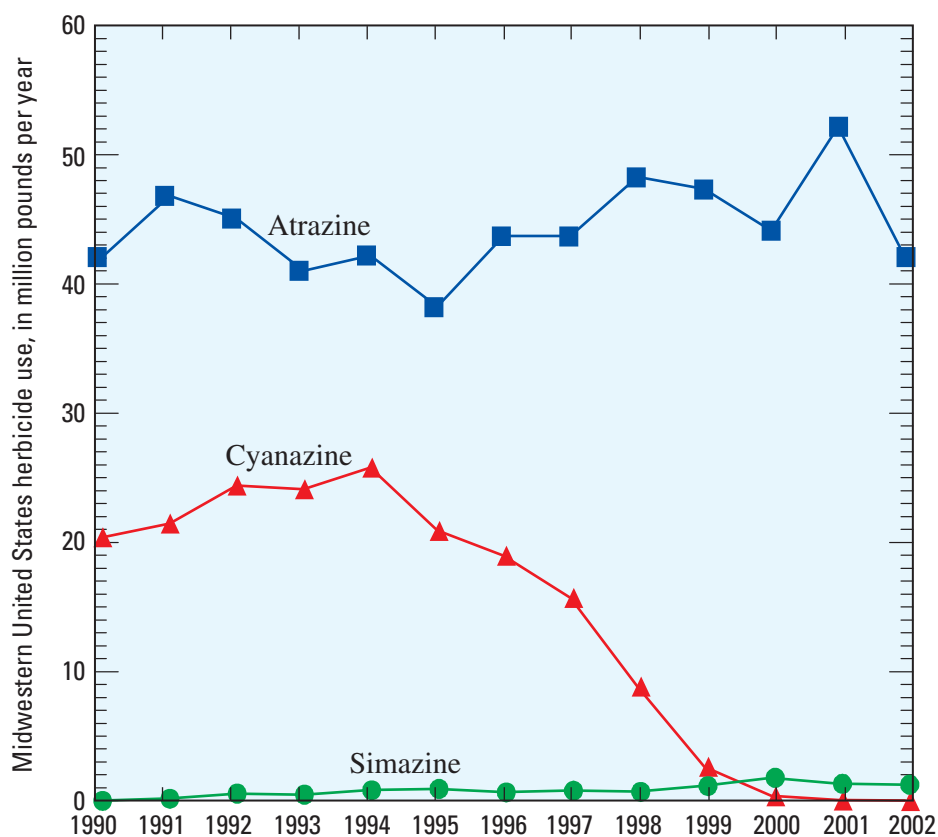


Summary of Significant Results from Studies of Triazine Herbicides and Their Degradation Products in Surface Water, Ground Water, and Precipitation in the Midwestern United States During the 1990s



Scientific Investigations Report 2005–5094

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By Elisabeth A. Scribner, E. M. Thurman, Donald A. Goolsby, Michael T. Meyer,
William A. Battaglin, and Dana W. Kolpin

Scientific Investigations Report 2005–5094

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Conversion Factors and Datum

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
inch (in.)	2.54	centimeter (cm)
microgram per liter ($\mu\text{g/L}$)	1	part per billion (ppb)
microgram per square meter per year [[$\mu\text{g/m}^2$]/yr]	0.003276×10^{-6}	ounce per billion (ppb)
mile (mi)	1.609	kilometer (km)
milligram per liter (mg/L)	1	part per million (ppm)
milliliter per gram (mL/g)	0.007491	gallon per ounce (gal/oz)
millipascal (mPa)	0.000208854	pound-force per square foot (lbf/ft ²)
mole per liter (mol/L)	1	gram molecular weight liter
pound (lb)	453.6	gram (g)
pound active ingredient per acre per year [(lb a.i./acre)/yr]	1.121	kilogram active ingredient per hectare per year [(kg a.i./ha)yr]
pound per acre (lb/acre)	1.121	kilogram per hectare (kg/ha)
square mile (mi ²)	2.590	square kilometer (km ²)

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Summary of Significant Results from Studies of Triazine Herbicides and their Degradation Products in Surface Water, Ground Water, and Precipitation in the Midwestern United States During the 1990s

By Elisabeth A. Scribner, E.M. Thurman, Donald A. Goolsby, Michael T. Meyer, William A. Battaglin, and Dana W. Kolpin

Abstract

Nonpoint-source contamination of water resources from triazine herbicides has been a major water-quality issue during the 1990s in the United States. To address this issue, studies of surface water, ground water, and precipitation have been carried out by the U.S. Geological Survey in the Midwestern United States.

Reconnaissance studies of 147 streams were conducted to determine the geographic and seasonal distribution of atrazine, cyanazine, propazine, and simazine. These studies showed that high concentrations of herbicides were flushed from cropland and transported through the stream system as pulses in response to spring and summer rainfall. The studies also revealed the persistence of herbicides and their degradation products in streams.

An investigation of 76 reservoirs showed that the occurrence and temporal distribution of herbicides and their degradation products in reservoir outflow could be related to reservoir and drainage-basin characteristics, water and land use, herbicide use, and climate. Significant findings showed that concentrations of atrazine and its degradation products remained elevated all summer and into the fall and that recently applied atrazine mixed with atrazine applied the previous year as water moved through a reservoir.

Reconnaissance studies of 303 ground-water wells were completed to determine hydrogeological and seasonal occurrence, concentration, and distribution of herbicides and their degradation products. Samples collected from across the Midwestern United States consistently revealed that triazine herbicide degradation products commonly were found more frequently than their parent herbicide and that ground-water age could be an important factor in explaining variations in herbicide contamination.

A final study investigated precipitation in the Midwestern United States, northeast to the Atlantic Ocean, and northward to the Canadian border. It found that the highest herbicide concentrations in precipitation occurred following herbicide

application to cropland. Atrazine was detected most often, followed by deethylatrazine, cyanazine, and deisopropylatrazine. Mass deposition of herbicides by precipitation was greatest in areas where herbicide use was intense and decreased with distance from the Midwest.

Findings of the 1990s studies include an improved understanding of the occurrence, persistence, chemistry, and transport of triazine herbicides and their degradation products in the hydrologic environment. A significant increase in knowledge of triazine herbicides and development and improvement of analytical methods were accomplished in the past decade. The results produced are not only significant for the present (2005) but provide an important data set for future use.

Introduction

The U.S. Geological Survey (USGS) Toxic Substances Hydrology (Toxics) Program provides unbiased scientific information on the behavior of toxic substances in the Nation's hydrologic environments. The objectives of the program include development and quantification of methods to measure contaminants and their degradation products at levels low enough to understand the fate and transport in hydrologic systems. Investigations are focused on identifying persistent pesticides and their degradation products in surface water, ground water, and precipitation. The research involves developing methods to measure these pesticides in water samples at low-level concentrations. Results then are used by manufacturers, farmers, regulators, researchers, and the public (Buxton, 2000).

Throughout the 1990s, a series of regional-scale water-quality studies were conducted by the Toxics Program in the Midwestern United States. The study area extended across parts of 12 States (fig. 1) and was selected because it is the largest and most intensive area of row-crop agriculture in the country. This area often is referred to as the Corn Belt (Thurman and others, 1991; Infoplease, 2004). Most of the agricultural application of triazine herbicides in the United States is to crops in this region.

2 Summary of Significant Results From Studies of Triazine Herbicides and Their Degradation Products

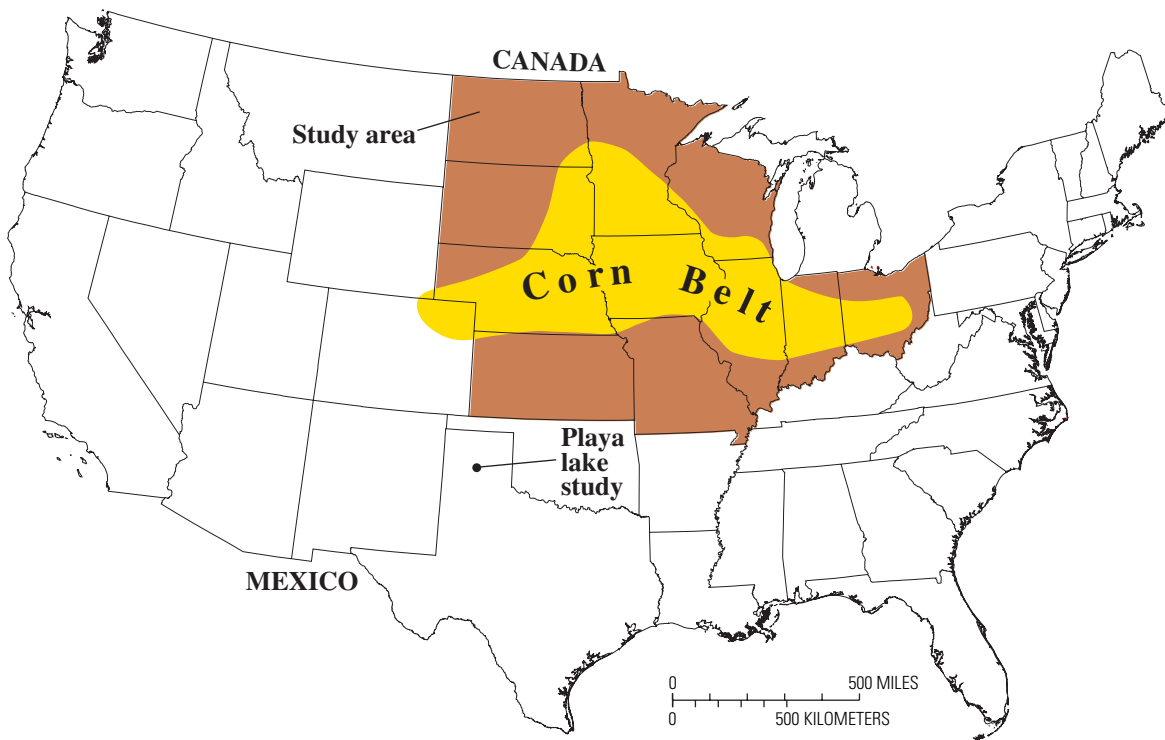


Figure 1. Location of U.S. Geological Survey Toxic Substances Hydrology Program study areas for triazine herbicides in the Midwestern United States.

The major Midwestern row crops include corn, sorghum, and soybeans, to which more than 52.8 million lb of triazine herbicides, such as atrazine, cyanazine, propazine, and simazine, were applied during 1997 (Gianessi and Marcelli, 2000). The regional-scale studies included reconnaissance of Midwestern streams, reservoirs, and ground water. Other studies were conducted to investigate herbicides dispersed by air currents, rain-fall, snow, and dry deposition.

Field-dissipation studies were conducted to examine the chemistry, fate, and transport of the triazine herbicides atrazine, cyanazine, propazine, simazine, and their degradation products in greater detail. These studies resulted in an improved understanding of the geochemical fate and transport of triazines and degradation products in hydrologic environments (Mills and Thurman, 1994a,b; Thurman and others, 1994).

USGS has emphasized analytical methods development to compliment studies of pesticide fate and transport. The USGS Organic Geochemistry Research Laboratory was established in 1987 in Lawrence, Kansas, to develop analytical methods and conduct research on the fate and transport of pesticides and their degradation products. Analytical methods developed for triazine compounds during the 1990s (table 1) included solid-phase extraction (SPE; Thurman and others, 1990; Mills and Thurman, 1992; Meyer and others, 1993; Thurman and Mills, 1998; Ferrer and others, 1999; Thurman and Snavely, 2000), gas chromatography/mass spectrometry (GC/MS; Zimmerman and Thurman, 1999; Kish and others, 2000), high-performance liquid chromatography (HPLC; Hostetler and Thurman, 2000), liquid chromatography/mass spectrometry (LC/MS; Ferrer and

others, 2000; Thurman and others, 2001; Lee and others, 2002), and enzyme-linked immunosorbent assay (ELISA; Thurman and others, 1990; Aga and Thurman, 1993; Pomes and others, 1996, 1998; Schraer and others, 2000). Analytical methods continue to be developed at the Organic Geochemistry Research Laboratory to measure concentrations of pesticides and their degradation products (Scribner and others, 2000b).

The purpose of this report is to provide a summary of triazine herbicide usage and water-quality effects, persistence, chemistry, and transport in hydrologic environments of the Midwestern United States using significant results from USGS studies conducted during the 1990s. The report also includes an extensive bibliography of publications resulting from these studies.

Triazine Herbicide Usage

Modern agricultural practices in the United States often involve widespread use of herbicides for production of crops. Because of concern about water contamination, several manufacturers voluntarily reduced the recommended application rates or, in other cases, removed herbicides from the market during the 1990s. Monitoring the effects of these usage changes is important in understanding the occurrence, persistence, chemistry, and transport of these herbicides and their degradation products.

The historical use of atrazine, cyanazine, and simazine in the Midwestern United States is shown in figure 2. In 1990, the

Table 1. Methods of analysis for triazine herbicides and their degradation products.

[SPE, solid-phase extraction; GC/MS, gas chromatography/mass spectrometry; HPLC/DAD, high-performance liquid chromatography with diode array detection; LC/MS, liquid chromatography/mass spectrometry; ELISA, enzyme-linked immunosorbent assay; x, method used; NA, not applicable]

Triazine compounds	Method				
	SPE	GC/MS	HPLC/DAD	LC/MS	ELISA
Parent compounds					
Atrazine	x	x	NA	x	x
Cyanazine	x	x	NA	x	x
Propazine	x	x	NA	x	x
Simazine	x	x	NA	x	NA
Degradation products					
Deethylatrazine	x	x	NA	x	NA
Deisopropylatrazine	x	x	NA	x	NA
Deethylhydroxyatrazine	x	NA	x	NA	NA
Deisopropylhydroxyatrazine	x	NA	x	NA	NA
Hydroxyatrazine	x	NA	x	x	NA
Cyanazine acid	x	NA	NA	x	NA
Cyanazine amide	x	x	NA	x	NA
Deethylcyanazine	x	x	NA	x	NA
Deethylcyanazine acid	x	NA	NA	x	NA
Deethylcyanazine amide	x	x	NA	NA	NA
Hydroxysimazine	x	NA	NA	x	NA

manufacturer of atrazine voluntarily reduced the maximum recommended application rate on corn and sorghum (U.S. Environmental Protection Agency, USEPA, written commun., January 23, 1990). In 1992, the maximum recommended application rate of atrazine on corn and sorghum was reduced again by the manufacturer to a range of 1.6 to 2.5 (lb a.i./acre)/yr (pounds active ingredient per acre per year) depending on soil organic residue and erosion potential. As much as 0.50 (lb a.i./acre)/yr could be used in subsequent applications (USEPA, written commun., March 8, 1993), with the total of all applications not to exceed 2.5 (a.i./acre)/yr (Scribner and others, 2000a).

As seen in figure 2, the use of atrazine decreased from about 47 million lb in 1991 to 39 million lb in 1995, fluctuating to 52 million lb in 2001, then declining sharply to 42 million lb in 2002. Besides voluntary reductions in application rates, herbicide use fluctuates in response to annual changes in planted corn and soybean acreage and the introduction of new herbicide products (U.S. Department of Agriculture, 1991–2003).

Cyanazine was historically one of the most intensively used herbicides in the country since its introduction in 1972. However, in 1996, the manufacturer of cyanazine voluntarily began reducing the maximum recommended application rate from 6.5 to 5 (lb a.i./acre)/yr to 3 (lb a.i./acre)/yr by January 1, 1999. The manufacture of cyanazine was discontinued on December 31, 1999, with distribution of existing supplies terminated in September 2002 (Tony Catka, Dupont, oral

commun., September 14, 2000). As shown in figure 2, approximately 20 million lb of cyanazine were used in the Midwestern United States in 1990, peaking at 26 million lb in 1994, then steadily declining to about 0.05 million lb usage by 2002 (U.S. Department of Agriculture, 1991–2003).

Simazine is applied to corn, primarily in Illinois, Indiana, Kentucky, Ohio, and on to the eastern seaboard. As can be seen in figure 2, simazine usage in the Midwestern United States increased from 0.80 million lb in 1990 to approximately 1 million lb in 2002 (U.S. Department of Agriculture, 1991–2003).

Propazine was voluntarily removed from the market by the manufacturer before 1990. However, there were many sorghum farmers who confirmed that propazine was still a necessary product in their region, and the manufacturer agreed to continue marketing the product to States that applied for U.S. Environmental Protection Agency (USEPA) Section 18 Emergency Exemption. For the 1993–97 growing seasons, USEPA granted Section 18 Emergency Exemptions for the use of propazine on sorghum to one or more of the following States: Colorado, Kansas, New Mexico, Oklahoma, and Texas (U.S. Environmental Protection Agency, 1998). As a result of USEPA Section 18 Emergency Exemption grants, propazine usage during 1993 was approximately 100,000 lb, increasing to approximately 360,000 lb in 1994, with a sharp decline in 1997 to 40,000 lb (Jim Bone, Griffin, L.L.C, written commun., 2005).

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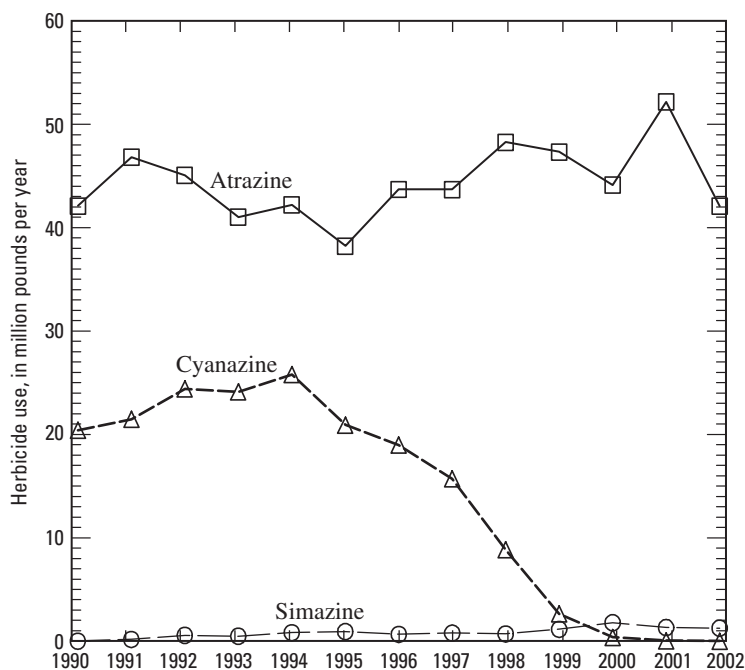


Figure 2. Triazine herbicide use in the Midwestern United States, 1990 to 2002 (data from U.S. Department of Agriculture, 1991–2003).

Water-Quality Studies

Surface Water

Since 1989, USGS has conducted periodic reconnaissance studies of streams located in the Midwestern United States to determine the occurrence, distribution, and concentrations of herbicides. The studies also included measuring concentrations of herbicide degradation products in surface-water samples to gain information about the transport and fate of herbicides in the environment (Battaglin, 2002). Sampling sites were selected at 147 USGS streamflow-gaging stations during 1989 to ensure geographic and seasonal distribution and regional-scale interpretation of the data (fig. 3). The streams were sampled before application of herbicides, during the first major runoff period after application, and during low-flow conditions in the fall when most of the streamflow was derived from ground water.

A follow-up sampling at 53 sites of the 147 sites (fig. 3) was conducted in 1990 because of increased concern about the findings of high post-application concentrations of herbicides in 1989. The distribution of major herbicide concentrations detected in these streams was essentially the same in 1989 and 1990 for both the pre- and post-application samples. Subsequent studies in 1994, 1995, 1998, and 2002 indicated that the flush of herbicides following application is an annual occurrence (Goolsby and others, 1991a, 1991b; Thurman and others, 1991, 1992; Scribner and others, 1993, 1994, 1998, 2000a, 2003; Goolsby and Battaglin, 1995; Battaglin and others, 2003, 2005).

The most striking feature of these reconnaissance data was that high concentrations of herbicides and their degradation products are mobilized by rainfall, then transported to streams with runoff. The majority of this transport takes place during the first rainfall or runoff after the application of herbicides. Subsequent runoff tends to produce lesser peaks in concentration. Because of these flushes, the detections of herbicides in larger Midwestern streams tends to be seasonal with higher percentages of detections in spring and early summer and lower percentages in fall and winter (table 2). Measurable amounts of atrazine, the most frequently detected herbicide, occurred in 91 percent of the pre-application samples and 76 percent of the harvest samples, providing an indication of its persistence in surface water. Also, deethylatrazine, a triazine degradation product, occurred more frequently in pre-application, post-application, and harvest samples than did deisopropylatrazine, also a triazine degradation product (table 2). These findings are significant because they indicate that some of the parent herbicides persist from year to year in soil and water, and that degradation products, such as deethylatrazine, both persist and are mobile. Results of studies of water samples collected from streams in eastern Iowa during the 1990s further substantiate these findings (Kalkhoff and others, 2003; Schnoebelen and others, 2003).

Herbicide concentrations in Midwestern streams were expected to change between 1989 and 2002 as a result of change in herbicide use. In 1994, 1995, 1998, and 2002 post-application runoff samples were collected at approximately 50 of the 147 sites sampled in 1989 (fig. 3). These samples were collected to assist in determining if changes in the application rates recommended by the manufacturer of atrazine had resulted in a decrease in atrazine concentrations in post-application runoff (Scribner and others, 1998, 2000a).

The percentage of samples with herbicides detected at or above the analytical reporting limit of 0.05 $\mu\text{g/L}$ was greater in 1995 than in 1989 for cyanazine and propazine, but less in 1995 than in 1989 for simazine. The detection frequency for atrazine was 100 percent for every year. The frequency of detection of deethylatrazine was the same in 1989 and 1995, but the frequency of detection of deisopropylatrazine was greater in 1995 than in 1989 (Battaglin and Goolsby, 1999; Scribner and others, 2000a).

The distribution of concentrations for surface-water samples collected during post-application runoff in 1989, 1990, 1994, 1995, 1998, and 2002 is shown in figure 4. Nondetections are plotted at the reporting limit of 0.05 $\mu\text{g/L}$. The use of atrazine and cyanazine was approximately the same in 1989 and 1995; however, the median concentrations of both herbicides were higher in 1989 than in 1995 or 2002. Although herbicide concentrations in Midwestern streams are quite variable during post-application runoff, the data suggest that changes in herbicide use do affect herbicide concentrations in streams (Battaglin and Goolsby, 1999; Scribner and others, 2000a). Studies during 1998 and 2002 of surface water in the Midwestern United States confirmed that herbicide degradation products were found to occur as frequently or more frequently and at concentrations

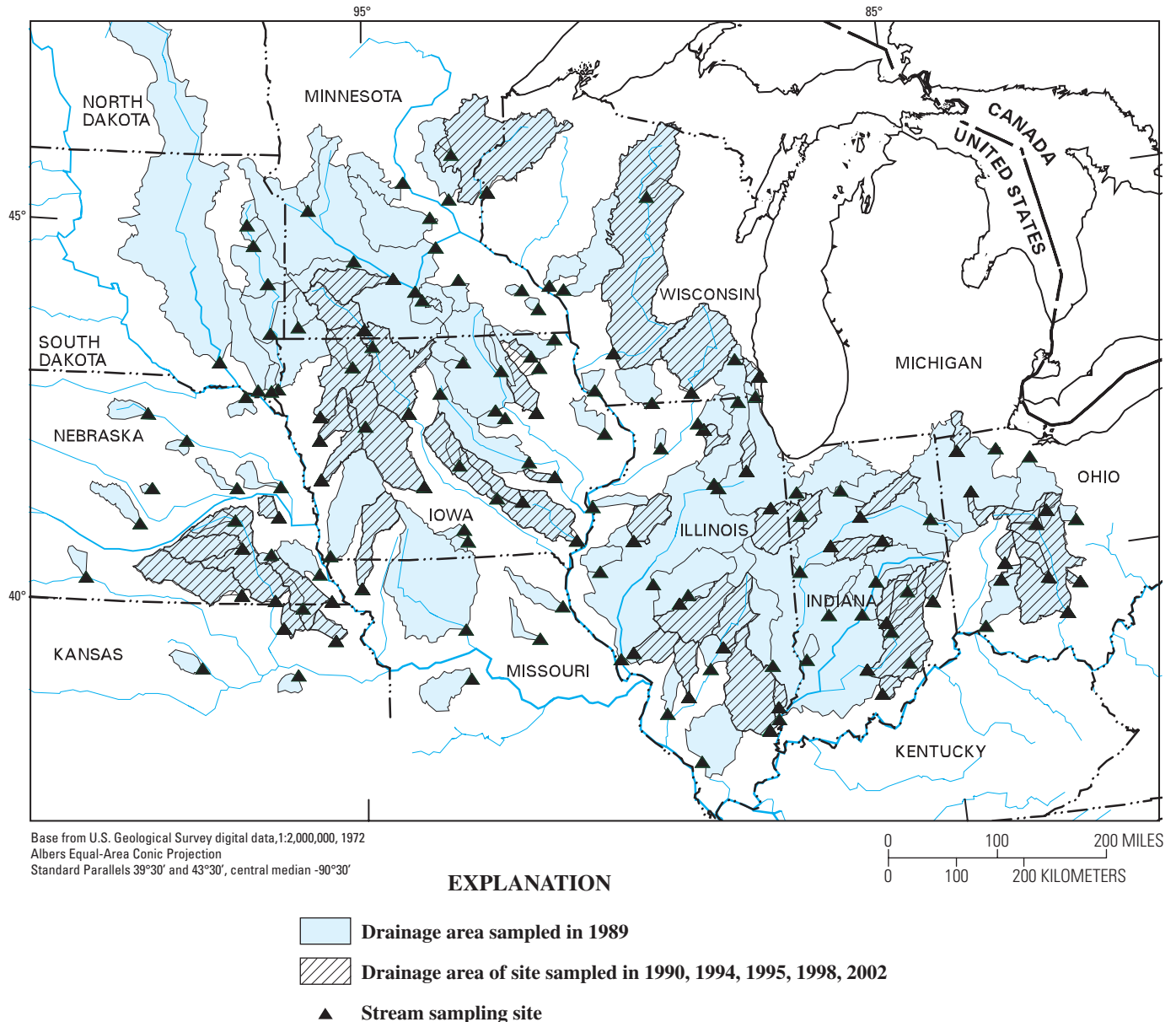


Figure 3. Location of study area, hydrologic units, and 147 sites sampled during 1989–2002 in the Midwestern United States.

that were frequently higher than the parent herbicides (Battaglin and others, 2003, 2005; Scribner and others, 2003).

In the summer of 1993, a persistent wet-weather pattern resulted in flooding in the upper Mississippi River Basin. Concentrations of selected herbicides were measured at several locations on the Mississippi River during this flood and in adjacent shallow wells after the floodwaters receded. These studies determined that record flooding did not dilute the concentrations of herbicides as expected. Instead, concentrations of herbicides such as atrazine were similar to those seen during normal spring and summer flows (Goolsby and others, 1993; Kolpin and Thurman, 1995).

Surface-water reservoirs in the Midwestern United States were also the focus of USGS studies as they are an integral

component of the supply, management, and quality of water resources in the United States. Many reservoirs are designed to catch and retain spring and early summer runoff for recreation, water supply, flood control, or irrigation use. Regional studies have shown that this water contains elevated concentrations of herbicides and their degradation products for several months of the year (Leonard, 1988; Baker and Richards, 1989; Pereira and Rostadt, 1990; Thurman and others, 1991, 1992; Squillace and Thurman, 1992; Goolsby and others, 1996; Battaglin and Goolsby, 1998). USGS designed a monitoring network of 76 hydrologically representative reservoirs (fig. 5) in the Midwestern United States described in Scribner and others (1996). Reservoir outflows were sampled eight times from April 1992 through September 1993 for a total of 608 samples. The timing

6 Summary of Significant Results From Studies of Triazine Herbicides and Their Degradation Products

Table 2. Percentage of detections of triazine herbicides and degradation products in surface-water samples collected from selected streams in the Midwestern United States during 1989 and 1990 (from Thurman and others, 1991).

[n= total number of samples analyzed; <, less than]

Triazine compound	Percentage of detections		
	Pre-application samples (n=53)	Post-application samples (n=132)	Harvest samples (n=145)
Parent compound			
Atrazine	91	98	76
Cyanazine	5	63	0
Propazine	0	40	<1
Simazine	7	55	3
Degradation product			
Deethylatrazine	54	86	47
Deisopropylatrazine	9	54	0

and frequency of sampling made it possible to determine approximately when maximum and minimum concentrations of herbicides occurred in the reservoir outflows (Stamer and others, 1998a).

One of the most significant findings from this study is the abundance and persistence of triazine herbicides and their degradation products in reservoirs. In many reservoirs, concentrations of atrazine and its degradation products remained elevated all summer and into the fall (Stamer and Zelt, 1992; Thurman and Fallon, 1996; Stamer and others, 1998a). As shown in table 3, atrazine occurred at the highest frequency (82.1 percent) and in the highest detectable concentration with a mean of 1.36 $\mu\text{g/L}$, whereas cyanazine was detected in only 47.2 percent of samples with a mean detectable concentration of 0.61 $\mu\text{g/L}$ (Stamer and others, 1998a).

As reported by Goolsby and others (1996), atrazine, deethylatrazine, and deisopropylatrazine were detected in more than one-half of the reservoirs during the fall sampling, whereas only atrazine was detected in more than one-half of the streams sampled in the fall of 1989. Another notable difference between the occurrence of herbicides in reservoirs and streams was the much greater frequency of detection of cyanazine and deisopropylatrazine in reservoirs. Neither cyanazine nor deisopropylatrazine was detected in streams during the fall because these compounds were no longer present in significant amounts on the agricultural fields where they were applied.

A detailed study of Perry Lake in northeast Kansas (fig. 5) was completed during 1992–93 by Fallon and others (2002). Water samples were collected monthly from four locations upstream and downstream from the reservoir, as well as within the reservoir throughout the year and from runoff during April to August (Thurman and Fallon, 1996; Fallon and others, 2002).

Three-dimensional images of the distribution of atrazine concentrations in Perry Lake during 1992 showed that recently applied atrazine mixed with atrazine applied the previous year as water moved through the reservoir (fig. 6). Relations between atrazine and the degradation product, deethylatrazine, indicated whether the atrazine in the reservoir had been flushed off the fields immediately prior to sampling or from the preceding year. Changes in atrazine concentrations in the reservoir resulted from several factors, including herbicide application, which fueled and reset the system, and precipitation, which drove the system by flushing atrazine into the reservoir and determining the residence time of water in the reservoir. Concentrations varied between the main inflow and the public water supply intakes located at the opposite ends of the reservoir. The concentration range in the outflow varied much less than concentrations in the upstream parts of the reservoir because of mixing (Fallon and others, 2002).

The frequency of occurrence, concentrations, both annual average and peak, and loads of pesticides in streams or reservoir outflows is related to the magnitude of the herbicide use in the upstream drainage areas. In most cases, the annual loss of herbicides to streams represents less than 5 percent of the amount applied. Pesticide losses are also affected by soils, climate, land cover, other basin characteristics, and management or application techniques. These studies demonstrate the strength of relations between the use of herbicides and their occurrence in streams and reservoirs (Battaglin and Goolsby, 1995, 1997, 1998; Clark and others, 1999; Clark and Goolsby, 2000).

Ground Water

During the 1990s, the Midwestern United States was also the focus of research on agricultural chemical contamination in ground water. A series of studies by USGS began in 1991 to investigate the occurrence of agricultural herbicides in near-surface aquifers of the Midwestern United States. To improve understanding of the movement and distribution of agricultural chemicals in ground water, USGS designed (Kolpin and Burkhart, 1991) a reconnaissance network that was geographically and hydrogeologically representative of near-surface aquifers in the corn- and soybean-producing region of the Midwestern United States (Burkart and Kolpin, 1993; Kolpin and others, 1994, 1996b; Thurman and others, 1998).

The objectives of the study were to determine the hydrogeological and seasonal distribution of herbicides in near-surface aquifers, determine the statistical relations of agricultural herbicides to natural factors, and obtain data on agricultural herbicide concentrations in ground water from geographic areas where few data existed (Burkart and Kolpin, 1993; Kolpin and others, 1994, 1996a). The report that sets the stage for these studies is Kolpin and others (1993a), which describes locations, detailed land use, and local features surrounding 303 wells sampled in the Midwestern United States during 1991 (fig. 7). During the summer of 1992, additional water samples were collected from 101 of the 303 wells to

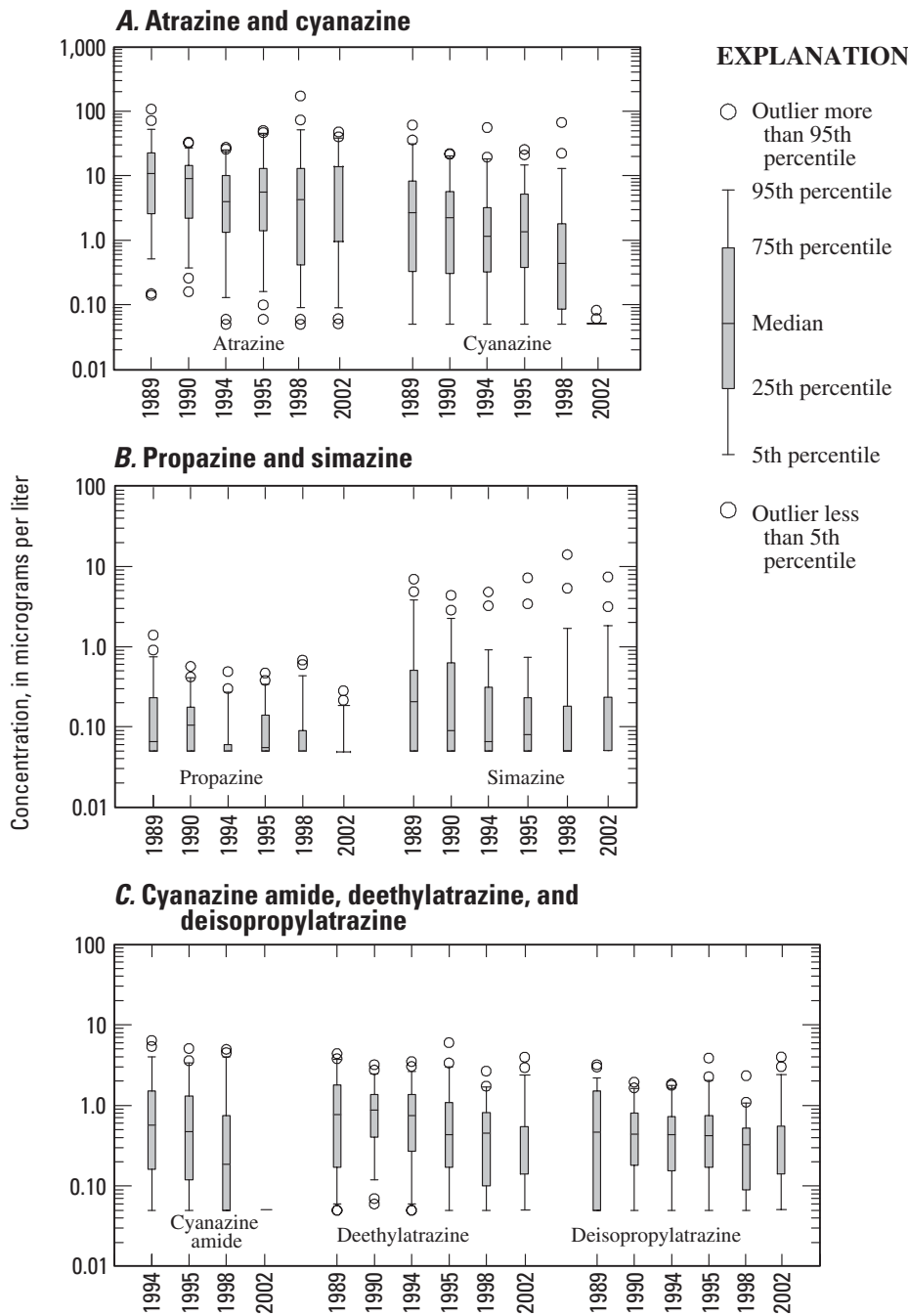


Figure 4. Concentrations in surface-water samples collected from 53 Midwestern streams during post-application runoff in 1989, 1990, 1994, 1995, 1998, and 2002 for (A) atrazine and cyanazine, (B) propazine and simazine, and (C) cyanazine amide, deethylatrazine, and deisopropylatrazine (data for 1989–98 from Scribner and others, 2000a; data for 2002 from Battaglin and others, 2003).

examine the occurrence of triazine herbicides and their degradation products not analyzed in 1991 (Kolpin and others, 1993b, 1995). Herbicides and their degradation products were detected in water samples from 28.4 percent of the 303 wells sampled during 1991. During 1992, herbicides and their degradation products were detected in 62 percent of the 101 wells sampled. The greater frequency of detection during 1992 was due primarily to the increased number of herbicide degradation products examined and a more sensitive analytical method that was available (Kolpin and others, 1993b, 1995, 1996b).

Although numerous studies were conducted during the early 1990s to investigate the occurrence of herbicides in

ground water, few had considered the degradation products of these herbicides. Information on degradation products is essential to fully understand the fate and occurrence of the parent herbicides and to determine the complete consequences of herbicide use on human health and the environment (Kolpin and others, 1995). Triazine degradation products, deethylatrazine and deisopropylatrazine, commonly were found in shallow aquifers across the Midwestern United States. As shown in table 4, during 1991, deethylatrazine (21.4 percent) was detected more frequently than its parent compound atrazine (20.8 percent) even though deethylatrazine had a higher reporting limit than atrazine, whereas deisopropylatrazine was

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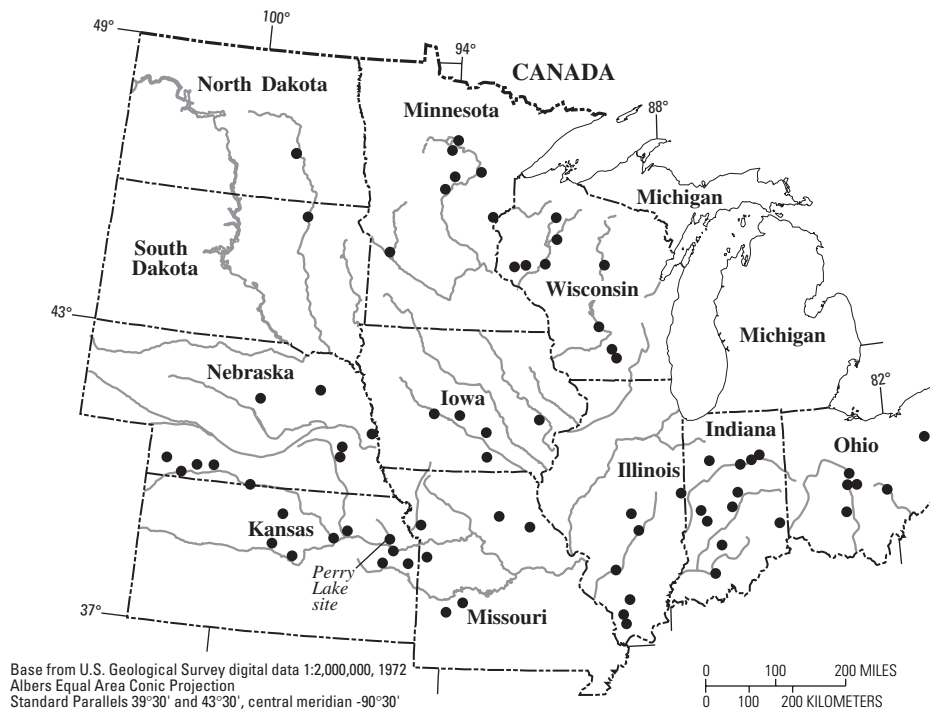


Figure 5. Location of 76 reservoirs sampled for herbicide analysis in the Midwestern United States during 1992 and 1993 (from Scribner and others, 1996).

Table 3. Triazine herbicides and their degradation products analyzed in samples collected from 76 Midwestern reservoir outflows, April 1992 through September 1993 (from Stamer and others, 1998a).

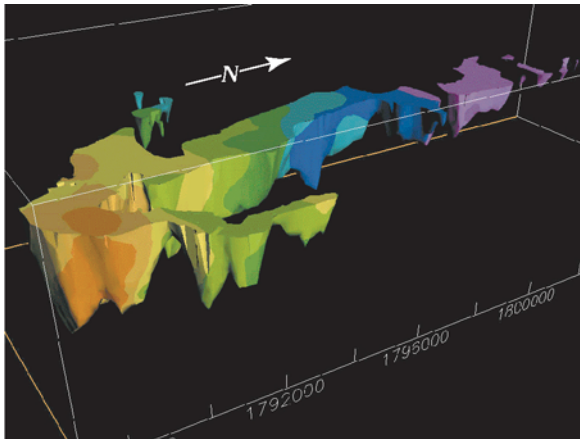
[$\mu\text{g/L}$, micrograms per liter; n, number of samples; <, less than]

Herbicide or degradation products	Reporting limit ($\mu\text{g/L}$)	Percentage of samples with detections	Median concentrations ($\mu\text{g/L}$)	Mean of samples with detectable concentrations ($\mu\text{g/L}$)
Herbicides (n=608)				
Atrazine	0.05	82.1	0.43	1.36
Cyanazine	.05	47.2	<.05	.61
Propazine	.05	4.1	<.05	.10
Simazine	.05	19.7	<.05	.21
Herbicide degradation products (n=511)				
Cyanazine amide	.05	49.3	<.05	.43
Deethylatrazine	.05	71.6	.17	.39
Deisopropylatrazine	.05	61.8	.08	.26
Deethylcyanazine	.05	25.2	<.05	.14
Deethylcyanazine amide	.05	2.0	<.05	.62

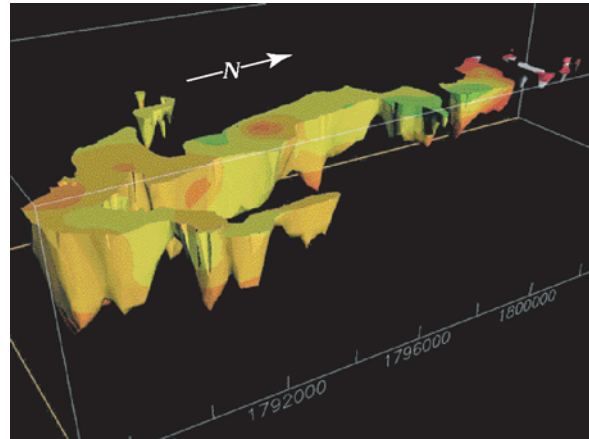
detected in 7.6 percent of the samples. In 1992 (table 4), deethylatrazine was detected in 31 percent, atrazine in 43 percent, and deisopropylatrazine in 18 percent of the samples collected. The reporting limits for atrazine and deethylatrazine were lower in 1992 than in 1991. The fact that deethylatrazine was detected more frequently than deisopropylatrazine supports conclusions from field-dissipation studies during the 1990s that deethylation

is the more stable, biotic degradation pathway (Adams and Thurman, 1991; Kolpin and others, 1994).

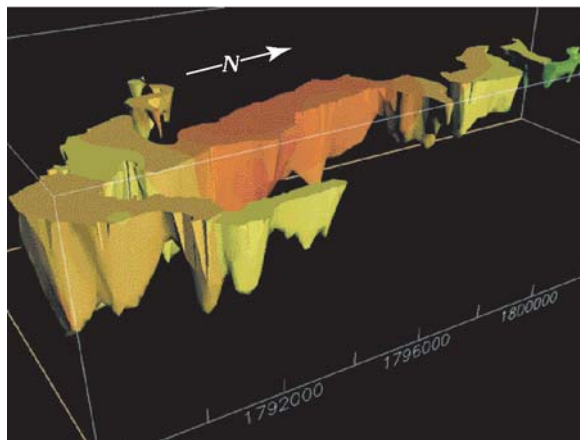
Cyanazine was used extensively during the early 1990s but was detected in only 1.3 percent of the water samples in 1991 and 3.0 percent of the water samples in 1992 (table 4). A method for cyanazine amide, a degradation product of cyanazine, was used to analyze water samples collected during 1992.



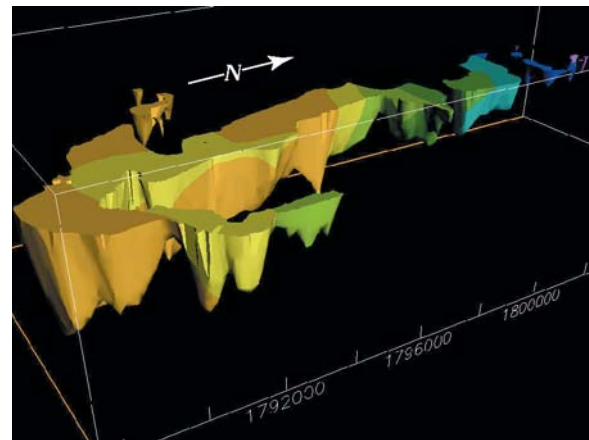
(A) Pre-application survey, March 30 to April 10, 1992



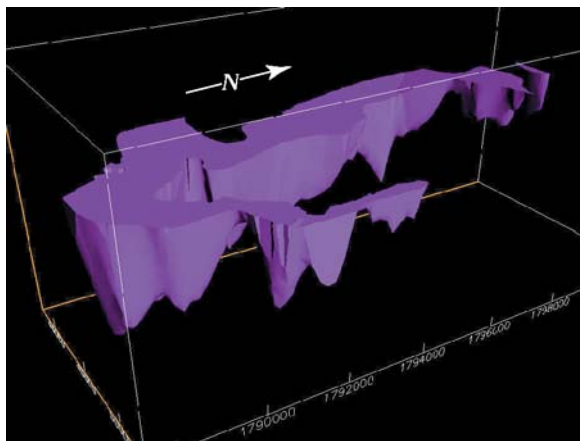
(B) First flush survey, June 16 to 25, 1992



(C) Summer survey, August 3 and 4, 1992



(D) Fall survey, September 16 to 22, 1992



(E) Pre-application survey, March 25 to 29, 1993

EXPLANATION

Triazine concentration, in micrograms per liter

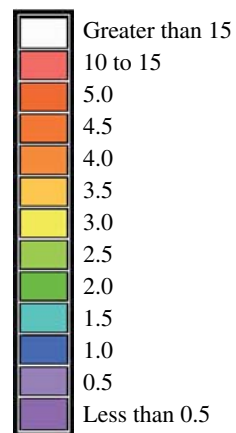


Figure 6. Three-dimensional computer images of atrazine concentrations in Perry Lake, northeastern Kansas, during (A) 1992 pre-application, (B) first flush, (C) summer, (D) fall, and (E) 1993 pre-application surveys (from Fallon and others, 2002).

10 Summary of Significant Results From Studies of Triazine Herbicides and Their Degradation Products

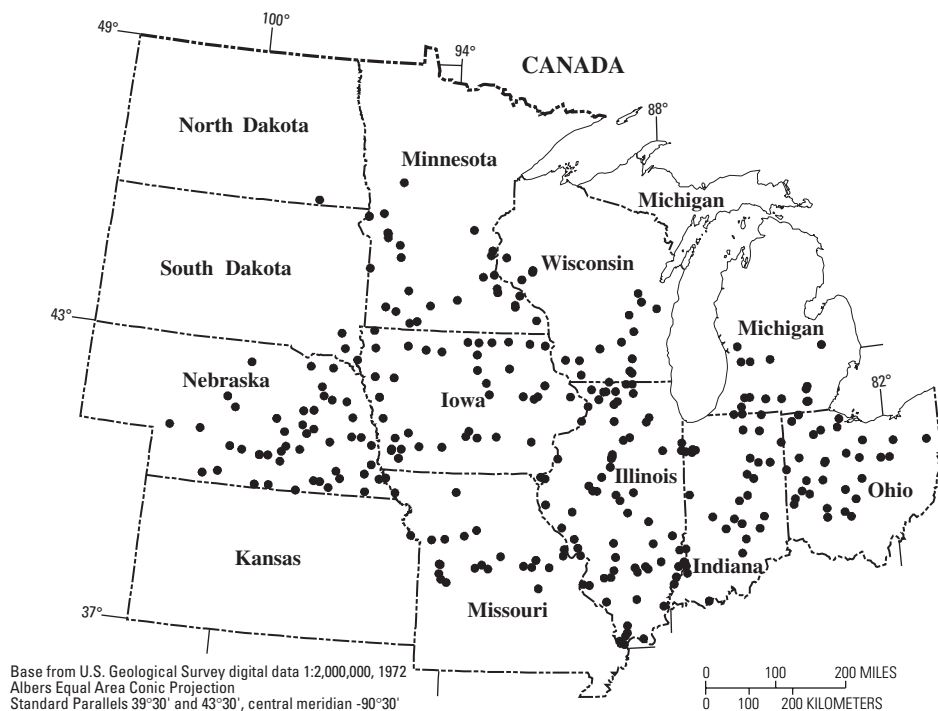


Figure 7. Location of wells in the U.S. Geological Survey Midwestern ground-water monitoring network sampled during 1991–94 (from Kolpin and others, 1995).

Table 4. Summary of analytical results for triazine herbicides and their degradation products in ground-water samples collected from wells in the Midwestern United States during 1991–93 (from Kolpin and others, 1993b, 1994; Kolpin and Thurman, 1995).

[$\mu\text{g/L}$, micrograms per liter; NA, not applicable]

Triazine compound	1991			1992			1993		
	Percentage of detection	Maximum concentration ($\mu\text{g/L}$)	Reporting limit ($\mu\text{g/L}$)	Percentage of detection	Maximum concentration ($\mu\text{g/L}$)	Reporting limit ($\mu\text{g/L}$)	Percentage of detection	Maximum concentration ($\mu\text{g/L}$)	Reporting limit ($\mu\text{g/L}$)
Parent compound									
Atrazine	20.8	2.1	0.05	43.0	1.0	0.005	23.6	1.8	0.05
Cyanazine	1.3	.68	.05	3.0	.02	.008	3.6	.88	.05
Simazine	1.6	.27	.05	13.0	.07	.005	NA	NA	NA
Degradation product									
Cyanazine amide	NA	NA	NA	9.3	.55	.05	NA	NA	NA
Deethylatrazine	21.4	2.3	.05	31.0	1.8	.015	23.6	1.7	.05
Deisopropylatrazine	7.6	1.2	.05	18.0	.28	.05	13.6	.48	.05

As shown in table 4, cyanazine amide was detected in 9.3 percent of the samples with a maximum concentration of 0.55 $\mu\text{g/L}$ (Kolpin and others, 1995). This greater frequency of detection suggests an increase in degradation product mobility to ground water after transformation from cyanazine. Cyanazine may degrade to deisopropylatrazine by the loss of a cyanoisopropyl group (Meyer, 1994; Thurman and others, 1994; Meyer and others, 2001). Simazine was detected in 1.6 percent of the samples in 1991 and 13 percent in 1992 (table 4). A study by Mills and Thurman (1994a) showed that

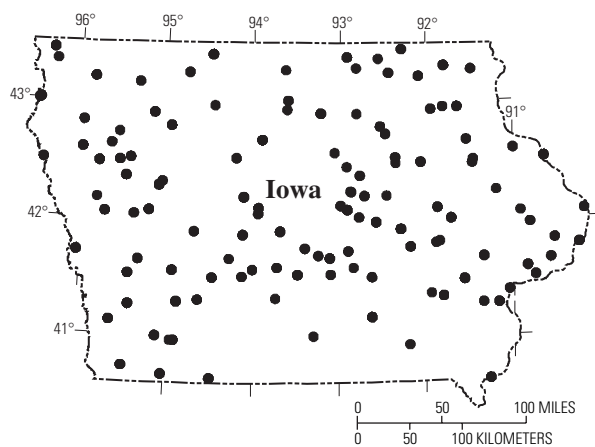
atrazine, cyanazine, and simazine also can degrade to deisopropylatrazine. The dealkylation of simazine to deisopropylatrazine contributes to the amount of deisopropylatrazine as it may degrade by two pathways to deisopropylatrazine (Mills and Thurman, 1992).

Water samples were collected during September and October from 110 wells during the historic 1993 flooding in the Mississippi River Basin (Goolsby and others, 1993; Kolpin and others, 1996b). There was a direct relation between increases in total herbicide concentration (between pre-flood and post-flood

samples) and the occurrence of stream flooding near wells (Kolpin and Thurman, 1995; Kolpin and others, 1996b). More than 60 percent of the wells that had at least a 20-percent increase in total herbicide concentration in water samples were located in areas that also were affected extensively by stream flooding. Water in shallow wells more quickly reflected changes in water quality in response to changes in recharge from the 1993 flooding than did deeper wells (Kolpin and others, 1996b). Of the 110 wells sampled, 30 were reported to be unaffected by flooding or intense rainfall, 45 were affected by stream flooding, and another 35 were affected by standing water from rainfall.

Results from these samples were compared with those samples obtained during 1991 and 1992 from the same wells. As shown in table 4, there was no statistically significant difference in either the frequency of herbicide detection or total herbicide concentration between the previous samples and those collected for the 1993 study (Kolpin and Thurman, 1995). An additional study during July to August 1994 of samples collected from 38 wells showed that herbicides and their degradation products were detected in water from 76 percent of the wells (Kolpin and others, 1996b).

An investigation of samples collected from 131 municipal wells completed in all the major aquifer types in Iowa (fig. 8) from 1995 to 1998 was made to compare the occurrence of herbicide degradation products in ground water with that of their parent compounds. An important finding of this study was the high frequency with which degradation products were detected in ground water (Kolpin and others, 1997, 1998, 2000). During 1995, more than one herbicide compound was detected in samples from 44 of the wells, with as many as nine compounds being detected in a single sample (Kolpin and others, 1997). Table 5 summarizes analytical results from 1995 through 1998. Atrazine is the only herbicide for which the parent compound was found more often than any of its degradation products. This



EXPLANATION

- Well sampled during 1995–98

Figure 8. Location of wells sampled in Iowa during 1995–98 (from Kolpin and others, 2000).

Table 5. Summary of analytical results for triazine herbicides and their degradation products in samples collected from 131 Iowa wells during 1995–98 (from Kolpin and others, 2000).

[$\mu\text{g/L}$, micrograms per liter]

Triazine compound	Percentage detection	Maximum concentration ($\mu\text{g/L}$)	Reporting limit ($\mu\text{g/L}$)
Parent compound			
Atrazine	37.4	2.1	0.05
Cyanazine	6.1	.51	.05
Simazine	0	0	.05
Propazine	0	0	.05
Degradation product			
Cyanazine amide	19.8	.64	.05
Deethylatrazine	32.1	.59	.05
Deisopropylatrazine	21.4	1.1	.05
Hydroxyatrazine	11.4	1.3	.20

could be because of the greater environmental stability of atrazine compared to the other parent compounds under investigation. Although herbicides commonly were detected, their frequencies of detection and concentrations varied significantly among the major aquifer types samples. These differences were much more pronounced when herbicide degradation products were included (Kolpin and others, 2000). Aquifer types presumed to have the most rapid recharge rates were those most likely to contain detectable concentrations of herbicides, indicating that ground-water age could be an important factor in explaining these variations in herbicide contamination (Kolpin and others, 2000). This study demonstrated that obtaining data on herbicide degradation products is critical for understanding the fate of herbicides in the hydrologic system (Kolpin and others, 2000).

A large-scale investigation of the occurrence of cyanazine and its degradation products, cyanazine acid, cyanazine amide, deethylcyanazine, and deethylcyanazine acid in samples from 64 Iowa wells was conducted during 1999. Cyanazine was detected in only 3.1 percent of wells sampled, but its degradation products were commonly detected, deethylcyanazine acid (32.8 percent), followed by cyanazine acid (29.7 percent), cyanazine amide (17.2 percent), and deethylcyanazine (3.1 percent) (Kolpin and others, 2001). The more frequent presence of cyanazine acid and cyanazine amide compared to cyanazine is in agreement with the reported greater stability of these degradation products after transformation from cyanazine (Ferrer and others, 2000; Kolpin and others, 2001). Thus, the results of the study emphasized that data on the cyanazine degradation products are critical for understanding its fate and transport in the hydrologic system (Kolpin and others, 2001).

As a continuation of the Iowa study, ground-water wells were sampled and analyzed for 21 herbicides and 24 herbicide degradation products during 2001. The frequency of detection increased from 17 percent when only herbicide parent

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compounds were considered to 53 percent when both herbicide parent compounds and degradation products were considered. A significant difference in results among the major aquifer types was apparent when both herbicide parent compounds and their degradation products were considered (Kolpin and others, 2004).

The ground-water samples collected across the Midwestern United States and in Iowa from 1991 through 2001 consistently revealed that triazine herbicide degradation products commonly were found more frequently than their parent herbicide, the frequency of herbicide detection was, in part, affected by a more sensitive analytical method, and ground-water age could be an important factor in explaining variations in herbicide contamination (Kolpin and others, 1994, 1996a, 2000, 2004).

Precipitation

During the late spring and summer of 1990 and 1991, another USGS study focused on herbicides transported in the atmosphere by various processes. In the atmosphere, these compounds can be dispersed by air currents and redeposited on the land surface, lakes, and streams by rainfall, snow, and dry deposition, often at considerable distances from their source areas. Triazine herbicides were reported in precipitation in the Midwestern United States by Goolsby and others (1997), which highlighted the major findings of this study. The report that describes the location of the study area, background areas, and sampling sites is Goolsby and others (1995).

Herbicide concentrations exhibited distinct geographic and seasonal patterns. The highest concentrations occurred in the Midwestern United States following herbicide application to cropland. The highest concentrations occurred following herbicide application to cropland. Rainfall-weighted concentrations of 0.20 to 0.40 µg/L for atrazine were typical

throughout the Midwest, and weighted concentrations as large as 0.60 to 0.90 µg/L occurred in precipitation at several sites. Concentrations of 1.0 to 3.0 µg/L were measured in a few individual samples. Atrazine was detected most often, followed by deethylatrazine, cyanazine, and deisopropylatrazine.

Table 6 contains a summary of the concentrations of triazine herbicides detected in 6,230 precipitation samples screened by enzyme-linked immunosorbent assay and then confirmed in 2,085 of the samples using gas chromatography/mass spectrometry (Pomes and others, 1998). The most frequently detected herbicide was atrazine, which was present in 30.2 percent of the samples analyzed by gas chromatography/mass spectrometry, followed by deethylatrazine at 17.4 percent. Cyanazine was detected in 7.2 percent of the samples. Although herbicides were detected in a significant number of samples, concentrations were relatively small (Goolsby and others, 1997; Stamer and others, 1998b; Thurman and Cromwell, 2000).

Because of the large temporal and spatial variation in the amount of rainfall, it is difficult to make meaningful comparisons of herbicide concentrations among sites or over time on the basis of individual samples. Instead, comparisons were made with rainfall-weighted concentrations. Overall, the spatial patterns of the weighted atrazine concentrations in 1990 and 1991 were similar and generally reflected the intensity of the use of atrazine. The total amount of atrazine deposited annually in precipitation in the study area represented about 6 percent of the atrazine applied annually to crops in the study area (Goolsby and others, 1997).

The study showed that the occurrence of atrazine in rainfall is highly seasonal. The detection frequency began to increase in mid-April following application of herbicides to cropland and peaked in late May or early June. Atrazine was detected in low concentrations at sites remote from cropland, such as Maine and Isle Royale in northern Lake Superior (Stamer and others, 1998b; Thurman and Cromwell, 2000).

Table 6. Summary of analytical results for triazine herbicides and their degradation product concentrations measured in precipitation samples from 81 sites across the Midwestern and Northeastern United States from March 1990 through September 1991 (from Goolsby and others, 1997).

[ELISA, enzyme-linked immunosorbent assay; GC/MS, gas chromatography/mass spectrometry; n, total number of samples analyzed; µg/L, micrograms per liter; <, less than; --, not determined]

Triazine compound	Percentage of detections	Concentration (µg/L) for indicated percentiles ¹				
		75th	90th	95th	99th	100 (maximum)
ELISA analysis (n=6,230)						
Triazine compounds	25.5	0.10	0.24	0.42	1.3	16
GC/MS analysis (n=2,085)						
Atrazine	30.2	.07	.23	.40	1.0	11
Cyanazine	7.2	--	<.05	.07	.27	2.0
Deethylatrazine	17.4	<.05	.11	.15	.39	.75
Deisopropylatrazine	2.6	--	--	<.05	.17	1.2
Simazine	1.5	--	--	<.05	.07	1.5

¹Reporting limits are 0.10 µg/L for triazine compounds analyzed by ELISA and 0.05 µg/L for all compounds analyzed by GC/MS.

Chemistry and Transport of Triazine Herbicides in Water

Degradation pathways may be followed from herbicide application on the soil to its entrance into an aquifer. These degradation pathways depend on the characteristics of the transport pathway (Adams and Thurman, 1991). Herbicides derived from point and nonpoint sources can be transported to streams by runoff from agricultural and urban areas, discharge from reservoirs and aquifers, and precipitation (Goolsby and others, 1993). The physiochemical properties of the triazine herbicides as well as the soil half-life and such factors as intensity of use, application methods, timing, intensity, duration of rainfall, and antecedent soil moisture conditions are also important in determining the amount of herbicides that can be transported into streams. Physiochemical properties shown in table 7 indicate that soluble and mobile herbicides, such as atrazine, cyanazine, propazine, and simazine are transported primarily in the dissolved phase.

Water solubility determines how easily herbicides wash off soil and crop residues and leach through the soil. Herbicides with solubilities greater than about 30 mg/L are likely to wash off the soil, whereas those with solubilities less than 1 mg/L are likely to remain on the soil surface during storms (Becker and others, 1989). The soil sorption coefficient (K_{oc}) is a measure of the tendency of a herbicide to sorb to soil particles. The larger the K_{oc} value, the more strongly the herbicide will be adsorbed to soil particles. Those herbicides with K_{oc} values less than about 500 mL/g tend to be transported primarily in the dissolved phase, whereas K_{oc} values greater than 1,000 mL/g are transported primarily on suspended-sediment particles (Becker and others, 1989; Goolsby and others, 1993). Half-life in soil is the length of time required for herbicides to degrade in the soil to one-half of their previous concentration. The longer the soil half-life, the more persistent the herbicide is, and the longer it will be available to wash off in storm runoff. Once herbicides are in surface water, the half-life generally is much longer than in soil because surface water contains much less organic matter and fewer microorganisms to degrade the herbicides (Goolsby and others, 1993). The water solubility of deethylatrazine is 670 mg/L and for deisopropylatrazine is 3,200 mg/L. The water

solubilities of triazine degradation products increase as carbon atoms are removed by dealkylation (Mills and Thurman, 1994a). The result is that the degradation products are more soluble and mobile than the parent compound.

A study of selected triazine herbicides and their degradation products was designed to define the relative rates and transport mechanisms of four parent triazine herbicides—atrazine, cyanazine, propazine, simazine—and two triazine degradation products—deethylatrazine and deisopropylatrazine—in the unsaturated zone and in surface runoff (Meyer, 1994; Mills and Thurman, 1994a; Thurman and others, 1994; Meyer and Thurman, 1996). This choice of parent herbicides was used because each degradation product had two parent herbicide sources, each source requiring the removal of either an ethyl or an isopropyl side chain. As shown by figure 9, atrazine and propazine degrade to deethylatrazine by deethylation and deisopropylation. Similarly, atrazine, cyanazine, and simazine can all dealkylate to deisopropylatrazine by removal of an isopropyl and ethyl side chain. Differences in the concentration of the dealkylated degradation product from the two different sources should indicate any preferential removal of ethyl versus isopropyl side chain. Furthermore, because deethylatrazine and deisopropylatrazine have different side chains remaining, their relative rate of removal should provide additional information on the stability of the ethyl side chain versus an isopropyl side chain (Thurman and others, 1994).

The dealkylation field study found the preferential removal of an ethyl side chain from atrazine relative to the removal of an isopropyl side chain. The high ratio of deethylatrazine to atrazine, referred to as the DAR, in shallow soil is evidence that simazine may degrade more rapidly to deisopropylatrazine (ethyl side chain removal) than propazine to deethylatrazine (isopropyl side chain removal). Furthermore, deethylation rates of atrazine and simazine are comparable, and approximately two to three times more rapid than the rates of deisopropylation from atrazine and propazine. This indicates that the removal of an ethyl side chain is preferential over an isopropyl side chain, regardless of parent triazine compound. Continued dealkylation of the degradation products in the unsaturated zone, where the parent compound is removed, also shows a preferential removal of ethyl side chains over isopropyl side chains, as deisopropylation can occur to a significant

Table 7. Physiochemical properties of triazine herbicides (from Goolsby and others, 1993).

[mg/L, milligrams per liter; mL/g, milliliters per gram; pKa, negative logarithm of the acid dissociation constant; mPa, millipascal]

Triazine herbicide	Water solubility (mg/L)	Soil sorption coefficient (K_{oc} , mL/g)	pKa	Soil half-life (days)	Vapor pressure (mPa)
Atrazine	33	100	1.7	60	0.04
Cyanazine	170	190	1.7	14	.0002
Propazine	5	154	1.7	45	.004
Simazine	6.2	138	1.6	75	.000810

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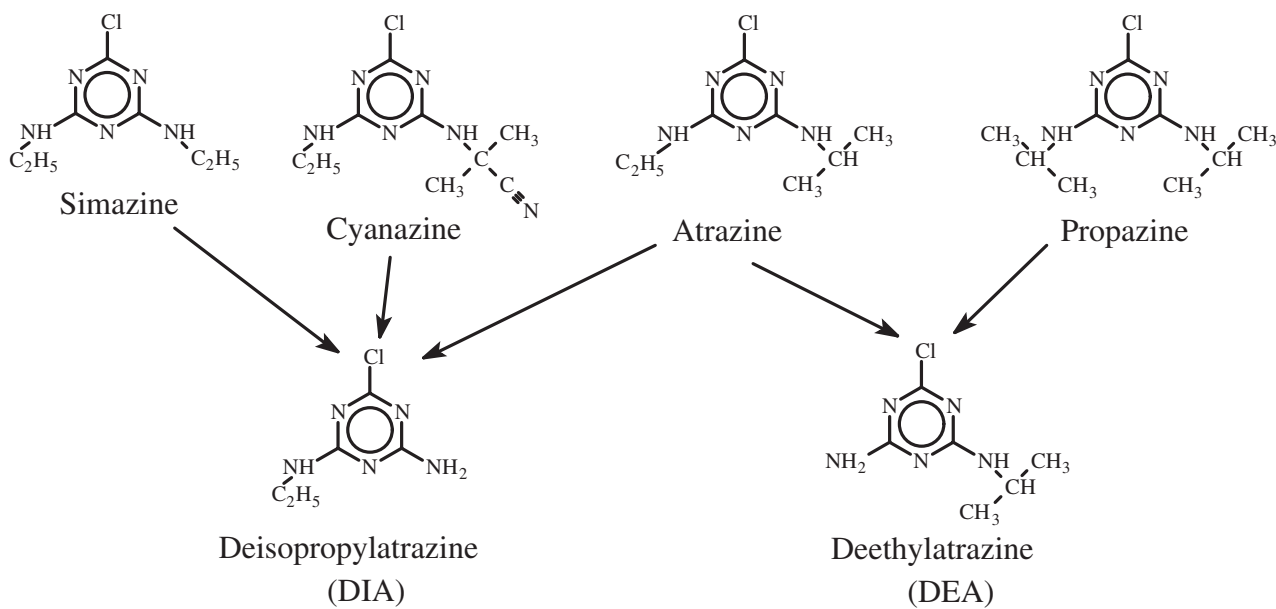


Figure 9. Degradation pathways for atrazine, cyanazine, propazine, and simazine to deethylatrazine and (or) deisopropylatrazine (from Thurman and others, 1994).

degree in the unsaturated zone. Therefore, the small concentrations of deisopropylatrazine commonly reported in the environment do not result purely from a smaller production of the degradation product but also to the more rapid removal of the isopropyl group once produced. The substantial turnover rate of deisopropylatrazine in the environment is evidence for the presence of a didealkylated degradation product in the unsaturated zone. The data supporting these conclusions are presented in Mills and Thurman (1994a).

To understand the geochemistry of the deethylatrazine-to-atrazine ratio (DAR) as an indicator of surface-water and ground-water interaction, it is valuable to compare the degradation product deethylatrazine to atrazine. The resulting ratio is called the DAR and is defined by Adams and Thurman (1991):

$$\text{DAR} = \frac{[\text{deethylatrazine, mol/L}]}{[\text{atrazine, mol/L}]} \quad (1)$$

The DAR may be a valid indicator of soil-mediated transport of atrazine to an aquifer. A DAR of unity (1.0) or greater could be an indicator of nonpoint-source contamination of an aquifer (Adams and Thurman, 1991), whereas a small DAR may be an indicator of point-source contamination of an aquifer. In clay- and silt-loam plots, the average concentrations of atrazine in the soil were about four times higher than the average concentrations of deethylatrazine. The concentrations of deethylatrazine, however, were significantly higher than the concentrations of atrazine in soil-water lysimeter samples collected at about the same time as the cores were collected (Adams and Thurman, 1991). These results indicate that atrazine is absorbed more strongly than deethylatrazine in clay- and silt-loam soils. Thus, the recharging ground water has a higher

concentration of deethylatrazine than atrazine giving rise to DAR values greater than 1.0 (Adams and Thurman, 1991).

The conversion of atrazine to deethylatrazine is primarily the result of the metabolic activity of soil bacteria and fungi. In the case of nonpoint-source contamination, soil microorganisms can convert significant quantities of atrazine to deethylatrazine, thereby increasing the DAR. Conversely, point-source contamination resulting from direct entry of atrazine into an aquifer by a natural or artificial conduit would not involve prolonged contact of the applied atrazine with soil microorganisms. In such a point-source-contamination occurrence, soil microorganisms would have little opportunity to degrade to deethylatrazine. Therefore, in the case of point-source contamination, the DAR may be expected to be much less than unity; that is, the concentration of deethylatrazine would be less than that of atrazine in the aquifer (Adams and Thurman, 1991).

The DAR hypothesis is predicated on the assumption that atrazine degrades slowly in an aquifer because of low organic carbon concentrations, small microbial populations, and anaerobic conditions. This is substantiated by Wehtje and others (1983) who determined that, under aquifer conditions, atrazine did not undergo deethylation or deisopropylation and only slowly underwent abiotic degradation to deisopropylhydroxyatrazine.

Adams and Thurman (1991) found that atrazine transport through the unsaturated zone gave DAR values greater than 1.0, whereas atrazine transported off the field by surface runoff had DAR values much less than 1.0. Deisopropylatrazine was rapidly degraded in the unsaturated zone but was an important persistent degradation product in surface runoff from the fields. Thus, the DAR may be an indicator of ground-water recharge by atrazine-laden water. Figure 10 shows that the

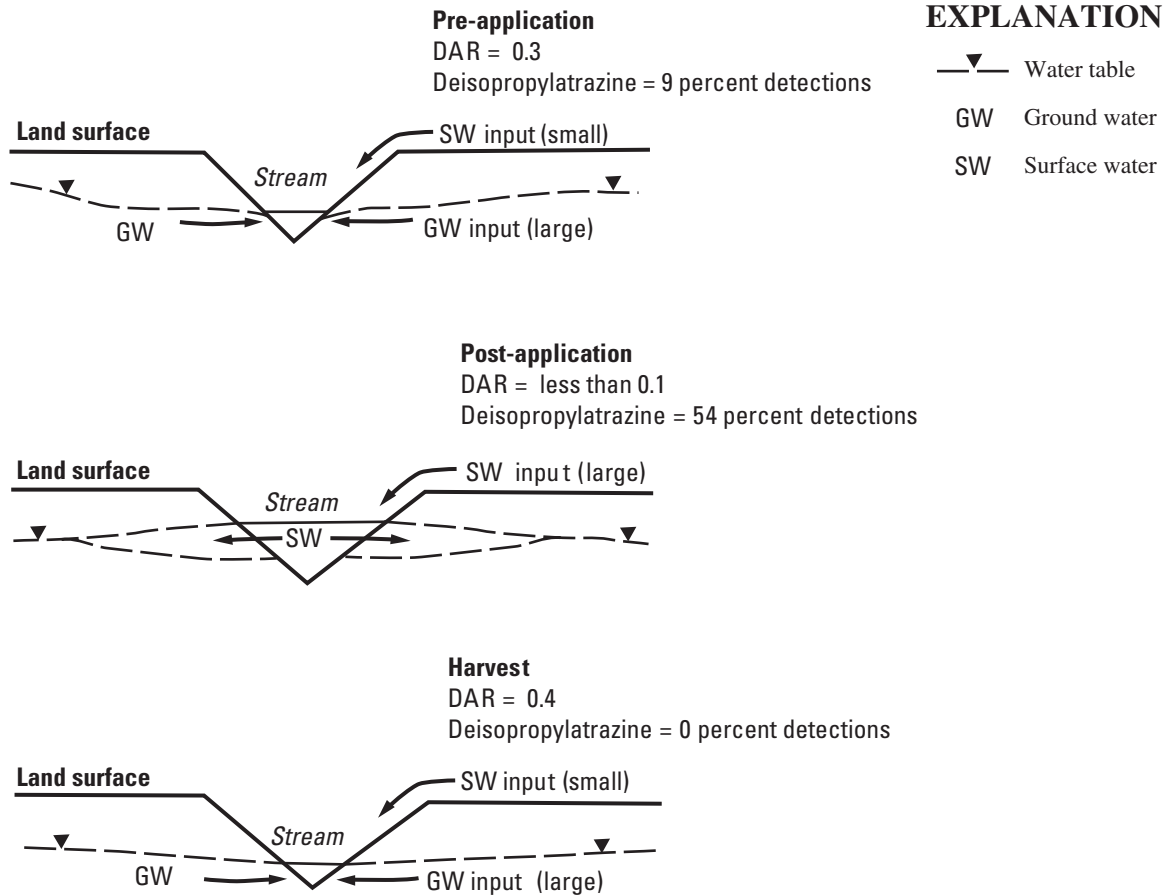


Figure 10. Deethylatrazine-to-atrazine ratios (DAR) for surface- and ground-water samples from Midwestern United States (from Thurman and others, 1992).

pre-application samples had a high DAR of 0.3 but also contained a few detections of deisopropylatrazine (9 percent). These results suggest both a surface-water and a ground-water origin of herbicides during this sampling period. The post-application samples collected during this period had a low DAR (less than 0.1) and the highest number of detections of deisopropylatrazine (54 percent), which indicate that surface runoff was the major contributor of herbicides. Finally, the post-harvest sampling during low streamflow had the highest DAR of 0.4 and detections of deisopropylatrazine, which indicate that alluvial ground water was likely the major source of herbicide (Thurman and others, 1992). Following the surface-water reconnaissance of Midwestern streams, Thurman and others (1992) reported DAR values less than 0.1 in streams shortly after herbicide application, whereas DAR values generally were 0.3 or higher in the fall at harvest during base-flow conditions. As shown by figure 11, the median DAR values obtained from USGS ground-water reconnaissance for both sampling periods were about 0.7. The DAR ranged from about 0.1 to 8.4. These results indicate that most of the atrazine detected in ground water was derived from nonpoint sources and had infiltrated the soil slowly (Kolpin and others, 1994).

Further field-dissipation studies of atrazine and cyanazine demonstrated that about 6 percent of the atrazine degraded to

deethylatrazine and about 3 percent degraded to deisopropylatrazine (Adams and Thurman, 1991; Mills and Thurman, 1994a). Cyanazine degraded only to the common degradation product, deisopropylatrazine. Thus, the ratios of deisopropylatrazine to deethylatrazine (D^2R) and atrazine to cyanazine (ACR) were used to differentiate the nonpoint source of deisopropylatrazine to surface water. Meyer and others (2001) successfully tested the D^2R discrimination diagram in two basins with very different application rates of atrazine and cyanazine to check the validity of the D^2R . The D^2R also was used to show that cyanazine contributed a considerable amount (40 percent) of the deisopropylatrazine that was transported during flooding of the Mississippi River in 1993. The D^2R is a useful water-quality monitoring tool to measure nonpoint-source contributions of deisopropylatrazine (Meyer and others, 2001).

A regional study of nine streams in the Midwestern Corn Belt confirmed that deethylatrazine and deisopropylatrazine occur frequently in surface water that has received storm runoff containing two parent triazine herbicides, atrazine and cyanazine (Scribner and others, 1994; Pomes and others, 1996). The concentrations of deethylatrazine and deisopropylatrazine in surface water varied with the hydrologic conditions of the basin and the timing of runoff, with maximum concentrations

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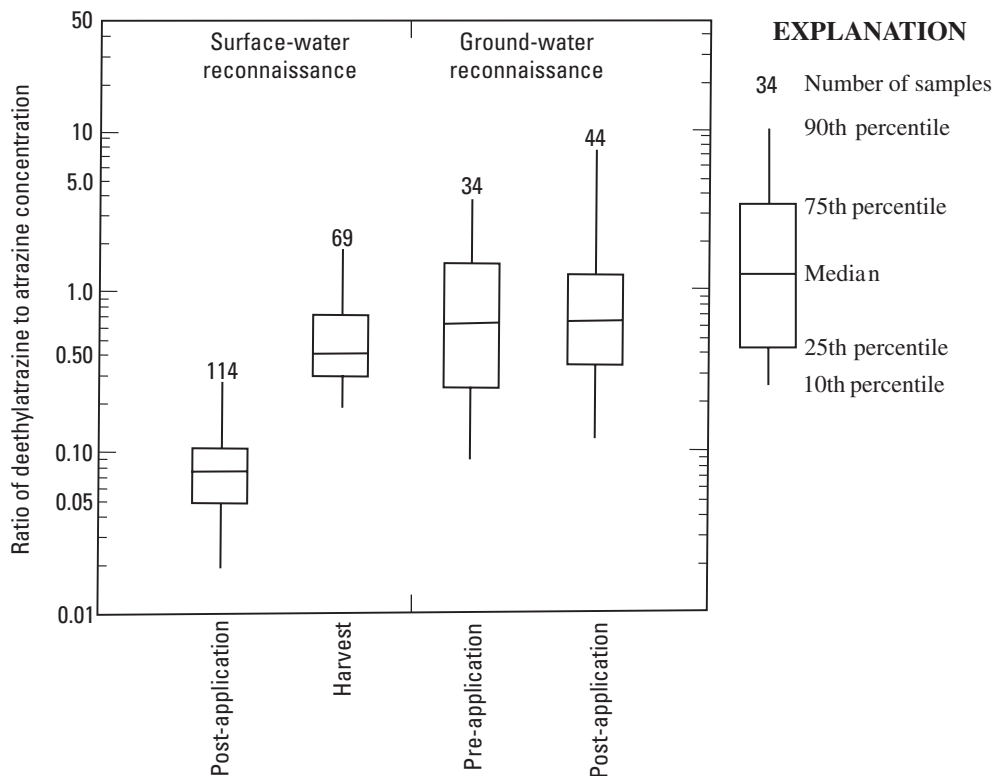


Figure 11. Deethylatrazine-to-atrazine ratios (DAR) for surface- and ground-water samples from Midwestern United States (from Kolpin and others, 1994).

reaching 5 $\mu\text{g/L}$ (deethylatrazine plus deisopropylatrazine). Early rainfall, followed by a dry summer, delayed the maximum concentrations, giving a second flush of triazine degradation products to surface water. Replicated field-dissipation studies of atrazine and cyanazine indicated that D^2R_s varied from 0.4 ± 0.1 , when atrazine was the major triazine compound present, to 0.6 ± 0.1 when significant amounts of cyanazine were present. A comparison of transport time of deethylatrazine and deisopropylatrazine from field plots to their appearance in surface water indicated that storage and dilution were occurring in the alluvial aquifers of the nine stream basins (Thurman and others, 1994).

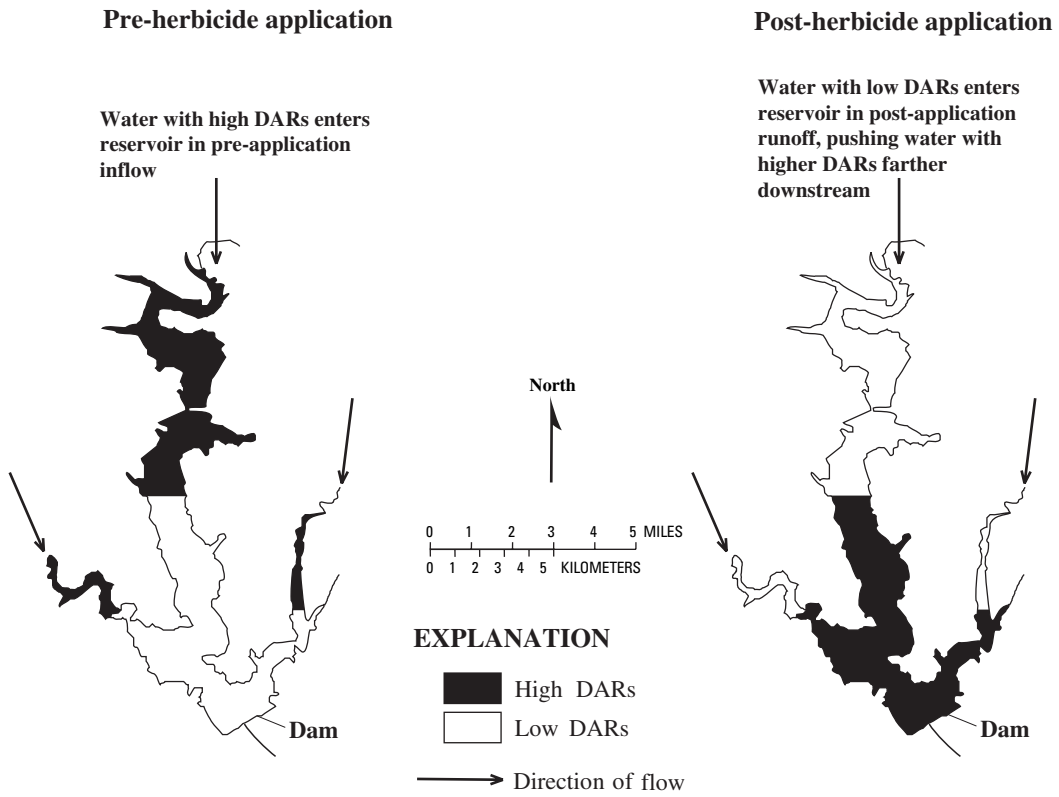
In a study by Thurman and Fallon (1996), a conceptual model was presented to explain how the DAR could be used to follow runoff through Perry Lake in northeast Kansas (fig. 12A). In the model, the reservoir already contained water with atrazine and deethylatrazine present from the previous year's runoff. The arrows show the direction of the flow with the dam at the downstream end of the reservoir. Near the dam, the water has been in the reservoir longer and contains water and herbicides from the previous summer, whereas the upstream water contains herbicides that had entered the reservoir during the fall and winter. Therefore, the DAR values were higher at the upstream end of the reservoir. The actual DAR values for each time period are shown in figure 12B. The concept of the DAR proved to be a useful tool in the ability to follow water movement through a reservoir.

In the precipitation study described earlier (Goolsby and others, 1997), deethylatrazine and deisopropylatrazine were detected in 17.4 and 2.6 percent, respectively, of the samples

analyzed. Deethylatrazine was present in more than one-half of the samples that contained atrazine and was the third most frequently detected compound. The median DAR value calculated for the 352 rainfall samples that contained both atrazine and deethylatrazine was 0.5. All of these DAR values were determined for rainfall samples collected from May through July of 1990 and 1991 when the median DAR values for streams in this area were less than 0.1 (Thurman and others, 1992). Considerably more deethylatrazine than atrazine was present in rainfall compared to streams draining the Corn Belt. There are several possible explanations for this observation. One is that deethylatrazine evaporates from the soil into the atmosphere faster than atrazine, resulting in a higher DAR value in rainfall. Another is that the high DAR value in rainfall is from atrazine transformed to deethylatrazine in the atmosphere by photochemical processes. Thus, it is possible that the high median DAR value of 0.5 in rainfall reflects the photocatalyzed degradation of atrazine in the atmosphere (Goolsby and others, 1997).

Finally, other important degradation products of atrazine that provide evidence of surface-water/ground-water interaction are hydroxylated atrazine degradation products (HADPs), which include hydroxyatrazine, deethylhydroxyatrazine, and deisopropylhydroxyatrazine. In general, HADPs are strongly bound to soil by two sorption mechanisms, cation exchange and hydrophobic interaction, which occur simultaneously. This is referred to as a mixed-mode model of sorption as shown in figure 13. Evidence of this model is provided by chromatographic studies, using solid-phase extraction and reverse-phase liquid chromatography, as well as soil-extraction studies that show

(A) Conceptual model



(B) Data from Perry Lake

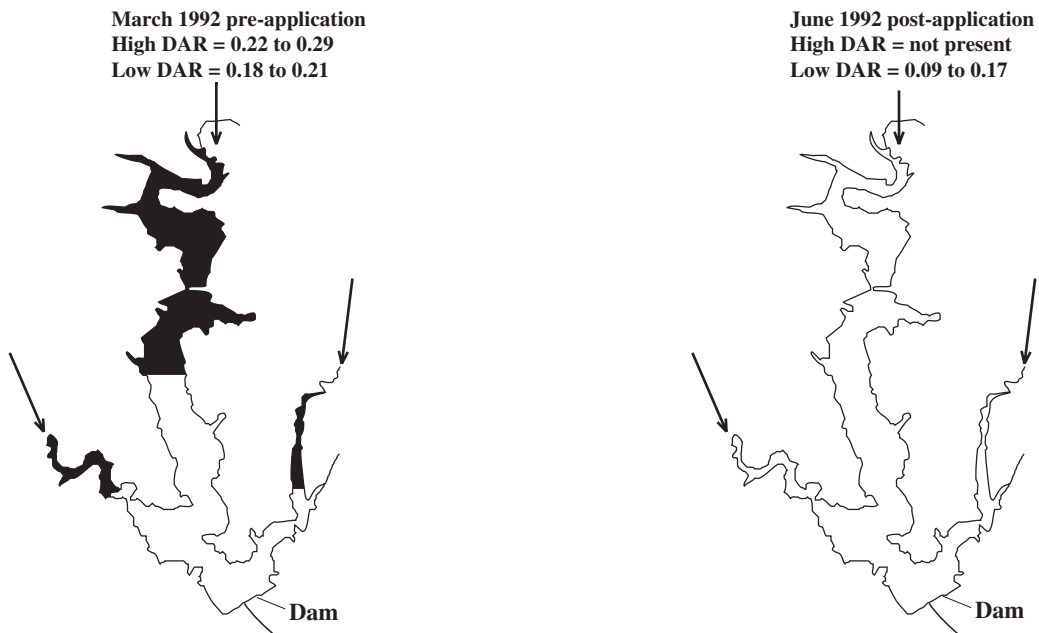


Figure 12. Conceptual model and data for deethylatrazine-to-atrazine ratios (DARs) in Perry Lake, northeastern Kansas, during March 1992–March 1993 (modified from Thurman and Fallon, 1996, fig. 5).

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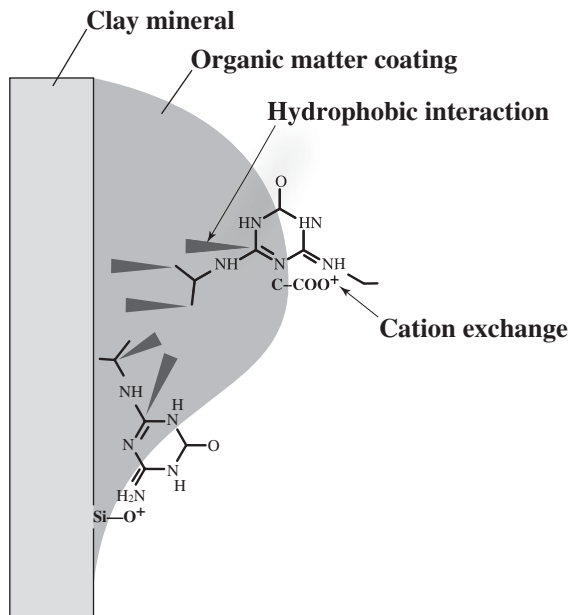


Figure 13. Mixed-mode model of sorption for hydroxylated atrazine degradation products (from Lerch and others, 1997).

the release of HADPs bound by mixed-mode sorption (Lerch and others, 1997).

As shown by figure 14A, during runoff conditions, a combination of dissolved-phase transport by surface runoff and desorption from suspended stream sediment is the source of

HADPs, whereas during base-flow conditions, the primary source of HADPs is desorption from bed sediments in the stream, as shown in figure 14B. Dissolved-phase transport of hydroxyatrazine by surface runoff has been measured directly in end-of-field samples from a north-central Missouri field treated with atrazine in 1994. Surface runoff from precipitation 6 to 7 days after atrazine application showed hydroxyatrazine concentrations of 3.3 to 5.4 $\mu\text{g/L}$ in flow-weighted samples collected throughout the course of the precipitation. Thus, surface runoff has the ability to extract or desorb a fraction of the hydroxyatrazine present in the soil. In addition, continuous monitoring of hydroxyatrazine in Goodwater Creek, also located in Missouri, showed that hydroxyatrazine mass flux was directly related to streamflow, indicating that increased hydroxyatrazine mass flux during runoff resulted from dissolved-phase transport (Lerch and others, 1998).

Persistence of Triazine Herbicides

Another important finding of USGS research during the 1990s was the persistence of triazine herbicides in surface water. Once applied to soil and crops, triazine compounds begin to degrade through biotic and abiotic reactions. Much of the research on the fate of triazine compounds prior to the late 1980s addressed only the parent herbicide because most of the triazine degradation products were assumed not to be effective herbicides and, therefore, were not of particular interest to the agronomists. During the 1990s, there was an increased focus on

(A) Runoff conditions

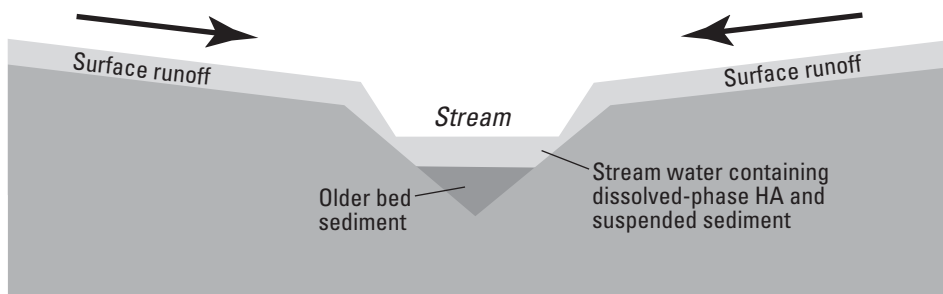
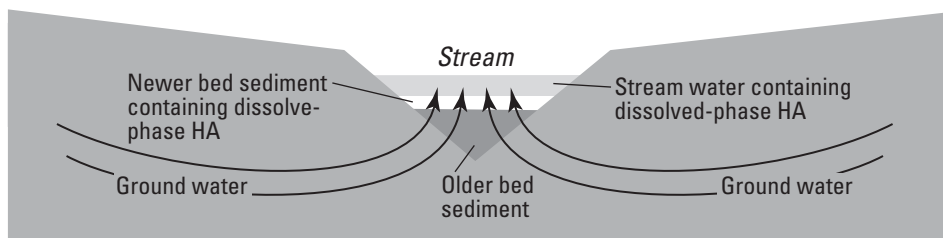


Figure 14. Proposed models for the mechanisms controlling concentrations of hydroxylated atrazine degradation products (HADPs) in streams. The figure depicts the cross-sectional view of a stream channel. (A) During runoff conditions, hydroxyatrazine (HA) is transported primarily from atrazine-treated fields to the stream in the dissolved phase. An additional source of HA in streams is suspended sediment derived from erosion of HA-contaminated soil. (B) During baseflow conditions (that is, ground water as the source of streamflow), HA is desorbed by ground water flowing through the HA-contaminated sediment deposited in the streambed (from Lerch and others, 1998).

(B) Base-flow conditions



accounting for the ultimate fate of triazine degradation products (Adams and Thurman, 1991; Thurman and others, 1994).

These studies found that the frequency of detection, or apparent order of stability, of triazine herbicides and their degradation products was atrazine, deethylatrazine, deisopropylatrazine, and cyanazine. It was also found that temporal trends in the number of detections in both pre-application and post-harvest samples, and in the range of the distribution during sampling periods, of various herbicides was significant. In a study by Thurman and others (1991, 1994), measurable amounts of atrazine, the most frequently detected herbicide, occurred in 91 percent of the pre-application samples, 98 percent of the post-application samples, and 76 percent of the harvest samples. The atrazine degradation product, deethylatrazine, was found in many pre-application, post-application, and harvest samples that contained atrazine.

Substantial evidence exists that another major biotic degradation process, dealkylation for atrazine by both bacteria and soil fungi, does occur. Several bacteria and fungi species have been shown to prefer deethylation, whereas others prefer deisopropylation. The presence of deethylatrazine in surface and ground water is ascribed almost exclusively to the degradation of atrazine by the removal of an ethyl group. Atrazine degradation pathways are shown in figure 15. Deethylatrazine is the most important degradation product found in water-quality studies throughout the Midwestern United States. Deisopropylatrazine is formed by the removal of an isopropyl group and also may occur from the degradation of cyanazine and simazine (Mills and Thurman, 1994a; Meyer and others, 2001). It may be degraded further to dideethylatrazine by removal of an ethyl group (fig. 15). Both the production of deethylatrazine and the degradation of deisopropylatrazine proceed by removal of an ethyl group. Therefore, the higher concentrations of deethylatrazine and the smaller concentrations of deisopropylatrazine during atrazine dealkylation may be a reflection of the greater ease of deethylation versus deisopropylation. These studies also show that concentrations of deethylatrazine and deisopropylatrazine in surface water vary with hydrologic conditions in the basin and the timing of runoff, with maximum concentrations reaching 5 µg/L (deethylatrazine plus deisopropylatrazine) (Mills and Thurman, 1994a; Thurman and others, 1994, 1998).

Early studies of atrazine degradation products focused on the chlorinated atrazine degradation products because of their greater water solubility, lower soil adsorption compared to the parent compound, and the fact that they are more amenable to gas chromatography/mass spectrometry analysis than the hydroxy degradation products. However, hydroxylated atrazine degradation products, particularly hydroxyatrazine, are the major degradation products of atrazine in most soils. Hydroxylated atrazine degradation products (HADPs), which include hydroxyatrazine, deethylhydroxyatrazine, and deisopropylhydroxyatrazine, are a major class of atrazine degradation products that form in the environment through chemical, biological, and photochemical hydrolysis of atrazine or dealkylated atrazine degradation products, resulting in replacement of chlorine with a hydroxyl group at the two-position of the triazine ring. In

soil or water, the rate of hydrolysis is enhanced by extremes in pH, dissolved organic matter, sorption to soil colloids, and the presence of photosensitizing compounds. HADPs have been shown to be more persistent in soil than atrazine and humic acids (Lerch and others, 1998).

Studies by Meyer (1994), Meyer and Thurman (1996), and Meyer and others (1996, 2001) suggest that cyanazine is more stable in the aquatic environment compared to the soil environment. The studies also showed that the half-life of cyanazine in the soil varied from 14 to 21 days (Meyer and Thurman, 1996). However, degradation products of cyanazine have been identified in the soil as long as 4 years after application (Meyer and Thurman, 1996). The cyanazine degradation pathway is shown in figure 16. The degradation process for herbicides generally increases the water solubility and the polarity of the compound. The increase in solubility is caused by the loss of carbon, the incorporation of oxygen, and the addition of carboxylic-acid functional groups. For every carbon atom that is removed, the water solubility will increase from two to three times (Meyer and Thurman, 1996).

A study by Meyer (1994) showed that atrazine and cyanazine were dissipated in the top 12 in. of the soil and they were not detected below 18 and 24 in. Deethylatrazine was the primary dealkylated compound produced from the degradation of atrazine. Stable production of deethylatrazine and deisopropylatrazine in the shallow soil was marked by relatively constant D^2R of about 0.4 throughout the growing season. In the deeper soil where the parent compound, atrazine, was diminished, the D^2R was generally less than 0.2 or nonexistent due to the absence of deisopropylatrazine. The systematic decrease in the concentrations of deisopropylatrazine relative to deethylatrazine with depth was determined to be from the preferential removal of the ethyl group from deisopropylatrazine and not from the preferential transport of deethylatrazine (Meyer, 1994; Meyer and others, 2001).

It was found that cyanazine amide dissipated rapidly and was not readily transported through the shallow soil (fig. 16). The concentration of cyanazine amide often was greater than cyanazine in both soil and pore water, and by mid-season, concentrations indicated that cyanazine amide was more readily transported through the unsaturated zone than cyanazine (Meyer, 1994; Meyer and others, 1996). The deethylated cyanazine degradation products, deethylcyanazine and deethylcyanazine amide, were identified only in the early season when the concentrations of cyanazine and cyanazine amide were high. They dissipated rapidly and were not transported at detectable levels deeper than 12 in. The primary degradation product of cyanazine that was measured with depth was deisopropylatrazine. It was detected as deep as 30 in. at concentrations greater than deethylatrazine (Meyer, 1994; Meyer and others, 2001).

The high DAR values showed that atrazine was not responsible for the deisopropylatrazine found in the soil-core samples in the cyanazine field plots. Also, deisopropylatrazine generally was detected later in the growing season and at deeper

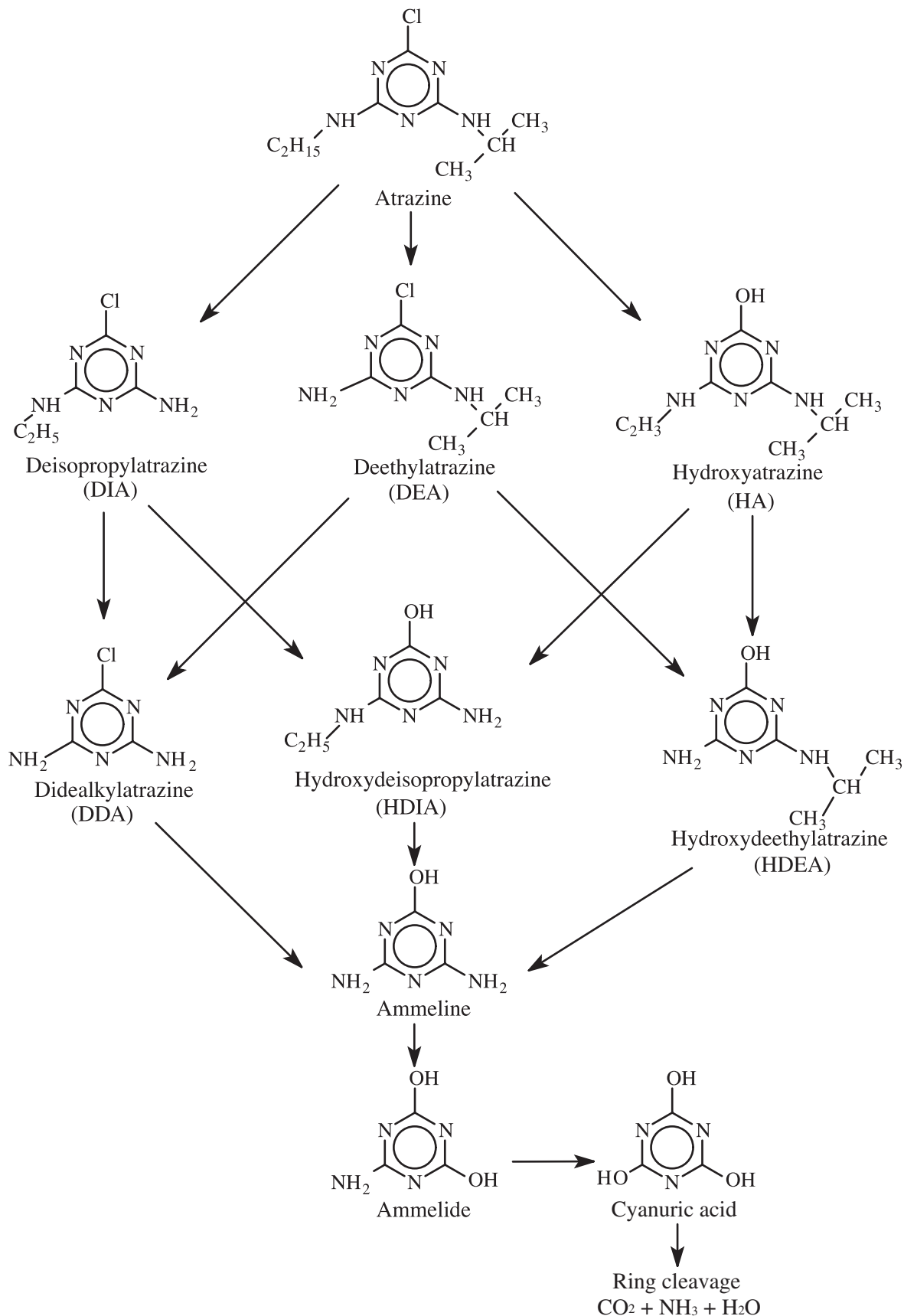


Figure 15. Degradation pathways for atrazine.

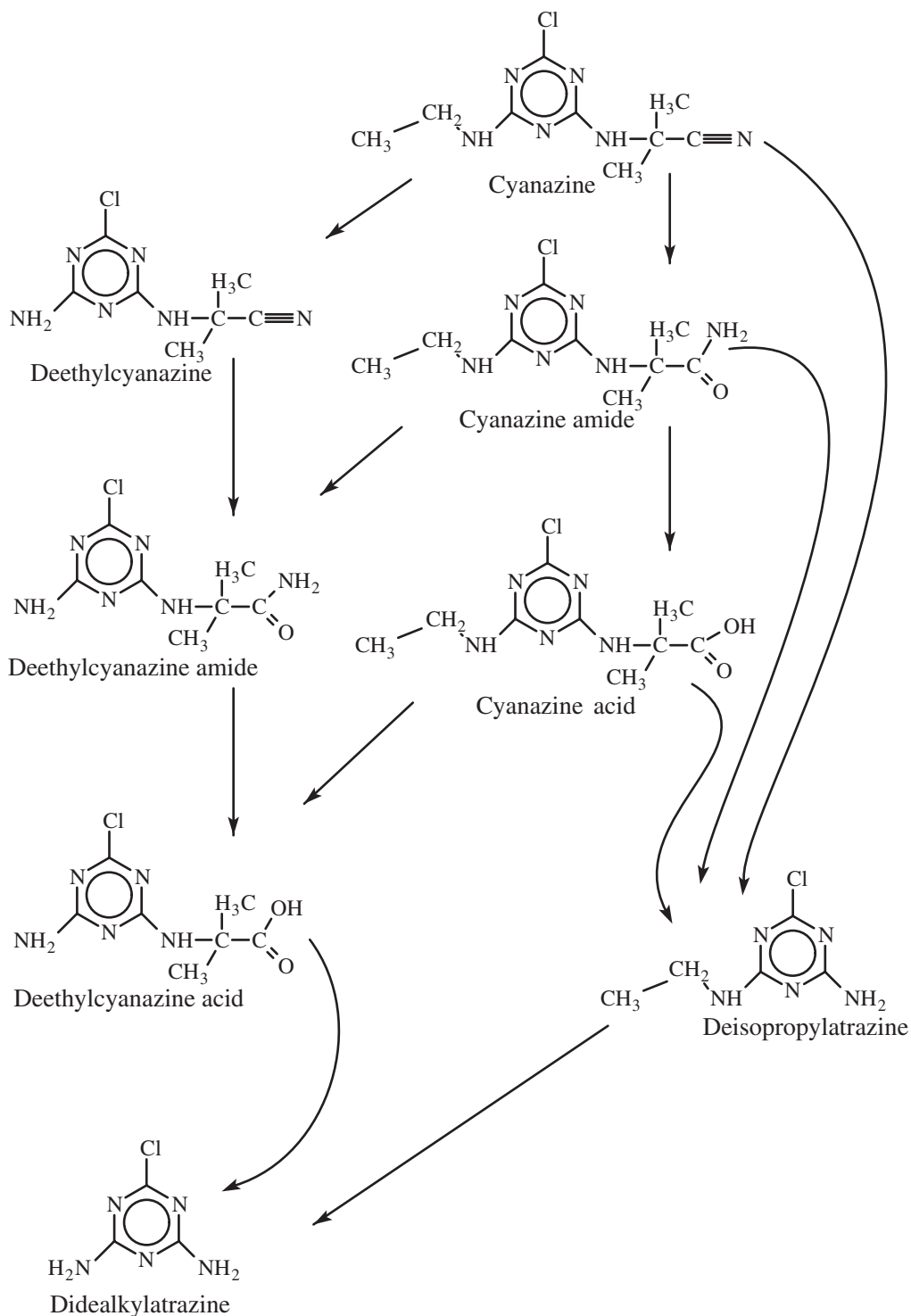


Figure 16. Degradation pathways for cyanazine.

levels than either cyanazine or cyanazine amide. Thus, the detection of deisopropylatrazine at depth is probably the result of the degradation of another cyanazine degradation product that is rapidly transported through the unsaturated zone, cyanazine acid. Cyanazine amide and cyanazine acid both have modified isopropyl moieties that may be removed by microbial degradation. The rapid dissipation of cyanazine amide suggests

that cyanazine acid is formed rapidly. Furthermore, because cyanazine acid is ionic at normal pH, it may be preferentially leached through the soil. As it is leached, it also may undergo deethylation and deisopropylation (Meyer and others, 1996, 2001).

As previously shown in figure 9, simazine also degrades to deisopropylatrazine. However, as already stated, about 15 to

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20 times more atrazine than simazine was applied in the United States during the early 1990s (Gianessi, 1992), which is why the presence of deethylatrazine and deisopropylatrazine in surface and ground water is ascribed almost exclusively to the degradation of atrazine.

Finally, propazine has not been sold since 1990, except to States that requested a USEPA Section 18 Emergency Exemption; however, it still occurred routinely in water because it was a contaminant present in atrazine at about 1 percent (Thurman and Fallon, 1996). Propazine is very persistent in the soil. It is broken down primarily by microbial action and, therefore, will persist longer in dry, cold conditions or in other conditions that inhibit microbial activity. In a study of playa lakes in the High Plains of Texas (fig. 1), atrazine and propazine were detected frequently (Thurman and others, 2000). Because propazine has a longer soil half-life (35 to 231 days) than atrazine (45 to 60 days), it is thought that atrazine was responsible for the majority of the deethylatrazine. Commonly, propazine was detected at much smaller concentrations than atrazine, perhaps because of little use during the 1990s. However, it is apparent from these data that propazine was still being used in Texas during the 1990s. Figure 9 also shows the structures of propazine and its respective dealkylation reactions to deethylatrazine by the removal of an isopropyl group (Thurman and others, 2000).

Summary

Triazine herbicides in surface water, ground water, and precipitation have been a major water-quality concern throughout the United States. The herbicides described in this report include atrazine, cyanazine, propazine, and simazine. Modern agricultural practices in the United States often require extensive use of these herbicides for crop production. Because of public concern about possible water contamination, several manufacturers have voluntarily reduced the recommended application rates and, in some cases, have removed herbicides from the market.

During the 1990s, numerous studies were conducted in the Midwestern United States as part of the USGS Toxic Substances Hydrology Program to document the usage of triazine herbicides and formation of their degradation products in the hydrologic environment. Studies showed that changes in application rates affected the frequency of detection of some of the triazine herbicides and their degradation products and revealed that herbicide use also fluctuated in response to annual changes in planted corn and soybean acreage as well as introduction of new herbicide products to the market. Monitoring the effects of these changes are important to understanding the occurrence, fate, and transport of these herbicides and their degradation products in surface water, ground water, and precipitation.

The first major source studied was surface water. A reconnaissance study of 147 stream sampling sites was conducted during 1989 with subsequent studies during 1990, 1994, 1995,

1998, and 2002 of about 50 of the 147 stream sampling sites to determine the geographic and seasonal distribution of herbicides. Results showed that large amounts of triazine herbicides and their degradation products were flushed into streams with runoff. Much of this transport took place during the first runoff period after application of herbicides. Subsequent runoff tended to produce lesser concentration peaks. Herbicide detections in larger Midwestern streams tended to be seasonal with higher percentages in spring and early summer and lower percentages in fall and winter.

The use of atrazine and cyanazine was approximately the same in 1989 and 1995; however, the median concentrations of both herbicides in stream samples were higher in 1989 than in 1995 or 2002. Although herbicide concentrations in Midwestern streams were quite variable during post-application runoff, the data suggest that changes in herbicide use affected herbicide concentrations in streams. These studies also confirmed that herbicide degradation products were found to occur as frequently or more frequently and at concentrations that were often higher than the parent herbicides. In 1993, a study during flooding in the upper Mississippi River Basin determined that flooding did not dilute the concentrations of herbicides but rather concentrations were similar to those seen in normal spring and summer flows.

A study of 76 reservoirs in the Midwestern United States reported an abundance and persistence of triazine herbicides and their degradation products in reservoirs. Significant findings showed that concentrations of atrazine and its degradation products remained elevated all summer and into the fall. A further study of the distribution of atrazine in Perry Lake (Kansas) during 1992 showed that recently applied atrazine mixed with atrazine applied the previous year as water moved through the reservoir. The reservoir studies demonstrated the relation between herbicide use and their occurrence in streams and reservoirs.

The second major source studied was ground water. Reconnaissance studies of 303 ground-water wells in the Midwestern United States began in 1991 with additional water samples collected from 101 of the 303 ground-water wells in 1992 to examine the occurrence of triazine herbicides and their degradation products. Triazine degradation products, deethylatrazine and deisopropylatrazine, commonly were found in ground water. During 1991, deethylatrazine was detected more frequently (21.4 percent of the samples) than its parent compound atrazine (20.8 percent of the samples) even though deethylatrazine had a higher reporting limit than atrazine, whereas deisopropylatrazine was detected in 7.6 percent of the samples. During 1992, the reporting limits for atrazine and deethylatrazine were lowered, and deethylatrazine was detected in 31 percent of the water samples while atrazine was present in 43 percent, and deisopropylatrazine was found in 18 percent of the samples collected.

Samples collected from 110 wells during the historic 1993 flooding in the Mississippi River Basin showed that there was a direct relation between increases in total herbicide concentration in ground water (between pre-flood and post-flood

samples) and the occurrence of stream flooding near wells. Results from these samples were compared to those samples obtained during 1991 and 1992 from the same wells. There were no statistically significant differences in either the frequency of herbicide detection or total herbicide concentration between the previous samples and those collected for the 1993 flood study. However, water from about 63 percent of the wells that had at least a 20-percent increase in total herbicide concentration also were severely affected by stream flooding.

An important finding of an investigation of samples collected from 131 municipal wells in Iowa was the high frequency with which degradation products were detected in ground water. Ground-water samples collected from across the Midwestern United States and in Iowa from 1991 to 2001 consistently revealed that triazine herbicide degradation products commonly were found more frequently than their parent herbicide, the frequency of herbicide detection was affected by a more sensitive analytical method, and ground-water age could be an important factor in explaining variations in herbicide contamination.

The third major source studied was precipitation. This study area included the upper Midwest (where the use of herbicides is most intense), the Northeast to the Atlantic Ocean, and northward to the Canadian border, a total of 26 States. The results identified the occurrence and temporal distribution of triazine herbicides and their degradation products in the Midwest. Because of the large temporal and spatial variation in the amount of rainfall, it is difficult to make meaningful comparisons of herbicide concentrations among sites or over time on the basis of individual weekly samples. Comparisons can best be made with rainfall-weighted concentrations. The highest concentrations occurred following herbicide application to cropland. Rainfall-weighted concentrations of 0.20 to 0.40 $\mu\text{g/L}$ for atrazine were typical throughout the Midwest, and weighted concentrations as large as 0.60 to 0.90 $\mu\text{g/L}$ occurred in precipitation at several sites. Concentrations of 1.0 to 3.0 $\mu\text{g/L}$ were measured in a few individual samples. Atrazine was detected most often, followed by deethylatrazine, cyanazine, and deisopropylatrazine. The large ratio (about 0.50) of deethylatrazine to atrazine in precipitation was greatest in areas where herbicide use was intense and decreased with distance from the Midwest.

Other important findings of the 1990s USGS studies included the chemistry, transport, and persistence of triazine herbicides and their degradation products in surface water and ground water. A number of field-dissipation studies were carried out for atrazine, cyanazine, propazine, and simazine in the unsaturated zone and in surface runoff. These dissipation studies resulted in outlining the structure and transport of many degradation products of triazine herbicides in the aquatic environment. A dealkylation field study found the preferential removal of an ethyl side chain from atrazine relative to the removal of an isopropyl side chain. The high ratio of deethylatrazine to atrazine (referred to as the DAR) in shallow soil was evidence that simazine degraded more rapidly to deisopropylatrazine than propazine to deethylatrazine. Furthermore, deethylation rates of atrazine and simazine were comparable. This indicates that the removal of an ethyl side chain was preferential

over an isopropyl side chain, regardless of parent triazine compound. It was also found that atrazine transport through the unsaturated zone gave DAR values much greater than 1.0, whereas atrazine transported in runoff had DAR values much less than 1.0. Deisopropylatrazine was rapidly degraded in the unsaturated zone but was an important degradation product in surface runoff from the fields.

An additional finding of USGS research was the persistence of triazine herbicides and their degradation products in surface water. Studies found that the frequency of detection, or apparent order of stability, was atrazine, deethylatrazine, deisopropylatrazine, and cyanazine. The temporal trends in the number of detections of various herbicides were also significant for several reasons. First, they indicated that some compounds persisted from year to year in soil and water. Second, degradation products, such as deethylatrazine, were both persistent and mobile in water. Third, the data showed that the DAR, which has been proposed as an indicator of nonpoint-source contamination of ground water, might be used also as a tracer of ground-water discharge to streams. Once it was applied, atrazine began to degrade through the action of soil microbes and abiotic losses and chemical reactions.

Findings of the 1990s studies by the USGS include an improved understanding of the occurrence, persistence, chemistry, and transport of triazine herbicides and their degradation products in the hydrologic environment. A significant increase in knowledge of triazine herbicides and development and improvement of analytical methods were accomplished in the past decade. The results produced are not only significant for the present but provide an important data set for future use.

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