do not transmit significant amounts of water. For this project, loamy and sandy soil were considered aquifer materials, and clayey soils were considered aquiclude materials. Groundwater in aquifer materials can drain rapidly due to gravity, allowing rapid refilling of wells positioned in sands and slower refilling in loams. Groundwater in aquiclude materials does not drain or drains very slowly due to gravity, therefore this type of well did not refill in a reasonable amount of time when pumped dry.

The positioning of the aquifer and aquiclude material define two kinds of groundwater aquifers, confined and unconfined. Unconfined aquifers are in direct contact with the above atmosphere through aquifer material, while confined aquifers are separated from the atmosphere by an aquiclude layer. Over time, rainfall, snowmelt, net lateral outflow and evaporative losses cause the depth to the surface/unconfined groundwater to fluctuate. The lower boundary of unconfined aquifer material was determined by observing the depth of saturated aquifer material, usually where underlying aquiclude materials cause saturation. The saturated zone was defined from the water table down to the aquiclude material, while the vadose zone was defined as the drained soil overlying the saturated zone. Surface/unconfined aquifers proved to be the best aquifer type for this project. Confined groundwater systems are surrounded on top and bottom by aquiclude material, which restricted the amount of recharge to the wells from above. Isensee and Sadeghi (1995) found that the unconfined groundwater tables consistently had higher atrazine concentrations than corresponding confined groundwater. Testing unconfined wells, therefore, allows for the worst case scenario for groundwater contamination.

Stratification of Shallow Wells

Specific site characteristics and chemical application practices were identified for each of the shallow well locations. The number of fields and shallow wells sampled are shown in Table 3.

Table 3. Number of Shallow Wells Sampled by Texture of the Vadose Zone and Drainage Class or Depth to Ground Water Table Class.

TEXTURE	DRAINAGE CLASS	DEPTH TO GROUND WATER		TOTAL
	PD-SPD	SHALLOW	DEEP	
CLY	3	5	6	14
LY	0	4	6	10
SY	0	11	3	14
TOTAL	3	20	15	38

Drainage classes were according to soil taxonomy. Vadose zone textures were based on the presence of a minimum 30 cm thickness of heavier textured horizons or strata. The heavier textured strata (Bt or other layer of the finer texture) were coded as follows:

CY - Clayey	SC, C, or SIC ≥ 30 cm
CLY - Clay loamy	SCL, CL, or SICL ≥ 30 cm
LY - Loamy	SL, L, SIL, or SI ≥ 30 cm
SY - Sandy	S or LS without heavier textures ≥ 30 cm

Seven sampling strata, which were used as site-types, are described as:

CLY_PD-SPD	poorly drained or somewhat poorly drained clay soils with shallow water tables
CLY_SHALLOW	drained clay loamy soils with groundwater at 0 to 240 cm (0-8 ft).
CLY_DEEP	drained clay loamy soils with groundwater within 240 to 610 cm (8-20 ft).
LY_SHALLOW	drained loamy soils with groundwater at 0 to 240 cm (0-8 ft).
LY_DEEP	drained loamy soils with groundwater within 240 to 610 cm (8-20 ft).
SY_SHALLOW	drained sandy soils with groundwater at 0 to 240 cm (0-8 ft).
SY_DEEP	drained sandy soils with groundwater within 240 to 610 cm (8-20 ft).

Of the 38 fields sampled, three poorly drained or somewhat poorly drained soils which were artificially drained were placed in the PD_SPD strata.

Site, Treatment and Concentration Variables

The variables analyzed were:

W - randomly assigned number identifying the well site
DW - randomly assigned number identifying the associated deep well

SPECIES - major species grown on field
GRSN - growing season age of current tree crop
TEXT-DEP - strata code based on texture, drainage and depth to groundwater

AvalTH - SUM [horizon thickness (cm) x (8 - Munsell value for A horizon)] ; higher means thicker and darker. (as measure of organic matter)

C150cm - Equivalent clay thickness to 1.5 meters calculated as SUM [thickness * percent clay] corrected for percent course fragments.

CVADcm - Equivalent clay thickness in soil above the groundwater zone

ABDEPcm - depth to base of B horizon

GWZcm - Depth to seasonal high water table (chroma<2 due to reduction)

GWDEPcm - Depth to groundwater at installation

A97 - Atrazine applied in last growing season (1997) in kg ae/ha.
A96 - Atrazine applied in 1996 in kg ae/ha.
A4 - Atrazine applied in four growing seasons (1994-1997) in kg ae/ha.
S97 - Simazine applied in last growing season (1997) in kg ae/ha.
S96 - Simazine applied in 1996 in kg ae/ha.
S4 - Simazine applied in four growing seasons (1994-1996) in kg ae/ha.
H97 - Hexazinone applied in last growing season (1997) in kg ae/ha.
H96 - Hexazinone applied in 1996 in kg ae/ha.
H4 - Hexazinone applied in four growing seasons (1994-1997) in kg ae/ha.
N97 - Nitrogen applied in last growing season (1997) in kg elemental N/ha.
N96 - Nitrogen applied in 1996 in kg elemental N/ha.
N4 - Nitrogen applied in four growing seasons (1994-1997) in kg elemental N/ha.

Appb - Shallow well atrazine concentration in µg/L
Sppb - Shallow well simazine concentration in µg/L
Hppb - Shallow well hexazinone concentration in µg/L
Nppm - Shallow well nitrate concentration in mg/L

ADWppb - Deep well atrazine concentration in µg/L.
SDWppb - Deep well simazine concentration in µg/L.
HDWppb - Deep well hexazinone concentration in µg/L.
NDWppm - Deep well nitrate concentration in mg/L.

The data subjected to summarization and statistical analysis consisted of the above variables for 38 shallow well sites and associated deep wells.

Shallow Well Installation and Development

Microsite Choice and Installation Pit

The wells were installed over the summer of 1996. The specific locations in the field were chosen to place the well on a relatively flat surface to prevent surface water from running toward the base of the well and down the well riser (see Figure 2). The first step to installing the well was to dig a circular 60-75 cm flat-bottomed installation pit, about 75-85 cm diameter. The soil was removed from the pit layer by layer, and each layer was placed on plastic sheets for later replacement. The pit was prepared to excavate to a least permeable layer (LPL) within the top 60 cm of soil. The LPL was defined as a soil layer that was two textural classes finer than the soil layer above it, or a layer where the underlying horizon had 20 percent more clay than the overlying horizon. Some sites, particularly sandy sites, did not have a LPL within 60 cm, so the pit was dug to the default depth of 60 cm. The intent of defining a LPL was to locate a layer that perches water in order to establish a site for the placement of the percolation seal. A subsurface percolation barrier was installed at the base of the installation pit, after the well was installed, to prevent percolating water from running down the well casing.

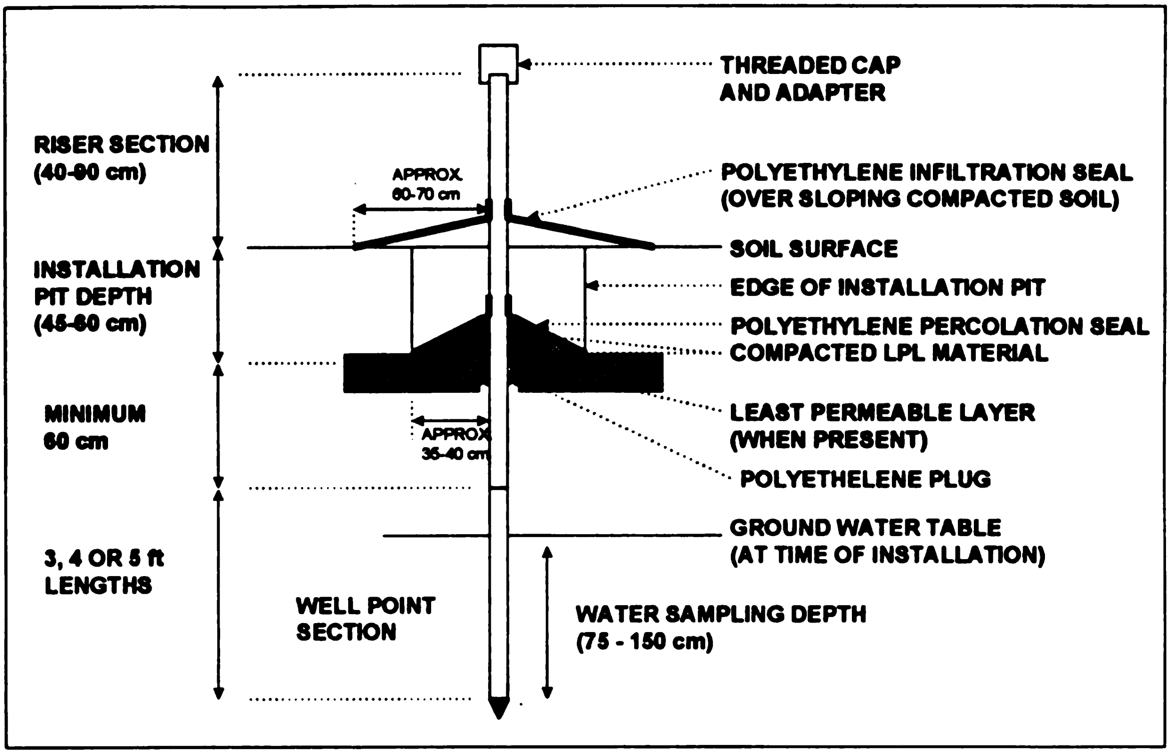

Figure 2. Schematic of Well Installation

Well Hole Augering and Well Logging

After preparation of the installation pit, a hole was augered through the bottom of the pit with a 3 ¼ inch (~10 cm) diameter AMS bucket auger with snap on extensions. Actions were taken to prevent soil from falling down the auger hole. The soil was removed in 15 cm increments and placed in sequential order on a plastic sheet. During the course of digging and augering, a detailed soil profile description was recorded for each well on the Well Log Data Form. Horizon depths, thickness, and properties such as texture and soil color were recorded in a well log. A strata break was recorded at the level of the groundwater table observed at the time of installation. The groundwater zone (GWZ) was defined as the zone with significant recurrent saturation. The top and extent of this zone was noted by the occurrence of reduced iron coloration (gley colors, chroma ≤ 2) caused by previous saturation and biological activity at that depth. The reduction did not occur with some soils, especially sands, so the occurrence of saturation was used to indicate the top of the groundwater zone.

Well Design and Screen Placement

The wells were made of 2 inch ID schedule 40 PVC well pipes and 1 cm slotted screens with points. To account for the differences in depths, the slotted screens were ordered in 5 foot (154 cm), 4 foot (122 cm) and 3 foot (91 cm) sizes. The depth of the top of the groundwater zone was used to determine the appropriate length and positioning of the slotted screening. The placement of the top of the screen was designed to coincide with the highest observed groundwater table at the beginning of the growing season or the reduction gley colors due to earlier water exposure. Efforts were made to place the top of the screens at least 60 cm below the percolation seal. The placement of the bottom of the screen was designed to allow for 75 - 150 cm of water to be present in the well at the times of sampling. Determination of the total length for the pipe, screening, and riser used the depth measurements recorded in the well log. The pipes were then measured, cut and assembled to the depth specifications for the well, and inserted by hand into the augered hole. In saturated sands, it was necessary to drive the well point down through the wet sand by firmly tapping the cap of the well with a rubber mallet.

Preparation of Percolation and Infiltration Seals

After well placement, the percolation seal was prepared at the bottom of the installation pit. The base of the installation pit was carefully cleaned to avoid knocking any soil down the well casing. A retaining ring of clean plastic was wrapped around the outside of the well casing and packed down into the borehole around the casing. The excavated LPL material was replaced into the installation pit and gently compacted in place around the well casing. The LPL material was compacted to a density greater than the original LPL, and sloped away from the casing. If LPL material was not available, then original soil material from the lower bore hole was used. A piece of polyethylene plastic, with a center hole removed for the riser, was slid down the riser to cover the soil percolation seal and sealed to the riser pipe with plastic tape. The resulting seal was intended to divert water away from the casing and to prevent direct flow of water down the well casing. Following preparation of the percolation seal, the overlying soil horizons were replaced and packed into the pit and built-up to form a sloping surface. This formed a surface infiltration barrier of tightly packed soil that sloped away from the casing to diverted water at least 1 foot away from the well to prevent direct water percolation down the pipe. A plastic sheet with a hole cut for the well pipe was placed over the surface to extend beyond the extent of the installation pit. The plastic was sealed to the well riser using plastic tape and weighted with soil and rocks around the edges.

Well Development

After each well was installed, it required development to establish maximum flow of water from the aquifer into the well. Prior to the first sampling, the wells were developed by surging and pumping the well water three times to condition the well and achieve sample clarity. Surging consisted of dropping a closed-bottomed 4.4 cm by 91 cm (3 foot) device from 91 cm above the surface of the water in the well, allowing it to sink to the bottom, and rapidly pulling it out of the water. The surging action produced a short sharp positive pressure to force water out of the well screens, followed by a suction into the well. This was intended to displace water in the well and any water in the void space outside the screening. Loose particles from the soil around the well screening were washed away to allow for optimum water flow. This was repeated three times. The well was then pumped to withdraw at least three volume equivalents of water, or until dry. For the last repeated pumping, the water was pumped until clear.

During development, two situations occurred: 1) wells in sandy or gravely aquifer materials refilled at a faster rate than pump removals and were named "refilling," or 2) wells in finer textured aquifers materials were pumped or bailed dry and were termed "dry." For the refilling situation, after the first surging and pumping of two volumes, surging and pumping were repeated two more times prior to sampling. For the dry wells, after the first volume was surged and pumped dry, a minimum of 1 liter of deionized water was added to the well. This water was surged as mentioned previously, and the well pumped until dry again. More deionized water was then readded, surged, and pumped. Refilling and pumping without surging was necessary, for some dry wells, to complete the development prior to sampling.

Sampling Protocol

Container Preparation

Pesticide sample bottles were Boston round amber glass cleaned to EPA protocol B. Nitrate samples were collected in 200 mL polyethylene bottles cleaned to EPA protocol B and preserved with 0.8 mL/L sulfuric acid for nitrate analysis per EPA approved methods. For the first sampling set, the glass containers were purchased pre-cleaned with adequate documentation, while for the plastic containers and all subsequent sampling sets, the containers were prepared in the following manner:

A. bottle, cap, and septum separated, then hand washed with laboratory grade non-phosphate detergent
B. rinsed in hot tap water
C. rinsed in methanol (for pesticide bottles only)
D. rinsed in triplicate with deionized water
E. air dried

Once the containers were cleaned and dried, each bottle was labeled with the date of sampling, sample identification number, sample preservatives, and tests to be performed on the sample. Appropriate preservatives were added to the containers while still in the laboratory, and the bottles were placed in the cooler for transportation.

Quality control (QC) samples were prepared for each sampling date, or one for every ten monitoring wells. The QC sample was a field blank, prepared at the sampling site, using the field supply of deionized water to account for field contamination. The QC samples were analyzed for the same parameters as the field samples.

Well Purging

Well purging is critical to obtaining representative samples. Purging strategies were dependent on the recovery times of the individual wells. The purging procedure was to pump three well volumes of water and achieve stability as measured by the field parameters of conductivity, pH, temperature and clarity rating. One bore volume was defined as the volume of water in the well, calculated by the following formula:

$$V = [\ TWD - DW\ ] \times [(\pi)(\ r\text{^}2)]$$

Where

V = volume (in ml) of water in the entire well
TWD = total well depth to bottom of the well, including the riser above the surface (in cm)
DW = measured depth to water from top of well, including the riser (in cm)
r = radius of well (in cm) [2 inch diameter pipe = 2.54 cm radius]

The purging at the initial sampling was done with a MasterFlex model 15 battery operated peristaltic pump with a 1715 pump head, 152 cm (5 feet) of C-flex tubing, and tygon tubing to the well point. For the subsequent sampling dates, the wells were fitted with a 0.63 cm (1/4 inch) polyethylene tube that was acid washed and triplicate rinsed with deionized water in the laboratory. The tubing was cut to well length and inserted into the well. The C-flex tubing attached to the pump was cleaned in the field, prior to use at each well, by pumping 18 percent HCl through the tubing for approximately 1 minute, and triplicate pumping with deionized water. The reusable C-Flex tubing was then attached to the well sampling tube and purging performed.

Pumping removed water at or just above the well point. The rapidly recovering wells, or refilling wells, had a minimum of three bore volumes removed by a peristaltic pump. The slowly recovering wells, or dry wells, had to be purged to dryness by the peristaltic pump. Since the dry wells took longer to refill, the subsequent purges had to be taken over a period of hours to days, depending on the flow rate. The samples were taken after stabilization of the field parameters. This was done by measuring and recording the field parameters in the purge water in eight 250 mL aliquots collected over the three volumes of purge water. Stability was evaluated by achieving +/- 10 us/cm conductivity, +/-0.1 pH units, +- .5 °C, and uniform clarity. The well was considered stable when two or three consecutive volumes had stabilized within the specified ranges.

Initial Sampling

The summer samples were obtained in each field from the surface groundwater wells immediately after installation. Wells were purged with a minimum of three volumes of water, pumped to clarity, and sampled with a 1 liter-capacity disposable polyethylene bailer attached to heavy string and lowered to the surface of the groundwater. After the bailer filled with water, it was slowly pulled up and emptied from the bottom into the sample containers. More than one bailerful was required to fill all of the sample containers, and in many cases, subsequent bailers were filled with murky water. When this would occur, the well would be pumped until clear again. After the water pumped clear, the bailer sampling would resume. The samples were then placed in the 4°C cooler for transport to the lab for refrigeration and analysis for atrazine, simazine, hexazinone, and nitrate.

September, November, and May Sampling

Between September 1 and September 10, all shallow wells were resampled using a modified procedure and equipment. September was chosen for the second sampling date because of estimations of soil recharge using evapotranspiration models from climatic data. For the September sampling, a comparison study examined the differences between bailer and pump samples for five wells. Gibb et al (1981) found that sampling with peristaltic pumps and bailers gave comparable data, with minimal changes in water quality. The results from the comparison study confirmed that equivalent samples were obtained by the two methods.

Dedicated polyethylene tubing and the peristaltic pump were used for all of the September sampling. It was found during the September sampling that all of the wells had stabilized before the end of three volumes. Due to occasional portable pH/temerature meter malfunction, a number of wells were stabilized using only the specific conductance parameter and the minimum three bore volumes until a new pH meter arrived. Similarly, a malfunction with the conductivity meter eliminated that parameter from the stabilization of a number of wells at the end of the sampling set. These wells were stabilized using pH, temperature, and the minimum three bore volumes. For all wells, samples were taken from the pump discharge following pumping of three well volumes for purging and confirmation of stability. Pesticides samples were collected and treated as stated for the initial sampling. Nitrate samples were collected in two 50cc polyethylene centrifuge containers with screw caps and preservatives equivalent to those used for the initial sampling, and all of the samples were transported to the laboratory in a 4 °C cooler.

Both the November 1996 and May 1997 sampling sets utilized the pump, tubing, and centrifuge tubes for purging and sampling the shallow wells. Dates in November and December were chosen for the third sampling date because of estimated groundwater recharge using evapotranspiration models from climatic data. Dates in May and early June were chosen for the last sampling date to follow herbicide and fertilization applications by a month.

Deep Well Sampling

For each shallow well installed and sampled, a correlating deep well, usually the house or office well, was also sampled. Water softeners were bypassed and samples taken directly from the faucet where possible. Water was allowed to run a sufficient time to empty house plumbing and the sample collected for comparison to the shallow groundwater in the nearby fields. If no deep well was available within an appropriate distance, then only the shallow well was sampled.

The same set of analyses were performed on both the deep well and shallow well samples.

Laboratory Analysis for Pesticides

The pesticide analyses were performed using a combination of the solid phase extraction (SPE) method and HPLC analysis. Literature review and preliminary laboratory analysis revealed that recovery by SPE is not significantly different than for solvent extraction, with SPE proving to be rapid and efficient (Craciun, 1996; Thurman et al., 1990). Ground water samples were vacuum filtered on nylon 66 membranes, 47 mm, 0.45 µm, from Alltech (Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015). The filtrates were extracted at a flow rate of 15-20 mL/min using Supelclean Envi-18 PK/54 solid-phase extraction cartridges, purchased from Supelco, Inc. (Bellefonte, PA), and were eluted with 2-3 mL methanol. HPLC analyses were performed on a Millipore Waters HPLC instrument, equipped with an autoinjection system, a thermostatically controlled column compartment, a spectrophotometer detector Millipore Waters LC Spectrophotometer Model 481, and a chromatographic column Econosil C18, 10 µm, 250×4.6 mm ID (288-138 category number); λ 254 nm; flow rate 1.5 mL/min; 45% acetonitrile + 55% water mobile phase composition; injection volume 25 µL. A standard curve was determined prior to each HPLC run, with standards checked throughout the analysis.

The detection limits for HPLC analysis of the three triazine herbicides, under the conditions described, are: atrazine 0.1 mg/L, simazine 1 mg/L, and hexazinone 0.01 mg/L. Since analysis pre-concentrated the samples from approximately 1 L volume to 2-3 mL, these detection limits correspond to real concentrations in the water samples of: atrazine 0.2 µg/L, simazine 2 µg/L, and hexazinone 0.02 µg/L.

Laboratory Analysis for Nitrate

Nitrate analysis was performed using a Lachat Flow Injection Analyzer and QuickChem Method No. 10-107-04-1-A, a cadmium reduction and colorimetric determination. The standards were preserved identically to the samples in 50 mL tubes. The standards ranged from 0.2 - 20 mg N per liter as nitrate (or nitrite). Dilutions were made as necessary to obtain concentrations within the analytical range. Twenty subsamples were analyzed for nitrite and only one sample had nitrite (0.13 mg/L) above detection limits. Ten percent duplicate nitrate samples were run and confirmed reliability.

Data Analysis and Statistical Methods

Statistical methods for analyzing the significance of the date included nonparametric correlations and logistic regression methods. Nonparametric statistics were used to analyze the correlations between groundwater concentrations of the herbicides and nitrates, and the site characteristics and treatment rates for the 38 wells. These methods were appropriate because the data were not normally distributed, having more data with low levels of contamination, and few very high levels.

The nonparametric methods included the Spearmans rank correlation. Tabulations, statistical summaries and correlation analyses were prepared to describe the site-type strata, number of wells by strata and species, and correlations of site variables and treatments presented above. Tabulations were prepared to display the frequency pollutant concentrations for site-type strata and treatment rates. Since there is a strong focus on pollutant concentrations by treatment rate and site-type, the mean, median, minimum, maximum and standard deviation were summarized for these factors. Tabulations were also developed to present and compare the pollutant concentrations of shallow and deep wells for the four sample dates.

The frequencies, means, medians, ranges, and standard errors of the mean are computed according to Steel and Torrie (1980) using Microsoft Excel spreadsheet functions and pivot tables. The graphs, correlations and regressions also follow the procedures of Steel and Torrie and were calculated using the MS Excel analysis functions and Statistical Analysis System programs (SAS Institute, 1995). No statistical justification exists to remove any outlying data points, therefore all data points were included for the nonparametric correlation and logistic regression analyses.

Logistic regression methods (SAS Institute, Inc., 1990) utilize binary responses for the chemical concentrations, i.e. 0 if less than critical concentrations or 1 if greater than critical concentrations. All site, treatment, and date variables were included in the regressions. The regression procedure included stepwise analysis with a retention criteria of p = 0.30 with a final predictive equation determined when no additional variables could be included or removed.

This technique can produce a regression model that predicts the probability of the presence of the chemical at the specified critical concentration. The general format for the predicted probability equation is:

$$\pi(x) = e^{\beta o + \beta 1x1 + \beta 2x2 + ... + \beta nxn} \; / \; (1 + e^{\beta o + \beta 1x1 + \beta 2x2 + ... + \beta nxn})$$

For the results and discussion section, this equation will be transformed and written as:

$$g(x) = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_n x_n$$

The critical concentrations used for the regression were the MCL, 1/3 the MCL, and the analytical detection limit. The MCL analysis indicates current health concerns and 1/3 the MCL serves as a warning for potential health concerns. The detection limit analysis indicates detection versus non-detection of the chemical in the groundwater.

This method allows greater utilization of data from wells with non-detections of the chemicals (Druliner, et al., 1996). By describing the distribution of the errors, the binomial distribution avoids the problems associated with non-normally distributed data (Hosmer and Lemeshow, 1989). Model results were examined in Microsoft Excel spreadsheets using three dimensional plots from pivot tables for predicted probability and significant predictor variables. The alpha levels used to determine significance for all analyses were alpha = 0.05 and 0.01.

RESULTS AND DISCUSSION

The results are presented in the general order the research objectives are listed in the introduction. First, the herbicide and fertilizer treatment rates and site-soil characteristics for the 38 fields with installed shallow wells are presented and correlations between site and treatment variables are discussed. Second, the groundwater depths and concentrations of agrichemicals for the shallow wells for the four sampling dates are reported and discussed. The shallow well concentrations are then compared to concentrations in established deep wells (DW). Lastly, the relationships between site variables, treatment rates, sampling dates, and groundwater concentrations are analyzed to develop logistic regression equations for predicting agrichemical occurrences in the shallow groundwater under Christmas tree fields. The equations identify the significant variables found to determine predictive models for each chemical at the MCL. This will combine the analysis for the last two objectives.

Site Factors and Treatment Rates for Shallow Wells

The site factors of soil texture, drainage class, and depth to groundwater, were successfully measured and used to locate fields for study using the stratified random sample design. Data on site characteristics, treatments, groundwater depths, and concentrations for the individual sites can be found in files in the Forestry department. Ranges and basic statistics of site characteristics for each site-type are listed in Table 4. The relationship between the site variables selected to characterize the well sites are presented using Spearmans Rank correlation coefficients in Table 5.

Table 4. Site Characteristics Summarized by Site-Type Strata.

SITE-TYPE	Count	GROUND WATER TABLE DEPTH (cm)at installation (GWDEPcm)				A HORIZON DEPTH - ORGANIC CODE /1 (AvalTHcm)			
		Min	Max	Average	Std Dev	Min	Max	Average	Std Dev
CLY_PD-SPD	3	90	160	137	40	90	157	113	38
CLY_SHALLOW	5	130	240	184	52	34	82	63	18
CLY_DEEP	6	260	480	392	90	72	118	89	16
LY_SHALLOW	4	140	235	195	41	62	92	76	14
LY_DEEP	6	250	620	398	137	39	106	76	26
SY_SHALLOW	11	125	230	180	40	43	107	73	20
SY_DEEP	3	285	430	355	73	73	93	86	11
TOTAL	38	90	620	260	125	79	157	34	23

/1 SUM [horizon thickness * (8 - Munsell value for A horizons)]; higher means thicker and darker.

Table 4 (continued)

SITE-TYPE	Count	CLAY TO 150cm DEPTH (cm) (C150cm) /2				CLAY IN VADOSE ZONE (cm) (CVADcm) /2			
		Min	Max	Average	Std Dev	Min	Max	Average	Std Dev
CLY_PD-SPD	3	28	47	38	10	20	48	32	15
CLY_SHALLOW	5	15	49	27	14	20	53	35	13
CLY_DEEP	6	9	37	21	10	21	63	38	19
LY_SHALLOW	4	10	12	11	1	9	18	14	4
LY_DEEP	6	9	18	11	4	10	31	21	8
SY_SHALLOW	11	3	9	5	2	4	8	5	1
SY_DEEP	3	4	5	5	0	10	30	18	10
TOTAL	38	3	49	15	12	4	63	21	16

/2 calculated as SUM [thickness * percent clay] corrected for percent course fragments.

Table 4 (continued)

SITE-TYPE	Count	A + B DEPTH (cm) (ABDEPcm)				GROUND WATER ZONE DEPTH (cm) (GWZcm)			
		Min	Max	Average	Std Dev	Min	Max	Average	Std Dev
CLY_PD-SPD	3	105	150	123	20	90	157	113	38
CLY_SHALLOW	5	34	85	66	18	34	82	63	18
CLY_DEEP	6	60	180	102	39	72	118	89	16
LY_SHALLOW	4	60	190	110	51	62	92	76	14
LY_DEEP	6	70	130	95	19	39	106	76	26
SY_SHALLOW	11	32	125	85	30	43	107	73	20
SY_DEEP	3	75	85	80	4	73	93	86	11
TOTAL	38	32	190	92	33	79	157	34	23

Table 5. Correlation Coefficients and Significance Among Site Factors.

	AvalTH cm	C150 cm	CVAD cm	ABDEP cm	GWZ cm
C150cm	0.115				
CVADcm	0.149	0.851 **			
ABDEPcm	0.421 **	0.124	0.088		
GWZcm	-0.005	-0.298	-0.028	0.180	
GWDEPcm, INSTALLATION	0.078	0.052	0.402 *	0.165	0.67 **

n= 38
** indicates significance at alpha = 0.01
* indicates significance at alpha = 0.05

Depth of A + B horizon (ABDEPcm) was positively correlated with a variable devised to represent the amount of organic material present in the A horizons (AvalTH). Soils with deeper soil horizons generally had darker and deeper A horizon, usually associated with increased soil organic matter. The amount of clay to 150cm depth (C150cm), and amount of clay in the vadose zone (CVADcm) were also directly related. The amount of clay in the vadose zone also varied in proportion to the depth to the groundwater table (GWDEPcm). Depth to groundwater zone, based on chroma < 2 morphological evidence of depth to a seasonal high water table, and depth to groundwater table at the time of installation were also correlated. In many of the sandy soil substrata, the only evidence of a high water table was the direct observation of the depth to saturation because there was no evidence of gleization by chroma < 2 due to seasonal high water tables.

The changes in groundwater depths between sampling dates ranged from a change of 335 cm in a CLY_DEEP soil to a change of 27 cm in a SY_DEEP soil. The average difference in groundwater depths between dates was only 70 cm, and the groundwater depths at each sampling date were significantly correlated (alpha= 0.0001). The groundwater depths at the four sampling dates were not significantly different, and data for dates were combined for statistical analysis.

Grower interviews determined species managed, chemical treatments used, and species-site-treatment combinations. Table 6 presents species grown on the fields by site-type strata. Chemical treatment practices for each species were reviewed from grower interviews. Most spruce and fir, but not pine, received fertilizer, atrazine, and simazine applications. Conversely, hexazinone applications were generally done for pine and not spruce or fir. Atrazine rates correlated with simazine rates, which was consistent with patterns of atrazine and simazine use. Simazine also correlated with fertilization rates. Atrazine and simazine were both negatively correlated to hexazinone rates because of species differences.

Table 6. Principal Species Grown in the Fields Installed With Shallow Groundwater Wells.

SITE-TYPE	NUMBER OF FIELDS GROWING PARTICULAR SPECIES					
	BALSAM FIR	BLUE SPRUCE	DOUGLAS FIR	FRASIER FIR	SCOTCH PINE	TOTAL
CLY_PD-SPD				2	1	3
CLY_SHALLOW		2		2	1	5
CLY_DEEP		1		3	2	6
LY_SHALLOW	1	1		2		4
LY_DEEP	1	1	1	2	1	6
SY_SHALLOW		3		3	5	11
SY_DEEP	1			1	1	3
TOTAL	3	8	1	15	11	38

The herbicide and nitrogen application rates for 1997, 1996, and the last four years are summarized in Table 7. The near zero mean and median application rates occur because rates were generally low and not all sites received treatment. For each chemical, the rates were correlated for the 1997, 1996, and 1994-1997 (four years) rates. This means, for example, that the atrazine rates for 1997, 1996, and annually for four years were applied at proportional rates.

Only 18 of the 38 sites (47%) weren't fertilized in 1994-1997. For all 38 sites, the treatment rates and groundwater concentrations were highly rank correlated (alpha = 0.01, r = 0.445), but rank correlations between groundwater concentrations and treatment rates for the 20 sites receiving fertilization were not significant. This suggests that there is no dose-response relationship between fertilization rate and groundwater concentration.

Table 7. Statistical Summary of Application Rates for Atrazine, Simazine, Hexazinone, and Nitrogen.

VARIABLE CODE	TIME	MEAN	STD DEV	MEDIAN	MIN	MAX
		ATRAZINE (kgai/ ha)				
A97	1997	0.2	0.4	0.0	0.0	1.3
A96	1996	0.4	0.7	0.0	0.0	3.0
A4	1994-97	1.5	2.0	0.9	0.0	7.0
		SIMAZINE (kgai/ ha)				
S97	1997	0.8	1.0	0.0	0.0	3.5
S96	1996	1.2	1.3	1.0	0.0	4.0
S4	1994-97	5.1	3.6	4.5	0.0	14.0
		HEXAZINONE (kgai/ ha)				
H97	1997	0.0	0.2	0.0	0.0	1.0
H96	1996	0.2	0.4	0.0	0.0	1.3
H4	1994-97	0.3	0.8	0.0	0.0	3.0
		NITROGEN (kg / ha)				
N97	1997	29.6	34.1	4.0	0.0	88.4
N96	1996	26.2	44.5	0.0	0.0	148.5
N4	1994-97	91.7	126.0	12.0	0.0	362.5

n=38

Correlations between site factors and chemical treatment rates are shown in Table 8. Growers calculate application rates based on surface soil factors, such as pH, organic matter, and texture, but only 9 of the 72 correlations were significant. Atrazine application rates were not correlated to any site characteristics, and only simazine 1997 rates were correlated to clay in the vadose zone and groundwater depth. Hexazinone application rates for 1997 were correlated to A+B thickness, groundwater zone depth, and groundwater depth. All nitrate rates were highly correlated to groundwater depth. No rates were correlated to organic content in the A horizon or clay in the top 150 cm of soil.

This concludes the summarization of the agrichemical application rates and soil characteristics for the 38 shallow wells, as specified in objective 1.

Table 8. Correlation Coefficients Between Site Characteristics and Treatment Rates.

VARIABLE CODE	AvalTH	C150CM	CVADCM	ABDEPCM	GWZCM	GWDEPCM
A97	0.261	0.220	0.285	0.073	-0.175	-0.031
A4	0.061	0.106	0.010	0.230	-0.130	0.006
A96	0.174	0.137	0.070	0.256	-0.232	-0.083
S97	-0.066	0.305	0.380 *	-0.217	0.104	0.239 **
S4	-0.036	0.220	0.235	-0.103	-0.170	0.072
S96	0.172	0.059	0.067	0.010	-0.216	-0.086
H97	0.249	0.062	0.159	0.355 *	0.333 *	0.284 **
H4	-0.111	-0.167	-0.096	0.116	0.338 *	0.064
H96	-0.138	-0.067	-0.038	0.125	0.138	-0.018
N97	-0.077	0.248	0.299	-0.017	0.026	0.283 **
N4	-0.016	0.275	0.285	-0.105	-0.065	0.246 **
N96	-0.085	0.307	0.372	-0.161	0.090	0.300 **
n for column	38	38	38	38	38	152

** is significant at alpha = 0.01

* is significant at alpha = 0.05

Agrichemical Concentrations in Groundwater at Four Dates

Shallow well concentrations

The shallow well concentrations of atrazine, simazine, hexazinone, and nitrate were determined for the four sampling dates and the analysis results are summarized in Table 9. Mean concentrations were well below the MCLs for all chemicals. Occurrences of the chemicals in groundwater were strongly right skewed, meaning that it was more frequent to find concentrations at near zero levels than at higher concentrations. The skewed frequency of nitrate occurrence in groundwater is demonstrated by nitrate results in Figure 3. Similar skewed distributions were seen with all of the herbicides. Skewed occurrences of agrichemical concentrations in groundwater have been reported in other studies (EPA, 1990; Richards, et al., 1996; Spalding and Exner, 1993). It has been concluded that groundwater in many agricultural regions is not particularly vulnerable to contamination from these chemicals. With such a skewed distribution, one would expect a few high concentrations, but most wells would have low concentrations. The data for atrazine, simazine, and hexazinone in the shallow wells concurs with this conclusion since less than 7 percent of the 147 groundwater samples exceeded the MCL for any of the three herbicides. Only 23 percent of the samples even had detectable levels of any of the three herbicides.

Table 9. Statistical Summary for Concentrations of Atrazine, Simazine, Hexazinone, and Nitrate in Shallow Groundwater at Four Sampling Dates.

	DATE	N	MEAN	STD DEV	MEDIAN	MIN	MAX
		ATRAZINE (µg/L)					
Summer	1	37	0.70	2.27	0.00✧	0.00✧	13.40
September	2	34	0.15	0.35	0.00✧	0.00✧	1.30✧
November	3	36	0.03	0.15	0.00✧	0.00✧	0.90✧
May	4	37	0.00	0.01	0.00✧	0.00✧	0.04✧
	total	144	0.22	1.19	0.00✧	0.00✧	13.40
		SIMAZINE (µg/L)					
Summer	1	37	0.67	1.52	0.00✧	0.00✧	7.30
September	2	34	0.31	0.61	0.00✧	0.00✧	2.30
November	3	36	0.01	0.03	0.00✧	0.00✧	0.20
May	4	37	1.06	5.14	0.00✧	0.00✧	30.80
	total	144	0.61	2.93	0.00✧	0.00✧	30.80
		HEXAZINONE (µg/L)					
Summer	1	37	0.27	1.02	0.00✧	0.00✧	4.80
September	2	34	0.04	0.15	0.00✧	0.00✧	0.80
November	3	36	0.00	0.00	0.00✧	0.00✧	0.00✧
May	4	37	0.99	4.47	0.00✧	0.00✧	26.60
	total	144	0.33	2.34	0.00✧	0.00✧	26.60
		NITRATE (mg/L)					
Summer	1	37	5.10	7.07	1.96	0.00✧	30.98
September	2	34	5.66	7.40	2.30	0.01	27.90
November	3	36	4.56	5.36	2.16	0.00✧	20.28
May	4	37	5.46	6.31	2.83	0.00✧	30.13
	total	144	5.20	6.53	2.31	0.00✧	30.98

Atrazine detection limit = 2 µg/L, MCL = 3 µg/L

Simazine detection limit = 0.2 µg/L, MCL = 4 µg/L

Hexazinone detection limit = 0.02 µg/L, MCL = 200 µg/L

Nitrate detection limit = 0.01 mg/L, MCL = 10 mg/L

✧ = identifies analysis results below analytical detection limit

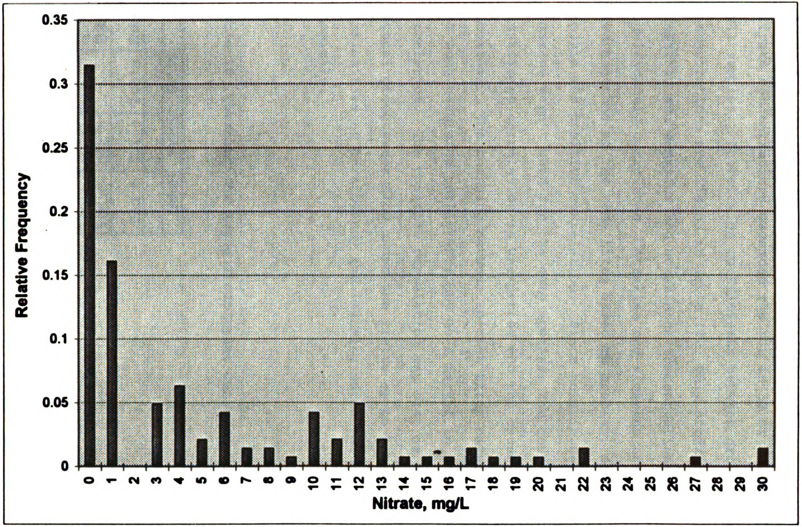

Figure 3. Relative Frequency of Nitrate Concentrations in 38 shallow wells.

Correlation coefficients (based on ranks) between chemical concentrations and treatment rates were highly significant (alpha = 0.01) only for nitrate and nitrogen rates (r= .445). Nitrate concentrations exceeded the MCL in 32 of 147 shallow well samples. Correlation coefficients between groundwater concentrations are listed in Table 10. Only atrazine and simazine, and simazine and hexazinone concentrations were significantly correlated. Atrazine and simazine are generally used together at the same sites based on species, so this would explain the positive correlation. Since hexazinone and simazine aren't used for the same species, the cause of the significant correlation is unexpected and the cause is uncertain. The changing between species after harvesting and the long herbicide persistency may be a factor in the correlation. The positive correlation may also be due to lateral groundwater flow under the fields or to the similarities of persistency and leaching potential between the chemicals.

Table 10. Correlations Among Groundwater Concentrations

	APPB	SPPB	HPPB
NPPM	0.059	0.125	0.002
APPB		0.280 **	-0.036
SPPB			0.319 **

N = 144 ** is significant at alpha = 0.01

This concludes the discussion concerning the agrichemical concentrations in the groundwater for the four sampling events, as specified in objective 2.

Deep well vs. shallow well concentrations

The statistics summarizing the concentrations in the established deep aquifer wells are reported in Table 11. Atrazine, simazine, and hexazinone levels were below the MCL for all samples, and nitrate levels exceeded the MCL in 9 of 138 samples. The herbicides were detected in 24 of the 138 samples. Only nitrate concentrations were significantly correlated (alpha= 0.01) between the deep and shallow wells (r= .234). However, the mean, median, and maximum concentrations were much lower in the deep wells than in the shallow wells. This is consistent with other studies comparing depths of groundwater wells.

Spalding and Exner (1993) showed significant trends of decreased nitrate concentrations with increased well depth. Halberg (1989) attributed the greater depth discrepancies to the hydrology of the vadose zone and to increased denitrification at greater depths. This may also be linked to a greater opportunity for degradation associated with the increased distance from soil surface to groundwater. Richards et al. (1996) also found greater contamination in shallow wells than in deep wells.

Table 11. Statistical Summary for Concentrations of Atrazine, Simazine, Hexazinone, and Nitrate in Deep Wells at Four Dates.

	DATE	N	MEAN	STD DEV	MEDIAN	MIN	MAX
		ATRAZINE (µg/L)					
Summer	1	32	0.1	0.4	0.0✧	0.0✧	1.5✧
September	2	37	0.0	0.3	0.0✧	0.0✧	1.6✧
November	3	33	0.1	0.3	0.0✧	0.0✧	1.5✧
May	4	36	0.0	0.0	0.0✧	0.0✧	0.0✧
	total	138	0.1	0.3	0.0✧	0.0✧	1.6✧
		SIMAZINE (µg/L)					
Summer	1	32	0.1	0.3	0.0✧	0.0✧	1.0
September	2	37	0.2	0.5	0.0✧	0.0✧	1.8
November	3	33	0.1	0.3	0.0✧	0.0✧	1.4
May	4	36	0.0	0.0	0.0✧	0.0✧	0.0✧
	total	138	0.1	0.3	0.0✧	0.0✧	1.8
		HEXAZINONE (µg/L)					
Summer	1	32	0.0	0.2	0.0✧	0.0✧	1.2
September	2	37	0.0	0.0	0.0✧	0.0✧	0.0✧
November	3	33	0.1	0.5	0.0✧	0.0✧	1.8
May	4	36	0.1	0.2	0.0✧	0.0✧	1.1
	total	138	0.1	0.3	0.0✧	0.0✧	1.8
		NITRATE (mg/L)					
Summer	1	32	1.7	3.2	0.1	0.0✧	10.9
September	2	37	1.9	3.3	0.1	0.0✧	11.7
November	3	34	1.7	2.8	0.2	0.0✧	11.6
May	4	35	1.6	3.0	0.0✧	0.0✧	12.1
	total	138	1.7	3.1	0.1	0.0✧	12.1

Atrazine detection limit = 2 µg/L, MCL = 3 µg/L

Simazine detection limit = 0.2 µg/L µg/L, MCL = 4 µg/L

Hexazinone detection limit = 0.02 µg/L, MCL = 200 µg/L

Nitrate detection limit = 0.01 mg/L, MCL = 10 mg/L

✧ = identifies analysis results below analytical detection limit

Lower concentrations at the greater depths may also be related to a greater dispersion of the chemical. Nitrate, atrazine, simazine, and hexazinone are known to stay near the top of the groundwater table. Frequently, concentrations in an aquifer are highest near the top of the water table, and decrease with depth (Power and Schepers, 1989). Once the atrazine and simazine reach the groundwater, the anaerobic conditions and small microbe community retard the degradation (Adams and Thurman, 1991; Kolpin et al., 1996; Nair and Schooner, 1992). Therefore, wells that don't extend very far into the groundwater table may have higher agrichemical concentrations. And, it may just take more time for pollutants to reach the groundwater at greater depths.

This concludes the comparison between the shallow wells and the established deep wells, as specified by objective 3.

Predicting Agrichemical Concentrations from Site Characteristics, Treatment Rates, and Dates

The concentration results were compared to critical values using logistic regression in SAS, as mentioned in the Methods and Materials section. The predictive equations and critical concentrations are presented for each chemical.

Nitrate Results and Discussion

Nitrate concentrations for this study were much higher in the shallow wells than in the deep wells. Concentrations ranged from 0 - 31 mg/L in the shallow wells and 0 - 12 mg/L in the deep wells. Concentrations exceeded the 10 mg/L MCL in 32 of 147 (22 percent) shallow well samples and in 9 of 138 (<7 percent) deep well samples.

Using logistic regression, there were four variables that could be used to predict the probability of exceeding the MCL of 10 mg/L. The variables were amount of nitrogen applied in 1997 (N97), A+B depth (ABDEPcm), groundwater depth (GWDEPcm), and amount of clay in the top 150 cm of soil (C150cm).

The probability of exceeding 10 mg/L nitrate is based on the equation:

$$P(> 10 \text{ mg/L}) = e^{g(x)} / 1 + e^{g(x)}$$

where:

$$g(x) = -5.3259 + 0.0452(N97) + 0.0240(ABDEPcm) - 0.0058(GWDEPcm) + 0.0462(C150cm)$$

The four significant variables were plotted, using the measurements from each site, against the predicted probability of exceeding groundwater concentrations of 10 mg/L nitrate (see Figure 4). Of the four variables, A+B thickness had the

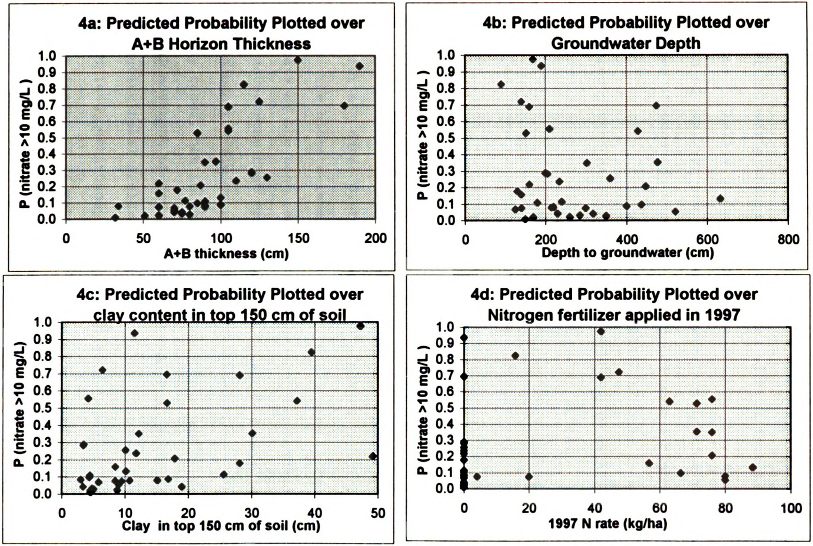

Figure 4. Predicted Probability of Exceeding 10 mg/L Nitrate Plotted over Four Variables.

greatest influence on the predicted probability. The thicker A+B horizons had the most significant relationship to greater probabilities of exceeding the 10 mg/L MCL for nitrate (Figure 4a), with lower probabilities at sites with thinner A+B horizons. Shallow groundwater depths (Figure 4b), higher amounts of clay (Figure 4c), and greater application rates of nitrogen (Figure 4d) were also associated with a higher probability of exceeding the MCL, although these three variables played a smaller role than A+B thickness in changing the calculated probability for the research sites. Probabilities of nitrate contamination, using all four variables, were generally below 75 percent probability for the research sites, but some cases approached certainty.

Logistic regression data indicated that nitrogen applied in 1997 and A+B depth were significant variables at 3 mg/L (~1/3 MCL). Figure 5 shows nitrate concentrations in shallow wells for all dates plotted over 1997 nitrogen rates and A+B depth. The nitrate levels are near zero in many instances, with bars at the base representing the non-zero concentrations. It is noteworthy that many wells had detectable nitrate levels even though the fields were not N fertilized in 1997, and even in many cases, not in the last 8 years. This may be due to the lateral movement of groundwater, especially at sites located near agricultural fields using fertilizers. It may also reflect long persistency once nitrate gets into groundwater, even at depths of <6 meters, as well as the possibility of obtaining nitrate from the mineralization and nitrification of

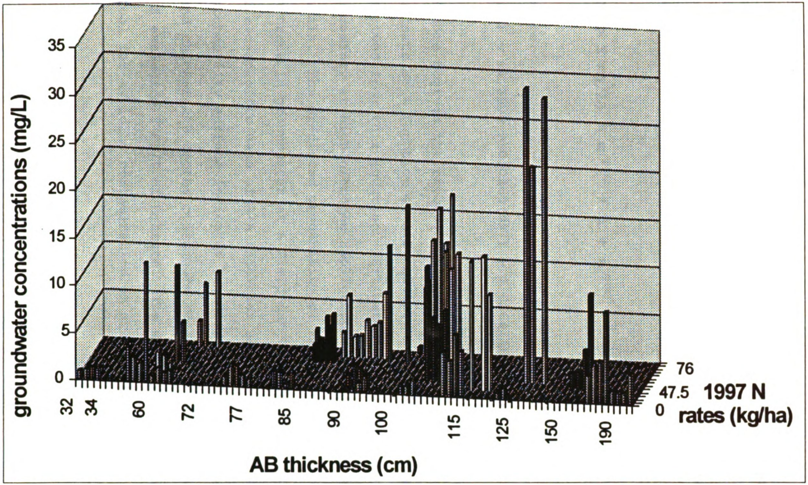

Figure 5. Nitrate Shallow Well Concentrations Plotted by A+B Thickness and 1997 Nitrogen Fertilization Rates

soil organic matter. These are discussed more fully in the following sections.

The logistic regression provided a predictive equation incorporating the variables found to be significant. The probability of exceeding 3 mg/L nitrate is based on the equation:

$$P(> 3 \text{ mg/L}) = e^{g(x)} / 1 + e^{g(x)}$$

where:

$$g(x) = -4.3509 + 0.0360(N97) + 0.0264(ABDEPcm)$$

Figure 6 gives the probability surface for exceeding 3 mg/L nitrate as a function of A+B thickness and 1997 nitrogen rates derived from this equation. Estimated probability approaches certainty at high nitrogen application rates and for deep A+B soils. The predicted probability of exceeding 3 mg/L of nitrate in groundwater at a field can be calculated using field-specific data of A+B thickness and nitrogen applied. The probability surface indicates that increased application rates and thicker A+B depths contribute to an increased probability of exceeding 3 mg/L of nitrate. The model provides a potential tool for avoiding contamination of groundwater.

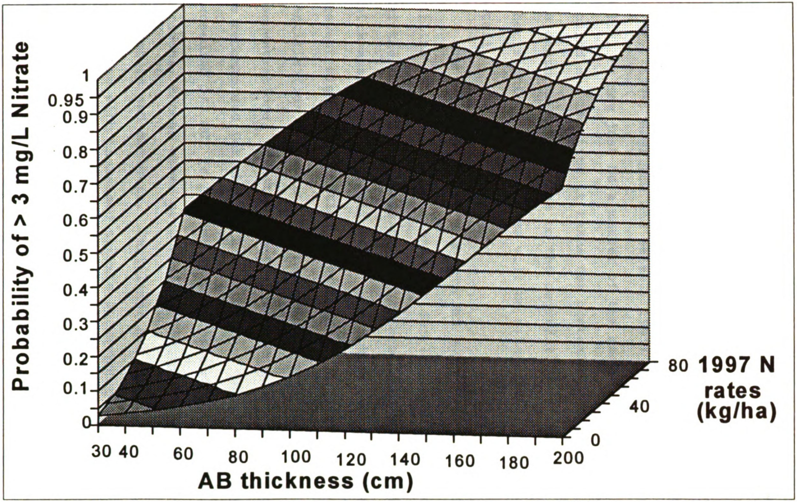

Figure 6. Predicted Probability of Exceeding 3 mg/L Nitrate as Predicted from A+B Thickness and 1997 Nitrogen Fertilization Rates

Significance of variables

Many studies have indicated relationships between well depth and nitrate contamination similar to those found in this study. As previously discussed, shallow wells repeatedly have shown higher nitrate concentrations than deep wells (Richards, et al., 1996; Hamilton and Helsel, 1995; Chen, 1996). For deep wells, it may just be a matter of the amount of chemical applied and the time it takes for contamination to occur, or the depth may contribute to the degradation of nitrate. The other significant variables will be discussed in greater detail.

The logistic models for both MCL and 1/3 MCL nitrate utilize nitrogen application rates for 1997 and A+B horizon thickness. This suggests that by determining the A+B horizon thickness, nitrogen application rates could be adjusted to prevent high probabilities of contamination. If N fertilization is causing the higher groundwater nitrate concentrations, then the use of lower fertilization rates could be recommended for thicker A+B horizons. The probability of exceeding 1/3 MCL is greater than 90 percent for thicker A+B horizons, though other probabilities could be selected by regulators and managers. Fertilizer use could logically be associated with increased nitrate occurrences, but the role of thicker A+B horizons is less obvious. And, there may be other causes of higher nitrate concentrations.

It has been assumed that thicker A+B horizons would allow for more nitrate uptake by plants, decreasing the amount of nitrate reaching the groundwater. The contrary finding that thicker A+B horizons are related to contamination may be linked to increased volumes of aerobic, surface soil available for microbial nitrifiers of ammonium. Deeper soils could hold more exchangeable ammonium, which could subsequently be nitrified and leached. Autotrophic nitrifiers generally depend on ammonium for energy and an increase in nitrate is seen when these nitrifiers are present in the soil (Van Miegroet and Johnson, 1993).

Theories have been made that repeated nitrogen input can enhance the nitrifier populations, so fertilized sites have a greater potential for nitrification (Johnson and Todd, 1988). As mentioned in previous sections, 1997, 1996, and 4-year nitrate application rates were correlated, indicating repeated addition of fertilizer. This may contribute to the continued survival of the nitrifying bacteria populations. The increases in nitrate may also be related to less depth, and a lower volume, of anaerobic soil available to denitrifying bacteria in the unsaturated zone below rooting depth.

Thicker A+B horizons can also be more productive for weeds, and once the weeds, especially leguminous ones such as clover, are killed and turned into the soil, decomposition and nitrification can release additional nitrate. The site soils with thicker A+B horizons were significantly rank correlated to the variable representing organic matter content (AvalTH) using Pearsons rank correlations ($r = 0.488$, α = 0.01).

Mineralization and nitrification of organic matter may then play a role in increasing nitrate concentrations in groundwater.

Nitrate concentrations were correlated to A+B depth (r = 0.174, alpha = 0.05) and clay in top 150 cm of soil (r = 0.280, alpha = 0.01). This suggests that clay content information can be useful for interpretation of groundwater concentrations of nitrate. It is also possible that sandy sites with thinner A+B horizons, shallow groundwater, and less clay content, may have nitrate leaching prior to the dates of sampling. This may be true since sampling only reflects conditions at a specific time.

Soil structure can also influence the rate of nitrate transport through the soil. Increased clay content may contribute to preferential flow to groundwater. Preferential transport is thought to be maximized in structured clay soils when rain occurs 1-2 days after application and by high intensity rains that produce ponding (Isensee and Sadeghi, 1996). This has been seen to initiate leaching, especially in clay loam soils (Sorenson, et al., 1994). Barbash and Resek (1996, p 193) also discuss that preferential transport of nitrate through the soil may occur during unsaturated conditions at sites with higher amounts of clay, and associated structure, near the surface. Cultivation practices, such as no-till practices, have also been proven to affect soil structure and preferential flow to groundwater (Isensee and Sadeghi, 1995). No-till practices allow for soil structures to remain intact, contributing to preferential flow through macropores. Preferential flow could potentially reduce the soil contact and residence time for nitrate in soil, decrease denitrification potentials, and contribute to direct flow of the nitrate to the groundwater table.

Because there are other cultural practices and natural processes that could cause increased nitrate in soils, it is possible that fertilization additions are not the direct cause of nitrate in groundwater. It may be necessary to control other practices, as well as decrease fertilization with nitrogen, to decrease nitrate in groundwater under productive soils with deep A+B horizons.

Simazine Results and Discussion

Simazine concentrations for this study ranged from 0 - 31 µg/L in the shallow wells and 0 - 1.8 µg/L in the deep wells. Concentrations exceeded the 4 µg/L MCL in 3 of 147 (2 percent) shallow well samples and in none of the deep wells. Figure 7 shows the simazine concentrations plotted by date and clay content in top 150 cm of soil, variables selected only to display the results. The simazine concentrations were near zero in most cases, with a few high concentrations. Most simazine concentrations were not at levels causing concerns about water quality.

There were no significant variables for predicting the probability of exceeding simazine MCL (4 µg/L), 1/3 the MCL (1.3 µg/L), or the analytical detection limit (0.2 µg/L).

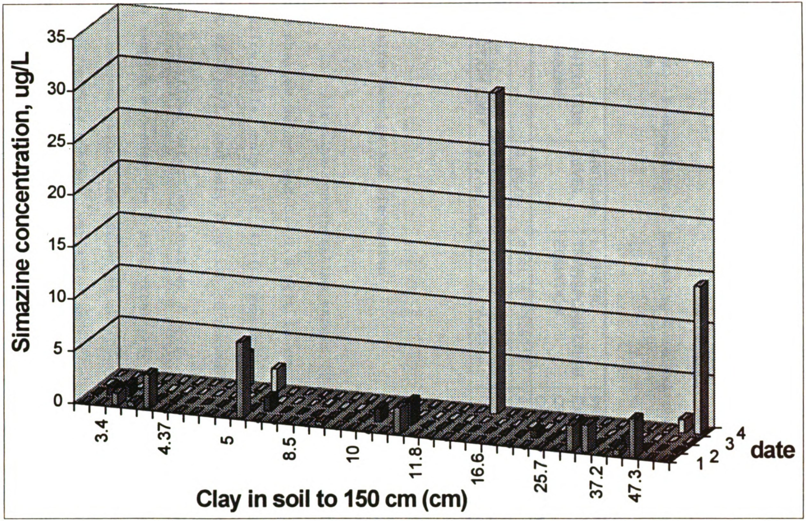

Figure 7. Simazine Shallow Well Concentrations Plotted by Date and Clay Content to 150cm

Table 12 shows the probability of exceeding the given critical concentrations without any significant variables. This analysis substantiates low probabilities of critical concentrations.

Table 12. Probability of Exceeding Critical Concentrations for Simazine

TEST CONCENTRATION FOR SIMAZINE	CRITICAL LEVEL	LOGISTIC TRANSFORMATION EQUATION	PROBABILITY OF EXCEEDING CRITICAL CONCENTRATION
MCL	4 µg/L	$g(x) = -3.8712$	0.042
1/3 MCL	1.3 µg/L	$g(x) = -2.4202$	0.178
DETECTION LIMIT	0.2 µg/L	$g(x) = -1.6848$	0.371

Atrazine Results and Discussion

Atrazine concentration ranged from 0 - 13.4 µg/L in the shallow wells, and 0 - 1.8 µg/L in the deep wells. In the shallow wells, only 1 of 147 (<1 percent) samples exceeded the MCL of 3 µg/L, and only 3 of 147 (2 percent) samples exceeded the analytical detection limit of 2 µg/L. In the deep wells, no samples exceeded the 2 µg/L detection limit. The shallow well concentrations are presented in Figure 8 by date and organic matter content, variables selected only to display concentration results. Most atrazine concentrations were at

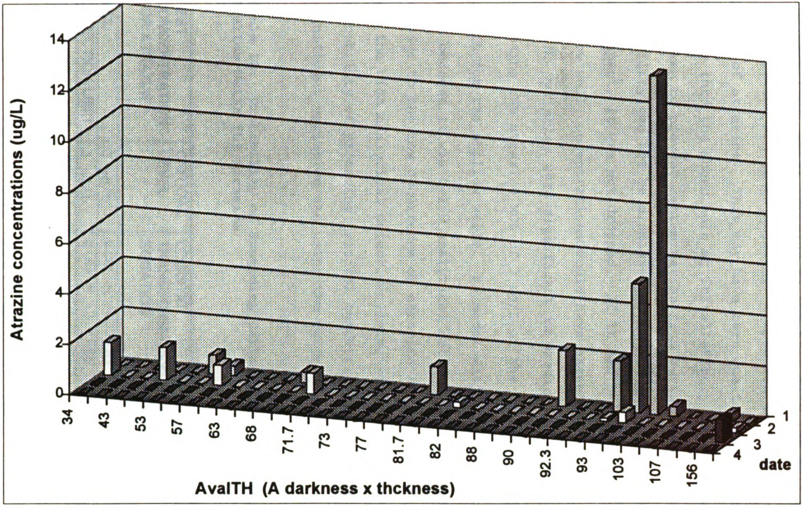

Figure 8. Atrazine Shallow Well Concentrations Plotted by Date and A Darkness x Thickness Variable

low levels not causing concerns about water quality. The highest concentrations were seen in samples taken at installation. Later sampling at the well with the 13.4 µg/L concentration and at an adjacent, comparison well revealed low levels of atrazine. This may have been due to surface soil falling into the auger hole at installation. Every precaution was taken to prevent contamination from surface soil, but the possibility can not be dismissed. Even though the concentration is suspect, it was not dropped. If it had been removed, no shallow well concentrations would have exceeded the MCL.

No variables were significant in predicting probability of exceeding the atrazine MCL of 3 µg/L or the detection limit of 2 µg/L for the shallow wells. No model was developed for 1/3 MCL, because it was below analytical detection limits. This was due to the low occurrence of atrazine in the shallow wells and the high analytical detection limit. Table 13 shows the probability of exceeding critical concentrations without any significant variables and using the fitted constants.

Table 13. Probability of Exceeding Critical Concentrations in Shallow Wells for Atrazine

TEST CONCENTRATION FOR ATRAZINE	CRITICAL LEVEL	LOGISTIC TRANSFORMATION EQUATION	PROBABILITY OF EXCEEDING CRITICAL CONCENTRATION
MCL	3 µg/L	$g(x) = -4.9836$	0.014
DETECTION LIMIT	2 µg/L	$g(x) = -3.5766$	0.056

This research result predicts only low probability of high concentrations of atrazine in groundwater. Detection of atrazine metabolites was beyond the objectives of this study, but other studies have shown concern over metabolites in groundwater (Adams and Thurman, 1991). Despite the low detection limits, these results are similar to other studies concerning atrazine. Groundwater contamination from atrazine does not appear to be a significant health concern for Christmas tree production.

Hexazinone Results and Discussion

No samples exceeded the MCL and only 10 of 147 (7 percent) shallow wells and 8 of 138 (6 percent) deep wells exceeded the detection limit. The shallow well concentrations are presented in Figure 9 by 1996 application rates and organic matter content, variables selected only for purposes of displaying concentration results. It is noteworthy that 3 of the highest concentrations were found at sites lacking hexazinone applications. Hexazinone concentrations were not at levels to cause health concerns. No variables were significant in logistic regressions for predicting the probability of exceeding the hexazinone MCL of 200 µg/L or the detection limit of 0.02 µg/L. This was partially due to the low occurrence of hexazinone in groundwater. The analysis was limited because only 9 fields with shallow wells were used to grow scotch pine and had hexazinone applied. From this data, no apparent water quality problems can be linked to hexazinone.

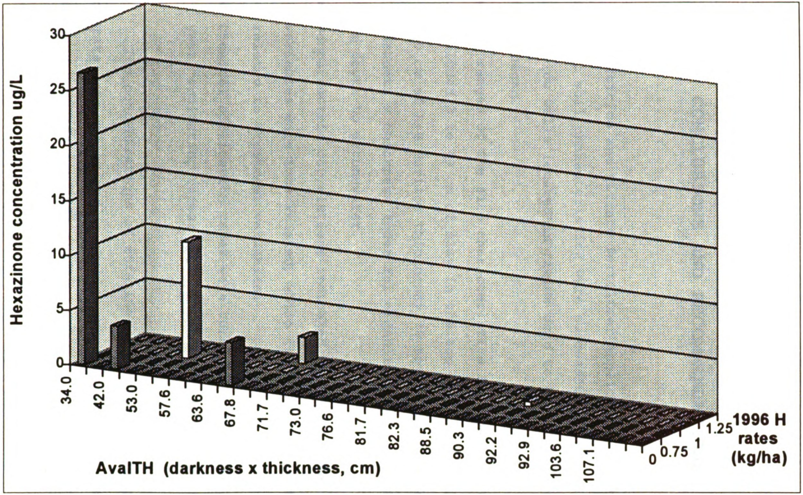

Figure 9. Hexazinone Shallow Well Concentrations Plotted by 1996 Treatment Rates and A Darkness x Thickness Variable

CONCLUSIONS AND RECOMMENDATIONS

Herbicide and nitrate fertilizer application practices and specific soil characteristics were successfully determined for 38 shallow wells located in fields used to grow Christmas trees in Michigan.

- The ranges of the site characteristics for the site-types included 3 to 49 cm of clay in the top 150 cm of soil, 32 to 190 cm of A+B horizon thickness, 79 to 157 cm of A horizon darkness x thickness index for organic matter, and 90 to 620 cm depth to groundwater.
- Nonparametric correlations indicated that some site variables were interrelated, while few site variables were related to treatment variables.
- Chemical application rates were correlated from year to year, indicating repeat application at proportional rates.

The concentrations of atrazine, simazine, hexazinone, and nitrate were determined in shallow groundwater under the fields at four separate sampling events.

- Skewed distributions of chemical concentrations in groundwater resulted with few high concentrations and many low concentrations.
- Less than 3 percent of the 147 groundwater samples exceeded the MCL for any herbicide, and 22 percent of the groundwater samples exceeded the MCL for nitrate.

Chemical concentrations in shallow groundwater under fields were compared to nearby established deep aquifer wells (DW) used for drinking water supplies.

- The deep wells had a lower incidence of chemicals than the shallow field wells.
- All herbicide concentrations were below the MCLs for the deep wells, and 7 percent of the 138 deep well samples exceeded the MCL for nitrate.

Concentration of groundwater pollutants were compared to the federal and state drinking water standards for each chemical and models were developed using logistic regression to predict probabilities of exceeding the critical concentrations of the MCL, 1/3 the MCL, and the analytical detection limit.

- The 4 µg/L MCL for simazine was exceeded in 2 percent of the shallow well samples, the 3 µg/L MCL for atrazine was exceeded in less than 1 percent of the samples, and the 200 µg/L MCL for hexazinone was not exceeded in any sample.

- Only 9 of the 38 well sites had applied hexazinone, which may be too few to base a conclusion of this magnitude. Studies with greater hexazinone use may be required to confirm the conclusions from this research.
- Due to the low occurrences of the herbicides in groundwater, logistic regression could not identify variables that significantly predicted exceeding the critical concentrations for atrazine, simazine, or hexazinone.
- Probabilities of shallow groundwater concentrations exceeding the 10 mg/L MCL for nitrate were predicted by 1997 nitrogen treatment rates and site characteristics of A+B horizon thickness, clay content in the top 150 cm of soil, and depth to groundwater. The predicted probabilities in the model approached certainty.
- The probability of exceeding 3 mg/L of nitrate in groundwater could be predicted using 1997 application rates and A+B thickness. The predicted probabilities also approached certainty. This provides a tool for modeling potential water quality problems.
- Some fields not fertilized in the past 8 years had significant nitrate groundwater concentrations. Nitrate sources appear to be from both fertilization and other sources, possibly from adjacent areas via lateral flow, mineralization and nitrification of organic matter, leguminous weed decomposition, and preferential flow to groundwater.

- Probabilities may be reduced by reducing treatment rates on soils with deep A+B horizons.

This research concludes that the herbicides atrazine, simazine, and hexazinone appear to not cause environmental quality problems for groundwater with current Christmas tree management practices. The results should provide useful information to the Michigan Department of Agriculture for the implementation of groundwater management plans for Christmas tree production.

The nitrate results indicate a high probability of occurrence for nitrate contamination of groundwater. Reducing the probability of exceeding high groundwater concentrations of nitrate requires greater focus on specific soil characteristics. Using the predictive equations can help determine protective nitrogen application practices using specific site characteristics.

There is still a need for further research.

- Hexazinone is not a likely environmental problem, but the number of treated sites was low. In general, this research allows conclusions that the herbicides atrazine and simazine are not water quality problems with current use for Christmas tree production.
- Analysis for atrazine metabolites was beyond the scope of this study, but other studies have investigated metabolite

occurrence in groundwater. More research is needed to determine the toxicity and occurrences of the metabolites.

- Further research is needed to determine the roles of land use in adjacent areas in influencing groundwater under Christmas trees via lateral flow. Nitrate was frequently found even in cases where fertilizers have not been applied in the last 8 years. Detailed investigation of the application practices and rainfall for each site would be necessary to determine if high nitrate levels are caused by fertilization, cultivation practices, lateral groundwater flow, or natural sources.
- Research is needed to confirm that limiting nitrogen application rates on soils with thick A+B horizons will help to prevent groundwater contamination.
- Research is also needed on predicting deep aquifer contamination from shallow aquifer measurements and time needed for such deep aquifer contamination.

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