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GROUNDWATER
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Wisconsin Department of Natural Resources

Analytical Determination of Atrazine, Alachlor and their Selected Degradation Products in Contaminated Groundwater: Implications For Wisconsin Groundwater Standards

by

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Abstract

Little is known of the occurrence of pesticide degradation products in groundwater. Therefore, methods were developed for the analysis of degradation products of atrazine and alachlor in water. Atrazine and alachlor were targeted because they are among the most widely used herbicides in Wisconsin. Two breakdown products of alachlor (2,6-diethylaniline (DEA), and 2- Cl-2',6'-diethylacetanilide) and two of atrazine (deethylatrazine and deisopropylatrazine) were focused upon. . These were selected based upon a) their likelihood to occur in groundwater as determined by literature review, b) the existing toxicological information on the products, and c) the availability of analytical standards. Samples were collected from four sites in Wisconsin known to have groundwater contaminated by atrazine or alachlor. These samples were analyzed for atrazine, alachlor, and their targeted breakdown products using the study methods. The data indicate that neither DEA or 2-Cl-2',6'-diethylacetanilide are important groundwater breakdown products of alachlor. Deethylatrazine was detected in all 32 of the study wells where atrazine was detected, and in three wells where atrazine was below the detection limit. Deisopropylatrazine was detected in 11 of the wells with atrazine detections and in two wells where atrazine was below the detection limit. The data was used to develop a mathematical model to predict atrazine breakdown product levels as a function of the concentration of atrazine in groundwater. If this model was used to adjust the enforcement standard to account for the presence of atrazine breakdown products in atrazine contaminated groundwater, the Enforcement Standard in Wisconsin for atrazine would decrease from 3.5 to 1.1 µg/l.

Table of Contents

List of Tables

List of Figures

Chapter 1
Introduction

1.1 Study Rationale

The contamination of rural aquifers by pesticide residues is a growing concern (Hallberg, 1986). Studies and monitoring programs throughout the country have indicated an increasing incidence of pesticides in groundwater (Pye, et al., 1983; Hallberg, 1986). The occurrence of these pesticides in groundwater poses a threat to public health in those areas which are affected. Groundwater is an important source of drinking water. In rural areas, including rural Wisconsin, nearly 100% of the rural population relies on groundwater for their source of drinking water (Pye et al., 1983). The chronic health risks of ingesting low levels of pesticide residues are unclear and difficult to study; however, many pesticides have been implicated as potential carcinogens (Evans, 1986).

The increased dependence of agriculture on pesticides and fertilizers over the last 40 years has resulted in increased productivity, both by lowering labor costs and by contributing to higher yields (Hallberg, 1986). It was originally believed that pesticides applied at or near the soil surface would be degraded in the soil profile and would not reach the groundwater (Kelley, 1986). Numerous studies and monitoring programs have since proven this incorrect. In Wisconsin, the discovery of the potato herbicide, aldicarb, in nonpotable groundwater in 1980 and its detection in potable groundwater in 1981 was the first indication that even supposedly non-persistent herbicides could be leached to groundwater (Kessler, 1986).

Most chemicals, when applied to a soil surface, degrade to form other compounds via chemical, physical, and biological reactions as they pass from the soil surface through the soil profile into the saturated zone. Thus, an application of a chemical at the soil surface may result in

a mixture of compounds in the groundwater beneath an application site. In general, current groundwater monitoring programs conducted by environmental agencies measure only the pesticide parent compound. Environmental fate models usually consider degradation only as a means of dissipating the parent compound; the models estimate the concentration or persistence of the parent compound while ignoring the fate of the degradation products. Health risk analyses on pesticide contaminated groundwater do not address the potential health risk component contributed by degradation product concentrations. Groundwater standards based on these risk analyses may not account for the total groundwater contamination, and thus the total health risk posed, by a given pesticide. This is largely due to the fact that degradation pathways and processes are complex and difficult to predict. The degradation processes are also greatly influenced by several environmental factors, further complicating the prediction of the extent of, and the health risk posed by, a contamination incident.

The frequency of occurrence of degradation products in contaminated aquifers has not been studied. Concern has been expressed that, by ignoring the presence of these degradation products, researchers may be underestimating the health risk involved in a pesticide groundwater contamination incident (Hallberg, 1986). The fact that these degradation products do appear in the soil profile, and may contribute to the health risk posed by a pesticide contamination, warrants their study.

1.2 Study Purpose

The primary objective of this study is to investigate the contribution of atrazine and alachlor degradation products to the total groundwater contamination by the parent compounds. Atrazine and alachlor are the two most popular corn herbicides in Wisconsin, and are of particular concern because they have been appearing in the state's

rural groundwater under normal field application conditions. The questions addressed by the study are:

•Are the soil degradation products of atrazine and alachlor present in groundwater contaminated by the parent compounds?

•Is there any pattern to the occurrence of the breakdown products relative to the occurrence of the parent compounds?

•Do the current Wisconsin atrazine and alachlor groundwater standards adequately account for the potential contribution to the health risk posed by the degradation products of atrazine and alachlor?

1.3 Scope of Study

A literature search was conducted in order to determine the degradative pathways for atrazine and alachlor in soils (and, when possible, in aquifer materials). From the resulting myriad of degradation products, four degradation products were selected for study based upon: a) their likelihood to occur in groundwater as determined by the literature, b) the existing toxicological information on the products, and c) the availability of analytical standards. The targeted atrazine breakdown products were deethylatrazine and deisopropylatrazine, while the selected alachlor breakdown products were 2,6-diethylaniline and 2-Cl-2',6'-diethylacetanilide.

Methods were developed to analyze for these compounds in water. It was a goal of the project to keep the project methods consistent with the pesticide analytical methods currently in use at the Wisconsin State Laboratory of Hygiene (WSLH). In this way, the methods could be easily adopted by the WSLH in the future. Most pesticide analyses of water samples at the WSLH use liquid/liquid extraction and packed column gas chromatography for identification and quantitative measurement.

Using the methods developed for the project, atrazine and alachlor concentrations were measured in contaminated groundwater from four sites in Wisconsin. The concentrations of the two atrazine breakdown

products and the two alachlor breakdown products were measured in the same samples. The four study sites were selected because of known atrazine or alachlor contamination. The sites also represented a variety of aquifer types, and from a practical point of view, were accessible for sampling. At three of the four sites, the contamination was due to spills occurring at mixing/loading operations. These can be considered to be point source incidents. Contamination at the fourth site is due to field application of atrazine, and can be considered a non-point source incident.

The levels of the degradation products were compared to the parent compound concentrations in samples from the four sites. Next, the data were analyzed for possible relationships between the concentrations of breakdown products and the concentrations of the parent compounds, where both appeared. In the case of atrazine, possible methods of adjusting either the current monitoring efforts or the Wisconsin atrazine groundwater standard were investigated as possible means to account for the presence of the degradation products.

Chapter 2
Background

2.1 Introduction

Atrazine, a chlorinated triazine herbicide, is used primarily for selective, pre-emergent control of broadleaf weeds and annual grasses in corn and sorghum. Alachlor, a substituted acetanilide herbicide, is registered for pre-emergent control of annual grasses and some annual broadleaf weeds. The majority of its use occurs on corn, soybeans and peanuts. Atrazine was introduced in 1958 (United States Environmental Protection Agency [USEPA], 1988), while alachlor has been registered for use since 1969 (USEPA, 1984). The molecular structures of atrazine and alachlor are depicted in Figures 2.1 and 2.2, respectively. Tables 2.1 and 2.2 list the chemical and physical properties of atrazine and alachlor.

Both atrazine and alachlor are widely used throughout the United States. Alachlor is the most widely used corn herbicide as well as the most popular soybean herbicide nation-wide. Atrazine is second to alachlor in use as a corn herbicide in the US. In Wisconsin, these trends are reversed, with atrazine being the most popular corn herbicide, followed by alachlor. The extent of use of these herbicides in Wisconsin is illustrated by the following figures:

> In 1985, 4,300,000 acres were planted in corn in Wisconsin; of these, 98% were treated with herbicides. Atrazine was used on 77% of the corn acres and alachlor was used on 40%. Soybeans accounted for 350,000 of Wisconsin's cropped acres, of which 96% were treated with herbicide. Alachlor was used on 47% of these acres (Wisconsin Agricultural Statistics Service, 1986).

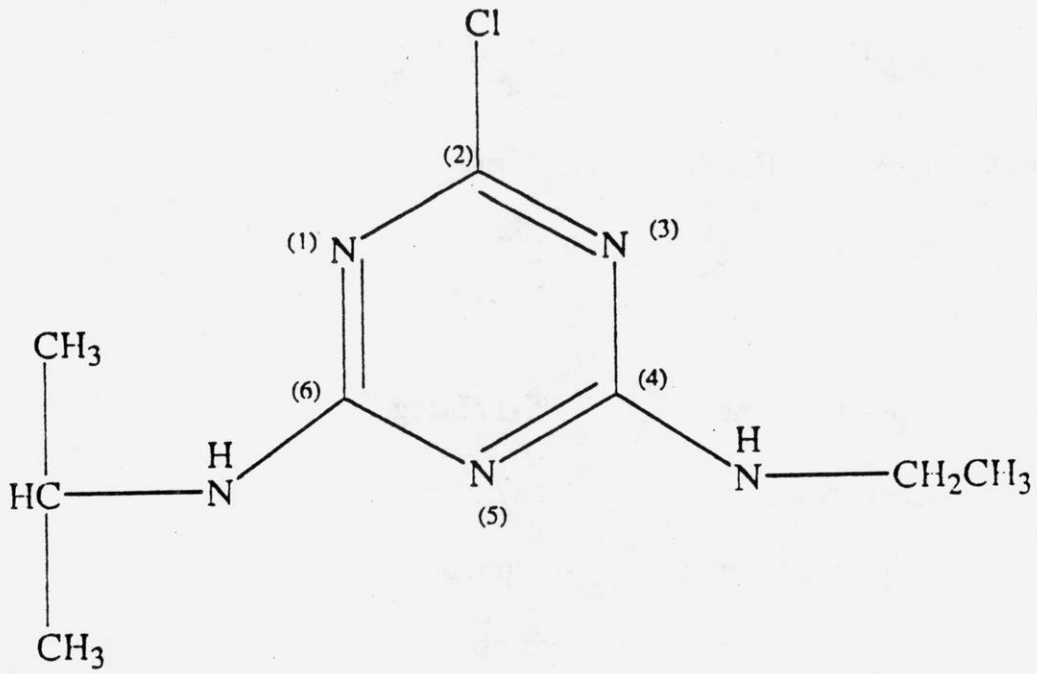


Figure 2.1

Atrazine*

*Numbers in parentheses refer to carbon position in triazine ring

Table 2.1
Physical and Chemical Properties of Atrazine[a]

Property	Value
Chemical Name	2-Chloro-4-ethylamino-6-isopropylamino-s-triazine
Trade Names	Aatrex, Aatram, Atrasol, Atratol, Bicep, Gesaprim, Primatol, Zeazin
Chemical Formula	$C_8H_{14}N_5Cl$
Molecular Weight	215.7
pKa	1.68
Melting Point	175-177 deg C
Density	1.187 g/cm^3
Aqueous Solubility	70 ppm at 22 deg C
K_{ow}	259.5[b]
LD_{50}	737 mg/kg (rat, oral) -3,000 mg/kg (mouse,oral)

a) References: USEPA, 1988; Carsel, 1989.
b) Adapted from Carsel, 1989

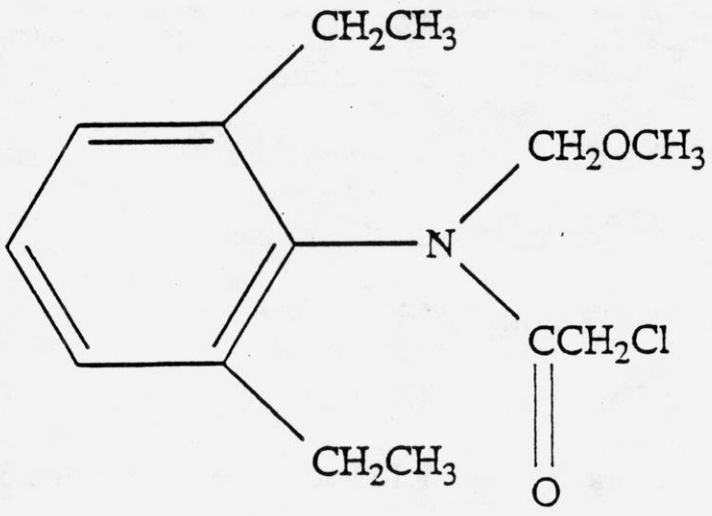


Figure 2.2

Alachlor

Table 2.2
Physical and Chemical Properties of Alachlor[a]

Property	Value
Chemical Name	2-Chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide
Trade Names	Lasso, Alanex, Alanox, Alazine, Lazo, Pillarzo
Chemical Formula	$C_{14}H_{20}ClNO_2$
Molecular Weight	269.8
Melting Point	40-41 deg C
Specific Gravity	1.133 at temperature range 25-15.6 deg C
Aqueous Solubility	242 ppm at 25 deg C
Kow	434
LD50	1800 mg/kg (acute, rat, oral)

a) References: USEPA (OPP), 1986; Meister Publishing Company, 1987.

The fate of atrazine and alachlor in soils has been well documented. A survey of the current body of literature on the fate and degradation of both herbicides reveals a wealth of lab and field studies evaluating both the primary dissipation processes for the herbicides and the effect of various environmental factors on these processes. Most of this work adresses the fate and degradation of the herbicides at the soil surface or in the root or vadose zones. Very little analysis has been done of the dissipation of atrazine or alachlor in the saturated zone. No work to date has identified degradation products of these herbicides in groundwater or in aquifer materials. This chapter provides an overview of the degradation pathways of atrazine and alachlor in soil and aquifer systems. It also explains the choice of degradation products for inclusion in this study.

2.2 Environmental Fate of Atrazine and Alachlor

This study focuses on the degradation products of atrazine and alachlor. However, degradation is one of many dissipation processes for chemicals in the subsurface. The four primary processes of pesticide dissipation are: uptake and retention by crops and their residues; volatilization; transport away from the application site by groundwater (leaching) or surface water (runoff); and degradation. Subsurface transport is primarily affected by two processes: hydrodynamic transport, and adsorption to organic matter and clay mineral surfaces (Weber and Miller, 1989; Anderson and Balogh, 1989). Each of these processes is influenced by the chemical and physical properties of the pesticide, by the chemical, biological and physical properties of the soil/subsurface involved, and by climatic conditions (Weber and Miller, 1989). Crop type and management also influence these processes, and, thus, the environmental fate of the pesticide. Due to the large number of possible combinations of these factors, the environmental fate of a pesticide is somewhat site specific.

The primary physiochemical properties of the pesticide affecting its environmental fate are: the aqueous solubility of the chemical, the acidity or basicity of the chemical (it's ability to ionize), its volatility, its polarity, the ability of the chemical to partition into an organic phase, and the persistence of the chemical in the soil environment (Anderson and Balogh, 1989; Weber and Miller, 1989).

The primary soil properties which affect the environmental fate of a pesticide are: the structure of the soil, the clay content, the organic matter content, the content of hydrous oxides, the pH, and the soil moisture content (Weber and Miller, 1989). Climatic properties which are important to the fate of chemicals include: the frequency, intensity, and amount of precipitation, the evaporation and transpiration rates, and the temperature (Weber and Miller, 1989).

Crop management affects pesticide environmental fate mainly by altering soil properties or by altering climatic properties at the soil surface. The microclimate at the soil surface is altered, for example, by a no-till residue cover protecting a field from contact with a strong wind. This decreases evaporation and volatilization losses. Irrigation alters the soil moisture content and increases the rate of leaching.

2.2.1 Degradation of Atrazine and Alachlor in Soil

Figures 2.3 and 2.4 summarize the degradative pathways for atrazine and alachlor, respectively. Tables 2.3 and 2.4 accompany these figures. The degradation of herbicides passing from the soil surface to groundwater occurs primarily by three reaction types: photolytic, chemical, and biological (Hacque and Freed, 1974). Several environmental factors determine which mechanism is dominant at any given site. The literature is conflicting on the effects of certain environmental factors, on the relative importance of the mechanisms and, thus, on the consequent occurrence of the degradation products under a given set of conditions. These schemes represent the primary

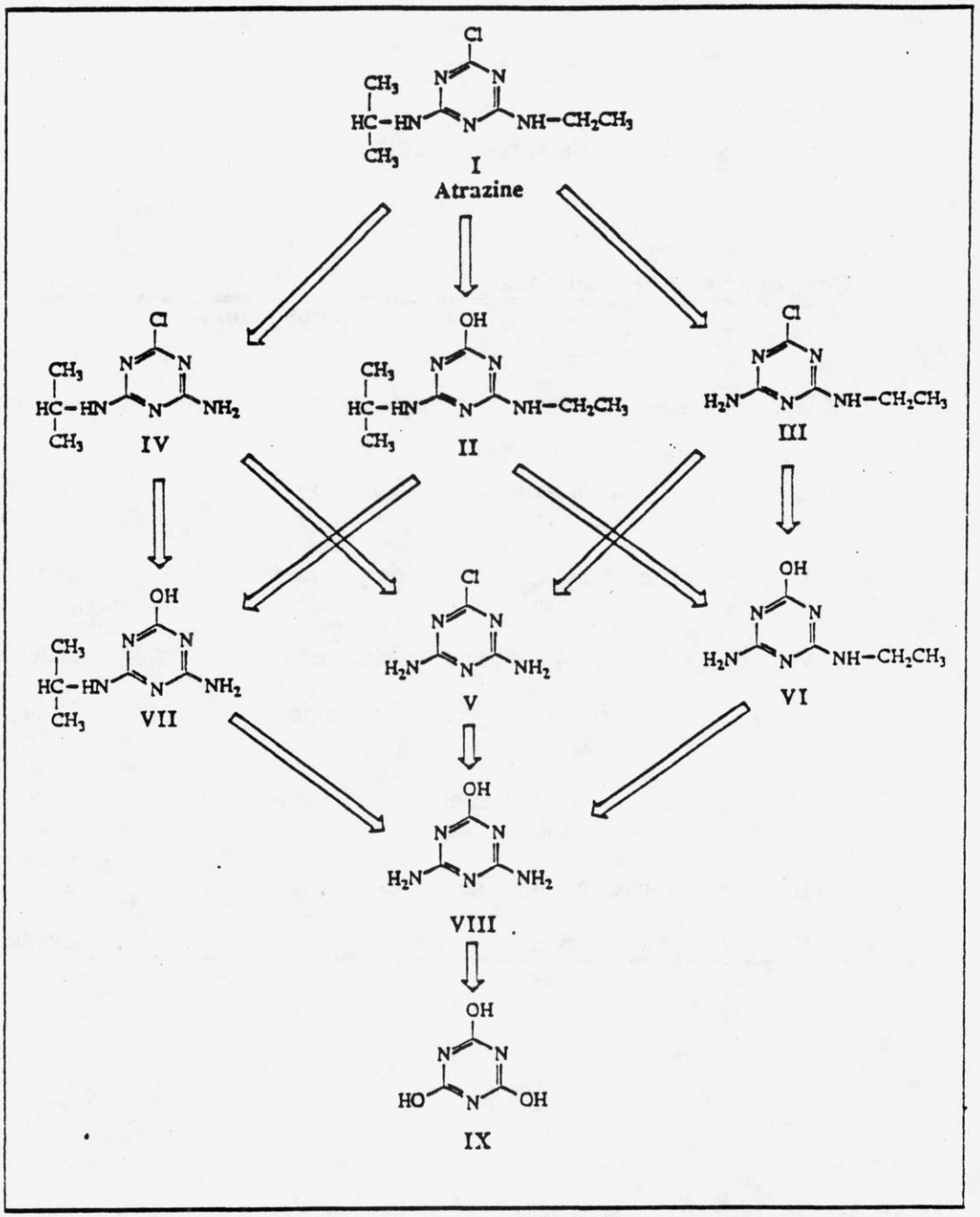


Figure 2.3 Degradation of Atrazine in Soils

Table 2.3
Atrazine Soil Degradation Products

Compound #	Chemical Name	Common Name
I	2-chloro-4-ethylamino-6-isopropylamino-s-triazine	Atrazine
II	2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine	Hydroxyatrazine
III	2-chloro-4-ethylamino-6-amino-s-triazine	Deisopropyl-atrazine
IV	2-chloro-4-amino-6-isopropylamino-s-triazine	Deethylatrazine
V	2-chloro-4,6-diamino-s-triazine	Didealkylatrazine
VI	2-hydroxy-4-ethylamino-6-amino-s-triazine	Deisopropyl-hydroxyatrazine
VII	2-hydroxy-4-amino-6-isopropylamino-s-triazine	Deethylhydroxy-atrazine
VIII	2-hydroxy-4,6-diamino-s-triazine	---
IX	2,4,6-trihydroxy-s-triazine	Cyanuric acid

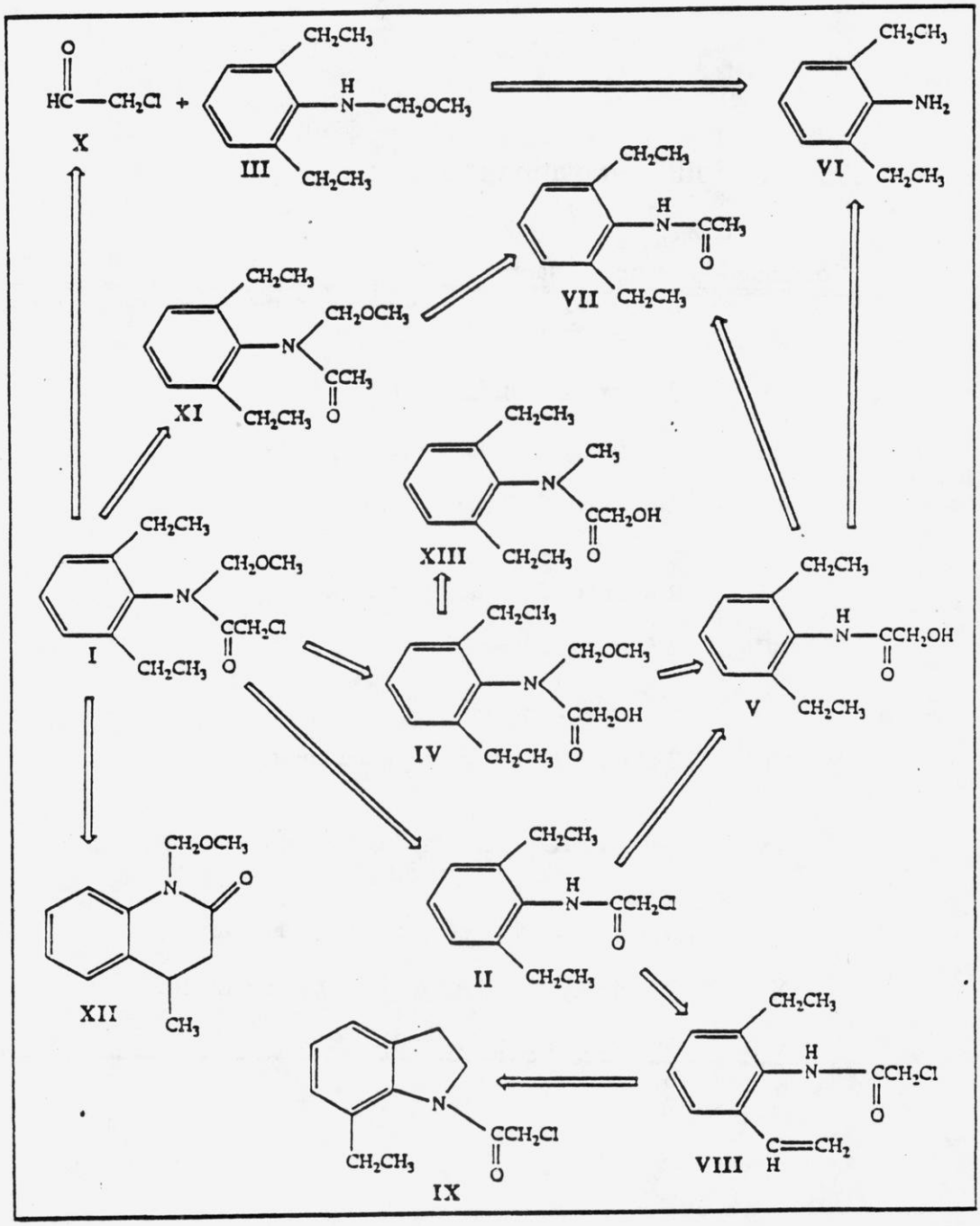


Figure 2.4 Degradation of Alachlor in Soils

Table 2.4
Alachlor Soil Degradation Products

Compound#	Chemical Name	Common Name
I	2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide	Alachlor
II	2-chloro-2',6'-diethyl-acetanilide	
III	2'6'-diethyl-N-(methoxymethyl)-aniline	
IV	2-hydroxy-2',6'-diethyl-N-(methoxymethyl)-acetanilide	Hydroxyalachlor
V	2-hydroxy-2',6'-diethyl-acetanilide	
VI	2,6-diethylaniline	DEA
VII	2',6'-diethyl-acetanilide	
VIII	2-chloro-2'-ethyl-6'-vinyl-acetanilide	
IX X	1-chloroacetyl-2,3-dihydro-7-ethylindole-monochloroacetic acid	
XI	2',6'-diethyl-N-(methoxymethyl)-acetanilide	Norchloralachlor
XII	2-hydroxy-2',6'-diethyl-N-methyl-acetanilide	
XIII	(unamed alachlor lactam)	

soil metabolites in the degradation pathways for atrazine and alachlor as outlined by the literature in the field.

Atrazine

Photolytic Degradation

Ultraviolet irradiation of atrazine in water results in hydrolysis of the chlorine at the 2- position as demonstrated in laboratory experiments (Pape and Zadik, 1970). This reaction is probably of minor importance to the environmental fate of atrazine because it must occur at the soil surface.

Chemical and Microbial Degradation

Four primary reaction mechanisms contribute to the degradation of atrazine. These are: hydrolysis of the chlorine at the 2- position, N-dealkylation of either amino side chain, deamination of a dealkylated nitrogen, and ring cleavage. The initial transformation of an atrazine molecule will be either hydrolysis or N-dealkylation, resulting in hydroxyatrazine (II), deisopropylatrazine (III), or deethylatrazine (IV). Which of these is preferred will depend on several environmental factors (Esser et al., 1975, Bekhi and Khan, 1986; Kaufman and Blake, 1970).

Armstrong et al. (1967) studied atrazine hydrolysis in soil perfusion systems. Hydrolysis occurred when soil was present, but did not take place in perfusate in the absence of soil. The authors theorized that that atrazine was adsorbed onto clay and organic matter surfaces where hydrolysis was then catalyzed. They also found that hydrolysis was favored in both highly acidic and highly basic solutions, but not in the pH range between. It was concluded that pH and organic matter content were the most important soil factors affecting the reaction. Harris (1967) showed that hydrolysis occurred in soil in the presence of microbial inhibitors, further establishing the nonbiological nature of the hydrolysis reaction. Other researchers (Skipper and Volk, 1972; Beynon et al., 1972; Dao et al., 1979) found hydroxyatrazine to be the

primary soil degradation product in laboratory and greenhouse experiments, although the dealkylation products were also present. Hydroxyatrazine is more susceptible to ring cleavage than atrazine (Skipper et al., 1967; Goswami and Green, 1972). It also binds more tightly to soil than atrazine or its dealkylated products (Muir and Baker, 1976; Schiavon, 1988; Hayes, 1970; Weber, 1970). Increased soil moisture and temperature increase the hydrolysis reaction rate (Esser et al., 1975).

Dealkylation of the amino side chains of atrazine is an important degradative reaction (Skipper et al, 1967; Skipper and Volk, 1972; Kaufman and Blake, 1970). A variety of soil bacterium and fungi have demonstrated the ability to dealkylate either side chain of atrazine (Bekhi and Khan, 1986; Kaufman and Blake, 1970). There are qualitative and quantitative differences as to which side chain is preferred by the various species (Bekhi and Khan, 1986). A few species have the ability to degrade atrazine by hydrolysis, but this is less common (Bekhi and Khan, 1986; Esser et al, 1975). Skipper and Volk (1972) found that the ethyl side chain was removed 12 times more rapidly than the isopropyl side chain in laboratory experiments. Work by Goswami and Green (1971) agreed with these results. Both dealkyl products retain some degree of phytotoxicity, with deethylatrazine being the more phytotoxic of the two (Kaufman and Blake, 1970). The possibility of these compounds contributing to carryover in agricultural fields has made them of interest to agronomists.

The hydrolysis product, II, can undergo dealkylation to form compound VI or VII. These same products can also be formed by the hydrolysis of compounds III and IV, respectively. The product compounds, deethylhydroxyatrazine (VII) and deisopropyl-hydroxyatrazine (VI), have been identified in a number of field studies (Muir and Baker, 1978; Khan and Marriage, 1977; Khan and Saidak, 1981). It is unclear which reaction (dealkylation or hydrolysis) proceeds the other (Khan and Marriage, 1977; Khan and Saidak, 1981). Khan and Saidak concluded that either reaction can occur first since

compounds displaying both Cl- and OH- moieties with and without dealkylation have been found in soils. Other researchers have concluded that since adsorption onto clay and organic matter enhances hydrolysis (Armstrong et al., 1967), it may be that dealkylation occurs prior to adsorption; the dealkylation products may then sorb and subsequently be hydroxylated. There is evidence that deethylatrazine is less tightly sorbed than atrazine (Muir and Baker, 1976; Schiavon, 1988). If adsorption is followed by hydrolysis, then deethylatrazine would be less lilely to be hydrolyzed. This explanation is compatible with the results of Khan and Marriage (1977) and Khan and Saidak (1981) who found deethylhydroxyatrazine to be present in lower concentration than deisopropylhydroxyatrazine in field studies, although it is generally conceded that deethylatrazine is the primary dealkylation product.

Further dealkylation of III and IV will result in didealkylatrazine (V). Products VI and VII can be dealkylated, resulting in compound VIII. Compound VII can be deaminated to form cyanuric acid (IX). Both V and VIII have been identified in soils treated with atrazine (Esser et al., 1975; Schiavon et al., 1988; Beynon et al., 1972). Product V has been identified as being highly polar, and is known to form unextractable (bound) residues (Schiavon et al., 1988); it is unlikely that it would leach to groundwater. Degradation of V and IX has been shown to be rapid (Wolf and Martin, 1975). In this way, these products may be considered as removal pathways for atrazine from soils.

Laboratory studies help to clarify reaction mechanisms or potential degradative pathways, but they may not reflect what occurs in the field, where many competing processes are affected by a myriad of environmental factors. Several studies have identified degradation products in soil from cultivated fields. These studies have, for the most part, concentrated on the first two "tiers" of products, II, III, IV, VI, and VII. Muir and Baker (1976) studied the occurrence and movement of atrazine and its degradation products in the top 40 cm of sandy clay loam soil planted in maize. The field had been treated with atrazine for three years prior to the study. They found hydroxyatrazine to be the

predominant residue, followed by atrazine. Deethylatrazine was also present, but in lesser quantities than both atrazine and deethylhydroxyatrazine. Deisopropylatrazine was present in almost negligible quantities. The study also showed deethylatrazine to be more mobile than atrazine, which was more mobile than hydroxyatrazine. Deethylhydroxyatrazine was less mobile than deethylatrazine.

Muir and Baker (1976) reported on the occurrence of atrazine and its degradation products in tile drain water from beneath the same fields used in the later studies (Muir and Baker, 1978). The tile drains were 1.2 m below the soil surface. The concentration of deethylatrazine in the water was equal to, or greater than, the atrazine concentration. Deisopropylatrazine was present in very small amounts, and the authors concluded that it was a minor product. The authors suggested that the more polar deethylatrazine had a higher aqueous solubility than atrazine, and thus moved more quickly through the soil profile. The authors did not look for hydroxyatrazine, as preliminary studies indicated that it would not be present.

Sirons et al. (1973) found that deethylatrazine was the primary dealkylated product in clay loam soil from the top 25.4 cm of a corn field which had been treated with atrazine. Over the period of a year, deethylatrazine was present in levels that were from 10%-100% of the atrazine levels. Deisopropylatrazine was a minor product and couldn't be detected 5 months post application.

Khan and Marriage (1977) identified atrazine and its metabolites in soil taken from a field which had received nine consecutive annual applications of atrazine. They identified hydroxyatrazine, deethylatrazine, deisopropylatrazine, deethylhydroxyatrazine, deisopropylhydroxyatrazine, and atrazine in samples taken from the top 15 cm of the field, 2-3.5 years post-application. Both deisopropylhydroxyatrazine and hydroxyatrazine were present in levels greater than those of atrazine. Deisopropylhydroxyatrazine was the primary product present, followed by hydroxyatrazine. Deethylhydroxyatrazine was present in higher levels than

deethylatrazine, suggesting that, in soils, the 2-hydroxy dealkylated compound is more prevalent than the 2-chloro dealkylated compound.

Khan and Saidak (1981) found that, following 20 consecutive annual atrazine applications, hydroxyatrazine was the primary compound present, followed by deisopropylhydroxyatrazine in the top 15 cm of a sandy loam soil. Deethylhydroxyatrazine was again present in levels greater than those of deethylatrazine. The authors also noted an appreciable loss of total atrazine which was not accounted for in the total residue. They suspected leaching as a primary dissipation mechanism which removed the residues from the plough layer.

These studies have focused on atrazine behavior in the surface layer; its degradation and movement under subsurface and aquifer conditions have not been as well studied. Wehtje et al. (1983) found that microbe populations isolated either from contaminated aquifers or from contaminated surface soil could not degrade atrazine under simulated aquifer conditions. Some hydrolysis did occur in the same samples, albeit slowly. The authors concluded that atrazine hydrolysis is the only viable degradation mechanism in aquifer conditions. Roeth et al. (1969) compared atrazine degradation in silt loam and silty clay loam in the topsoil and subsoil. They found that atrazine ring cleavage occurred two to three times more rapidly in the topsoil than in the subsurface. Also, hydrolysis occurred 100-194 times more rapidly than dealkylation. The authors suggested that because the microorganism population, temperature and clay content decrease with depth, atrazine adsorption and degradation also decrease. Wolf and Martin (1972) found that the rate of ring cleavage of atrazine, cyanuric acid (compound IX) and didealkylatrazine (V) were greatly decreased under saturated soil conditions in laboratory experiments. Goswami and Green (1971) found that hydroxyatrazine was much more quickly degraded than atrazine in submerged soils in lab experiments.

Schiavon (1988a) compared the migration and degradation of ring labelled atrazine compounds in water leached from 60 cm soil columns. The compounds were applied to individual columns which were buried

in the field. The leached water was collected and analyzed over the course of a year. The applied compounds included atrazine, hydroxyatrazine, deethylatrazine, deisopropylatrazine and didealkylatrazine. Deethylatrazine was the compound at highest concentration in the water leached from the atrazine treated column. Schiavon ranked the compounds in order of increasing "power of (groundwater) contamination" with the following results: deethylatrazine> atrazine> deisopropylatrazine> didealkylatrazine> hydroxyatrazine. The author did detect the hydroxydealkyl- compounds in small quantities in leached water, with deethylhydroxyatrazine> deisopropylhydroxyatrazine. The author noted that all the degradation products were present, although in low quanitities, in the groundwater. Schiavon concluded that isopropyl attack is very slow relative to ethyl attack, and that the hydroxylated compounds are highly immobile. Contaminaton of leached water was due primarily to deethylatrazine, which is contrary to the results of Muir and Baker (1978).

Schiavon (1988b) followed the leaching studies by evaluating the amount of radioactivity present at different levels in the soil columns. This enabled him to examine the ability of the different products to penetrate into the soil. The radioactive residues were classified as extractable or unextractable (bound). Extractable residues are susceptible to leaching while the unextractable residues are not. Schiavon found that deethylatrazine was the most susceptible to leaching while hydroxyatrazine was the least susceptible. His results showed that increasing the degree of dealkylation favored the formation of bound residues; conversely, hydroxylation seems to block the formation of unextractable residues. Thus, while hydroxyatrazine adsorbs tightly to soils, it remains extractable, or susceptible to leaching, while didealkylatrazine is capable of forming the largest amount of unextractable residues. The author found that bound residues were more susceptible to ring cleavage, so that the order of unextractable resiude formation and susceptibility to ring cleavage was as follows: didealkylatrazine> deisopropylatrazine> deethylatrazine> atrazine>

hydroxyatrazine. This is contrary to the findings of Skipper and Volk (1972) and Goswami and Green (1972) who found that hydroxylation guaranteed faster degradation. It could be that both the tightly adsorbed (hydroxy-) compounds and the bound residues are more quickly degraded.

In view of the literature cited here, the degradation products most likely to be found in atrazine contaminated groundwater are deethylatrazine and deisopropylatrazine. Hydroxyatrazine, the primary soil degradation product, is tightly bound to the soil matrix and is unlikely to leach to groundwater. Didealkylatrazine was demonstrated in one study (Schiavon, 1988a) to leach to groundwater. No other study corroborates this. Didealkylatrazine has also been shown to form unextractable residues in the soil matrix. On the basis of these results, it is unlikely to be a groundwater compound.

Alachlor

The environmental fate of alachlor has not been as well studied as that of atrazine. There is some disagreement between the academic literature and industry literature as to which degradation products are most prevalent. Several studies have focused on factors affecting the degradation rate of alachlor in soils. Zimdahl and Clark (1982) found that alachlor degraded faster in clay loam than in sandy loam soil, and that increased temperature enhanced degradation. They suggested that the higher soil moisture content and microbial activity of the clay loam soil were responsible for the increased rate of degradation. Walker and Brown (1985) compared the alachlor degradation rate in soil under different incubation conditions in laboratory experiments. They found that increased temperature caused an increased rate of loss. Increased soil moisture content also increased degradation.

Photolytic

Fang (1977) studied the effect of sunlight on alachlor exposed on glass surfaces or incorporated into soil samples. Degradation did not

occur in the dark. Six degradation products were identified: 2-Cl-2',6'-diethylacetanilide (II), 2',6'-diethyl-N-(methoxymethyl)-aniline (III), 2',6'-diethylaniline (VI), 2',6'-diethylacetanilide (VII), 1-chloroacetyl-2,3-dihydro-7-ethylindole (IX), and chloracetic acid (X). Two further compounds, 2-hydroxy-2',6'-diethyl-N-(methoxymethyl)-acetanilide ["hydroxyalachlor"] (IV), and 2-hydroxy-2',6'-diethylacetanilide (V), were not observed, but were proposed as likely intermediates in the conversion of alachlor to VII. Degradation rates increased in conditions of low or high pH and with a decrease in organic matter content. Degradation was more rapid in soils than on glass surfaces. Later experiments (Fang, 1979) showed that photodegradation occurred most rapidly on soils of lower pH.

Somich et al. (1988) investigated the use of UV irradiation and ozonation as a possible disposal process for alachlor contaminated groundwater. This process was tested in water in laboratory conditions. Contrary to the results of Fang (1977), dechlorination was found to be the first step of alachlor photolysis. A number of products were formed by UV irradiation, all of which retained the aromatic ring and carbonyl carbons of the alachlor molecule. The identified compounds were compounds IV and VII, norchloralachlor (XI), an unnamed lactam (XII), and 2-hydroxy-2',6'-diethyl-N-methylacetanilide (XIII).

Chemical and Microbial

Hargrove and Merkle (1979) studied the effects of temperature and relative humidity on degradation and volatilization of alachlor in soil. The authors found that degradation was rapid at high or low relative humidity. The authors identified one degradation product, compound II, which was also formed in acidic solution. The authors concluded that this product resulted from acid hydrolysis of alachlor by acidic water films at mineral surfaces. At constant relative humidity, product formation is favored by increased temperature. Increased relative humidity increases the film thickness, with a concomitant decrease in film acidity, and thus decreased hydrolysis. Degradation

does increase with high relative humidity, but this was attributed to volatilization.

Sethi and Chopra (1975) also identified compound II in soil in lab studies by thin layer chromatography. They found that alachlor adsorption was accompanied by degradation to compound II. Adsorption was found to increase with increased clay or organic matter content. They determined that pH was the most important factor affecting degradation but concluded that alkaline hydrolysis was more important than acid hydrolysis, even though higher pH decreases adsorption. Compound III was proposed as an alternative hydrolysis product, but was not identified.

Beestman and Deming (1973) conducted laboratory studies to assess the major routes of alachlor dissipation from soils, and their relative contributions to total dissipation. Alachlor was dissipated 50 times more slowly in sterile soil than in nonsterile soil. This indicates that microbial decomposition is more important than chemical decomposition, which was calculated as accounting for less than 2% of alachlor field losses. The authors also concluded that leaching was not an important dissipation mechanism as no residues were detected beneath 4 cm depth. Work by Eschel (1969) supports this finding.

Chou (1977) identified two products, II and IX, in field studies and also found degradation rates of alachlor in sterile soil to be much slower than in nonsterile soil, corroborating Beestman and Deming's results. Chou determined alachlor degradation to be more rapid in aerobic conditions than in anaerobic conditions.

Work by Kaufman and Blake (1973) showed that alachlor could be degraded in enrichment solutions by pure cultures of *Fusarium oxysporum*. In this case, chloride was released, but no aniline (compounds III and VI) could be detected. Chanal et al (1976) had found that two species of soil fungi, a *Penicillium* and a *Trichoderma* species, were capable of degrading alachlor. Two degradation products were produced by both species, but were not identified.

The degradation of alachlor in isolated *Chaetomium globosum* cultures was studied by Tiedje and Hagedorn (1977). Sixty percent of the alachlor incubated with *C. globosum* cultures in nutrient broth had disappeared after sixty hours. Within that same time span, 68% of the chlorine had been released as chloride, suggesting that most of the residues were nonchloro- aromatic moieties. Four metabolites were positively identified: II, III, VI, and IX. Compound V was not observed but was proposed as a likely intermediate for the conversion of II to VI. Compound VIII is proposed as an intermediate from II to IX. Compound II, when incubated with *C. globosum* cultures, degraded at a slower rate than alachlor, indicating that II is a minor intermediate in the *C. globosum* pathway. Six other soil fungi were unable to degrade alachlor. Studies with ^{14}C ring-labeled alachlor incubated with *C. globosum* cultures showed no $^{14}CO_2$ release, indicating that no ring cleavage occurred. Previous studies by the same authors (Tiedje and Hagedorn, 1973) had indicated that alachlor was rapidly biodegraded in soils, but that very little of the ring labelled carbon had been converted into $^{14}CO_2$. The majority of the radioactivity could be recovered from soil only after alkaline hydrolysis, suggesting that the degradation products were bound to soil organic matter.

A separate body of soil degradation products has been identified by Monsanto, the producers of alachlor (Malick, J.M., 1987). Figure 2.5 depicts the degradation products that Monsanto has identified as those most likely to leach to groundwater. There is little available information about these products.

From the available literature, it is difficult to assess which degradation products are most likely to occur in groundwater. Available studies indicate that hydroxyalachlor (IV) and 2-Cl-2',6'-diethylacetanilide (II) are common to two pathways each while 2',6'-diethylaniline (VI) is the end product of at least two pathways. The adsorption and leaching of these compounds has not been studied, so it is unclear which are most mobile in the hydrologic system. The rate of degradation or accumulation of these products is also unknown;

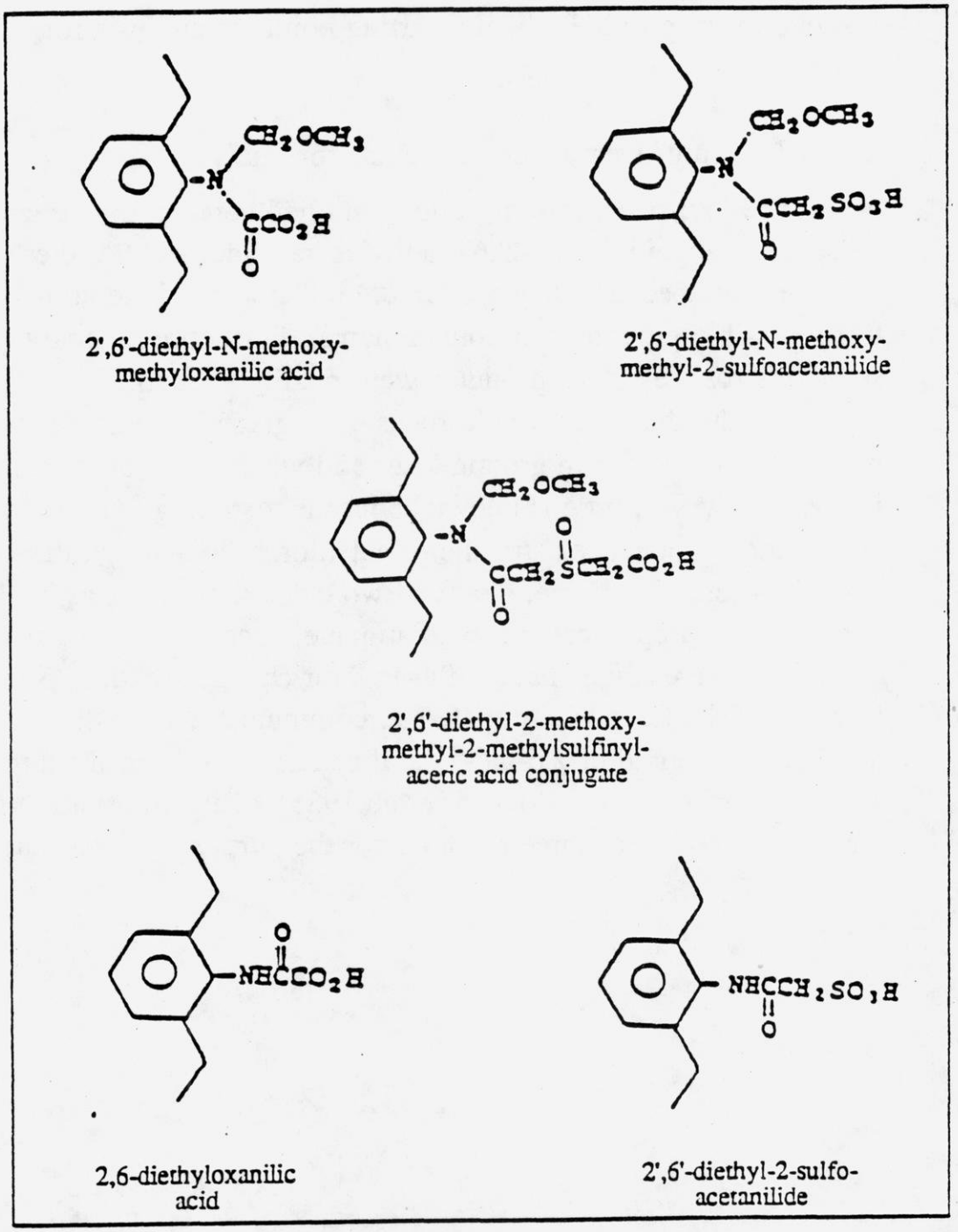


Figure 2. 5 Alachlor Soil Degradation Products Recognized by Monsanto (Malick, 1987)

however, they provide a likely starting point for analysis for this project.

2.3 Selection of Degradation Products for Study

The four degradation products studied here-deethylatrazine, deisopropylatrazine, 2-Cl-2',6'-diethylacetanilide, and 2,6-diethylaniline-were selected because they appeared, on the basis of literature research, to be possible groundwater contaminants. Furthermore, analytical standards for these four products were readily available.

Ideally, this study would focus on degradation products which were known to occur in groundwater and which were of toxicological interest. However, little is known about the toxicology of any of the degradation products of atrazine or alachlor. Ciba-Geigy, the manufacturers of atrazine, treat the two dealkyl products as having toxicological properties similar to atrazine, because they retain the chlorine and are somewhat similar in their chemical action (Sumner, Darryl of Ciba Geigy Corp, personal communication, 1988). The mutagenic potential of 2,6-diethylaniline has been determined to be significant in Ames tests (Lyons et al.,1985). This information supports the selection of these three products for the purposes of this study.

Chapter 3
Methods

3.1 Introduction

A primary goal of this study was the development of methods for the analysis of selected atrazine and alachlor breakdown products in water. Ideally, these methods were to be compatible with those in use by the Wisconsin State Lab of Hygiene (WSLH) for the analysis of pesticides in water. The WSLH uses liquid-liquid extraction and packed-column gas chromatography for the majority of its pesticide analyses, as this technique combines sensitivity and efficiency. Consequently, in this study packed-column gas chromatographic methods were given first consideration for analyzing metabolites. This chapter describes the methods used for the collection of drinking water samples, for the extraction of the samples, and for the chromatography of the extracts. Quality control and quality assurance measures are also described.

3.2 Samples and Sample Preservation

All groundwater samples, whether from sample tap or from monitoring wells, were collected in one-liter round amber glass bottles fitted with teflon-lined septum caps. For each well sampled, two or three one-liter bottles were collected. Each sample bottle was filled to the bottom of the screw cap, ensuring a volume of one liter.

Wells were purged before samples were collected to ensure that the water collected for the sample was, indeed, from the well itself. In the case of drinking water samples, all taps were allowed to run for at least two pump cycles prior to filling the sample bottles, when the pump was audible. When the pump was not audible, the tap was allowed to run for ten to fifteen minutes prior to sampling. In the case of monitoring wells, the wells were bailed using a bailer made of PVC

plastic, four or five well volumes of water were removed from each well and discarded prior to collecting the water for the sample.

All sample bottles were washed and rinsed before field use. Ten percent of all bottles processed were analyzed for contaminants before being used for sampling. Further discussion of sample preparation may be found in the Wisconsin Laboratory of Hygiene Methods Manual (1988).

In order to ensure correct identification of field samples, each sample bottle was labelled, at the time of collection, with the well site, the collector's name, a field number and a description of the sample tap or well. Each sample was also accompanied by a field sheet which was filled out with the same information.

All samples were refrigerated at 4 ° C upon return to the lab and prior to extraction. Extractions were performed within one week of sampling and the total analysis was generally performed within twenty days of sampling.

3.3 Reagents and Standards

Table 3.1 lists the reagent used for the extraction and chromatography of the water samples. The NaCl was baked in a muffle oven for 8 hours at 500 ° C prior to use in order to remove impurities. Table 3.2 lists the pure chemical standards for the pesticides and pesticide-breakdown products used in this study.

3.4 Analytical Standards

Stock standard solutions of pesticides and pesticide breakdown products were prepared by accurately weighing out about 0.01 g of pure compound into a 50 ml erlenmeyer flask. Each compound was dissolved in isooctane and transferred to a 100 ml volumetric flask with several rinsings. The standard was brought to volume with isooctane. In some cases, the pure compound was initially dissolved in a small

Table 3.1 Reagent Descriptions

Reagent	Manufacturer	Reagent Grade
Methylene Chloride	Baxter, Burdick&Jackson	Pesticide Grade
Isooctane	Baxter, Burdick&Jackson	Pesticide Grade
Hexane	Baxter, Burdick&Jackson	Pesticide Grade
Acetone	Baxter, Burdick&Jackson	Pesticide Grade
NaCl	VWR Scientific Reagents	
Anhydrous Sodium Sulfate (Na_2SO_4)	Mallinckrodt	

Table 3.2 Analytical Standards Used

Compound	Source	Purity
Atrazine	USEPA RTP/gratis	99.9
Alachlor	USEPA RTP/gratis	99.7
Deethylatrazine	Ciba-Geigy Corporation/gratis	99
Deisopropylatrazine	Ciba-Geigy Corporation/gratis	98
2-Cl-2',6'-diethyl-acetanilide	Monsanto Corporation/gratis	97
2,6-diethylaniline	Aldrich Chemical Co./purchased	99

amount of acetone before being transferred to the volumetric flask with isooctane. All stock standards were stored in the freezer.

Dilutions were made from the stock standards by pipetting a calculated amount of the stock standard into an appropriate volumetric flask and bringing that flask to volume with isooctane. The dilution standards were used for fortification and distilled-water spikes or as calibraton standards. The spiking standards were stored in the freezer while the calibration standards were stored at room temperature.

3.5 Extraction

Method A

For each sample, a 2 liter separatory funnel was rinsed with about 50 ml of methylene chloride. This rinse was percolated through a one inch diameter drying tube filled with a plug of glass wool and two to three inches of anhydrous sodium sulfate. The glass wool was soxlhet-extracted with methylene chloride for four hours prior to use in order to remove organic impurities. The rinse was collected in a 500 ml round-bottom flask, the flask was rinsed and the solvent discarded.

Each liter sample was transferred to a 2 liter separatory funnel. Fifty g of NaCl were added to the funnel and the funnel was shaken vigorously for thirty seconds. One hundred ml of methylene chloride was added to the separatory funnel. The funnel was shaken vigorously for two minutes with frequent venting.

The water and the organic phases were allowed to separate for a minimum of ten minutes, or until the top water surface and the interfacial surface were clear of bubbles. The separated methylene chloride was percolated through the prepared sodium sulfate column and into the rinsed round bottom flask. The water sample was extracted with three more 100 ml volumes of methylene chloride; each time the separatory funnel was shaken for two minutes, and phases were allowed to separate for a minimum of ten minutes prior to percolating the methylene chloride through the sodium sulfate. The three extract

volumes were collected in the 500 ml round bottom flask. The sodium sulfate column was rinsed with 20 ml of methylene chloride, and the solvent was collected in the round bottom flask.

The extract was concentrated on a rotary evaporator to about 5 ml. Ten to 15 ml of hexane were added to the round bottom flask. Concentration of the extract was continued on the rotary evaporator until the solvent volume was about 2 ml. The extract was transferred, with 3-4 hexane rinses, to a 15 ml graduated centrifuge tube. The hexane was dried under air until the extract volume was less than 2 ml. The volume of the extract was corrected to 2 ml with hexane.

Extracts were stored in the centrifuge tubes fitted with ground-glass stoppers. The extracts were stored at room temperature during analysis and were brought to the original 2 ml volume each day prior to gas chromatographic analysis.

Method B

Method B was performed the same as method A, except that 200 g of NaCl was used instead of 50 g in the extraction step. This method was used for the Bear Creek samples and was replaced with method A, as discussed in Chapter 5.

3.6 Gas Chromatography

Contaminant identification and quantitation in the sample extracts was done by gas chromatography. To confirm the identity and quantitation, each tentatively identified contaminant was analyzed on two unique gas chromatographic systems. A gas chromatographic system is defined, for these purposes, as the combination of detector and column. Thus, following identification and quantitation on one column-detector combination, identification was then be confirmed on either: (1) a column of the same polarity using a second detector, (2) a column of different polarity using the same detector, or (3) a column of different polarity using a second detector. Table 3.3 describes the initial, or

Table 3.3 Primary and Secondary Chromatographic Systems

Compound	Primary System			Secondary System		
	instrmnt.	det.	column	instrmnt	det.	column
Atrazine	HP 5790	NPD	1% SP-1000	Var 3700	ECD	SE30/OV210
Alachlor	Var 3700	ECD	SE30/OV210	HP 5790	NPD	1%SP-1000
Deethyl-atrazine	HP 5790	NPD	1% SP-1000	HP 5890	ECD	DB-1; 60 M
Deisopropyl-atrazine	HP 5790	NPD	1% SP-1000	HP 5890	ECD	DB-1; 60 M
2,6-Diethyl-aniline	HP 5790	NPD	5%-DEGS	HP 5790	NPD	10%-Cwax
2-Cl-2',6'-diethyl -acetanilide	Var 3700	ECD	1%-SP-1000	HP 5890	ECD	DB-1; 60 M

instrmnt = instrument; det = detector;
NPD= Nitrogen Phosphorus Detector; ECD = Electron Capture Detector
HP = Hewlett Packard; Var = Varian; Cwax = Carbowax 20M

primary, chromatographic system and the confirmatory, or secondary, system used for each pesticide and breakdown product.

3.6.1 Packed Column Chromatography

The majority of the gas chromatographic analysis done for this project was performed on packed columns. Table 3.4 indicates the preferred operating conditions for each instrument for each compound that was analyzed on packed columns. Any deviations from the preferred conditions are noted in Chapter 5.

The general scheme employed for the identification and quantitation of the selected compounds on any given packed column was as follows:

1. Establish the retention times of the analytes by injecting 4 µl of the mixed spiking standard.

2. Inject 4 µl of the sample extract. A 4 µl injection volume is preferred, but a maximum injection volume of 6 µl and a minimum of 2 µl can be used. The injection volume must be adequate to allow an analyte occurring in the sample extract at the concentration of the detection limit to result in a reproducible peak. The subsequent peak height must be at least twice the height of the baseline noise of the chromatogram.

3. If the extract chromatogram displays a peak matching the retention time of one of the compounds in the mixed standard, the sample extract is reinjected to ascertain the presence and quantity of the compound.

4. Quantitation of the identified compounds is done using individual standards of each compound. The standard is injected and the resulting peak height is used to determine the compound's concentration in the extract, and hence in the sample. The peak height of the standard injection used for quantitation must be within 20%, and preferably within 10%, of the peak height of the sample peak.

Table 3.4 Operating Conditions For Packed Column Gas Chromatography

Compound	Parameter	Primary System	Secondary System	Alternative System
Atrazine	Instrument	HP 5790	Varian	HP 5790
	Detector	NPD	ECD	NPD
	Column	1% SP-1000	SE 30/OV 210	SE 30/ OV 210
	Carrier Gas	Helium	Argon-Methane	Helium
	Carrier Gas Flow Rate	40-50 psi	40 psi	40 psi
	Column Temperature	225 deg C	215 deg C	215-225 deg C
Alachlor	Instrument	Varian	HP 5790	Varian
	Detector	ECD	NPD	ECD
	Column	SE 30/OV 210	1% SP-1000	1% SP-1000
	Carrier Gas	Argon-Methane	Helium	Argon-Methane
	Carrier Gas Flow Rate	40 psi	40-50 psi	40 psi
	Column Temperature	215 deg C	225 deg C	195 deg C
Deethyl-atrazine	Instrument	HP 5790	**	
	Detector	NPD		
	Column	1% SP-1000		
	Carrier Gas	Helium		
	Carrier Gas Flow Rate	40-50 psi		
	Column Temperature	225 deg C		
Deisopropyl-atrazine	Instrument	HP 5790	**	
	Detector	NPD		
	Column	1% SP-1000		
	Carrier Gas	Helium		
	Carrier Gas Flow Rate	40-50 psi		
	Column Temperature	210-225 deg C		
2-Cl-2',6'-diethyl-acetanilide	Instrument	Varian	**	
	Detector	ECD		
	Column	1% SP-1000		
	Carrier Gas	Argon-Methane		
	Carrier Gas Flow Rate	40 psi		
	Column Temperature	195 deg C		
2,6-diethyl-aniline	Instrument	HP 5790	HP 5790	
	Detector	NPD	NPD	
	Column	5% DEGS	10% C-wax/KOH	
	Carrier Gas	Helium	Helium	
	Carrier Gas Flow Rate	40-50 psi	40-50 psi	
	Column Temperature	180 deg C	225 deg C	

**Capillary Column GC, see table 3.5
HP= Hewlett Packard, Var = Varian;
NPD = Nitrogen Phosphorus Detector; ECD = Electron Capture Detector

5. Confirmation is performed on a second column and/or a second detector as indicated in table 3.3.

All injections were done using the solvent flush method of injection (Grob, 1985). In some samples, the concentrations of the pesticides or the breakdown products were large enough to require that the sample extract be diluted for analysis by a given detector. If the dilution required was six-fold or less, the extract was diluted in the graduated centrifuge tube which the extract was stored in. If the extract required greater dilution, one ml of the original two ml was measured out with a one ml pipette and transferred to an appropriate volumetric flask. The flask was then brought to volume, and analysis proceeded as described. Since only three of the compounds were ever present in amounts necessary to warrant dilution (atrazine, alachlor and deethylatrazine), packed-column analysis for the other compounds was completed prior to dilution of the extract.

3.6.2 Capillary Column Gas Chromatography

Capillary column gas chromatography was used for the confirmation of deethylatrazine, deisopropylatrazine and 2-Cl-2',6'-diethylacetanilide. Packed column chromatography would have been preferred for the analysis of these compounds due to its relative simplicity and speed as well as the more general availability of packed column equipment in most labs. However, in the case of deethylatrazine and deisopropylatrazine, a second packed column could not be found which adequately separated these compounds. In the case of 2-Cl-2',6'-diethylacetanilide, the Nitrogen-Phosphorus detector was not adequately sensitive for quantitation at its detection limit. A second column for the Varian 3700 with the Electron-Capture Detector could not be found which adequately separated the 2-Cl-2',6'-diethylacetanilide from atrazine, in some cases, or alachlor, in others.

Samples were prepared for the capillary column by changing the extract solvent to isooctane. Two ml of isooctane were pipetted into each centrifuge tube. For those extracts which had been halved for dilution purposes, one ml of isooctane was added. The additional solvent was dried down under air until the extract volume was less than 2 ml (or 1 ml for those samples which had been halved for dilution). The extract volume was then corrected to 2 ml (or 1 ml) with isooctane. Sample extracts were diluted with isooctane when necessary in order that all the extracts, when injected onto the gas chromatograph, would be within a two-order of magnitude range of concentrations. A smaller range of sample analyte concentrations would enable the use of a more compact calibration curve, and would thus require fewer standard injections.

Individual standards for each compound were pipetted into autosampler vials. Standards of at least three concentrations were used for each compound. These concentrations were chosen to bracket the expected concentrations of the compounds in the extracts. The results of these injections were used to construct a calibration curve for each analyte. The autosampler vials were fitted with aluminum caps with rubber septa; the caps were crimped to seal.

Approximately 1 ml of each sample extract was pipetted into an individual autosampler vial. These vials were also fitted with caps and crimped. The vials were loaded onto the autosampler (Hewlett Packard 7673A) which injected each sample onto the gas chromatograph. The instrument conditions which were used are listed in table 3.5.

Quantitation of the analytes was done by the external standard method. For each analyte, at least three concentrations of standard were injected. A calibration curve was constructed for each analyte by plotting the standard concentration relative to the peak height for each concentration of analytical standard injected. The calibration data were fitted with a straight line and an equation was derived to describe the line with concentration as the unknown variable. The calibration curves were generated using Cricket Graph (Aldus Corp.) for the Apple Macintosh.

Table 3.5 Operating Conditions For the Hewlett Packard 5890

Parameter	Value
Instrument	Hewlett-Packard 5890
Detector	Electron Capture
Column	60M DB-1
Carrier Gas	Argon Methane
Carrier Gas Flow	55 psi
Injection Mode	Splitless
Injector Temperature	250 deg C
Detector Temperature	320 deg C
Initial Temperature; Hold Time	90 deg C; 1 minute
Initial Rate	10 deg C/min
Initial Final Temperature; Hold Time	150 deg C; 0 minutes
Rate A	1 deg C/min
Final Temp A; Hold Time	170 deg C; 0 min
Rate B	20 deg C/min
Final Temp B; Hold Time	270 deg C; 0 min

The sample chromatograms were screened for peaks whose retention times matched those of the standard peaks. The concentrations of the analytes were calculated using the calibration equations generated for the calibration curves.

3.7 Quality Assurance/ Quality Control (QA/QC)

A quality assurance program was designed in order to continually assess the accuracy and precision of the generated data and to assure the quality of the data within defined limits. This section describes the quality control points which were identified and controlled throughout the sample handling and analysis processes.

3.7.1 Lab Notebook and Sample Sheets

A lab notebook was maintained in which daily laboratory activities were recorded. This information included mixing and dilution of standard solutions, sampling dates and well numbers, extraction dates and anomalies, dates of spikes, blanks and duplicates, chromatographic data, example calculations, and results. Sample sheets accompanied each sample from the field to the lab. The date of collection, well location, and sample type were recorded for each sample on its respective sample sheet. The result for each analyte was listed on the sample sheet at the end of analysis.

3.7.2 Sample Batches

A sample batch is defined as a group of samples collected on the same day from the same field area and analyzed as a group. A single sample batch was carried through the analysis process at the same time. Each batch was accompanied by at least one blank and one tap water spike. Occasionally, both a tap water spike and a fortification spike were included. In general, at least one duplicate analysis was included

per batch; however, the guideline for duplicate measurements was that approximately 10% of all samples were analyzed in duplicate.

3.7.3 Method Detection Limit and Limit of Quantitation

The Method Detection Limit (MDL) is defined as "the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix" (Longbottom et al., 1982). The limit of detection (LOD) is considered to be the lowest concentration level that can be measured as statistically different from a blank. The MDL approaches the LOD as the background contamination (interference) approaches zero (Kieth et al., 1983). The LOD is generally accepted to be three standard deviations (3σ) from the mean or true concentration of the analyte. For the purposes of this study, the background contamination for all compounds on their primary chromatographic systems was determined to be zero; thus, the MDL was equivalent to the LOD for all analytes. The limit of quantitation (LOQ) is equal to the concentration of analyte above which measurement results may be assigned a certain degree of confidence. Confidence levels of 95% percent were used to define the LOQ for the analytes in this study.

The statistical MDL and LOQ for each analyte were calculated from the standard deviation of the concentration of analyte recovered from each of seven replicates. The statistical method used to determine the MDL and LOQ is described in Appendix A of the USEPA Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (Longbottom et al., 1982). The seven replicates used for this study were made by spiking 7 L of distilled water with each analyte so that the final concentration of each analyte was 2 µg/L. Each of these seven replicates was carried through the entire extraction and analysis method described in the methods section of this chapter.

3.7.4 Precision and Accuracy: Duplicates and Spikes

Precision is defined as the reproducibility of method results of replicate analyses under controlled conditions. Precision was measured by analyzing a minimum of 10% of all samples in duplicate and calculating the average difference, R, between the measured concentrations of each analyte. The samples performed in duplicate were randomly selected and analyzed along with the appropriate sample batch. The results of the duplicate analyses were considered in control if they were within 20% of each other for each analyte:

$$R=([dup\#1]-[dup\#2])/\ (ave\ dup\#1,dup\#2)\ x\ 100 \leq 20.$$

If duplicates did not meet the 20% criteria, the duplicates were considered out of control and the batch of samples associated with the duplicates was suspect. If this situation arose, a second duplicate pair was usually analyzed and the batch results carefully audited to determine a possible error. Note that the 20% control limit was arbitrarily selected, although it is similar to the statistically determined control limits for other pesticides (Wisconsin State Laboratory of Hygiene, 1988)

Accuracy refers to the agreement between the true amount of analyte and the measured concentration of analyte in a sample. Accuracy was measured by spiking tap water and calculating the percent recovery of the spike. A known amount of analytical standard was added to a liter of tap water. The spiked liter was then extracted and analyzed along with the sample batch. The percent recovery for any given analyte is given by:

$$(C_m/C_a)\ x\ 100$$

C_m= measured concentration of analyte
C_a= actual (known) concentration of analyte.

The recovery of a spike must be within the upper control limit (UCL) and lower control limit (LCL) calculated for each analyte. As a general practice, upper and lower control limits are set for spike recoveries for a given compound and method. In commercial analytical laboratories, these control limits are determined using a statistical method (Wisconsin State Laboratory of Hygiene, 1988). This requires large amounts of data which have been collected over the course of many analyses. The size of the data set and the duration of the project didn't allow for the use of such a statistical method. Instead, upper and lower control limits were set arbitrarily, based on familiarity of percent recoveries from establishing the method. The selection of upper and lower control limits for this study is discussed in Chapter 5, and the UCLs and LCLs for spike recovery are listed in table 5.9. These limits for all the compounds but deispropylatrazine are similar to those used by the Wisconsin State Laboratory of Hygiene for atrazine and alachlor (Wisconsin State Laboratory of Hygiene, 1988).

3.7.5 Method Blanks: Background Contamination

Blanks were used to determine the presence of background contamination introduced during the analysis process. One blank was run with each sample batch. Ordinary tap water from the laboratory tap was used as the blank matrix. One liter of water was carried through all steps of the analytical process and was treated exactly as a field sample for all parameters being measured. When background contamination was measured at the retention time of any of the analyte sample peaks on any of the chromatographic systems, measures were taken to discover the source of contamination and to correct for it.

3.7.6 Interlaboratory Control- Split Samples

Samples were occasionally split with Dr. Marty Ondrus (Department of Chemistry, University of Wisconsin, Stout). Dr.

Ondrus has developed a method for the analysis of atrazine and deethylatrazine by HPLC. The results for these two analytes were compared between the two labs.

Chapter 4
Site Descriptions

4.1 Introduction

The four sites sampled in this study— Bear Creek, Cottage Grove, Lone Rock and the Hartung facility— were selected because of known atrazine and/or alachlor groundwater contamination. In addition, the sites represented a variety of aquifer types and, from a practical point of view, were accessible for sampling. As shown in Figure 4.1, three of the four sites are located in southern Wisconsin.

A detailed description of the study sites is given below, including a description of the geology and hydrogeology of each site. Information on well location and depth is also included. Where possible, well drillers' logs are summarized for the wells at a site. Ideally, well drillers' logs are submitted to the Wisconsin Department of Natural Resources (WDNR) whenever a well is constructed. However, well driller's logs are notoriously poor at clearly defining the location of a given well. This means that it is often unclear which well a well driller's log actually describes. Furthermore, the data in the logs are not field checked by any agency, and there is no industry standard as to level of detail maintained. What one well driller may describe as hardpan, another may describe as clay and sand. Only well logs for which the wells were adequately located were used in this chapter. Well logs are not corrected to any altitude datum, so they were not used in this study to create cross sections, and should not be interpreted as such.

4.2 Bear Creek

The first record of pesticide contamination of private wells in the town of Bear Creek dates from February of 1986 (Wisconsin Department of Natural Resources, Green Bay, unpublished data). The suspected responsible party is the Waugamie FS Co-op, a pesticide storage and distribution facility. Several herbicides have been

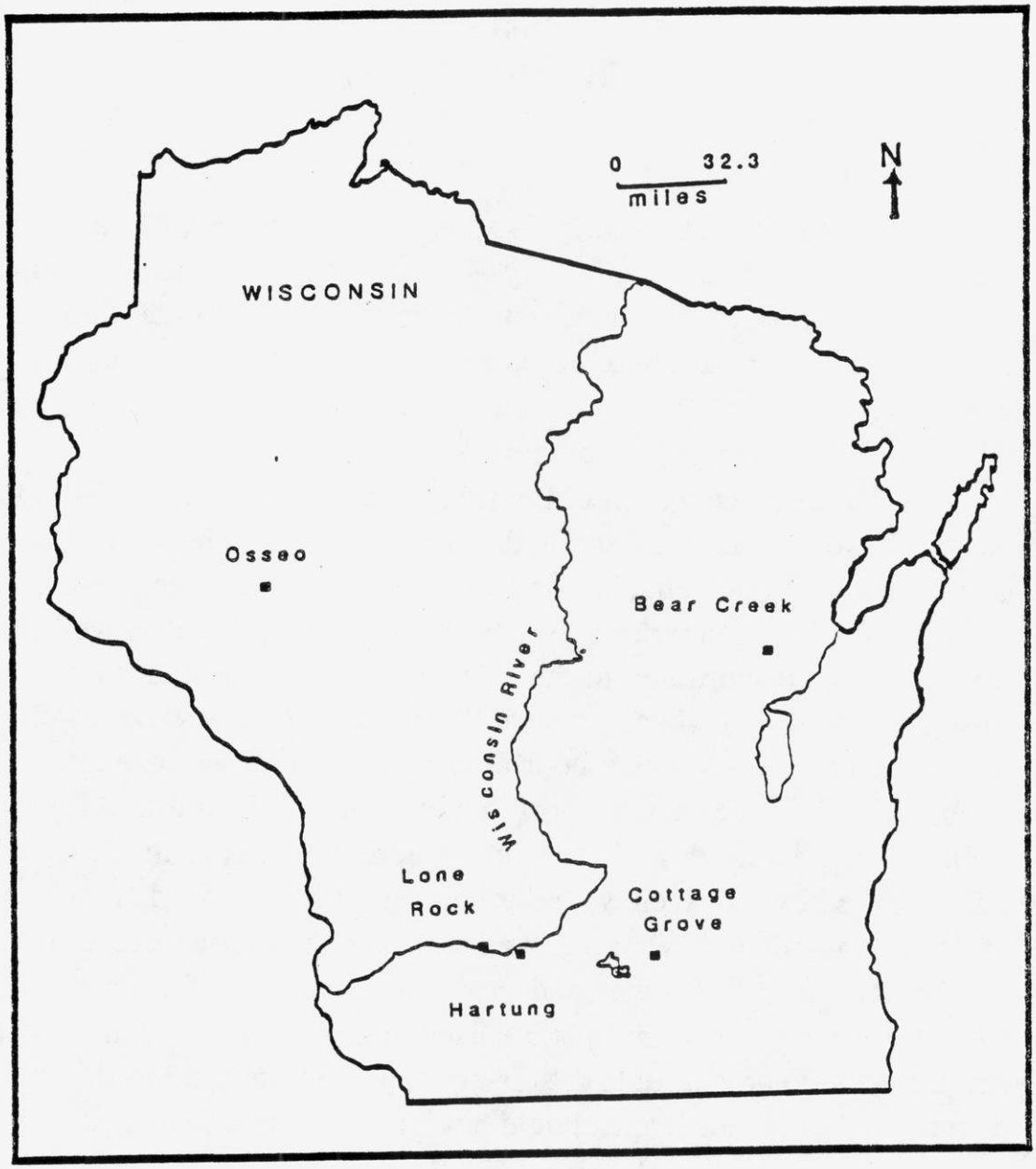


Figure 4.1
Study Site Locations

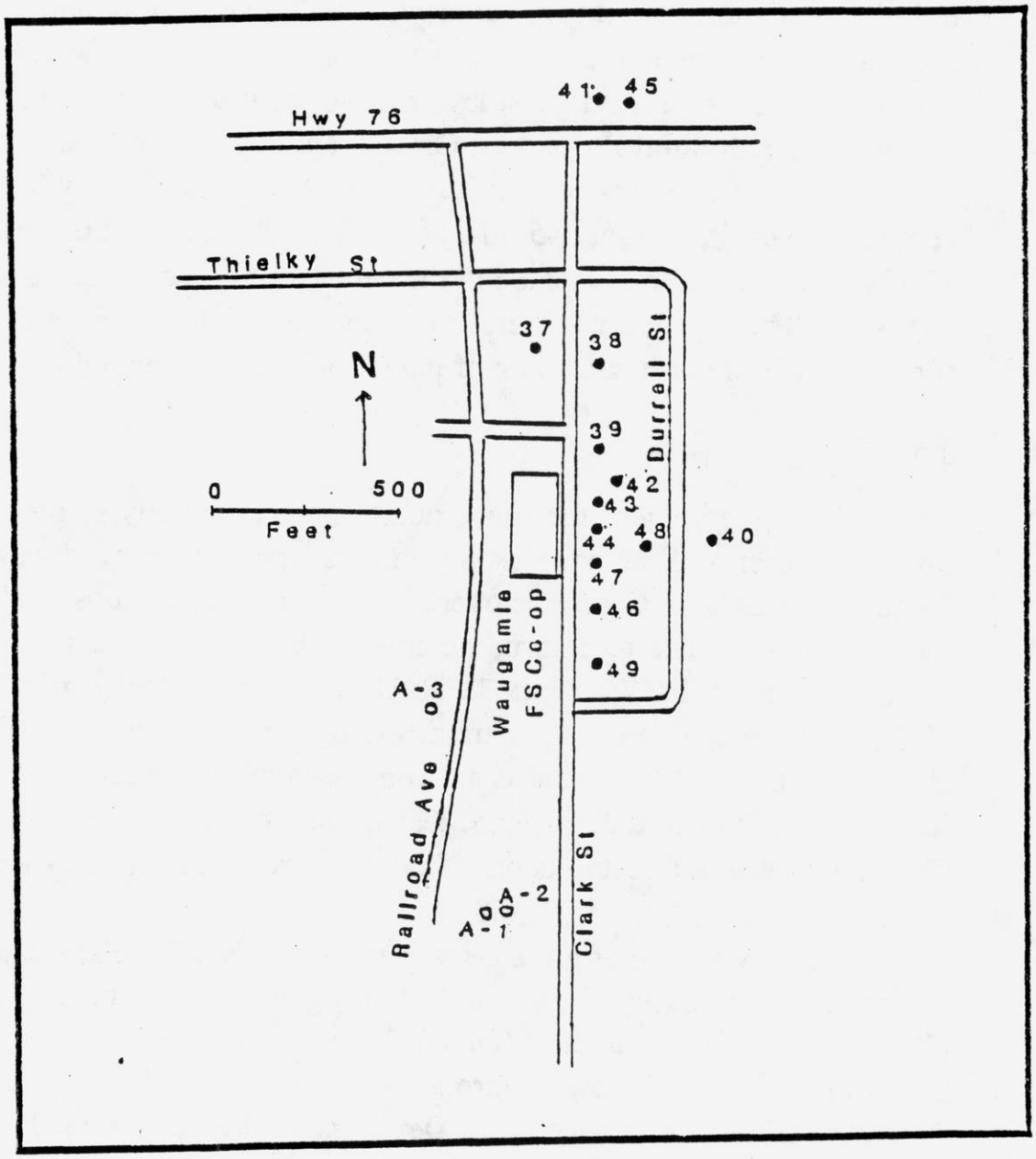


Figure 4.2
Bear Creek:
Well Location

previously identified in private wells from the town, including atrazine, alachlor, metolachlor, cyanizine, dicamba, butylate, thimet, linuron, terbofus, diazinon, chloraben, carbaryl, eptam, carbofuran, and picloram . Atrazine and alachlor are the compounds which are most consistently found in the highest levels throughout the site (Wisconsin Department of Natural Resources, Green Bay, unpublished data).

The town of Bear Creek is located in Outagamie County in east-central Wisconsin, roughly 45 miles (72.7 km) due east of Stevens Point. The Waugamie Co-op is located in the center of town on Clark Street (fig. 4.2). The affected wells are primarily east of the co-op, although some wells both north and south of the co-op are also contaminated.

4.2.1 Physical Description

The topography of the site is nearly level to slightly sloping. The Precambrian crystalline bedrock which characterizes the northwestern corner of Outagamie County is overlain by glacial lake deposits of Pleistocene age. These, in turn, are covered by recent flood-plain deposits (Leroux, 1957; Olcott, 1968; U.S. Department of Agriculture, 1978). The lacustrine deposits are primarily fine-grained sand, silt and clay, while the outwash deposits are composed of coarse sand and gravel (Leroux, 1957; Olcott, 1968; U.S. Department of Agriculture, 1978). The Pleistocene and recent deposits range from 90-200 ft (27.4 - 61 m) thick (Leroux,1957; Olcott, 1968).

The only source of groundwater at the site is the Pleistocene and recent deposits; this aquifer yields 100-500 gallons per minute (gpm) (379 - 1894 liters per minute) (Olcott, 1968). The water table is less than 100 ft (30.5 m) below the ground surface, and can be as high as 20 ft (6.1 m) below the surface (U.S. Department of Agriculture, 1978). The underlying Precambrian rock is essentially impermeable, and does not supply significant amounts of water (Leroux, 1957; Olcott, 1968). Surface water drainage at the site flows east, toward the Embarass River (Leroux, 1957). Groundwater flow in the glacial deposit aquifer is

controlled mainly by the surface and bedrock topography, and thus also flows east (Leroux, 1957; Olcott, 1968).

Soils at the site are primarily of the Menominee-Gray-Rousseau association (U.S. Department of Agriculture, 1978). These are well-drained to moderately well-drained fine sands and loamy fine sands. The surface layer is fine sand or loamy fine sand while the subsoil and substratum are fine sand or sandy loam to a depth of about 5 ft. (1.52 m). The soils contain low organic matter and tend to be weakly to strongly acidic. They display rapid to moderate permeability and low available water capacity (U.S. Department of Agriculture, 1978).

4.2.2 Sampling Locations and Well Information

There were 13 private domestic water wells sampled at the Bear Creek site; 12 supplied drinking water to homes, while BrCrk 40 supplied drinking water to a small apartment complex. The approximate locations of the wells are indicated in fig. 4.2. Most of the study wells are east and northeast of the co-op, although wells BrCrk 41 and 45 were north of the co-op. A well driller's log was available for study-well BrCrk 40. Figure 4.3 illustrates the data for the well; the well was screened over the 67-75 ft. (20.43-22.87 m) depth interval, which is in the sand and gravel of the glacial deposit aquifer. Well logs were available for four additional wells in the area; the location of these is indicated in fig 4.2. Two of these wells supply water to the Sauerkraut factory (A1 and A2) south of the co-op. The other (A-3) supplies water to a private residence. These three well logs are also illustrated in fig. 4.3. The fourth additional well log available for the town of Bear Creek indicates a clay layer from 4 - 21 ft. (1.22-6.40 m) below the ground surface. The location information for this well is incomplete, so that it is not indicated on the map. The well logs collectively indicate that there are clay lenses throughout the till, and that layers of silt or silty sand are also present. The data, however, are not adequate to determine the extent of the clay layers.

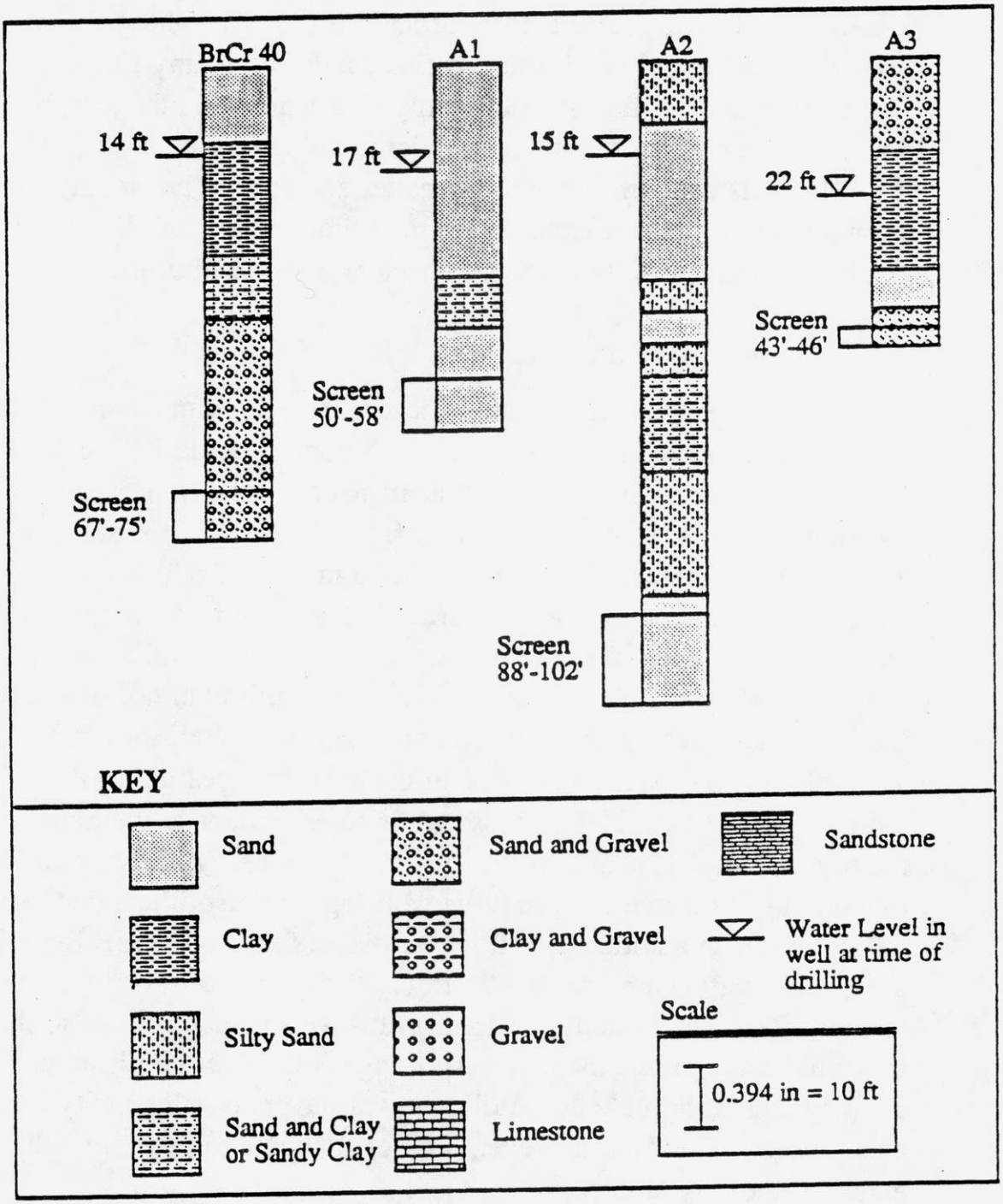


Figure 4.3 **Bear Creek Well Logs**

4.3 Cottage Grove

Pesticides were first identified in water samples from wells on the Dane County Farmers' Union co-op property in July, 1985. Since that time, the WDNR and WDATCP have regularly identified pesticides in groundwater and soil samples from the co-op. Herbicides identified in groundwater at the co-op include atrazine, alachlor, cyanizine, metolachlor, metribuzin, and pendimethalin (Prowl) (Dofahl, 1988). In November, 1988, atrazine was detected in drinking water from private wells directly east of the co-op (Wisconsin Department of Natural Resources, 1988). In inquiries stemming from this contamination of private wells, the WDNR was informed of two prior pesticide spills occurring at the co-op including a large Bicep (liquid mix of atrazine and alachlor) spill in 1986. Subsequent site examinations revealed evidence of other spills at various locations around the co-op land (Wisconsin Department of Natural Resources, 1988).

The Cottage Grove study site is located in eastern Dane County in south-central Wisconsin. The Dane County Farmers' Union Co-op facility, the suspected source of contamination, is located south of Cottage Grove near the intersection of Uphoff Road and county Highway N (see fig. 4.4). The co-op is a retailer and commercial applicator of agricultural fertilizers and pesticides. The facility handles pesticides stored in bulk forms and provides mixed formulations for spray application (Dofahl, 1988).

4.3.1 Physical Description

Eastern Dane County is characterized by rolling topography and low-relief drumlins and ridges. Quarternary glaciers moving from northeast to southwest left unconsolidated deposits of varying thickness and developed the topography in the region (Cotter et al., 1969). This area is underlain by a layer of Cambrian sandstone. The sandstone layer, which is up to 350 ft. (106.7 m) thick, is overlain in spots by

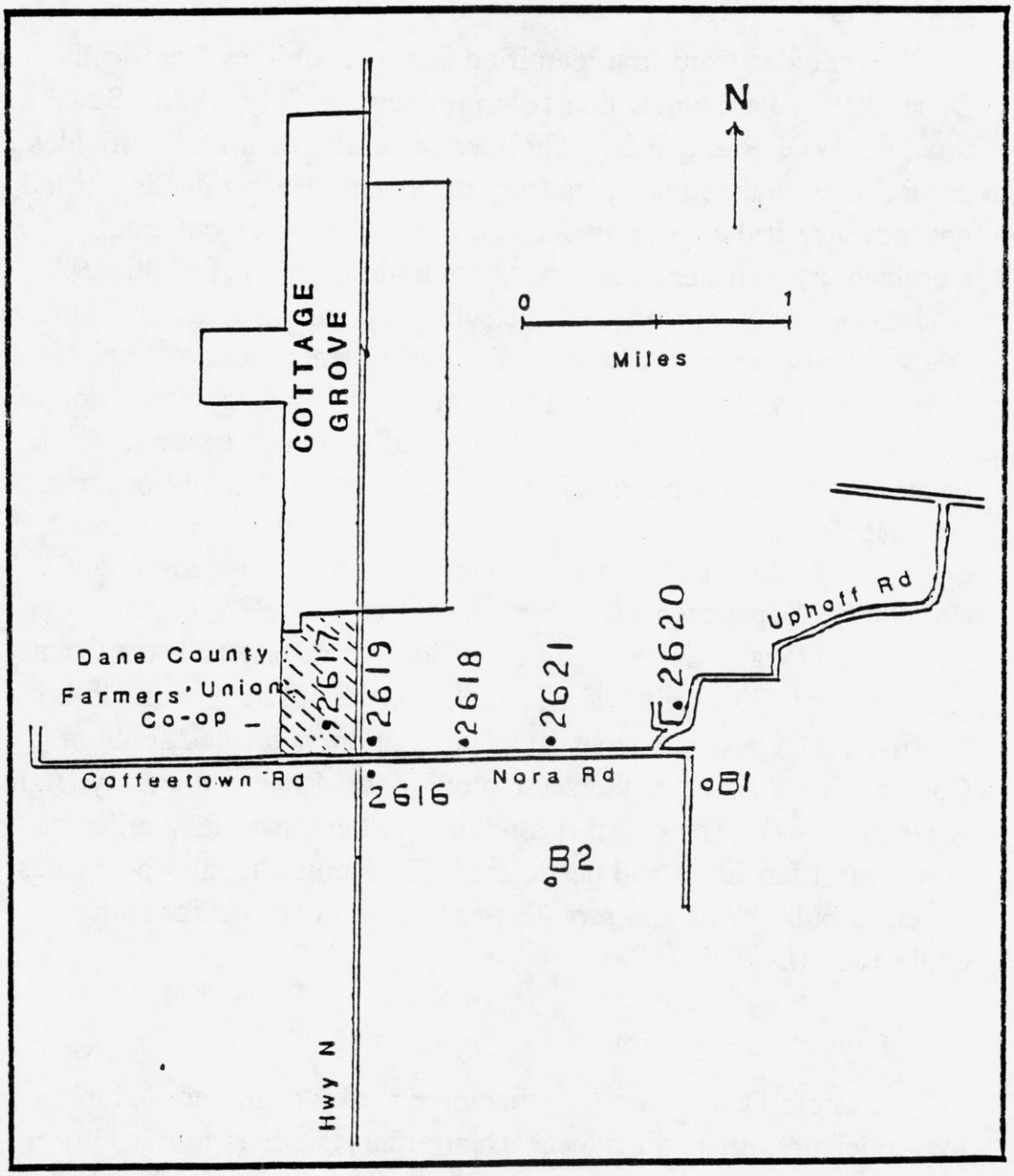


Figure 4.4
Cottage Grove:
Well Location

Ordivician dolomite of the Prairie Du Chien group (Cotter et al., 1969). In the Cottage Grove area, the bedrock is overlain by unconsolidated and unsorted Pleistocene glacial deposits consisting of clay, silt, sand, gravel and boulders. The glacial till is overlain by glacial outwash deposits, which are in turn crowned by several feet of loess and/or fine grained silt and clay deposits (Dofahl, 1988). The primary aquifer in the region is the glacial drift sand and gravel aquifer. The general direction of groundwater flow is nearly due east (Dofahl, 1988).

Soils at the site are generally classified as silt loams of the Batavia and Sable formations. The Batavia silt loams are formed in outwash material and range from well to poorly drained. Batavia soils are deep and are underlain by silt, sand and gravel. The Sable silty clay loams are deep and poorly drained, and are generally underlain by sandy loam glacial till (U.S. Department of Agriculture, 1978). The soils in this area are weakly to strongly acidic, and are highly fertile, with a high humus content (Mickelson, 1983).

4.3.2 Sampling Locations and Well Information

There were six sampling points for the Cottage Grove study site. All six were private wells which provided drinking water to homes and businesses. One well was located on the co-op property; the remaining 5 were located along Nora and Uphoff Roads. Figure 4.4 shows the approximate locations of the six sites. The well driller's reports were available for CtGr 2619 and 2617; these are summarized in fig 4.5. Two additional well logs from the area are included as representative of the wells at the site. All four wells tap the limestone/sandstone beneath the glacial till. One of the study wells, CtGr 2621, is a jetted point well. The maximum depth of a jetted point well in till is 50 ft. (15.24 m). A fifty foot well most likely would enter the glacial outwash or glacial till. The remaining wells are drilled wells, but their well logs are unavailable. It is assumed that they tap the limestone or sandstone beneath the till.

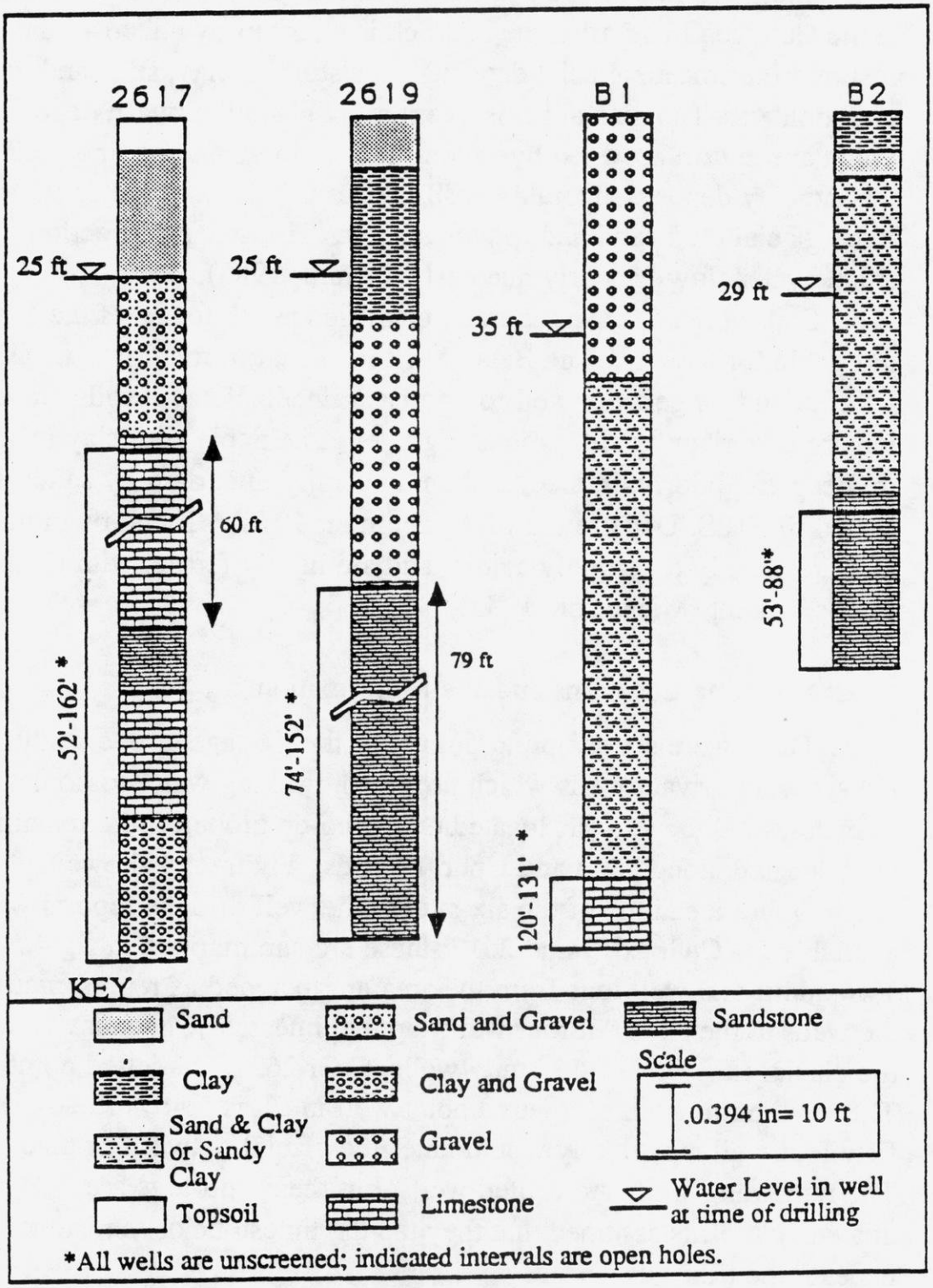


Figure 4.5 **Cottage Grove Well Logs**

4.4 Lone Rock

The WDNR first identified atrazine in private well water samples from the Lone Rock area in 1986. The apparent source of atrazine at the site is the regular application of atrazine to the surrounding farm fields. Farmers in the area rely on the intensive use of center pivot irrigation systems. The combination of heavy herbicide use and intensive irrigation is a common source of ground water contamination in rural areas (Anderson and Balogh, 1988). This is the one study site where the contamination is a non-point-source incident.

The Lone Rock study site is located north of the town of Lone Rock, straddling the Richland and Sauk County line. The fields to the north and east of the sample wells are most likely the source of the atrazine.

4.4.1 Physical Description

The Lone Rock site lies north of the Wisconsin River in the alluvial outwash plain. The terrain in the area is nearly level. The topography is defined by unconsolidated stratified sand and gravel outwash deposits laid over Cambrian sandstone bedrock (Hindall and Borman, 1974). The soil parent material in this area is the outwash sand and gravel; the permeability of the resulting coarse-grained soil is 2.5-5 ft/hour (0.76-1.52 m/hour). The soil is of the Sparta-Plainfield-Sparta variant. It is an excessively drained to moderately well drained, coarse textured soil underlain by sand and gravel. The surface layer is sand to loamy fine sand underlain by a loose sand to a depth of 5 ft. (1.52 m) (U.S. Department of Agriculture, 1977). The soil exhibits rapid permeability, low water holding capacity, and low organic matter content (U.S. Department of Agriculture, 1977).

The Wisconsin River is a gaining stream in this region (Hindall and Borman, 1974). Consequently, the regional groundwater flow is south, toward the river. The primary groundwater source for the area

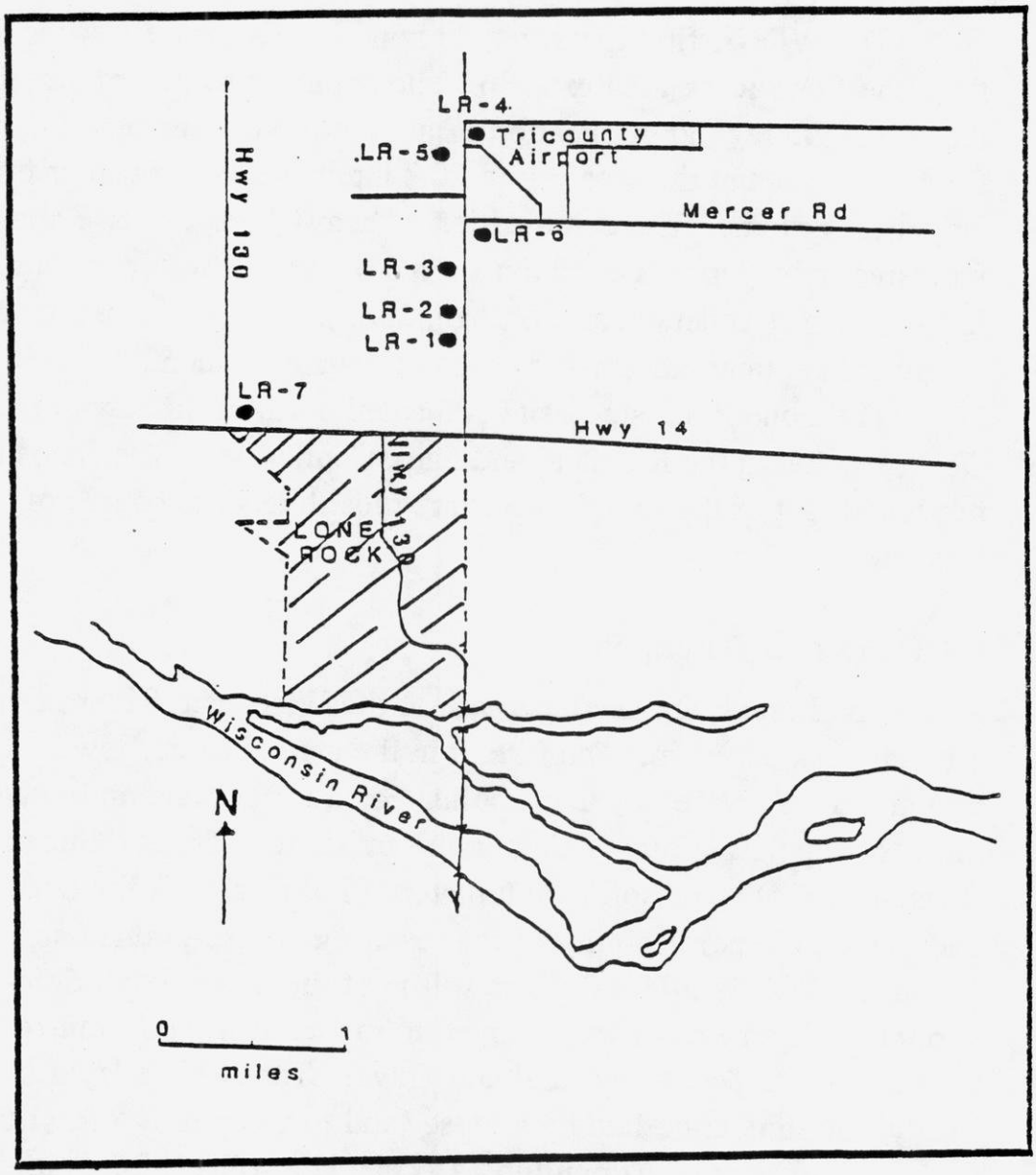


Figure 4.6
Lone Rock:
Well Location

is the upper, unconfined sand and gravel aquifer which is characteristic of the preglacial bedrock valleys along the Wisconsin River. It ranges in thickness from 0-390 ft (0-119 m) and can yield up to 1000 gallons per minute (3788 liters/minute). The water table in this area is near the surface; during the wet season, it can be as shallow as 2.5-5 ft. (0.76-1.52 m). The sand and gravel aquifer is underlain by the Cambrian sandstone aquifer which can be a significant source of groundwater (Hindall and Borman, 1974).

4.4.2 Sampling Locations and Well Information

Seven private wells were sampled at this study site; the locations of the wells are indicated on fig 4.6. Five of the wells provide water to homes while LR-4 provided water to the local airport and LR-7 provided water to a small business. All wells in this area are driven point wells, and are approximately 20-50 ft (6.10-15.24 m) deep (Dunn, J., Wisconsin Department of Natural Resources, personal communication). The wells tap the sand and gravel aquifer. Well drillers' reports are not required for driven and jetted point wells; consequently, there is no information on well depths or on the screened intervals for this site.

4.5 Hartung Facility

Contamination of the wells at the Hartung Arena facility was first detected in May of 1986 (Wisconsin Department of Natural Resources, 1987). The facility is a fertilizer and pesticide storage and distribution center. It is located north and west of the town of Arena (Iowa County). The facility is licensed as a commercial applicator and bulk storage area by the state (General Engineering Co., 1988). The facility is located one mile (1.61 km) south of the Wisconsin River on a nearly level river terrace.

4.5.1 Physical Description

The topography of the Hartung site is defined by the alluvial outwash plain; it is nearly level with some gently sloping areas. The surficial bedrock in this area is sandstone of the Trempeleau group. Overlying the bedrock is a thick layer of stratified sand and gravel deposits (Hindall and Borman, 1974). The sand and gravel provide the parent material for the soil in this region. The soils at the site are primarily of the Sparta-Plainfield-Sparta variant. These soils are excessively drained to moderately well drained coarse textured soils underlain by outwash sand. The surface and subsurface soil is generally sand or sandy loam. The soil exhibits low organic matter content, low water holding capacity, and rapid permeability (U.S. Department of Agriculture, 1962).

The Wisconsin River is a gaining stream in this area, and the regional groundwater flow is north, toward the river (Hindall and Borman, 1974). General Engineering Co. (GEC) determined the direction of flow at the site to be in the north-northwest direction in the spring of 1989. This may vary during the irrigation season (GEC, 1988). The water table in the area can be as shallow as 2.5-5 ft (0.76-1.52 m) during the wet season (U.S. Department of Agriculture, 1962) and was measured at 5-15 ft (1.52-4.57 m) throughout the site by GEC in 1988. The sand and gravel aquifer is an important source of drinking water along the Wisconsin River Valley. This unconfined aquifer is from 0-390 ft (119 m) thick and yields more than 1000 gpm (3788 liters per minute). The sand and gravel aquifer is underlain by a Cambrian sandstone aquifer, which is capable of yielding 500 gpm (1894 liters/minute) (Hindall and Borman, 1974).

4.5.2 Sampling Location and Well Information

The 10 sampling wells at this site were all monitoring or industrial wells on the Hartung facility land. The location of the wells is indicated on fig. 4.7a and fig. 4.7b. Five of the wells (044, 045, 053,

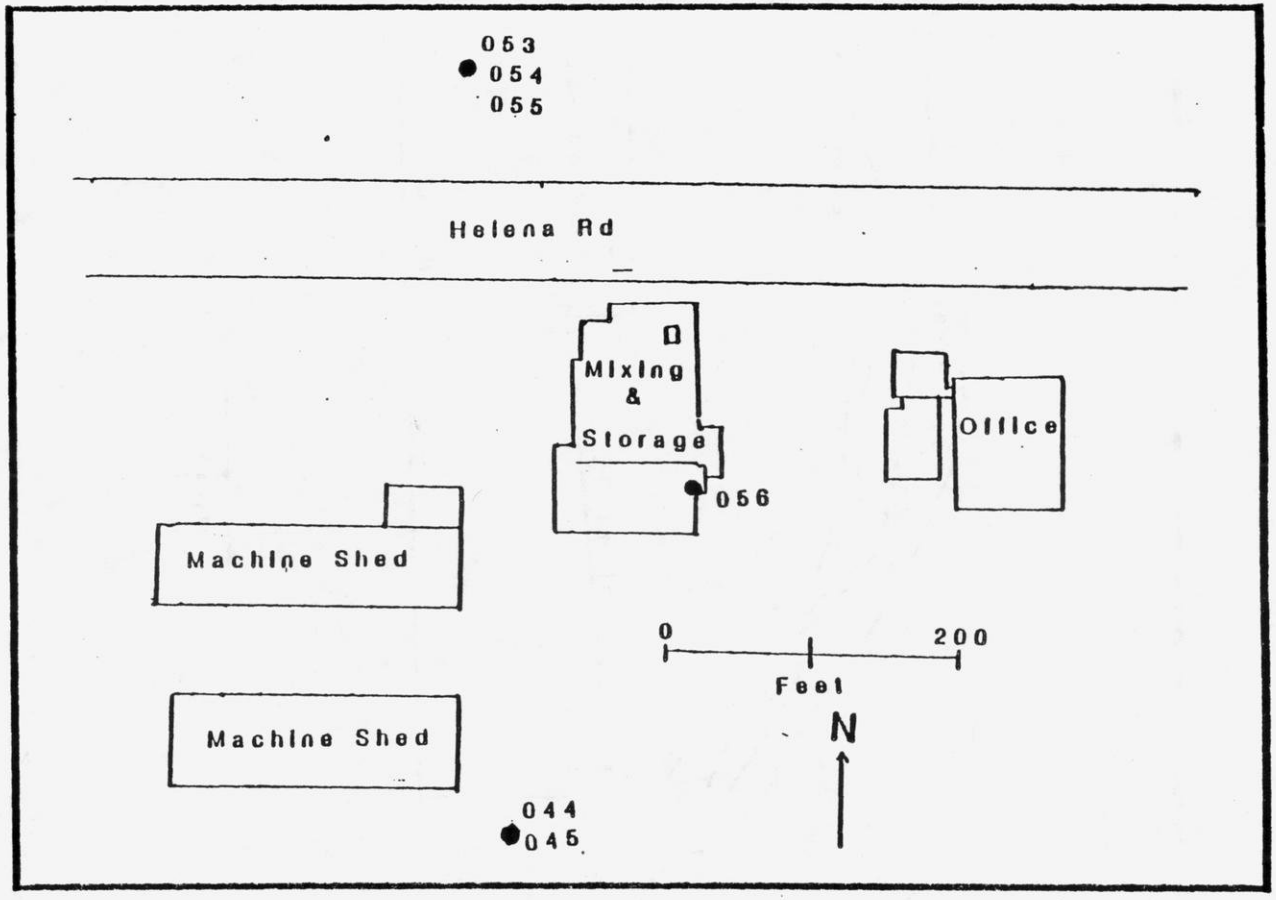


Figure 4.7a

Hartng Facility:
Well Location on Facility Property

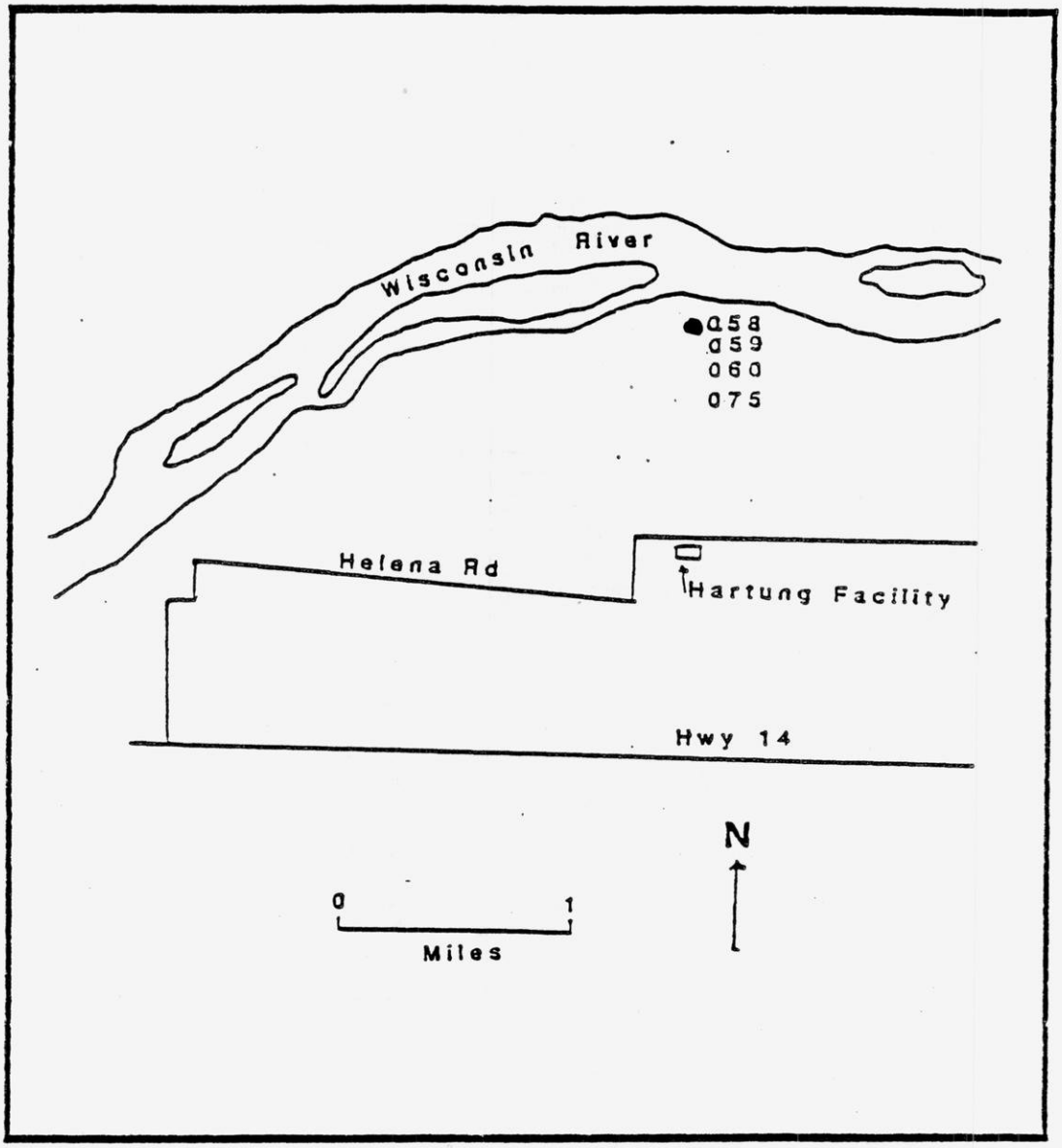


Figure 4.7b

Hartung Facility:
Location of Well Nest off Facility Property

054, and 055) were installed by GEC to monitor the contamination at the mixing and storage facility. These are grouped into two well nests. Wells 044 and 045 are in one well nest south of the facility buildings. Wells 053, 054 and 055 are in a second well nest north of the facility across Helena Road. Well 056 was installed by the Hartung corporation; it supplied non-potable water to a facility building for use in fertilizer mixing. The remaining four wells (058, 059, 060, and 075) were installed and maintained by the WDNR and WDATCP; these are located north of the facility, across Helena Road and north of the adjacent corn field. These four wells are in one well nest. The depths and screened intervals of all the wells are noted in table 4.1. All the study wells tapped the sand and gravel alluvial outwash aquifer. Municipal well logs from both Arena and Spring Green (towns in the outwash plain, east and west of the study site, respectively) indicate that the depth of the sand and gravel is 170-181 feet (51.83-55.18 m).

Table 4.1 Well Information for Hartung Facility

Well #	Diam. (cm)	Well Depth (m)	Depth to Screen Top (m)	Screen Length (m)	Depth to Water (m)
044*	5.08	9.45	8.23	1.22	1.96
045*	5.08	6.40	5.18	1.22	1.98
053*	5.08	9.45	8.23	1.22	2.11
054*	5.08	6.40	5.18	1.22	2.11
055*	5.08	3.35	.304	3.04	2.08
056*	15.24	14.02	NA	NA	NA
058**	5.08	4.45	3.66	1.52	3.66
059**	5.08	5.52	4.21	1.52	3.66
060**	5.08	7.38	5.85	1.52	3.72
075**	5.08	18.14	17.84	0.30	3.75

Diam.=Well diameter
NA=Information not available
* Water depths taken 4/17/89
**Water depths taken 5/2/89

Chapter 5
Results

5.1 Introduction

The concentration data for the six chemical parameters are listed in Table 5.1 for each well in the study. Atrazine was detected more frequently than alachlor at each site. The atrazine degradation product, deethylatrazine, occurred in each well where atrazine was present. Deisopropylatrazine appeared less frequently, and in lower levels, than deethylatrazine. The alachlor degradation products, 2,6-diethylaniline (DEA) and 2-Cl-2',6'-diethylacetanilide, did not occur with any regularity.

5.2 Occurrence of Individual Chemical Parameters

The data for the six measured chemical parameters are summarized for each study site in Tables 5.2-5.5. Table 5.6 summarizes the cumulative data for the entire study by aggregating the results from the four study sites.

In Tables 5.2-5.6, the columns entitled "# Detects" list the number of wells at each site in which the concentration of the chemical parameter in question was equal to or exceeded the detection limit. In the "# Detects" columns, "ND" signifies that the chemical parameter was not detected at that site. For convenience, the detection limits are listed in Table 5.7. The 36 wells were not evenly distributed between the four sites; this was due to both varying availability of wells and varying ease of access to wells at the different study sites.

A Note on Graphs in this Section

Two types of graphs are used in this section to summarize the concentration data for each compound. Box plots are a convenient method for displaying, and comparing, batches of data (Cleveland, 1985). Figure 5.1 is an example box plot displaying the atrazine

Table 5.1 Cumulative Data (Concentrations in µg/l)

Sample #	Atrazine	Deetat	Deisoat	Alachlor	DEA	2Cldietac
BrCk37	1.1	1.1	0.74*	ND	ND	ND
38	3.9	1.7	0.62*	ND	ND	ND
39	1.3	0.63*	ND	ND	ND	ND
40	12	0.83*	ND	0.83	ND	0.35*
41	3.9	9.5	ND	ND	ND	ND
42	15	2.4	0.53*	22	ND	0.44*
43	160	8.7	1.8	460	ND	5.8
44	72	6.8	1.6*	53	ND	1.4
45	1.9	2.8	ND	ND	ND	ND
46	9.8	2.8	0.50*	3.5	ND	ND
47	22	4.8	1.4*	62	ND	0.61*
48	30	4.4	1.2*	8.7	ND	0.44*
49	1.1	1.7	ND	ND	ND	ND
CtGr 16	0.79*	2.0	ND	0.22*	ND	ND
17	20	5.4	0.70*	7.4	ND	ND
18	5.9	5.6	0.80*	ND	ND	ND
19	17	4.3	0.60*	1.0	ND	ND
20	1.4	0.84*	ND	ND	ND	ND
21	50	14	2.4	2.4	ND	ND
LnRk1	8.3	41	2.0	ND	ND	ND
2	8.4	20	ND	ND	ND	ND
3	ND	0.58*	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND
5	ND	0.47*	2.5	ND	ND	ND
6	ND	1.8	0.63*	ND	ND	ND
7	5.8	2.8	0.78*	ND	ND	ND
Hrt 44	14	9.4	0.87*	4.5	ND	ND
45	32	13	1.7	110	ND	0.45*
53	140	12	0.83*	140	3.6	3.8
54	56	8.4	ND	62	3.0	1.0
55	26	2.0	0.84*	7.9	ND	ND
56	14	13	0.68*	12	ND	ND
58	3.3	0.96	ND	ND	ND	ND
59	2.8	0.90*	ND	ND	ND	ND
60	4.5	0.31*	ND	ND	ND	ND
75	3.5	3.8	ND	ND	ND	ND

*Denotes concentration between LOD and LOQ (detection limit and quantitation limit); Deetat=deethylatrazine; Deisoat=deisopropylatrazine; DEA=diethylaniline; 2Cldietac=2-Cl-2',6'-diethylacetanilide; BrCk=Bear Creek; CtGr=Cottage Grove; LnRk=Lone Rock; Hrt=Hartung Farm

Table 5.2

Bear Creek
concentrations in µg/l
13 wells

Parameter	# Detects	Range	Median	Mean	Std.Dev.
Atrazine	13	1.1-160	9.8	25.6	44.8
Deethylatrazine	13	0.63-9.5	2.8	3.7	3.0
Deisopropylatrazine	8	0.50-1.8	0.95	1.0	0.53
Alachlor	7	0.83-460	22	87.1	166.1
2,6–Diethylaniline	ND	-	-	-	-
2–Cl–2',6'–Diethyl–acetanilide	6	0.35-5.8	0.5	0.64	1.5

Table 5.3

Cottage Grove
concentrations in µg/l
6 wells

Parameter	# Detects	Range	Median	Mean	Std.Dev.
Atrazine	6	0.79–50	11.45	15.8	18.54
Deethylatrazine	6	0.84–14	4.85	5.4	4.6
Deisopropylatrazine	4	0.60–2.4	0.75	1.1	0.85
Alachlor	4	0.22–7.4	1.7	2.8	3.2
2,6–Diethylaniline	ND	–	–	–	–
2–Cl–2',6'–Diethyl–acetanilide	ND	–	–	–	–

Table 5.4

Lone Rock
concentrations in µg/l
7 wells

Parameter	# Detects	Range	Median	Mean	Std.Dev.
Atrazine	3	5.8–8.4	8.3	7.5	1.5
Deethylatrazine	6	0.47–41	2.3	11.0	16.4
Deisopropylatrazine	4	0.63–2.5	1.4	1.5	0.92
Alachlor	ND	–	–	–	–
2,6–Diethylaniline	ND	–	–	–	–
2–Cl–2',6'–Diethyl–acetanilide	ND	–	–	–	–

Table 5.5

Hartung Farm
concentrations in µg/l
10 wells

Parameter	# Detects	Range	Median	Mean	Std.Dev.
Atrazine	10	2.8-140	14	29.6	42.3
Deethylatrazine	10	0.31–13	6.1	6.4	5.3
Deisopropylatrazine	5	0.68–1.7	0.84	1.0	0.4
Alachlor	6	4.5–138	37	55.9	57.8
2,6–Diethylaniline	2	3.0–3.6	3.3	3.3	0.42
2–Cl–2',6'–Diethyl–acetanilide	3	0.45–3.8	1	1.8	1.8

Table 5.6

Total Results
concentrations in µg/l
38 wells

Parameter	# Detects	Range	Median	Mean	Std.Dev.
Atrazine	32	0.79–160	9.1	23.4	37.5
Deethylatrazine	35	0.31–41	2.8	6.0	7.8
Deisopropylatrazine	21	0.53–2.5	0.83	1.1	0.63
Alachlor	17	0.22–460	8.7	56.3	111
2,6–Diethylaniline	2	3.0–3.6	3.3	3.3	0.42
2–Cl–2',6'–Diethyl–acetanilide	9	0.35–5.8	0.6	1.6	1.9

Table 5.7

Detection Limits
concentrations in µg/l

	Atrazine	Alachlor	Deetat	Deisoat	DEA	2Cldietac
LOD	.30	.20	.30	.50	.41	.22
LOQ	.93	.58	.91	1.7	1.4	.73

Deetat=deethylatrazine, deisoat=deisopropylatrazine, DEA=diethylaniline, 2Cldietac=2-Cl-2',6'-diethylacetanilide
LOD=Limit of Detection, LOQ=Limit of Quantitation (see chapter 3)

Figure 5.1

Example Box Plot

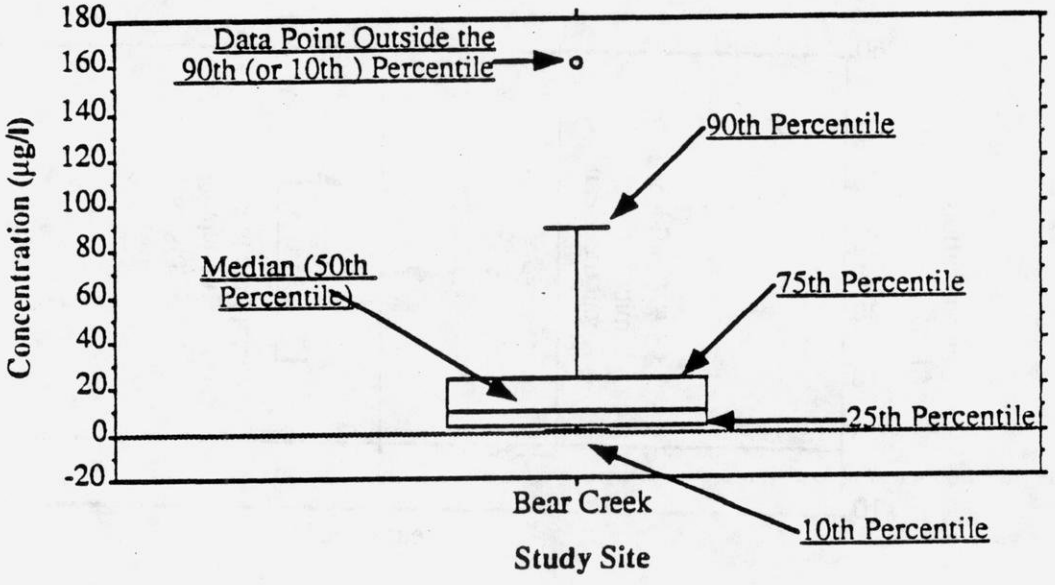
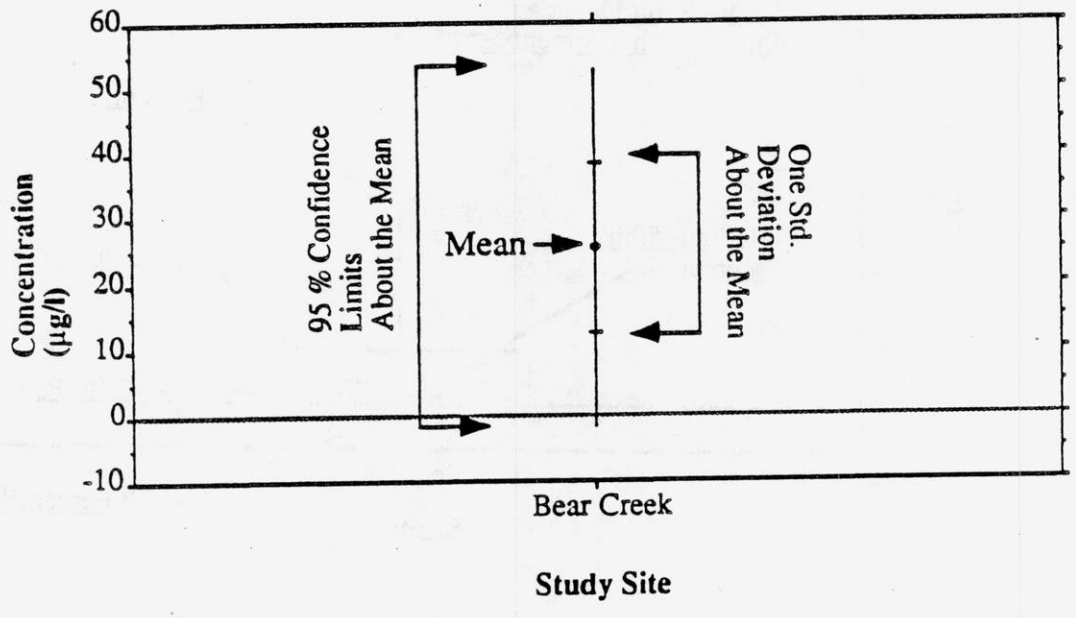


Figure 5.2

Example Mean, Std. Deviation, and 95% Confidence Limits for a Data Set



concentration data for the Bear Creek site. The values represented in the box plot are the 10th, 25th, 50th (median), 75th and 90th percentiles of the atrazine concentrations at Bear Creek. The interquartile range can be deciphered easily. Values lying outside of the 10th or the 90th percentile are represented by open circles. Graphs comparing the percentiles of two or more distributions can be more effective than those displaying mean values, because they do not omit high, low and middle values, which the means neglect (Cleveland, 1985).

The second graph used is a scatter plot representing the mean, one standard deviation above and below the mean, and the 95% confidence intervals about the mean. Figure 5.2 is a representative scatter plot displaying the atrazine concentration data for the Bear Creek site. Visual comparison of multiple batches is easily achieved. In Figure 5.4, for example, the 95% confidence levels about the mean overlap for all four sites, indicating that the means are roughly significantly similar at the 95% confidence level.

5.2.1 Atrazine

Atrazine was detected in all 4 of the study sites, and in all but 4 of the 36 total wells. The four wells where atrazine was not detected were located in the Lone Rock study site. Atrazine concentrations ranged from 0.80 µg/l to 160 µg/l for the entire study.

Figures 5.3 and 5.4 graphically compare atrazine contamination between study sites. Although the average concentration of atrazine is greatest at the Bear Creek and Hartung sites, the median concentration of atrazine is highest at the Hartung site, followed by the Cottage Grove site. The median atrazine values are very similar between the sites, all falling between 5 and 15 µg/l. The 95% confidence limits about the mean atrazine value overlap for all four sites, indicating that the general degree of contamination was similar at the four sites.

Figure 5.3

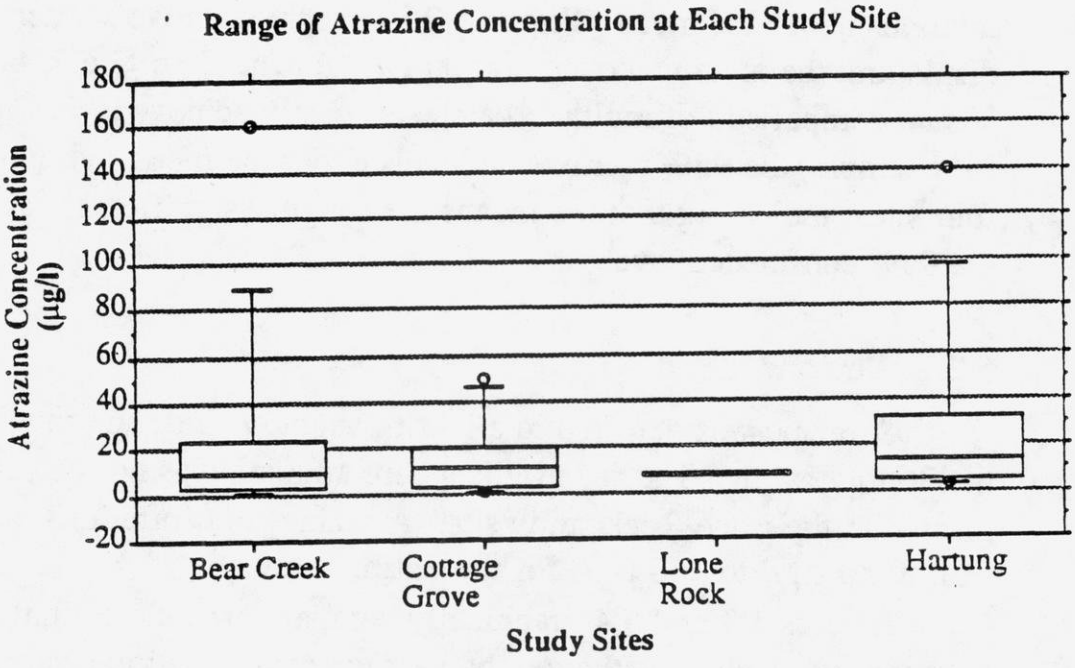
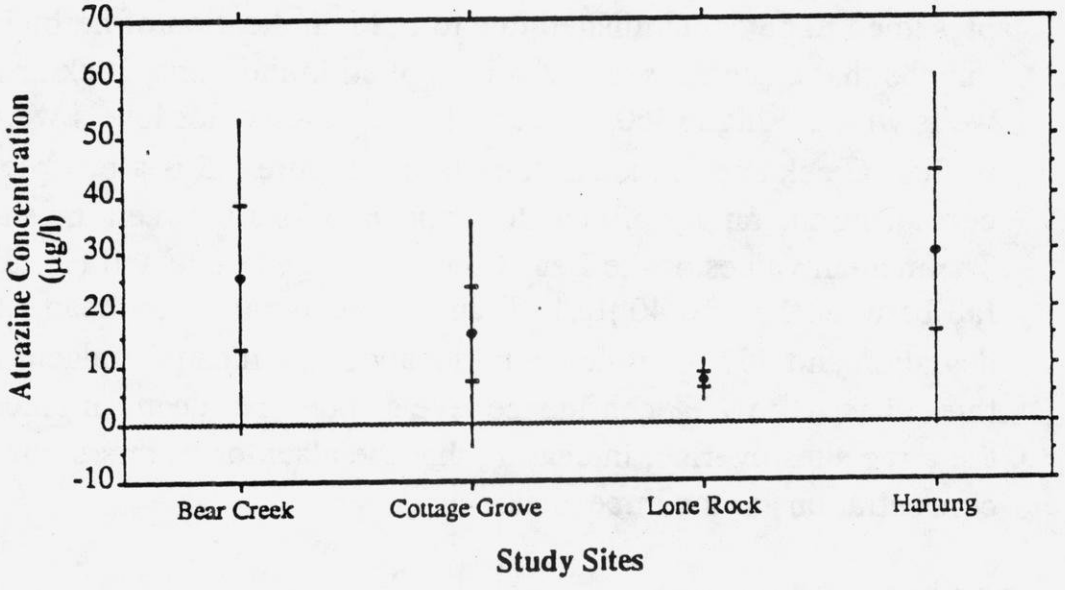

Range of Atrazine Concentration at Each Study Site
Atrazine Concentration (µg/l)
180
160
140
120
100
80
60
40
20
0
-20
Bear Creek
Cottage Grove
Lone Rock
Hartung
Study Sites

Figure 5.4

Mean, Standard Deviation, and 95% Confidence Limits for Atrazine Data



5.2.2 Alachlor

Alachor was detected in three of the four study sites and was less ubiquitous than atrazine at those sites where it was detected. Of the 36 wells sampled, 17 contained alachlor above the detection limit. However, the range of alachlor levels was broader than the atrazine range; alachlor concentrations ranged from 0.22 - 460 µg/l, where detected. The Lone Rock site, where alachlor was not detected, is presumed to be contaminated due to field application of herbicides. It may be that alachlor is not widely applied in the Lone Rock area. The wells with the high (460, 140 and 110 µg/l) alachlor levels were found in Bear Creek and at the Hartung farm. Figure 5.5 is a box plot comparing the ranges of alachlor concentrations between the study sites. The median values of the Bear Creek, Cottage Grove and Hartung sites fall between 1.5 and 40 µg/l. Figure 5.6 compares the mean, standard deviation and 95% confidence limits about the mean for alachlor at the three sites. The 95% confidence levels about the mean for alachlor at the three sites overlap, indicating that the alachlor occurs in similar concentrations at the three sites.

5.2.3 Deethylatrazine

Deethylatrazine was detected at all four of the study sites and in 35 of the 36 wells studied. The one well where deethylatrazine was not detected was located at the Lone Rock site. Three of the four wells at the Lone Rock site wherein atrazine was not detected contained deethylatrazine at levels above the detection limit. In these three wells, the deethylatrazine levels were at or near the limit of quantitation. The range of deethylatrazine concentrations for the entire study was 0.31 - 41 µg/l.

Figure 5.7 is a box plot comparing the ranges of deethylatrazine concentrations between the study sites. The ranges for the four sites

Figure 5.5

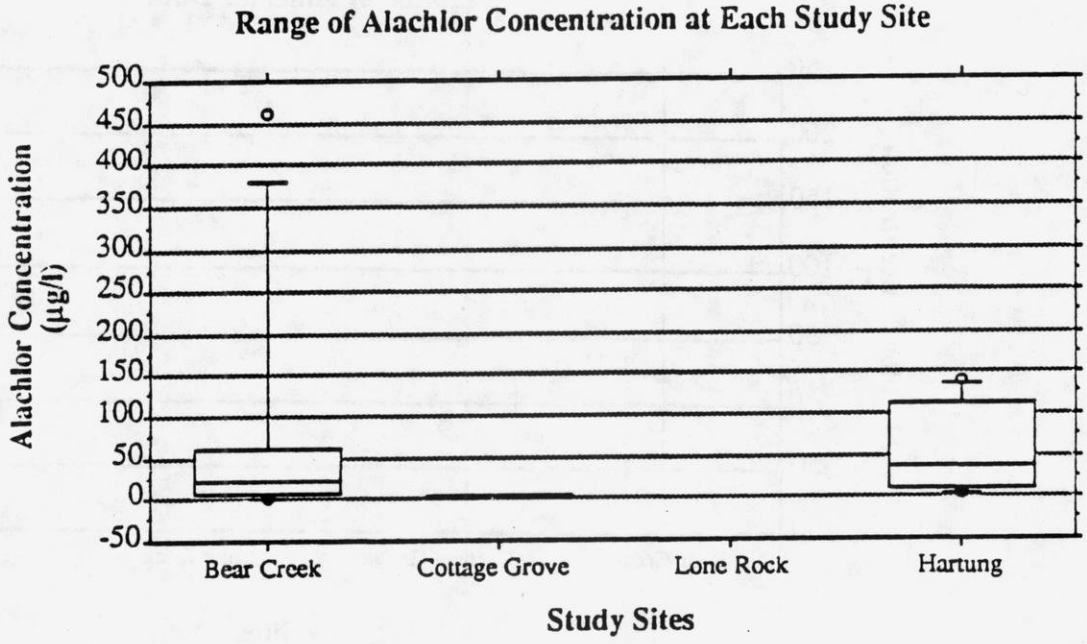

Range of Alachlor Concentration at Each Study Site
Alachlor Concentration (µg/l)
500
450
400
350
300
250
200
150
100
50
0
-50
Bear Creek
Cottage Grove
Lone Rock
Hartung
Study Sites

Figure 5.6

Mean, Standard Deviation and 95% Confidence Limits for Alachlor Data

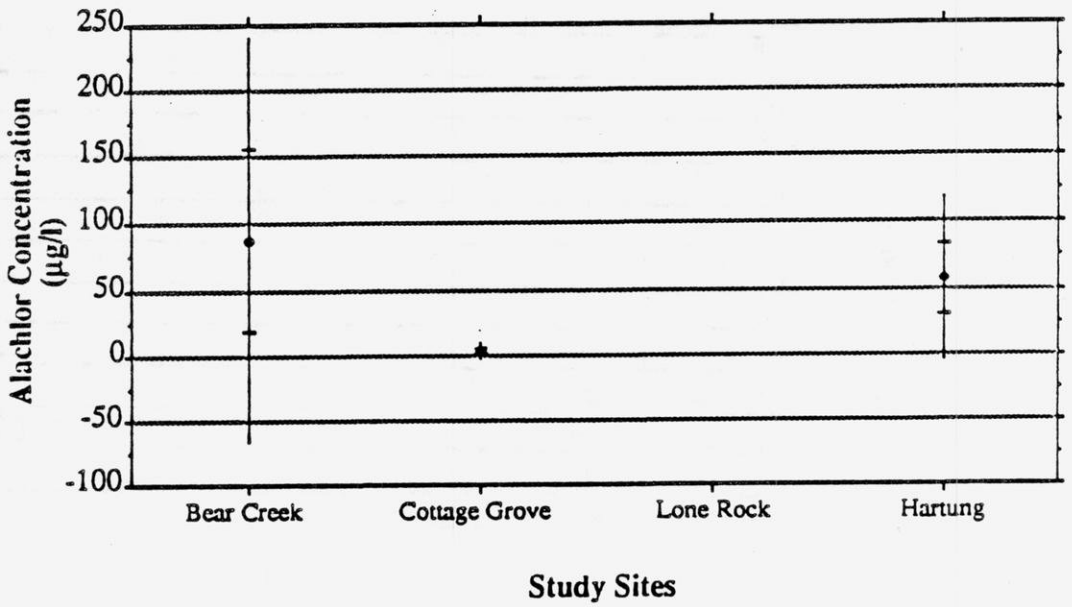


Figure 5.7

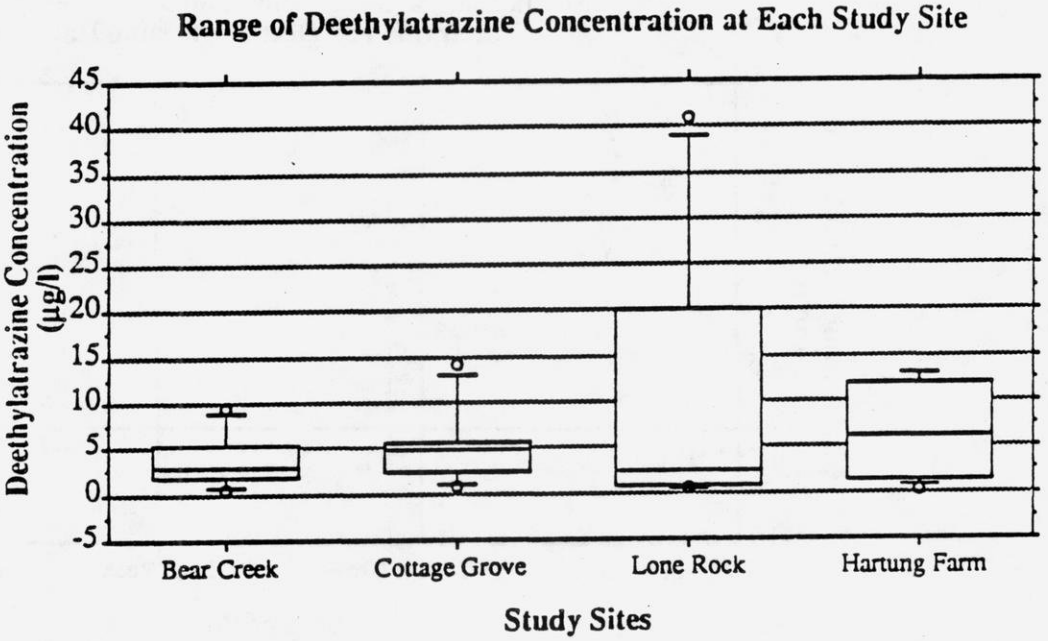
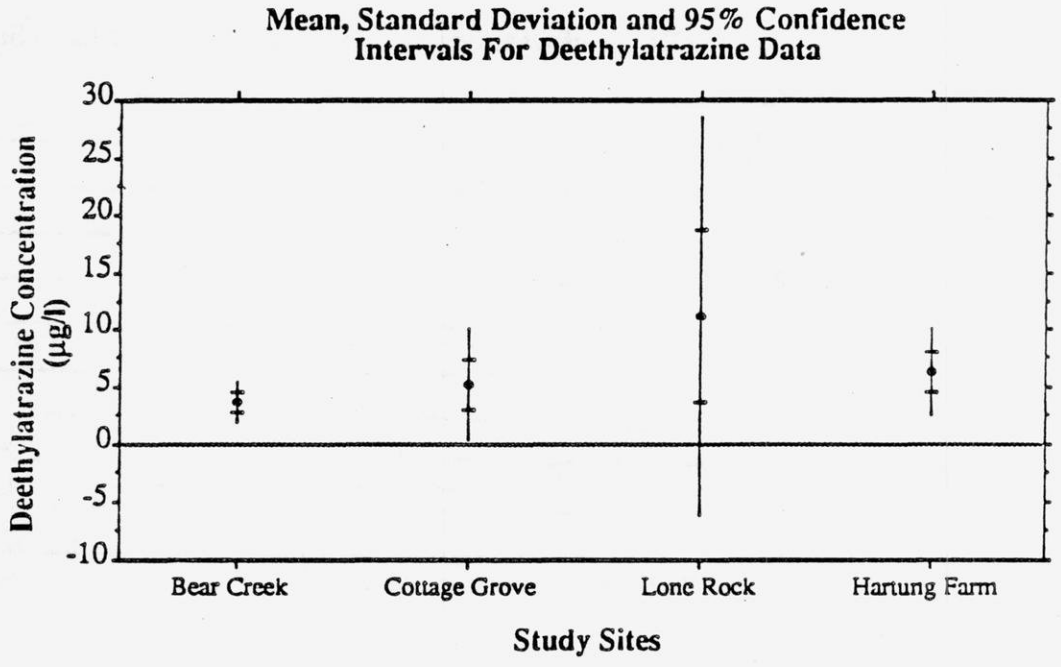

Range of Deethylatrazine Concentration at Each Study Site
Deethylatrazine Concentration (µg/l)
45
40
35
30
25
20
15
10
5
0
-5
Bear Creek
Cottage Grove
Lone Rock
Hartung Farm
Study Sites

Figure 5.8


Mean, Standard Deviation and 95% Confidence Intervals For Deethylatrazine Data
Deethylatrazine Concentration (µg/l)
30
25
20
15
10
5
0
-5
-10
Bear Creek
Cottage Grove
Lone Rock
Hartung Farm
Study Sites

compare favorably, although the range for Lone Rock is much broader than the remaining three sites. The medians range from 2.3 - 6.1 µg/l.

Figure 5.8 compares the mean, and the standard deviation and 95% confidence limits about the mean for deethylatrazine at the four sites. Although Lone Rock displays the highest mean concentration, it has the lowest median concentration; thus its mean is influenced by the one high value (42 µg/l) which lies outside of the 90th percentile. The 95% confidence levels for the mean deethylatrazine concentrations overlap for the four sites. These two figures, 5.7 and 5.8, indicate that the magnitude of the deethylatrazine contamination is similar at the four sites.

5.2.4 Deisopropylatrazine

Deisopropylatrazine was detected in 21 of the 36 wells tested in the entire study. Deisopropylatrazine was detected at all of the sites, although with less frequency and generally in lower concentrations than deethylatrazine. Deisopropylatrazine ranged from 0.5 - 2.5 µg/l for the entire study. The mean and median concentrations of deisopropylatrazine for the four sites all fell under 1.7 µg/l, which was the limit of quantitation for the compound. Fig 5.9 compares the ranges of deisopropylatrazine for the four study sites. Figure 5.10 compares the mean, standard deviation, and 95% confidence levels about the mean for the sites. These figures show that, for deisopropylatrazine, the levels of contamination at the four sites are of comparable magnitude. The range of deisopropylatrazine values at the four sites are very similar. The 95% confidence limits about the means of the four deisopropylatrazine distributions overlap.

5.2.5 2,6-Diethylaniline

2,6-Diethylaniline (DEA) was detected only at the Hartung site. The two wells where DEA was found were located in the same well nest (wells screened at different depths but located right next to each other),

Figure 5.9

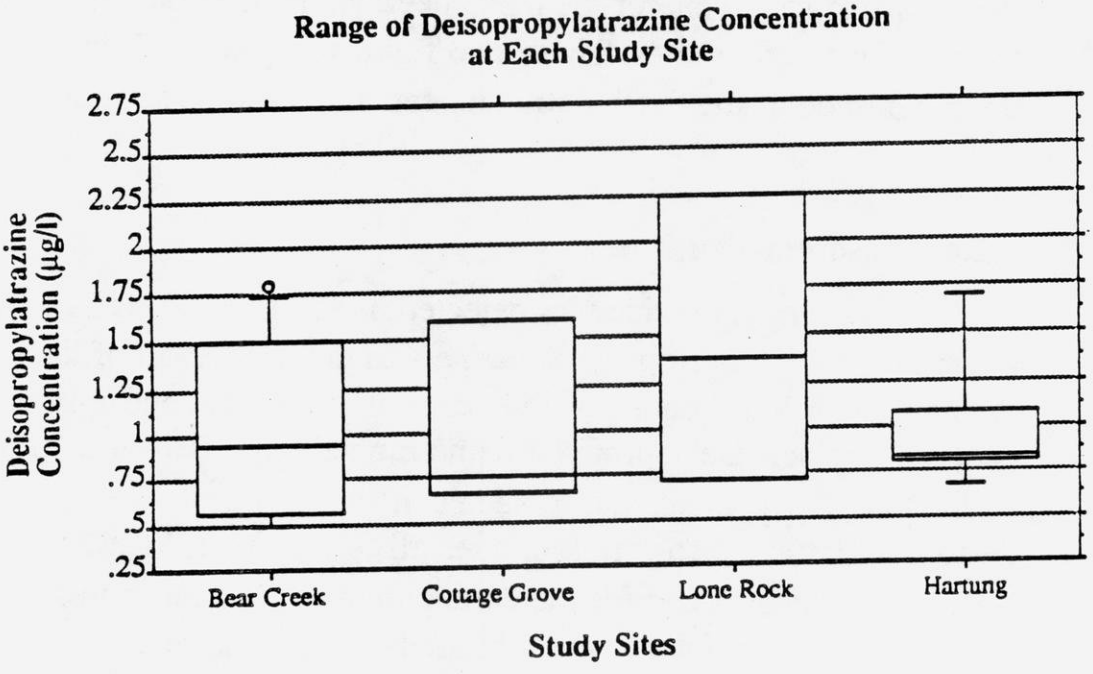
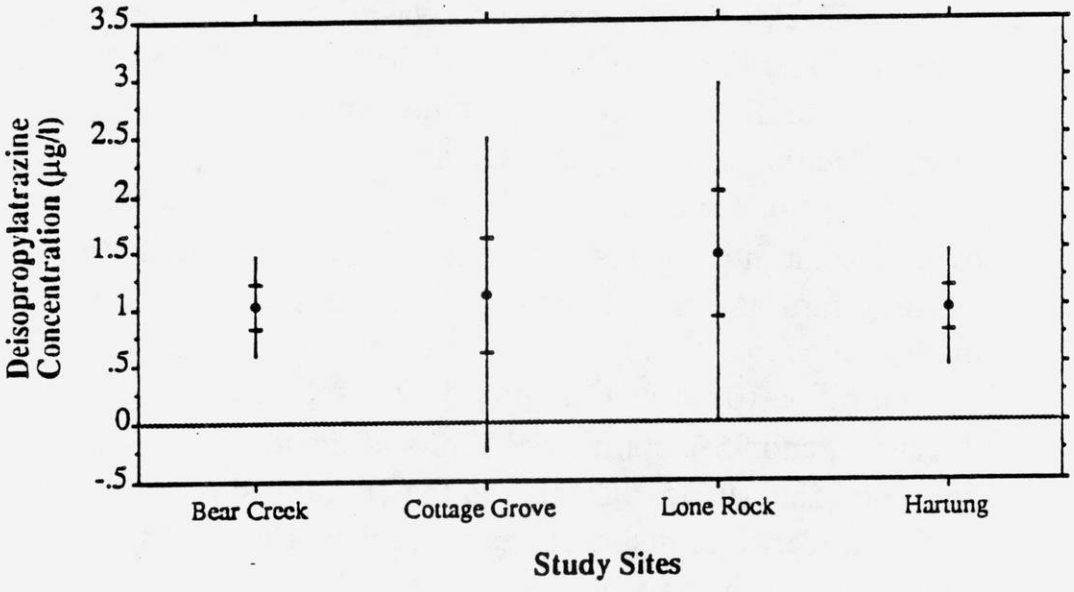

Range of Deisopropylatrazine Concentration at Each Study Site
Deisopropylatrazine Concentration (µg/l)
2.75
2.5
2.25
2
1.75
1.5
1.25
1
.75
.5
.25
Bear Creek
Cottage Grove
Lone Rock
Hartung
Study Sites

Figure 5.10

Mean, Standard Deviation, and 95% Confidence Intervals for Deisopropylatrazine Data



next to a chemical storage facility on the Hartung farm. At both of these wells, alachlor was detected at a high level (140 and 62 µg/l). A second well at the Hartung site contained high levels of alachlor (110 µg/l) but did not contain DEA above the detection limit. No DEA was detected at Bear Creek, where one well contained alachlor at 460 µg/l. DEA is a common chemical intermediate (Short et al., 1983), and could have potentially resulted from the degradation of various other chemicals.

5.2.6 2-Cl-2',6'-Diethylacetanilide

2-Cl-2',6'-diethylacetanilide was detected in nine wells at two sites, the Bear Creek study site and the Hartung farm. No diethylacetanilide was detected at the remaining sites, even in wells where alachlor was detected. Diethylacetanilide concentration ranged from 0.3 µg/l to 5.8 µg/l for the two sites. Figure 5.11 compares the diethylacetanilide ranges for the two sites. The distribution at the Hartung farm is drawn from only three detections. The Hartung median concentration (1.0 µg/l) is comparable to the Bear Creek median concentration (0.5 µg/l). Figure 5.12 displays the mean, standard deviation, and 95% confidence limits of the diethylacetanilide concentrations at Bear Creek and the Hartung site. The overlap of the 95% confidence limits indicates similarity of the diethylacetanilide distribution at the two sites.

5.3 Data Quality

5.3.1 Detection Limits

Table 5.8 lists the standard deviation, S, of the results of seven replicate spikes and the method detection limit (LOD) established for each of the chemical parameters using both extraction method A (50 g of NaCl) and extraction method B (200 g of NaCl). The statistical method used to derive these values is discussed in Chapter 3. Method B was used only for the Bear Creek samples and the Osseo interlaboratory control samples. For the remaining samples, method B was abandoned in favor

Figure 5.11

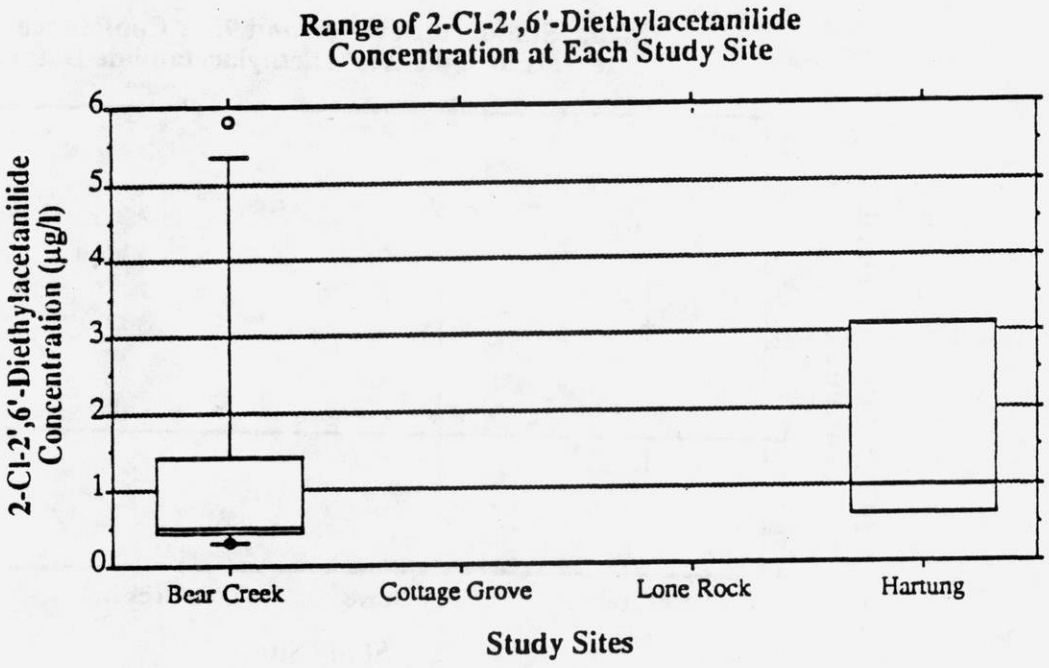

Range of 2-Cl-2',6'-Diethylacetanilide Concentration at Each Study Site
2-Cl-2',6'-Diethylacetanilide Concentration (µg/l)
6
5
4
3
2
1
0
Bear Creek
Cottage Grove
Lone Rock
Hartung
Study Sites

Figure 5.12

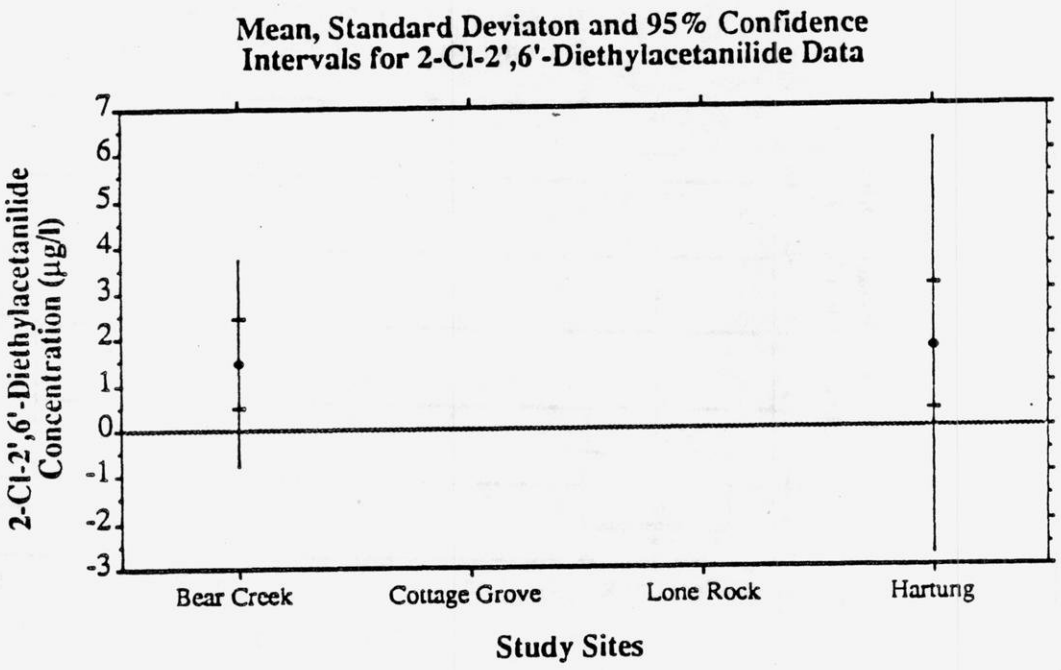

Mean, Standard Deviaton and 95% Confidence Intervals for 2-Cl-2',6'-Diethylacetanilide Data
2-Cl-2',6'-Diethylacetanilide Concentration (µg/l)
7
6
5
4
3
2
1
0
-1
-2
-3
Bear Creek
Cottage Grove
Lone Rock
Hartung
Study Sites

Table 5.8

Determination of LOD and LOQ
For 2 Variations of Extraction Method
A: 50 g NaCl
B: 200 g NaCl
--units: µg/l for S, LOD, LOD* and LOQ--

Compound	Method A		Method B		LOD*	LOQ
	S	LOD	S	LOD		
Atrazine	.0899	.283	.0339	.1067	.30	.93
Alachlor	.0560	.176	.0129	.041	.20	.58
Deethylatrazine	.0878	.276	.043	.136	.30	.91
DeisopropylAt.	.160	.502	.0453	.142	.50	1.7
2-Cl-2',6'-Dietal.	.0340	.107	.0705	.222	.22	.73
DEA	.130	.409	.081	.253	.41	1.4

LOD*=LOD used for study purposes. The LOD* was rounded up in selected cases (those where the calculated LOD was below 0.3 and 0.2 µg/l) in order to compensate for practical background complications at these low levels that are not accounted for in the statistical analysis.

of method A. This decision was made based on the difficulties raised by the large amount of salt used in method B; both because it came out of solution and because it resulted in eratic chromatogram baselines, especially in the case of the baseline produced with the electron capture detector.

In establishing the detection limits for method A, each one liter replicate was spiked with a mixed standard so that the final composition of each replicate was as follows:

Alachlor	1.92 µg/l
Atrazine	1.92 µg/l
Deethylatrazine	2.00 µg/l
Deisopropylatrazine	1.92 µg/l
2-Cl-2',6'-Diethylacetanilide	2.06 µg/l
DEA	2.00 µg/l.

The detection limits for method B were performed in four batches. The replicates were each spiked with individual standards to arrive at the following concentrations:

Batch 1:	Alachlor	0.80 µg/l
Batch 2:	Atrazine	0.80 µg/l
Batch 3:	Deethylatrazine	2.00 µg/l
	Deisopropylatrazine	2.00 µg/l
Batch 4:	2-Cl-2',6'-Diethylacetanilide	2.00 µg/l
	DEA	2.00 µg/l.

The statistical LOD for each compound for a given method was calculated from the standard deviation of the concentration of that compound recovered in each replicate, as described in Chapter 3. Because the LOD was determined statistically, the resulting limit was sometimes unrealistically low compared to chromatogram baseline noise and considering practical laboratory experience with the compounds' behavior on the requisite gas chromatographic systems. This was true of most of the LODs calculated for method A. Partly, this was due the use of four separate batches of seven replicates, resulting in less interference

between compounds. In the case of atrazine and alachlor, the replicate spiking level was too low, contributing to the low LOD values.

In order to correct for the low apparent LOD values, the greater of the two LODs calculated for each compound was used as the working LOD for the entire study. The corresponding limit of quanititation (LOQ) was then calculated by multiplying the LOD by 3.3. By choosing the largest LOD for each compound, the claims of actual detection of any compound were rendered more conservative.

5.3.2 Precision and Accuracy: Duplicates and Spikes

Tap water spikes were used to control the accuracy of sample analyses. Accuracy was measured by percent recovery of the spikes. The upper and lower control limits of percent recovery for each chemical parameter are listed in Table 5.9. The derivation of these values is discussed in Chapter 3. Table 5.10 lists the spike recoveries accompanying each sample batch. All sample batches were within accuracy control limits.

Duplicate analyses were used to control for data precision. The average difference, R, between the analytical results of two duplicates was required to be less than, or equal to, 20% for each analyte (see Chapter 3). A minimum of ten percent of all samples was to be analyzed in duplicate. During the study, seventeen percent of all samples were analyzed in duplicate. Table 5.11 lists the results of the duplicate analyses and the sample batch that they were associated with. The Bear Creek batch was not accompanied by a duplicate but was preceded by replicate spikes. The R values for these spikes are included in the Table, but are starred.

The only duplicate which was out of precision control was the Lone Rock duplicate, sample 7, and that was out of control only for deisopropylatrazine. However, on perusal of the data, there are three arguments for not discarding the deisopropylatrazine data for Lone Rock. The measured concentrations of deisopropylatrazine were 0.87

Table 5.9

Upper and Lower Control Limits For Spike Recovery
(percent recovery)

	Atrazine	Alachlor	Deetat	Deisoat	DEA	2Cldietac
UCL	120	120	120	100	120	120
LCL	80	80	80	60	80	80

UCL=upper control limit; LCL=lower control limit
Deetat=deethylatrazine, deisoat=deisopropylatrazine, DEA=diethylaniline,
2Cldietac=2-Cl-2',6'-diethylacetanilide

Table 5.10

Spike Recovery

	Chemical Parameter (% recovery)					
Study Site	Atrazine	Alachlor	Deetat	Deisoat	DEA	2Cldietac
Bear Creek*	96	104	99	98	77	98
Cottage Grove	103	95	91	78	80	98
Lone Rock	95	105	94	64	88	101
Hartung Farm	93	104	99	65	90	108

Deetat=deethylatrazine, deisoat=deisopropylatrazine, DEA=diethylaniline,
2Cldietac=2-Cl-2',6'-diethylacetanilide

* uses method A

Table 5.11

Duplicate Results

R Value (Average Difference) (µg/l)

Sample		Atrazine	Alachlor	Deetat	Deisoat	DEA	2Cldietac
CtGr	2616	10	9	16	0	0*	0*
	2617	4	2	1	0	0*	0*
	2618	3	0	1	0	0*	0*
LnRk	2	4	0*	8	0*	0*	0*
	7	2	0*	4	32**	0*	0*
Hrt	054	2	5	8	0*	0	16

Deetat=deethylatrazine, deisoat=deisopropylatrazine, DEA=diethylaniline, 2Cldietac=2-Cl-2',6'-diethylacetanilide

* Compound was below the deteciton limit in both duplicates.

** Out of control: see text.

and 0.63 µg/l for the duplicates. These values were near the LOD. Concentrations near the LOD are susceptible to greater error; this is the reason that the Wisconsin State Lab of Hygiene (WSLH) reports values falling between the LOD and the LOQ as being suspect (Wisconsin Laboratory of Hygiene, 1988). Secondly, the R values for the related compounds, atrazine and deethylatrazine, were in control. Thirdly, in a second duplicate accompanying the sample set, sample 2, deisopropylatrazine was below the detection limit for both duplicates, and the resulting R value was within precision control limits. These factors warranted considering the Lone Rock deisopropylatrazine data in the results.

5.3.3 Blanks

Method blanks accompanied each sample batch in order to control for any contaminants which would coelute with the component peaks, thus causing false positive results or over- estimation of the concentration of the monitored chemicals. In general, there was little contamination interfering with the gas chromatographic data peaks. The exceptions to this generalization were as follows:

1. Bear Creek samples, Osseo interlaboratory control samples, Cottage Grove samples: a contaminant peak interfered with deisopropylatrazine on the nitrogen phosphorus detector. This was remedied by using both a higher column temperature and a higher carrier gas flow rate in order to affect greater separation of the two peaks.

2. Hartung samples: A contaminant peak interfered with atrazine on the electron capture detector using the SE30/OV210 column. This was the confirmatory column for atrazine. Since the analytical results from the primary column were the ones which were reported and because the contamination was not large, it was ignored.

3. Hartung samples: A contaminant peak occurred at the retention time of 2-Cl-2',6'-diethylacetanilide on the capillary column (EC detector), which was the primary system. The peak height of this contaminant resulted in a concentration which was considerable lower than the detection limit. Furthermore, the confirmation results agreed with the primary results, thus, this contamination was ignored.

5.3.4 Confirmation

Confirmation of all concentration measurements which were above the detection limit on the primary chromatographic system was performed on a secondary chromatographic system, as described in Chapter 3. The confirmation data is listed in appendix A. When both the initial measurement and the confirmatory measurement were performed on packed columns, the two measurements were generally close. In the case of 2-Cl-2',6'-diethylacetanilide, the primary measurements were done on the DB-1 capillary column. These measurements were compatible with the confirmatory results from packed column (1% SP-1000) analysis.

The primary and confirmatory results for deisopropylatrazine and deethylatrazine did not demonstrate consistent agreement. The primary system for deethylatrazine and deisopropylatrazine was the Nitrogen-Phosphorus detector using the packed column, 1% SP-1000. The confirmatory system was the electron capture detector using the DB-1 capillary column. The two systems nearly always agreed on whether or not the compounds were detected in a given sample. The exceptions to this were:

1. Sample 2616, deisopropylatrazine: packed column result: 1.0 µg/l; capillary column result: not detected.
2. Sample Hrt O54, deisopropylatrazine, duplicates A and B: packed column: not detected (A and B); capillary column: 1.0, 0.92 µg/l (A and B, respectively).

3. Sample LnRk 2, duplicates A and B: packed column: not detected (A and B); capillary column 1.6 and 1.7 µg/l (A and B, respectively).

These differences may have been due to the presence of a compound which coeluted with the deisopropylatrazine on the column where there was an apparent detection, resulting in a false positive. In any event, whenever one system showed no detection, the result was reported as "no detect."

Capillary column measurements were nearly always greater than packed column measurements for deethylatrazine and deisopropylatrazine. The capillary column result was often greater than the packed column results by a factor of 1.5 - 3, and occasionally was greater by a factor of as much as 6. In the occasional instance where the packed column measurement was greater than the capillary column measurement, the difference between the two results was small.

The packed column measurements were the ones which were reported in the results for deethylatrazine and deisopropylatrazine; this was warranted by several factors. First, the same packed column (1% SP 1000) was used for the primary system for atrazine, the parent compound of these two parameters. The use of the same primary system for the three chemicals lent consistency to the results and was thus preferable for comparing the amounts of the three chemicals in any one sample. Secondly, the results from the packed column for deethylatrazine agreed more closely with interlaboratory sample comparisons (to be discussed subsequently) than did the capillary column results. Thirdly, if this work is continued by the WSLH, where most pesticide work is performed on packed columns, the search would continue for a second packed column which would adequately separate deisopropylatrazine and deethylatrazine.

5.3.5 Confirmation by Mass Spectroscopy

In addition to the gas chromatographic confirmation of sample peaks, mass spectroscopy (MS) was used to analyze roughly ten percent of the samples. GC-MS was used only to validate the presence or absence of a compound, but was not used to quantitate those compounds. The results of the GC-MS analysis are compared to the study results in Table 5.12. The MS detector had low sensitivity to deethylatrazine and deisopropylatrazine; deisopropylatrazine was not detected at concentrations of less than 2 ppb when tested with standards; deethylatrazine was detectable above 1 ppb when tested with standards. It is thus understandable that deisopropylatrazine was detected only in sample LnRk-5, where deisopropylatrazine was present at 2.5 ppb. Neither deethylatrazine nor deisopropylatrazine was detected in either Bear Creek sample, even though they were detected in both samples on the two GC systems. The Bear Creek samples, 43 and 42, contained high levels of many contaminants besides atrazine and alachlor. It could be that the baseline noise effectively "swamped" the deethylatrazine peak. Hydroxyalachlor, which was not monitored in this study, was identified by MS in all samples where alachlor was present.

5.3.6 Interlaboratory Checks

Interlaboratory checks were performed by splitting samples from various sites with two labs. This allowed for a validation of method results and for a check on laboratory practices. The two labs, the samples split with each of them, and the compounds compared in those splits are listed in Table 5.13. In general, the interlaboratory split samples indicate that the anaytical methods and lab practices used in this study gave results consistent with other analytical laboratories.

Dr. Martin Ondrus of the Department of Chemistry, University of Wisconsin, Stout, has developed a cartridge method for isolating and analyzing atrazine and its degradation products, deethylatrazine, deisopropylatrazine, and hydroxyatrazine, from water samples. The

Table 5.12

Comparison of MS Confirmation to GC/EC and GC/NPD Results

Sample	#	Atrazine	Deetat	Deisoat	Alachlor	DEA	2Cldietac
BrCk	42	15 √	2.4 •	0.53 •	22 √	ND √	0.44 √
	43	160 √	8.7 •	1.8 •	460 √	ND √	5.8 √
LnRk	5	ND *	0.47 √	2.5 √	ND √	ND √	ND √
Hrt	53	140 √	12 √	0.83 •	140 √	3.6 √	3.8 √
Hrt	54A	56 √	8.7 √	ND √	60 √	2.8 √	1.0 √

√=MS Confirmation agrees with GC results.
•=MS Detector does not detect compound; compound was detected and confirmed by GC/NPD
* =Detected by MS Detector, but not by GC/NPD.

quantitative analysis of the compounds is done with HPLC. The detection limits have not been calculated for this method, but are roughly 1.0 µg/l for the metabolites and 0.8 µg/l for atrazine (Ondrus, Dr. Martin, University of Wisconsin, Stout, personal communication).

Two sets of samples were split with Ondrus on two occasions. Three samples from the town of Osseo were provided by Ondrus, while six samples from the Lone Rock study site were sent to Ondrus. The results of the analyses by the two labs for these samples are compared in Table 5.14 Ondrus was monitoring solely for atrazine and atrazine degradation products, and the table reflects this.

Dr. Ondrus adjusts the results of the analyses with the percent recovery measured in an accompanying spike. Thus, if the percent recovery is 32%, the analytical result is divided by 0.32. The Ondrus method has low sensitivity to deisopropylatrazine; consequently results were not provided for deisopropylatrazine in the Osseo samples. Hydroxyatrazine was not detected in samples from either site.

The two methods show excellent agreement for atrazine and deethylatrazine in the Osseo samples, and to a lesser degree, in the Lone Rock samples. Considering that the methods use two completely different chromatographic systems (HPLC and GC), the agreement is especially good. There is a large discrepancy between the results for deisopropylatrazine in the Lone Rock samples. It is impossible to know which results are more accurate since control samples are not available for deisopropylatrazine. Considering the low recovery of deisopropylatrazine (32%) for the Lone Rock samples by Ondrus' method, the adjustment of the total using the recovery may introduce some error to the results.

Samples from the Hartung farm were split with the analytical laboratory of the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP). The DATCP laboratory monitored for a broad range of herbicides in these samples, but did not measure degradation products. Consequently, Table 5.15, which compares

Table 5.13

Interlaboratory Split Samples
(Participants and Samples)

Laboratories	Sample Source	Samples Split	Compounds Compared
1. Ondrus/ DeLuca	Osseo	MW-4 MW-6 MW-7	Atrazine Deethylatrazine
2. Ondrus/ DeLuca	Lone Rock	LR-1 through LR-6	Atrazine Deethylatrazine Deisopropylatrazine
3. WI DATCP/ DeLuca	Hartung	044, 045, 053 054, 055, 056 059, 060, 075	Atrazine Alachlor

Table 5.14

Comparison of Split Sample Results;
Ondrus* (Ond)/DeLuca (DeL)

Sample	Atrazine		Deethylatrazine		Deisopropylatrazine	
	DeL.	Ond.	DeL.	Ond.	DeL.	Ond.
OSSEO						
MW-4	4.0	3.8	1.6	1.2	0.4	NA
MW-6	1.6	2.1	1.0	1.0	0.3	NA
MW-7	4.6	5.4	5.6	3.3	0.8	NA
LONE ROCK						
1	8.3	6.7	41	24	2.0	7.3
2	8.4	8.0	20	13.6	ND	4.1
3	ND	0.6	0.58	0.7	ND	0.9
4	ND	0.3/ND	ND	ND	ND	ND
5	ND	0.3/ND	0.47	0.4/ND	2.5	11.9
6	ND	0.3**	2.8	1.6	0.63	ND

NA = Compound was not measured by Ondrus. ND = Not detected.
*Ondrus' results are the averages of two duplicates, in cases where one duplicate was a non-detect and the other was measureable, the two results are reported.
**One of the duplicates displayed interference and was not analyzed.

Table 5.15

Comparison of Split Sample Results;
DeLuca (DeL)/WI Department of Trade, Agriculture and Consumer Protection (DATCP)

Sample	Atrazine		Alachlor	
	DeL	DATCP	DeL	DATCP
044	14	38.8	4.5	11.4
045	32	51.7	110	131
053	140	156	140	139
054	56	72.9	62	60.7
055	26	23.8	7.9	8.6
056	14	14.7	12	11.8
059	2.8	2.3	ND	ND
060	4.5	3.1	ND	ND
075	3.5	2.64	ND	ND

ND = Not Detected

analytical results for the two labs, lists only the results for atrazine and alachlor.

The agreement between results for the two labs was generally good. There was a wide discrepancy between the two labs for samples 044 and 045 for both atrazine and alachlor. The two wells from which these samples were drawn exhibited very low water levels. The bottles for all split samples were filled sequentially; when one bottle was filled, it was capped and the next was filled, rather than filling all bottles from one pooled batch of water. Six one liter bottles were drawn from each well. The final liters drawn from both well 045 and well 044 contained more colloidal matter and sediment than the first liters drawn from the same wells due to the low water levels in both wells. In both cases, DATCP received the last two bottles to be drawn. This may have been responsible for the differences in measured concentrations, since colloidal matter may sorb organic molecules (McCarthy and Zachara, 1989), thus increasing the effective concentration of any measured substituent.

Chapter 6
Discussion

6.1 Introduction

This chapter describes the public health and groundwater policy implications of the data presented in Chapter 5. In order to assess the policy implications, the concentration of the degradation products of atrazine and alachlor must be compared to the concentration of the parent compounds in contaminated groundwater. Thus, the data are first analyzed for relationships between the occurrence of atrazine and alachlor and their respective breakdown products. For atrazine, such patterns are evident, while in the case of alachlor, the data are inconclusive.

In this chapter, the term "contribution," or "relative contribution," is used to describe the amount of breakdown product present relative to the corresponding parent compound. If deethylatrazine is detected at 5 µg/l, its "relative contribution" to the total atrazine contamination is more significant when atrazine is present at 5 µg/l than when atrazine is present at 75 µg/l. The ratio of:

[degradation product]/[degradation product + parent compound] x 100

is used as a comparative measure of the contribution of the breakdown product to the total contamination due to the parent compound. When the breakdown product concentration is equal to the parent compound concentration, the contribution is 50; a contribution greater than 50 indicates that the breakdown product is present at concentrations larger than the parent.

6.2 Occurrence of Alachlor Breakdown products Relative To Alachlor

There were seventeen wells where alachlor was present above the detection limit of 0.20 µg/l. Seven of these were at the Bear Creek site, four were at Cottage Grove, and six were at the Hartung facility. Of these, only two wells, both at the Hartung facility, contained detectable

diethylaniline (DEA), while six of the Bear Creek wells and three Hartung wells contained 2-Cl-2',6'-diethylacetanilide. Hydroxyalachlor was identified by mass spectroscopy in four out of four samples which contained alachlor and which were analyzed by mass spectroscopy.

6.2.1 2,6-Diethylaniline

The data indicate that DEA is not an important alachlor degradation product in groundwater at these sites. The two wells where DEA was detected, wells 53 and 54, were in a single nest at the Hartung facility. Wells 53 and 54 were the deep- and moderate-depth wells in the well nest immediately downgradient from the facility. DEA was not detected in the shallow well in the same nest (Hrt 55). The concentrations of DEA in the two wells were similar (3.6 and 3.0 µg/l, respectively), while the alachlor concentrations were quite disparate (140 and 62 µg/l, respectively). DEA was not detected in any other well, even those wells where alachlor was present in high concentrations (BrCk 43, 44 and 47, and Hrt 45; with alachlor at 460, 53, 62, and 110 µg/l). It is likely, based on this evidence, that the DEA in wells Hrt 53 and 54 was not the result of alachlor degradation. It may have been a breakdown product or process impurity of another agricultural chemical.

2.6.2 2-Cl-2',6'-diethylacetanilide

Although 2-Cl-2',6'-diethylacetanilide was detected with greater frequency than DEA, it did not, in general, contribute significantly to the total alachlor contamination when it did occur (table 6.1). At Bear Creek, the seven wells with alachlor detects all lay due east of the coop. The study wells north, southeast, and southwest of the coop did not contain alachlor. In six of the seven Bear Creek wells where alachlor was detected, 2-Cl-2',6'-diethylacetanilide was also detected. The alachlor concentrations range from 0.83 to 460 µg/l in the Bear Creek wells. The groundwater enforcement standard for alachlor is 0.5 µg/l,

Table 6.1 Contribution of 2,6-Diethylaniline and 2-Cl-2',6'-Diethylacetanilide to Total Alachlor Contamination

Well #		DEA Contribution	2-Cl-2',6'-Diethylacetanilide Contribution
BrCk	40	-	30
	42	-	2.0
	43	-	1.2
	44	-	2.6
Hrt	45	-	0.4
	53	2.5	2.6
	54	4.6	1.6

DEA = 2,6-diethylaniline
DEA Contribution = {[DEA]/([DEA]+[Alachlor])} x 100;
similar for 2-Cl-2',6'-diethylacetanilide

so all of these wells already exceed the state alachlor standard. In all but one of these wells, the 2-Cl-2',6'-diethylacetanilide contribution ranged from 1.2% to 2.6%. In well BrCk 40, where alachlor was detected at only 0.83 µg/l, the 2-Cl-2',6'-diethylacetanilide contribution was more significant (30%). Of all the wells containing alachlor, well BrCk 40 was the furthest from the coop. The alachlor in this well either represents an older spill incident than alachlor in wells nearer the source, or it is at the front of the contaminant plume resulting from a single incident. In the first case, the longer elapsed time means that there has been more time for alachlor to degrade, thus there is relatively more 2-Cl-2',6'-diethylacetanilide. Alternatively, 2-Cl-2',6'-diethylacetanilide may be more mobile than alachlor, so that the center of the 2-Cl-2',6'-diethylacetanilide plume resulting from alachlor degradation would lead the center of the alachlor plume. The data provided by this study does not differentiate between these possibilities.

At the Hartung facility, three of the six wells with alachlor detects also contained 2-Cl-2',6'-diethylacetanilide. Two of these wells (Hrt 53 and 54) were the deep and moderate depth wells in the well nest immediately downgradient of the Hartung facility. Diethylaniline was also detected in these wells. The third well, Hrt 45, was the shallow well in the nest upgradient from the facility. At the Hartung site, 2-Cl-2',6'-diethylacetanilide contribution ranged from 0.4% to 2.6%. The alachlor concentration in all three of these wells was high (>50 µg/l). The four wells in the well nest one mile north of the facility did not contain alachlor.

At the Cottage Grove site, where alachlor was detected in 4 wells, no 2-Cl-2',6'-diethylacetanilide was detected. Alachlor concentration was low in all four wells (<10 µg/l). If alachlor does degrade to 2-Cl-2',6'-diethylacetanilide in soils, it is possible that the resultant degradation product concentrations were below the detection limit in these wells. The soil at this site has higher organic matter content and is less sandy than the soil at the other two sites. The organic matter would promote the binding of the residues in the soil profile while the

decreased sandiness would slow the percolation of water, and thus the transport of the residues, through the soil profile.

6.2.3 Hydroxyalachlor

Mass spectroscopy was used to confirm the gas chromatographic results on five samples. Alachlor was identified by mass spectroscopy in four of these; this agreed with the gas chromatographic analysis. In all four of these samples, hydroxyalachlor was also identified. Since hydroxyalachlor was not measured or identified during routine analysis, nothing is known about the quantities present. The alachlor concentration ranged from 22 to 460 µg/l. The occurrence of hydroxyalachlor in alachlor contaminated groundwater is a potential area of further study.

6.3 Occurrence of Atrazine Breakdown products Relative To Atrazine

Atrazine was detected in thirty-two of the thirty-six wells in the study. Deethylatrazine was detected in all of these wells, and also in three wells at the Lone Rock site where atrazine was not detected. Deisopropylatrazine was detected in five of thirteen Bear Creek wells, four of six Cottage Grove wells, and two of three Hartung facility wells wherein atrazine had been detected. Additionally, deisopropylatrazine was detected in two Lone Rock wells where atrazine was not detected.

Figures 6.1-6.8 plot the concentrations of deethylatrazine and deisopropylatrazine against the concentration of atrazine at each well within the individual study sites. The general trend for this set of graphs is for the concentration of deethylatrazine or deisopropylatrazine to increase with increased atrazine concentration. This relationship is not surprising. Common sense would dictate that degradation products would be present in greater concentrations where the parent compound concentration is greater. A greater amount of parent compound will potentially degrade to more of its various daughter products. However,

Figure 6.1: Bear Creek
Deethylatrazine Concentration vs. Atrazine Concentration

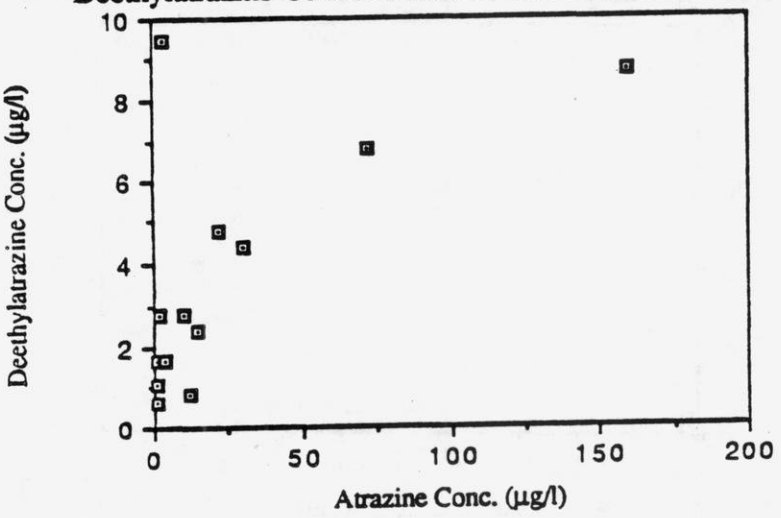


Figure 6.2: Cottage Grove
Deethylatrazine Concentration vs. Atrazine Concentration

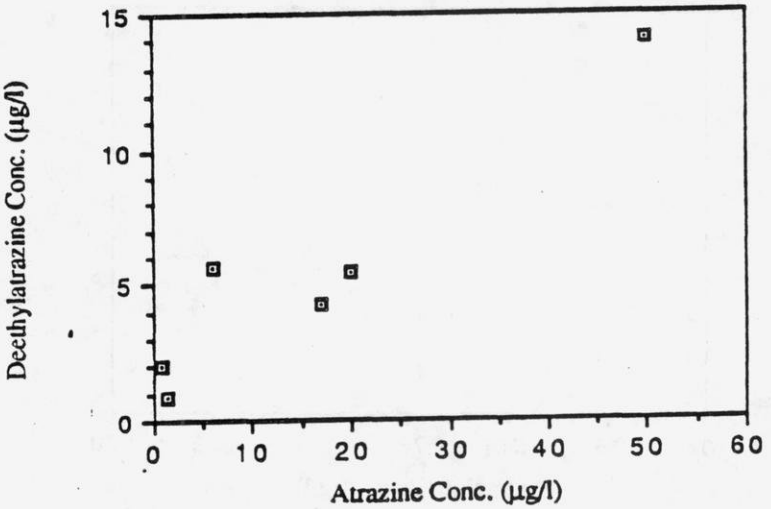


Figure 6.3: Lone Rock
Deethylatrazine Concentration vs. Atrazine Concentration

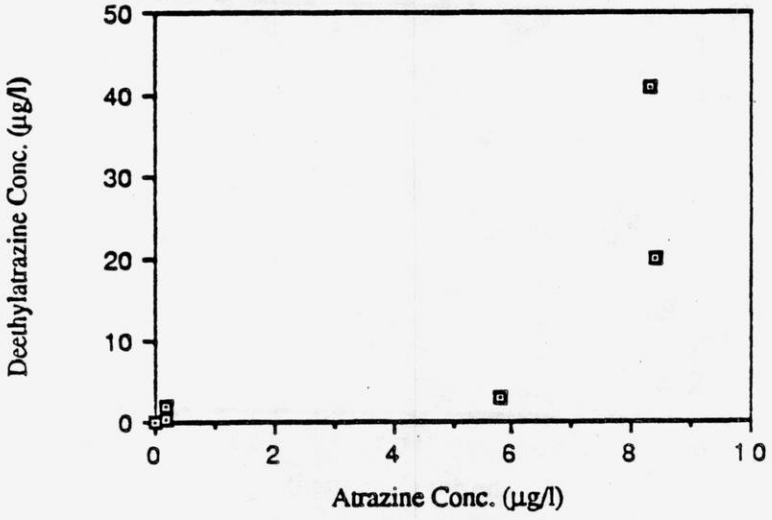


Figure 6.4: Hartung Facility
Deethylatrazine Concentration vs. Atrazine Concentration

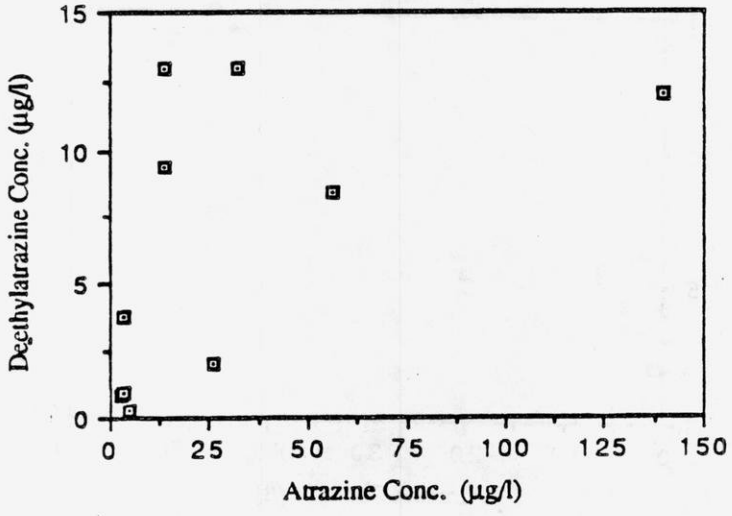


Figure 6.5: Bear Creek
Deisopropylatrazine Concentration vs. Atrazine Concentration

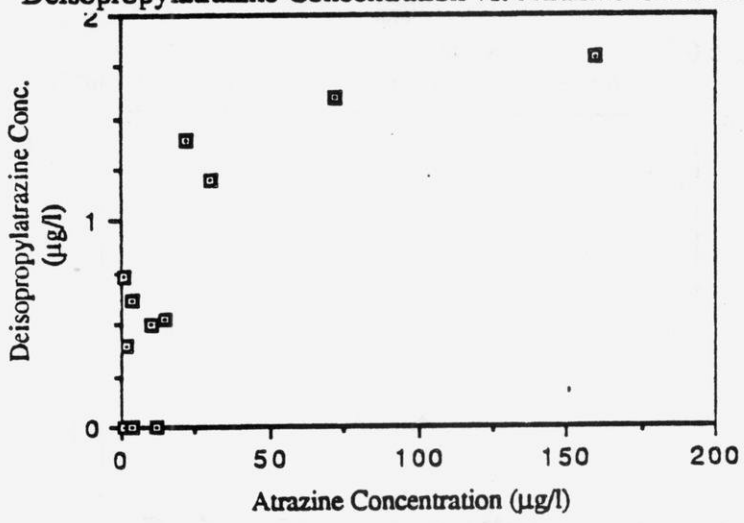


Figure 6.6: Cottage Grove
Deisopropylatrazine Concentration vs. Atrazine Concentration

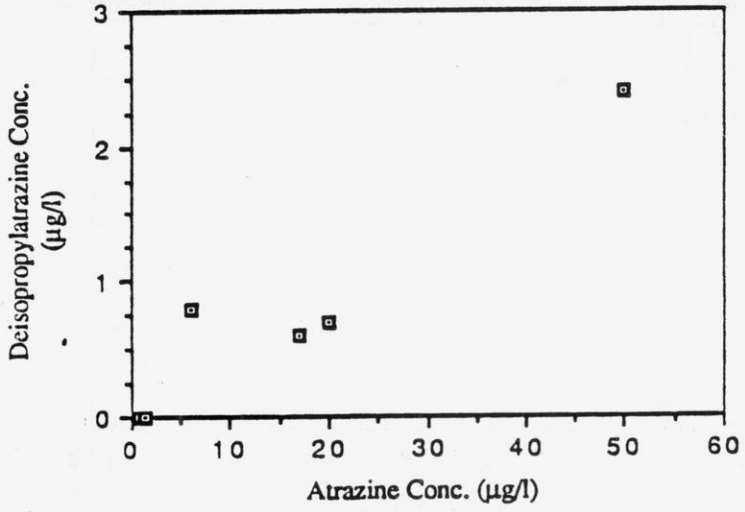


Figure 6.7: Lone Rock
Deisoropylatrazine Concentration vs. Atrazine Concentration

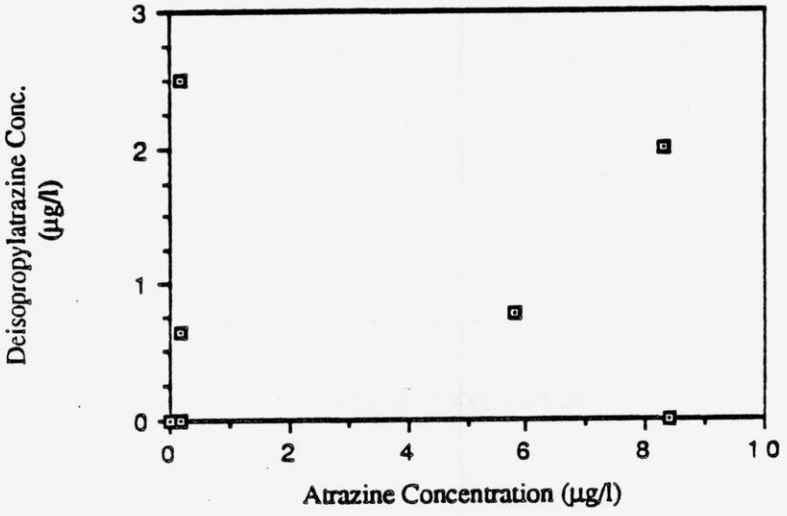


Figure 6.8: Hartung Facility
Deisopropylatrazine Concentration vs. Atrazine Concentration

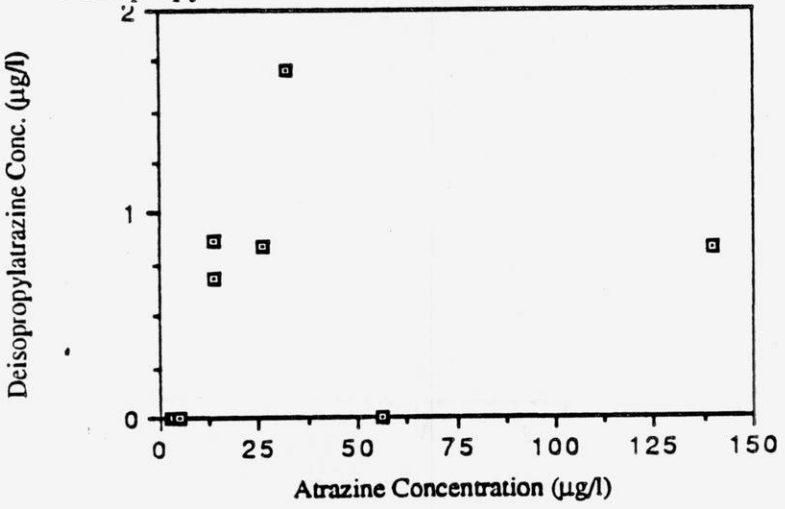


Table 6.2 Contribution of Deethylatrazine and Deisopropylatrazine to Atrazine Contamination

Well #		Deetat Contribution	Deisoat Contribution	Corrected Deisoat Contribution*
BrCk	37	50	40	40
	38	30	14	14
	39	33	-	-
	40	65	-	-
	41	71	-	-
	42	14	3.4	3.4
	43	5.2	1.1	1.1
	44	8.6	2.2	2.2
	45	60	-	-
	46	22	4.9	4.9
	47	18	6.0	6.0
	48	13	3.8	3.8
	49	61	-	-
CtGr	16	72	-	-
	17	21	3.4	4.3
	18	49	12	15
	19	20	3.4	4.3
	20	38	-	-
	21	22	4.6	5.8
LnRk	1	83	19	27
	2	70	-	-
	3**	74	-	-
	4**	-	-	-
	5**	70	92	95
	6**	90	76	83
	7	33	12	17
Hrt	44	40	5.9	8.7
	45	29	5.0	7.6
	53	7.9	0.6	0.9
	54	13	-	-
	55	7.1	3.1	4.7
	56	48	4.6	7.0
	58	23	-	-
	59	24	-	-
	60	6.4	-	-
	75	52	-	-

Deetat = deethylatrazine Deisoat = deisopropylatrazine

Deethylatrazine Contribution = {[deethylatrazine]/[atrazine + deethylatrazine]} x 100; similar for deisopropylatrazine

* For Cottage Grove, Lone Rock and Hartung, where deisopropylatrazine spike recovery was less than 90%, concentration is corrected by dividing by spike recovery. Spike recovery values: CtGr=78%, LnRk=64%, Hrt=65%

** No atrazine detected

these graphs give little information about the relative contribution of the degradation products to the total contamination.

Table 6.2 lists the contributions of deethylatrazine and deisopropylatrazine to the total atrazine contamination at each study well. In those cases where atrazine was not detected, but at least one of the degradation products were, atrazine is treated as being present at 0.2 µg/l. This artifice is justified because the atrazine detection limit is 0.3 µg/l, and it is doubtful that the concentration of atrazine at these wells is actually 0. By using a non-zero value for atrazine, the estimate of the dealkyl-breakdown product contribution is made more conservative.

Deethylatrazine contributed more significantly than deisopropylatrazine to the total atrazine contamination at all but one well (LnRk 5). For three of the sample batches, the deisopropylatrazine spike recoveries were 78, 64, and 65%, as compared to the usual 90 to100% recovery of the remaining compounds. When the deisopropylatrazine concentrations are corrected for low recovery, the contribution of deethylatrazine is still more important, as indicated by table 6.2 and Figure 6.9. Figure 6.9 employs box plots to compare the distributions of deethylatrazine and deisopropylatrazine contributions for the total data set. The median deethylatrazine contribution is 33, while the median deisopropylatrazine contribution (corrected for spike recovery), is 6. The mean contributions for deethylatrazine and deisopropylatrazine are 38 and 16.9, respectively. Furthermore, the frequency of deethylatrazine occurrence (35/36 wells with detects) is greater than that of deisopropylatrazine (21/36 wells). Thus, the study data favor deethylatrazine as the primary monodealkylated atrazine breakdown product in groundwater. This agrees with the results of Schiavon (1988a and 1988b), Skipper and Volk (1972), Goswami and Green (1971), Muir and Baker (1976), and Sirons et al. (1973).

Figures 6.10-6.17 depict the contribution of the deethylatrazine and deisopropylatrazine relative to the atrazine concentration at each well in the individual study sites. For those wells where atrazine was not detected, but the degradation products were, atrazine is treated as being

Figure 6.9

Comparison of Contributions of Deethylatrazine and Deisopropylatrazine for Combined Data

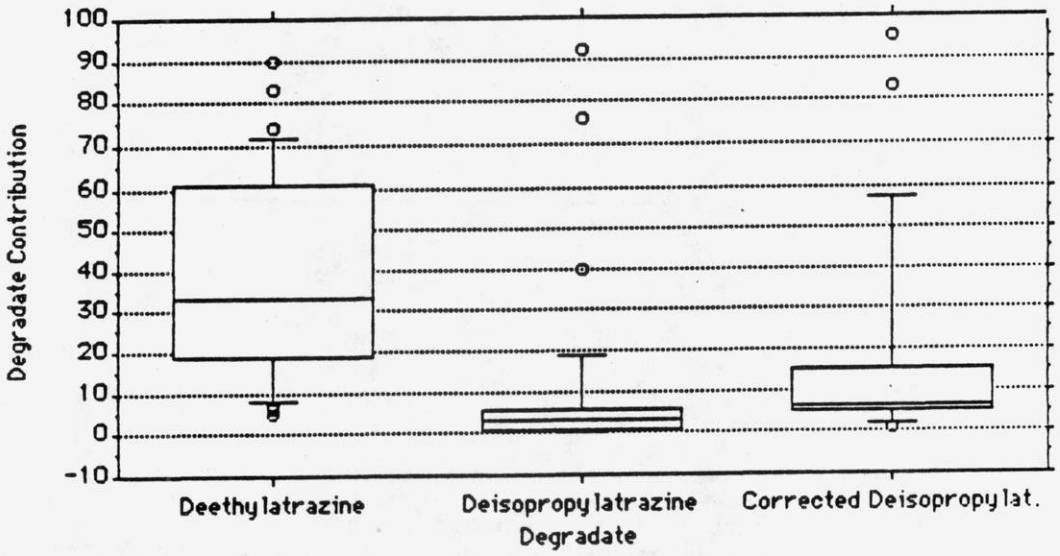


Figure 6.10: Bear Creek
Deethylatrazine Contribution Relative To Atrazine Concentration

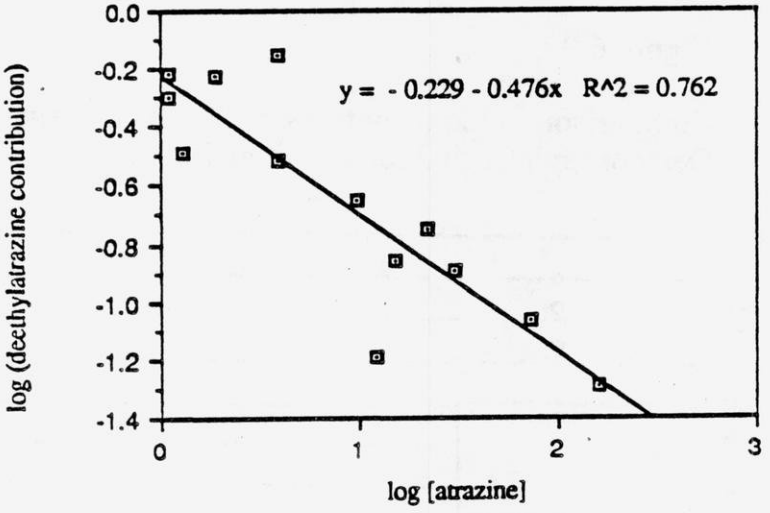


Figure 6.11: Cottage Grove
Deethylatrazine Contribution Relative to Atrazine Concentration

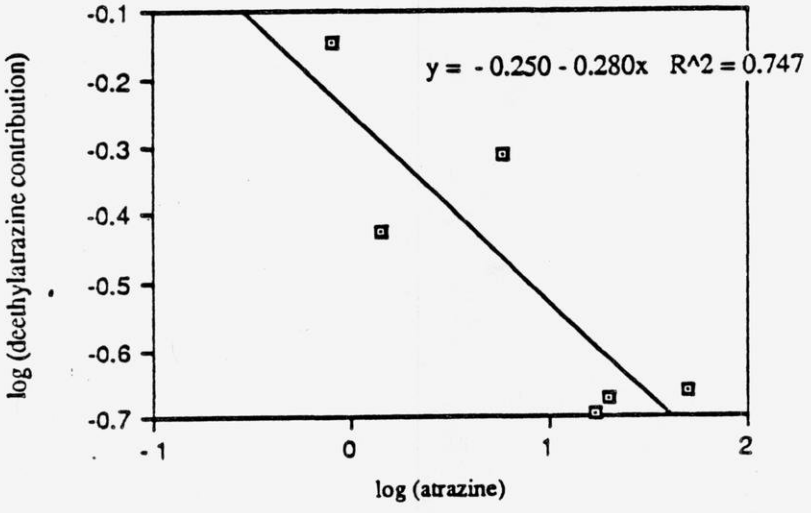


Figure 6.12: Lone Rock
Deethylatrazine Contribution Relative To Atrazine Concentration

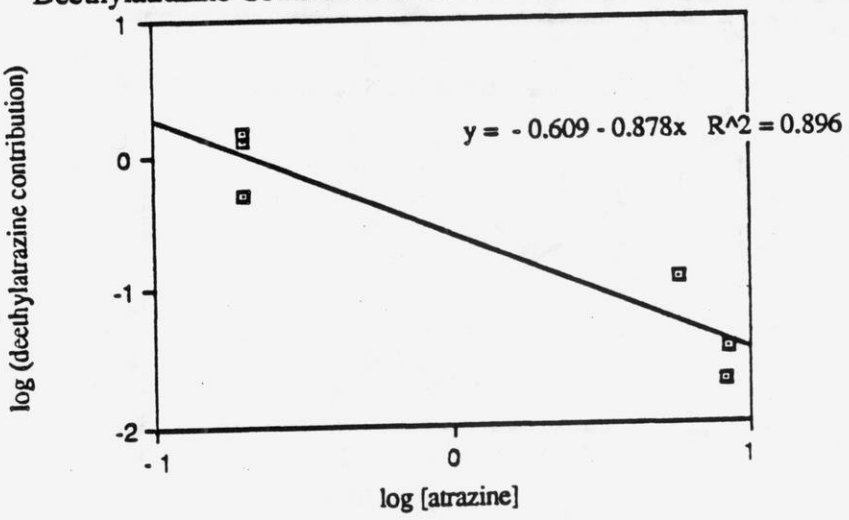


Figure 6.13: Hartung Facility
Deethylatrazine Contribution Relative To Atrazine Concentration

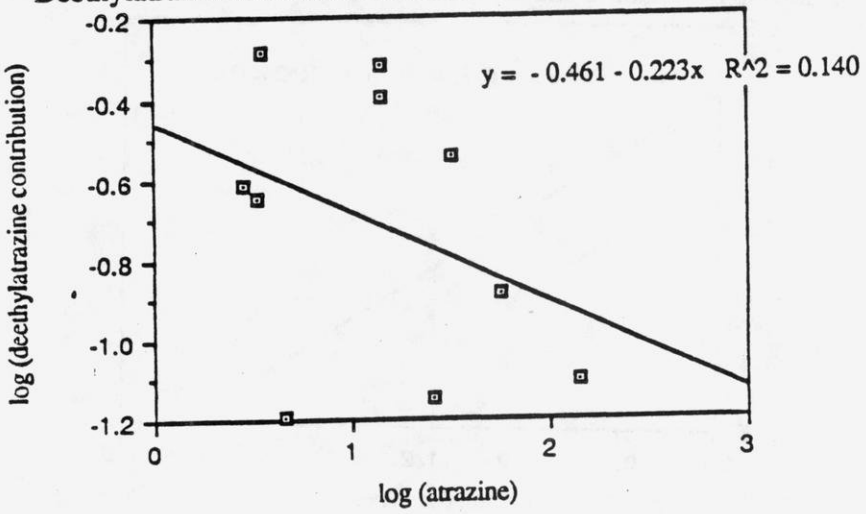


Figure 6.14: Bear Creek
Deisopropylatrazine Contribution Relative to Atrazine Concentration

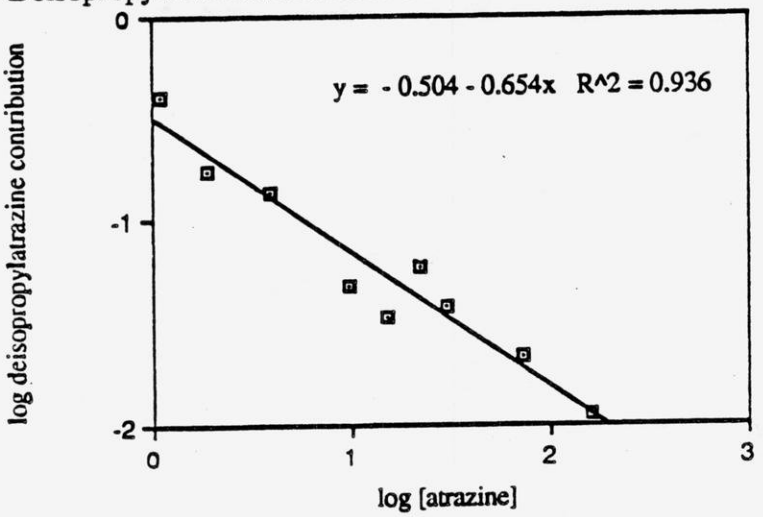


Figure 6.15: Cottage Grove
Deisopropylatrazine Contribution Relative to Atrazine Concentration

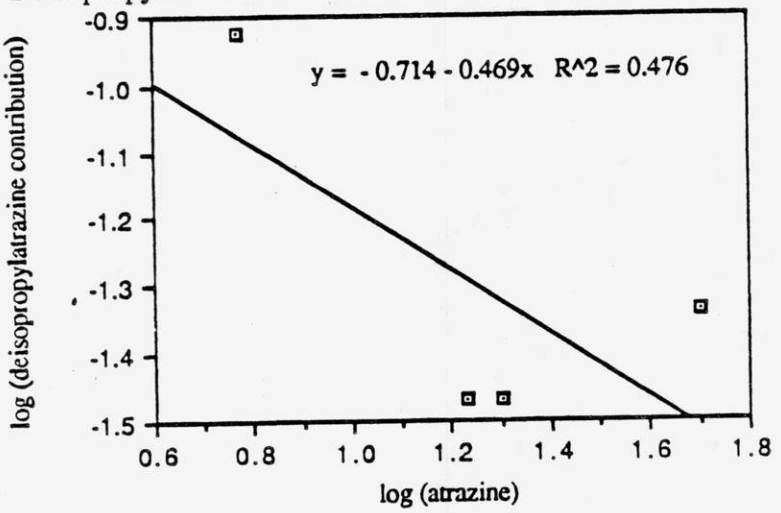


Figure 6.16: Lone Rock
Deisopropylatrazine Contribution Relative To Atrazine Concentration

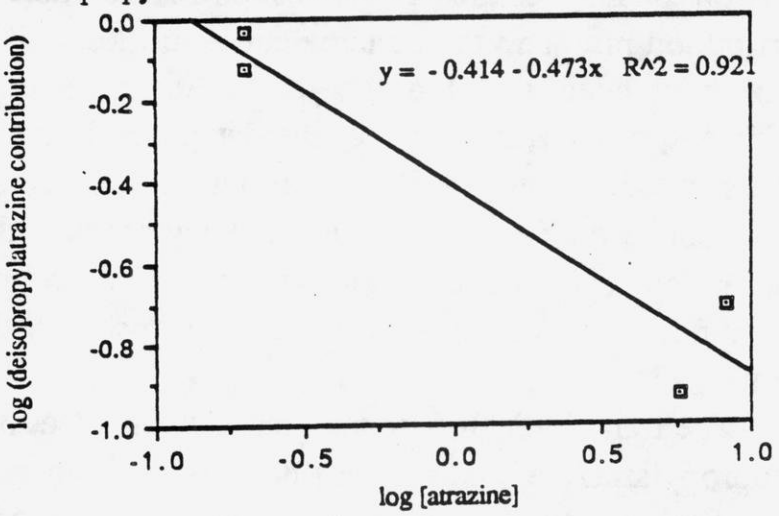
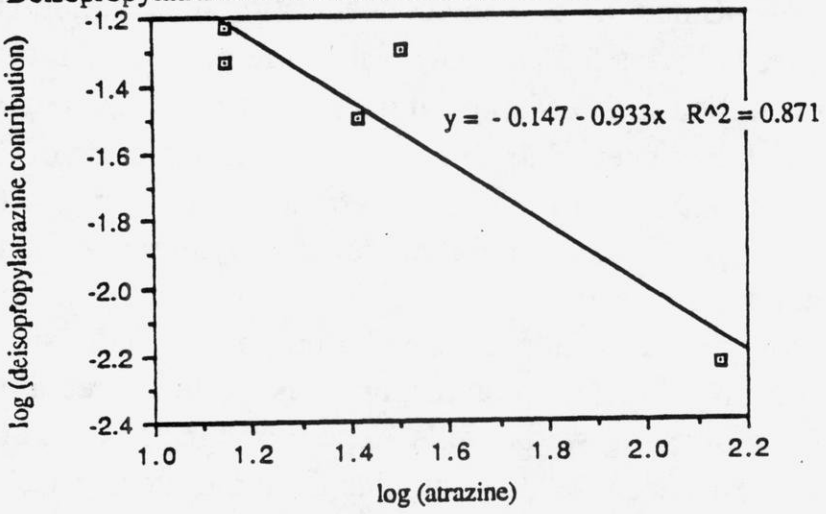


Figure 6.17: Hartung Facility
Deisopropylatrazine Contribution Relative To Atrazine Concentration



present at 0.2 µg/l. This series of graphs uses the log/log transformation of both axes. For the study data, a log/log transformation of both axes most consistently resulted in the best correlation between the contribution ratio and the atrazine concentration. The line of best fit has been included in each of the graphs, and is accompanied by the coefficient of determination for the data. The line equations should not be interpreted as being definite relationships between the breakdown product and atrazine concentrations. They are intended to illustrate the trend of decreasing contribution with increasing concentration of parent compound, while the correlation indicates how well the data fit the trend.

The trend indicated by the graphs is that deethylatrazine and deisopropylatrazine contributions decrease with increasing atrazine concentration. For deethylatrazine the correlation of fit for the four sites is fair, ranging from r=0.37 for the Hartung facility to r=0.95 for the Lone Rock site. The trend is similar for deisopropylatrazine; the correlation value for the four sites ranges from r=0.69 for Cottage Grove to r=0.97 for Bear Creek. The line equations vary from site to site for both breakdown products.

Since the atrazine concentration distribution is similar at the four sites (Figures 5.3 and 5.4), data were combined into one set, and plotted, even though the edaphic and geologic conditions vary between sites. The combined deethylatrazine data still show a trend of decreasing contribution with increasing atrazine concentration (Figure 6.18; r=0.72). For the combined deisopropylatrazine data, (Fig. 6.19), the correlation is excellent, (r=0.95). To address the implications to groundwater standards, the Hartung data should be excluded since the Hartung wells are monitoring wells while the remaining samples came from drinking water wells. The monitoring wells are shallower than the domestic wells. Also, samples from monitoring wells often contain sediment. For these reasons, Figures 6.20 and 6.21 show the deethylatrazine and deisopropylatrazine contribution relative to atrazine concentration for the total drinking water data only.

Figure 6.18: Total Data
Deethylatrazine Contribution Relative to Atrazine Concentration

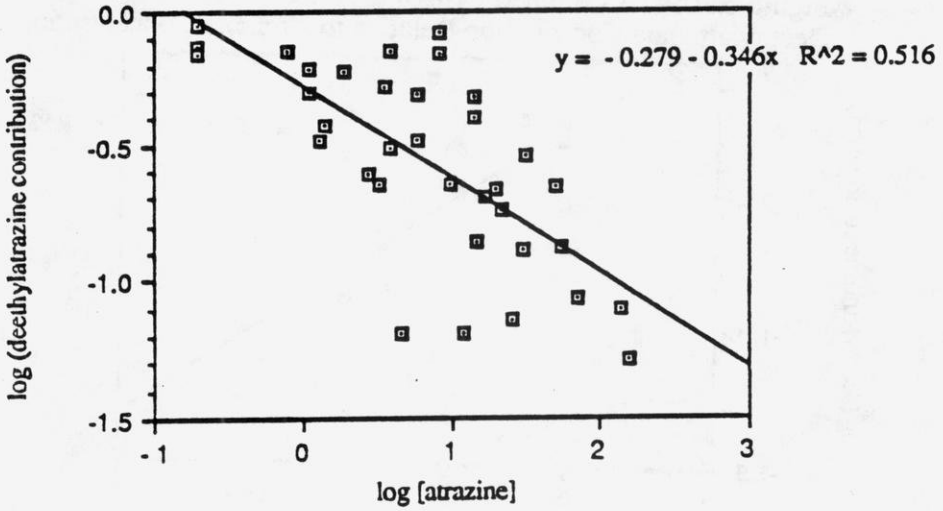


Figure 6.19: Total Data
Deisopropylatrazine Contribution Relative to Atrazine Contribution

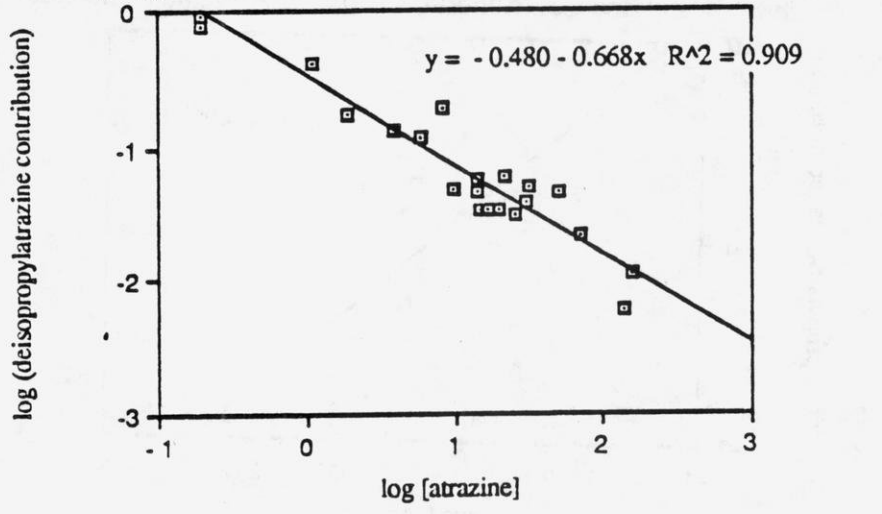


Figure 6.20: Combined Drinking Water Data
Deethylatrazine Contribution Relative to Atrazine Concentration

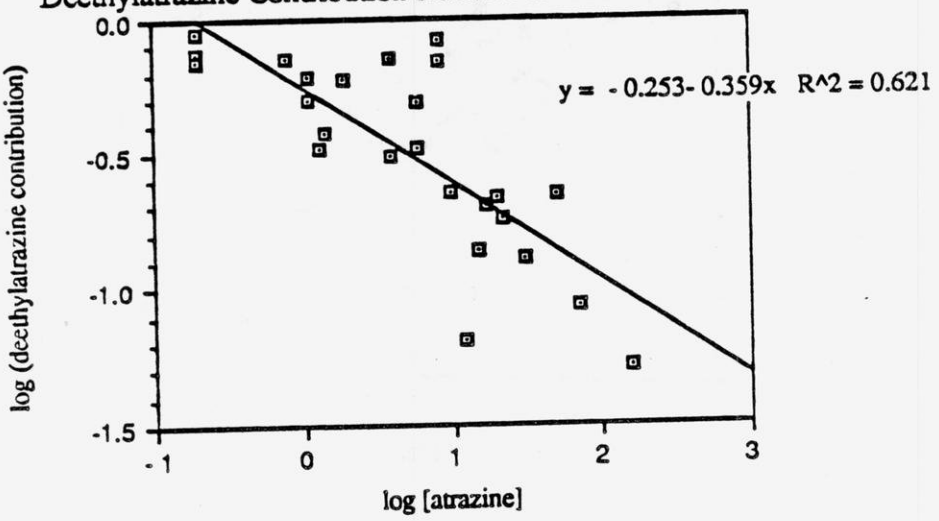


Figure 6.21: Combined Drinking Water Data
Deisopropylatrazine Contribution Relative to Atrazine Concentration

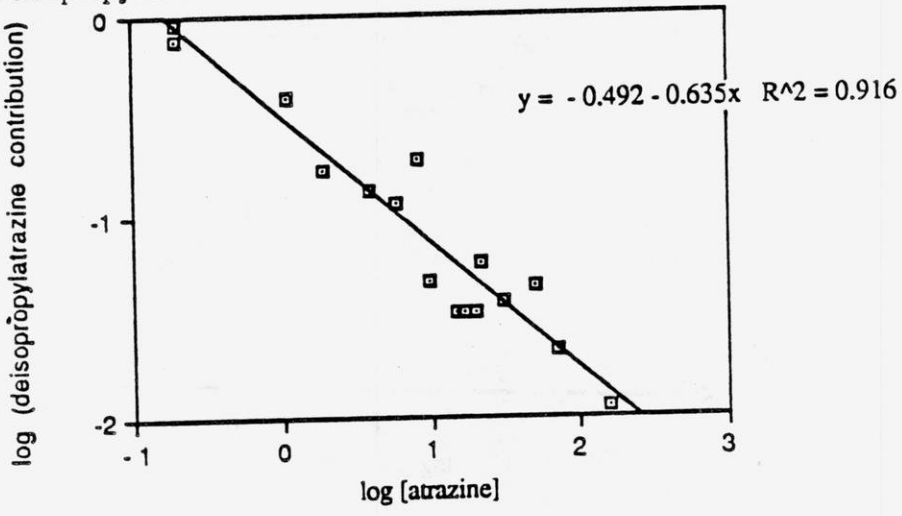


Figure 6.22

Deethylatrazine Contribution At Each Study Site

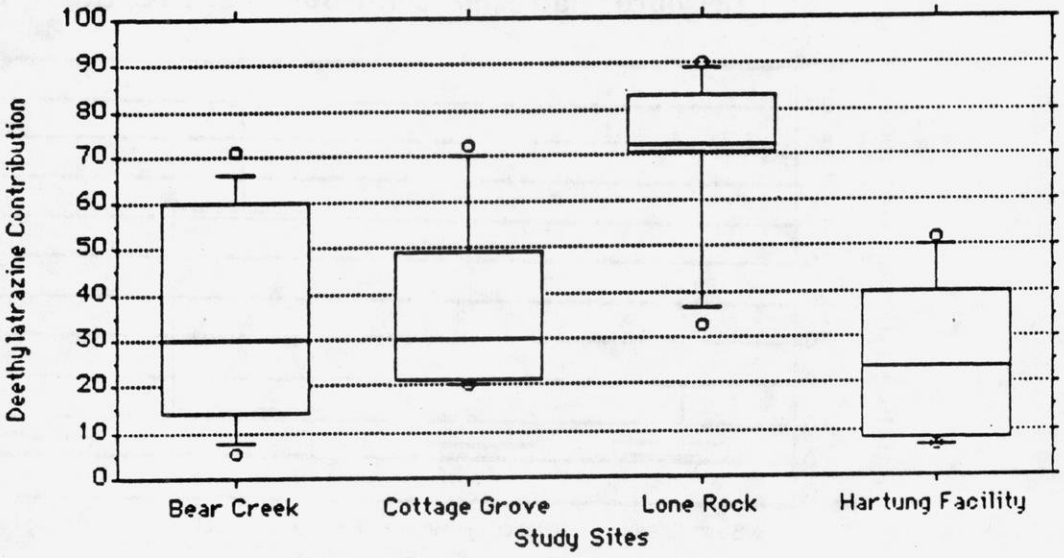
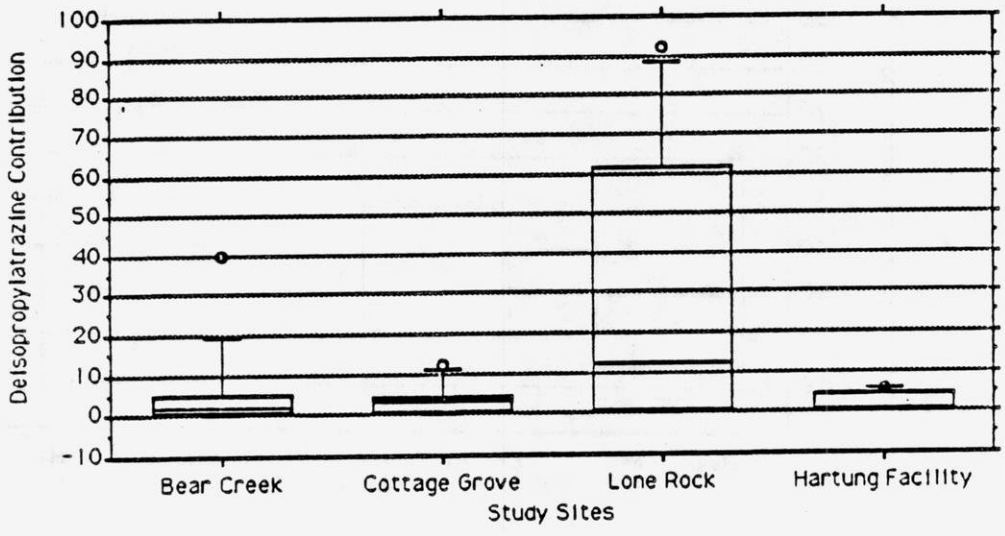


Figure 6.23

Deisopropylatrazine Contribution at Each Study Site



There are several factors which affect the degradation process at any site (see section 2.2), thus the relative contribution of a given breakdown product may be expected to vary between sites. This is illustrated for deethylatrazine in Figure 6.22, and for deisopropylatrazine in figure 6.23. For deethylatrazine, the contribution distributions are similar for the four sites. The Lone Rock site deviates the most. This is also true for deisopropylatrazine. In both cases, the medians for the Bear Creek, Cottage Grove and Hartung sites are very similar, while the Lone Rock site displays a higher median contribution. This may be due, in part, to the small size of the data set at the Lone Rock site. Also, there were three wells at the Lone Rock site where atrazine was not detected but at least one breakdown product was. In these instances, the contribution of both breakdown products are very high, even though the contribution estimates are conservative. The Lone Rock site is the only one of the study sites which was contaminated due to a non-point source incident, although whether this had any effect on the contribution can not be determined from this study. In any event, the relative contributions of deethylatrazine and deisopropylatrazine generally compare favorably between sites, despite edaphic, geologic, and climatic differences.

In summary, deethylatrazine was consistently found in the wells studied and measureably contributed to total atrazine contamination. Deisopropylatrazine, although found less often than deethylatrazine, is present often enough and at high enough concentrations to be of importance to total atrazine contamination. How these two breakdown products can be accounted for in the current groundwater standards is the subject of rest of this chapter.

6.4 Wisconsin Groundwater Standards

The Wisconsin Groundwater Law (1983 Wisconsin Act 410), adopted in 1984, requires that the Wisconsin Department of Natural

Resources (WDNR) and the Department of Health and Social Services (DHSS) collaborate on the establishment of groundwater standards for targeted chemicals. The groundwater standards are based on human toxicology data, when available, or, more commonly, on animal toxicology data. Each chemical of concern is assigned two standards, an Enforcement Standard (ES) and a Preventative Action Limit (PAL). The ES is the level needed to protect human health; it defines when a violation has occurred. When a contaminant is found in groundwater at a concentration equal to, or greater than, its ES, immediate enforcement action must be taken by a regulatory agency against the activity responsible for the contamination. The PAL is an indicator level intended to draw attention to a potential exceedance of the ES, and to allow for cessation of the contaminating activity before the ES is attained (Belluck and Anderson, 1988). The PALs are set at 10% or 20% of the ES, based on the toxicological characteristics of the substance in question. If the substance is a carcinogen, mutagen or teratogen, the PAL factor is 10% of the ES; in all other instances, the PAL factor is 20% of the ES (Anderson et al., 1989).

The DHSS has the responsibility of performing risk assessments to calculate recommended groundwater standards. The WDNR reviews the recommendations, holds public hearings on the potential standards, and sends the resultant comments to the DHSS. The DHSS makes its final recommendations to the WDNR Board. The standards, once accepted by the WDNR Board, must be approved by the Wisconsin State Legislature. Upon legislative approval, the standards are enforceable by law (Belluck and Anderson, 1988).

6.5 Process For Development of Groundwater Standards

The U.S. Environmental Protection Agency (USEPA) has developed Maximum Contaminant Levels (MCLs) for a large number of chemicals. The MCLs were developed to regulate municipal drinking water quality and are based partially on non-health related data, such as

cost effectiveness. The DHSS uses the MCLs as a point of departure in establishing ESs. If no MCL is established for a given chemical, or if the DHSS feels that the MCL does not adequately protect the public health, they may calculate a unique ES based on a numerical health risk assessment. The risk assessment approach differs for carcinogens and non-carcinogens (Department of Health and Social Services, 1989).

6.5.1 Non-Carcinogens

In order to quantitate non-carcinogenic health effects, the DHSS calculates a Reference Dose (previously the Average Daily Intake or ADI). The Reference Dose (RfD) estimates the greatest concentration of a contaminant in drinking water to which a human population (including sensitive subgroups) can be exposed daily for an entire lifetime with no deleterious health effects (Belluck and Anderson,1988; USEPA, 1988). The RfD is based on the No-Observed-Adverse-Effect Level (NOAEL), which is the quantity of a compound which, when administered to experimental animals, results in none of the adverse effects measured at a higher dose. In the absence of a NOAEL, the Lowest-Observed-Effect Level (LOAEL) is used. The NOAEL or LOAEL is determined using data from animal feeding studies (USEPA, 1988). The equation for calculating the RfD is (USEPA, 1988):

$$RfD = \frac{\text{NOAEL or LOAEL}}{\text{Uncertainty Factor}} \quad \text{(units= mg/kg body weight/day)}$$

The Uncertainty Factor (UF) accounts for inter- and intra- species differences in toxicological response. Additional uncertainty factors may be included to account for inadequacies of the available data base. The selection of an uncertainty factor requires a scientific judgement on the body of data used to derive the NOAEL or LOAEL. The UF ranges from 10 to 1000. An additional uncertainty factor of 10 is incurred for compounds ranked as possible human carcinogens (Class C Carcinogens

on the USEPA scale). This is intended to account for the difference in mechanism of action between carcinogens and noncarcinogens (DHSS, 1989).

The RfD is used by the DHSS to calculate an ES. In calculating the ES, the DHSS assumes that the target human is a 10 kg child who drinks 1 liter of water a day. It is also assumed that the only route of exposure to the chemical is through drinking water. The ES equation is as follows (Anderson et al., 1989):

$$ES = \frac{\text{NOAEL or LOAEL x 10 kg (100\%)}}{\text{(UF) x 1 liter/day}} \quad \text{OR}$$

$$ES = \frac{\text{RfD x 10 kg (100\%)}}{\text{1 liter/day}}$$ (units: mg/l, convert to µg/l).

6.5.2 Carcinogens

The USEPA ranks chemical carcinogenicity based on whether there is adequate evidence to support a cause-and-effect relationship between exposure to the chemical and cancer incidence. The rankings are (USEPA, 1988):

A) Human Carcinogen
B) Probable Human Carcinogen
C) Possible Human Carcinogen
D) Not Classified as to Human Carcinogenicity
E) Evidence of Noncarcinogenicty for Humans.

Cancer is assumed by the USEPA to be a nonthreshold effect, in other words, exposure to even one molecule of a carcinogen theoretically may contribute to the risk of developing cancer. Because of this, the sub-threshold approach of NOAEL calculation does not apply to carcinogens. Thus, a "risk-specific" level is used to formulate

water quality criteria for known carcinogens rather than the "safe level" used for non-carcinogens (USEPA, 1988).

If evidence supports the classification of a chemical as a class A or B carcinogen, mathematical models are used to estimate carcinogenic potency factor for humans and an upper-bound excess cancer risk associated with lifetime ingestion of the chemical. Data from lifetime exposure studies in animals are usually used to formulate these estimates (USEPA, 1988). The model used by the DHSS (and the USEPA) is a linear multistage model, although other models may be used. The potency factor is then used to determine the concentration of the chemical in drinking water associated with theoretical upper bound excess lifetime cancer risk of 1 in 1,000,000, using the same exposure assumptions as those applied to the non-carcinogen case. This DHSS uses this concentration as the ES for carcinogens (USEPA, 1988; Belluck and Anderson, 1988).

6.6 Wisconsin Atrazine Groundwater Standards

Atrazine is classified by the USEPA as a possible human, or Class C, carcinogen. Although Ciba Geigy has submitted studies to the USEPA which have indicated that atrazine causes an increased incidence of mammary carcinomas in female Sprague Dawley rats, there has been no evidence of any carcinogenic tendencies in human systems (USEPA, 1988). Currently, the USEPA has established neither a carcinogenic potential nor a carcinogenic risk estimate for atrazine. The DHSS thus calculates its ES using the non-carcinogenic RfD approach (DHSS, 1989). Chronic health effects of atrazine may include ataxia, effects to kidney, nervous system and adrenal gland functions, and histopathological effects on the kidney, liver, and lung (USEPA, 1988).

The USEPA has recommended a RfD based upon a NOAEL of 0.35 mg/kg/day and a UF of 100 (this NOAEL was derived from a two year chronic dog feeding study conducted in 1964). The DHSS agreed with these figures but felt that it was necessary to use an additional UF

of 10 in order to account for carcinogenic effects (DHSS, 1989). The calculation of current Wisconsin atrazine groundwater standards is based on the following (DHSS, 1989):

NOAEL	0.35 mg/kg/day
UF	100; accounts for inter and intraspecies differences
Additional UF	10; accounts for difference in activity between carcinogens and non-carcinogens.
RfD (ADI)	0.0035 mg/kg/day
ES	3.5 µg/l
PAL factor	10%
PAL	0.35 µg/l.

6.7 Accounting For Degradation Products in Groundwater Standards

The data from this study indicate that deethylatrazine is consistently present where atrazine is detected. Although deisopropylatrazine is not as predictable, it may contribute significantly to the atrazine contamination at some sites. There is inadequate toxicology data available to form a health risk estimate for the degradation products of atrazine. This is a common problem in the health risk arena: little to no animal feeding data exist for most chemicals; the corresponding chronic health effects and carcinogenicity can only be approximated. In cases such as these, toxicology and carcinogenesis data for chemicals with similar structure can be used to formulate the risk estimate. This method is called "risk by analogy" (Crouch et al., 1983). By this reasoning, the toxicology of deethylatrazine and deisopropylatrazine can be assumed to be similar to that of atrazine. This agrees with the stance Ciba-Geigy has taken, which is to treat the chlorinated degradation products as having toxicological action similar to atrazine (personal communication; Dr. Darryl Sumner, Ciba-Geigy, Greensboro, NC, 2/11/87).

There are several models which could be proposed to account for the presence of deethylatrazine and deisopropylatrazine in atrazine contaminated water. The breakdown products could be accounted for by revising the atrazine ES, by measuring only atrazine and estimating the amount of breakdown product present, or by measuring all three compounds. These alternatives are described below, accompanied by the advantages and disadvantages of each. These models are described using the Wisconsin system as an example. With the exception of alternative 2, all assume that the toxicologies of the three compounds are identical.

1. Quantitation of All Breakdown products of Concern

The analytical lab charged with analyzing environmental samples for the state (the Wisconsin State Laboratory of Hygiene, or SLH) would quantitate all three compounds in water samples submitted for atrazine analysis. The three concentrations would be summed and the resultant total concentration would be compared to the current ES. The primary disadvantage of this model is the increased laboratory time required for analysis of all three compounds. The method developed for this study, though similar to the current analytical method used for atrazine by the SLH, is not identical. Unless an alternative packed column could be found for the confirmation of the breakdown products by gas chromatography, the analysis of the compounds is too time intensive to fit efficiently into the current routine of the SLH pesticide lab. There are currently many environmental contaminants for which analysis is not performed, or for which analytical methods are not developed, and the state resources dedicated to monitoring are limited. The priorities of limited lab resources must be resolved; either a greater number of samples can be analyzed, analysis for a greater number of unique compounds in fewer samples can be performed, or analysis can be performed on fewer samples for all the residues related to a few individual compounds.

2. Separate Standards For Each Breakdown product

Unique groundwater standards could be developed for each breakdown product. This would require a considerable amount of toxicological data which is currently unavailable. The requisite studies could require several years, considering that the USEPA is still awaiting definitive studies on atrazine toxicology. Once the ESs are developed, the same disadvantages facing alternative 1 would hold for this model as well. The advantage of this model would be that public health risk posed by the contamination would be more accurately estimated by the combination of direct measurement of all residues and ESs based upon the individual toxicology of each residue. However, the activity causing an atrazine contamination is release of atrazine, not its breakdown products. The knowledge on the factors affecting the environmental fate of atrazine is limited. It would be difficult to direct action to keep the concentration of the breakdown products below the PAL.

3. Atrazine Concentration as Analogue For Total Atrazine Contamination

Under this model, only atrazine would be measured, using the current SLH analytical methods. The atrazine concentration would be used to estimate the concentrations of the other compounds. The estimate of the total contamination would be compared to the atrazine ES. This would have the advantage of conforming to current pesticide laboratory practices. The obvious disadvantage would be the possibility of false ES exceedances (false positives) or false negatives. A variation of this model would use a two-tiered approach; if the atrazine measurement fell within a certain percentage of the ES, a second analysis would be required to measure the breakdown product concentrations. If the atrazine concentration already exceeded the ES, then it would not be necessary to measure the breakdown product concentrations. This approach is justified because many samples are submitted not only for atrazine analysis, but for a whole pesticide scan. Atrazine is extracted and measured with the rest of the "base neutral" pesticides. A large

percentage of the samples do not contain atrazine. Thus, only the samples containing atrazine near the ES would be submitted for the more time consuming breakdown product analysis.

4. Establish A Lower ES for Atrazine

A lower ES could be set for atrazine, and this is the "model" favored here for accounting for degradation products in groundwater standards. The adjusted ES would account for the possible presence of deethylatrazine and deisopropylatrazine. This would essentially be the same as including an additional uncertainty factor in the determination of the ES. This alternative is strongly supported by the data of this study: deethylatrazine is present whenever atrazine is present, while the relationship between deisopropylatrazine and atrazine concentrations is predictable (r=0.96). The primary disadvantage lies in the process of resetting the ES; this would require that the DHSS make recommendations to the DNR for the new ES. Acceptance of the recommencations would require time. However, this is true for any of the models. This alternative does avoid the disadvantage of inexact measurement, since only the atrazine concentration is reported. A possible method for correcting the ES is described in the next section.

6.8 Adjusting the Atrazine ES to Account For Degradation Products

This analysis assumes that the current atrazine ES correctly accounts for the toxicology of atrazine, and by extrapolation, its dechlorinated daughter compounds, deethylatrazine and deisopropylatrazine. It is then necessary to determine at which atrazine concentration the sum of the dealkylbreakdown products and atrazine concentrations is equal to the atrazine ES. This atrazine concentration becomes the adjusted ES. The adjusted ES is termed "ES_{Total}" and is calculated as follows:

Figure 6.24: Combined Drinking Water Data
Deethylatrazine/Atrazine Ratio Relative To Atrazine Concentration

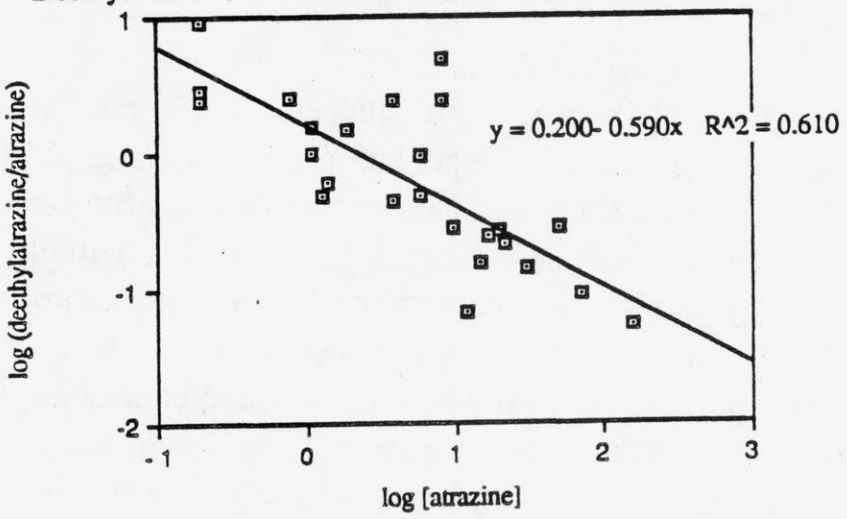
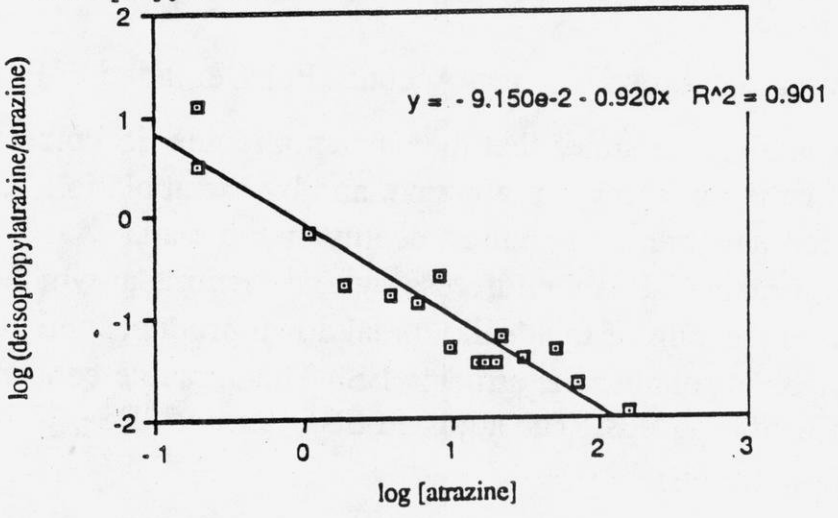


Figure 6.25: Combined Drinking Water Data
Deisopropylatrazine/Atrazine Relative to Atrazine Concentration



(a) ES_{Total} = [atrazine] + [deethylatrazine] + [deisopropylatrazine] = 3.5 µg/l

The relationships established with the drinking water data were used to calculate ES_{Total}. The graphs in figures 6.24 and 6.25 are similar to the contribution graphs in figures 6.20 and 6.21, except that the contribution ratios have been replaced with the ratios of [breakdown product]/[atrazine]. This is done to simplify the final calculation. Only the drinking water data (Bear Creek, Cottage Grove, and Lone Rock) were used for this purpose.

The equations relating the breakdown product concentrations to atrazine concentration are (from figures 6.24 and 6.25):

(b) log[deethylatrazine/atrazine] = 0.200 - 0.590 x log[atrazine]
(c) log[deisopropylatrazine/atrazine] = -0.092 - 0.920 log[atrazine]

Equations (b) and (c) were simplified and substituted into the ES_{Total} equation (a). The solution to equation (a) was arrived at by iteration:

(d) ES_{Total} = 1.06 µg/l

The ES_{Total}, based on the data collected for this study, is 1.1 µg/l; the corresponding PAL for total atrazine would be 0.11 µg/l. The data supporting this adjustment came from three sites diverse in geologic and edaphic conditions. A broader data base is recommended in order to certify both this ES_{Total} value and the validity of this type of calculation. Also, there may be other important groundwater breakdown products of atrazine which were not measured in this study that could add to the atrazine ES_{Total}.

Chapter 7
Conclusions and Recommendations For Further Study

Methods were developed to identify and quantify the atrazine degradation products, deethylatrazine and deisopropylatrazine, and the alachlor degradation products, 2,6-diethylaniline (DEA) and 2-Cl-2',6'-diethylacetanilide, in water. Samples were collected from four sites in Wisconsin known to have groundwater contaminated by atrazine and/or alachlor. Samples from three of the sites were from drinking water wells while the samples from the remaining site were from monitoring wells. These samples were analyzed for atrazine, alachlor and their targeted breakdown products using the methods developed for this study.

The data for alachlor indicate that neither DEA nor 2-Cl-2',6'-diethylacetanilide are important groundwater breakdown products. However, hydroxyalachlor may occur frequently in alachlor-contaminated groundwater, and should be investigated further. The atrazine data indicate that the atrazine breakdown products can contribute significantly to total atrazine groundwater contamination. Deethylatrazine was detected in all 32 of the study wells where atrazine was detected, and in three wells where atrazine was below the detection limit. Deisopropylatrazine was detected in 11 of the 32 wells where atrazine was detected, and in two wells where atrazine was below the detection limit. By failing to measure, or otherwise account for deethylatrazine and deisopropylatrazine in atrazine-contaminated groundwater, the amount of atrazine-associated contamination that contributes to the health risk may be underestimated.

Several "models" were proposed in order to account for the occurrence of atrazine degradation products in the regulatory framework outlined by the Wisconsin Groundwater Law. The model which is most practical in terms of cost and efficiency adjusts the atrazine enforcement standard (ES) for the presence of the breakdown products. The empirical linear relationship between:

log(breakdown product concentration/ atrazine concentration) and log (atrazine concentration)

was used to calculate an adjusted ES (ES_{total}) of 1.1 µg/l. The current ES for atrazine is 3.5 µg/l.

Further study is recommended in order to expand the data base of degradation product and atrazine concentrations to include data from a wider variety aquifer- and soil- types. The monitoring data should also be designed to investigate the temporal characteristics of the relationship between the breakdown product and the parent concentrations. The expanded study could include monitoring for the presence of 2-Cl-4,6-diamino-s-triazine (didealkylatrazine). Before this is done, an initial screen for the presence of didealkylatrazine should be run on samples from at least three contaminated aquifers. New methods of analysis would be required for didealkylatrazine. Literature indicates that this breakdown product may occur in groundwater, although it has been shown to form unextractable residues in the soil profile. If didealkylatrazine proved to be present in the initial screening, then it should be included in the larger monitoring study.

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Table A.1 **Atrazine Confirmation Data** (concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR CREEK	37	1.11	1.5	30
	38	3.94	4.44	12
	39	1.27	0.95	29
	40	11.57	12.93	11
	41	3.9	3.42	13
	42	14.6	16.54	12
	43	163.43	170.25	4
	44	71.72	67.53	6
	45	1.91	2.06	8
	46	9.88	13.92	34
	47	21.74	26.24	19
	48	29.97	37.6	23
	49	1.13	2.3	68
COTTAGE GROVE	2616	0.79	0.67	16
	2617	19	17	11
	2618	5.9	4.8	21
	2619	17	17	0
	2620	1.4	1.6	13
	2621	50	48	4
LONE ROCK	1	8.3	7.51	10
	2A	8.5	10.3	19
	2B	8.2	9.7	17
	3	ND	-	DA
	4	ND	-	DA
	5	ND	-	DA
	6	ND	-	DA
	7A	5.84	6.92	17
	7B	5.74	6.57	1
HARTUNG	44	14	19	30
	45	32	44	32
	53	135	142	5
	54A	56	68	19
	54B	55	64	15
	55	26	21	21
	56	14	19	30
	58	3.3	8.8	91
	59	2.8	2.1	29
	60	4.5	6.9	42
	75	3.5	3.8	8

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

Table A.2 **Alachlor Confirmation Data** (concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR CREEK	37	ND	ND	0*
	38	ND	ND	0*
	39	ND	ND	0*
	40	8.25	9.74	17
	41	ND	ND	0*
	42	22.31	28.8	25
	43	455.67	407.58	11
	44	52.51	56.1	7
	45	ND	ND	0*
	46	3.53	3.23	9
	47	61.9	72.6	16
	48	8.68	8.47	2
	49	0.1	0.11	10
COTTAGE GROVE	2616	0.22	ND	DA*
	2617	7.4	7.5	1
	2618	ND	ND	0*
	2619	1	0.6	50
	2620	ND	ND	0*
	2621	2.4	2	18
LONE ROCK	1	ND	-	DA
	2A	ND	-	DA
	2B	ND	-	DA
	3	ND	-	DA
	4	ND	-	DA
	5	ND	-	DA
	6	ND	-	DA
	7A	ND	-	DA
	7B	ND	-	DA
HARTUNG	44	4.5	5.4	18
	45	110	110	0
	53	138	110	23
	54A	60	52	14
	54B	63	59	7
	55	7.9	8	1
	56	12	12.5	4
	58	ND	-	DA
	59	ND	-	DA
	60	ND	-	DA
	75	ND	-	DA

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

Table A.3 **Deethylatrazine Confirmation Data** (concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR	37	1.09	1.91	55
CREEK	38	1.69	2.45	37
	39	0.63	0.91	36
	40	0.83	1.88	77
	41	9.47	6.3	40
	42	3.21	3.44	7
	43	8.69	25.45	98
	44	6.78	10.27	41
	45	2.8	3.25	15
	46	2.83	3.68	26
	47	4.8	7.3	41
	48	4.41	6.84	43
	49	1.67	1.75	5
COTTAGE	2616	1.9	2	5
GROVE	2617	5.4	5.6	4
	2618	5.5	6.12	11
	2619	4.3	4.98	15
	2620	0.84	0.95	12
	2621	14	14.53	4
LONE ROCK	1	42	32	27
	2A	19.4	19	2
	2B	21	21	0
	3	0.58	1.51	89
	4	ND	ND	0*
	5	0.47	0.96	69
	6	1.8	3	50
	7A	2.8	6.8	83
	7B	2.7	8.3	102
HARTUNG	44	9.4	9.8	4
	45	13	18	32
	53	12	23	63
	54A	8.7	6.8	25
	54B	8	12	40
	55	2	5	86
	56	13	12	8
	58	0.96	3.6	116
	59	0.9	2.6	97
	60	0.31	2.3	152
	75	3.8	7.3	63

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

Table A.4 **Deisopropylatrazine Confirmation Data** (concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR CREEK	37	0.74	1.55	71
	38	0.62	1.09	55
	39	0.38	0.45	17
	40	0.35	0.5	35
	41	0.33	0.57	53
	42	0.53	0.49	8
	43	1.75	2.86	48
	44	1.63	2.63	47
	45	0.37	0.6	47
	46	0.5	0.84	51
	47	1.4	1.44	3
	48	1.15	2.04	56
	49	0.32	0.63	65
COTTAGE GROVE	2616	1	ND	DA*
	2617	0.7	1.14	48
	2618	0.7	1.39	66
	2619	0.3	1.28	124
	2620	0.6	0.45	29
	2621	2.4	3.39	34
LONE ROCK	1	2	3.4	52
	2A	ND	1.6	DA**
	2B	ND	1.7	DA**
	3	ND	ND	0*
	4	ND	ND	0*
	5	2.5	6.2	85
	6	ND	ND	0*
	7A	0.63	1.3	69
	7B	0.87	1.8	70
HARTUNG	44	0.87	4.1	130
	45	1.7	5.5	106
	53	0.83	1.7	69
	54A	ND	0.92	DA**
	54B	ND	1.1	DA**
	55	0.84	0.92	9
	56	0.68	4.7	149
	58	ND	-	DA
	59	ND	-	DA
	60	ND	-	DA
	75	ND	-	DA

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

Table A.5 2-Cl-2',6'-Diethylacetanilide Confirmation Data
(concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR CREEK	37	ND	ND	0*
	38	ND	ND	0*
	39	ND	ND	0*
	40	0.26	0.14	60
	41	ND	ND	0*
	42	0.35	ND	DA*
	43	5.79	6.68	14
	44	1.35	1.57	15
	45	ND	ND	0*
	46	ND	ND	0*
	47	0.61	0.67	9
	48	0.44	0.67	41
	49	ND	ND	0*
COTTAGE GROVE	2616	ND	ND	0*
	2617	ND	ND	0*
	2618	ND	ND	0*
	2619	ND	ND	0*
	2620	ND	ND	0*
	2621	ND	ND	0*
LONE ROCK	1	ND	ND	0*
	2A	ND	ND	0*
	2B	ND	ND	0*
	3	ND	ND	0*
	4	ND	ND	0*
	5	ND	ND	0*
	6	ND	ND	0*
	7A	ND	ND	0*
	7B	ND	ND	0*
HARTUNG	44	ND	ND	0*
	45	0.45	0.39	14
	53	3.8	4.6	19
	54A	1	1.4	33
	54B	1	1.2	18
	55	ND	ND	0*
	56	ND	0.17	DA**
	58	ND	ND	0*
	59	ND	ND	0*
	60	ND	ND	0*
	75	ND	ND	0*

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

Table A.5 **2,6-Diethylaniline Confirmation Data** (concentrations in µg/l)

Study Site	Sample #	1% Column	2% Column	% Difference
BEAR CREEK	37	ND	ND	0*
	38	ND	ND	0*
	39	ND	ND	0*
	40	ND	0.46	DA**
	41	ND	ND	0*
	42	ND	ND	0*
	43	ND	ND	0*
	44	ND	ND	0*
	45	ND	ND	0*
	46	ND	ND	0*
	47	ND	ND	0*
	48	ND	ND	0*
	49	ND	ND	0*
COTTAGE GROVE	2616	ND	ND	0*
	2617	ND	ND	0*
	2618	ND	ND	0*
	2619	ND	ND	0*
	2620	ND	ND	0*
	2621	ND	ND	0*
LONE ROCK	1	ND	-	DA
	2A	ND	-	DA
	2B	ND	-	DA
	3	ND	-	DA
	4	ND	-	DA
	5	ND	-	DA
	6	ND	-	DA
	7A	ND	-	DA
	7B	ND	-	DA
HARTUNG	44	ND	ND	0*
	45	ND	ND	0*
	53	3.6	3.6	0
	54A	2.8	2.8	0
	54B	3.3	3.3	0
	55	ND	ND	0*
	56	ND	ND	0*
	58	ND	ND	0*
	59	ND	ND	0*
	60	ND	ND	0*
	75	ND	ND	0*

0*=Both columns show no detect; thus percent difference is 0. ND=Was not detected.
DA=Does not apply; the compound was not detected on the primary column, and consequently was not measured on the confirmatory column.
DA*=Was detected on the primary column, but not on the confirmatory column.
DA**=Was detected on the confrimatory column, but not on the confirmatory column.

050874- Analytical Determination of Atrazine, Alachlor, and their Selected Degradation Products in Contaminated Groundwater: Implications for