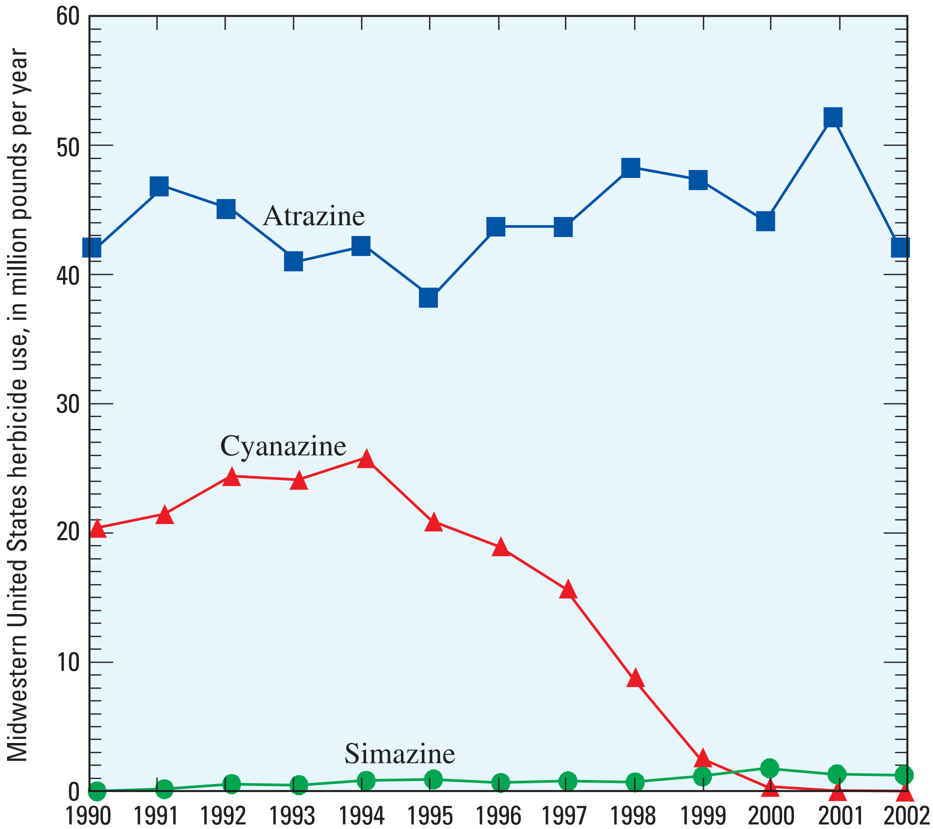
Summary of Significant Results from Studies of Triazine Herbicides and Their Degradation Products in Surface Water, Ground Water, and Precipitation in the Midwestern United States During the 1990s



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

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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 (µg/L)	1	part per billion (ppb)
microgram per square meter per year [(µg/m^2)/yr]	0.003276x10^{-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

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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 deisoproplyatrazine. 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.

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 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. 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.

References Cited

Adams, C.D., and Thurman, E.M., 1991, Formation and transport of deethylatrazine in the soil and vadose zone: Journal of Environmental Quality, v. 20, p. 540–547.

Aga, D.S., and Thurman, E.M., 1993, Coupling solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) for ultratrace analysis of herbicides in pristine water: Analytical Chemistry, v. 65, p. 2894–2898.

Baker, D.B., and Richards, R.P., 1989, Herbicide concentration patterns in rivers draining intensively cultivated farmlands of northwestern Ohio, *in* Weigmann, D., ed., Pesticides in the terrestrial and aquatic environments, Proceedings of a National Research Conference, May 11–12, 1989, Blacksburg, Virginia: Blackburg, Virginia Polytechnic Institute & State University, p. 103–120.

Battaglin, W.A., 2002, Using ratios of atrazine transformation products to atrazine to determine its source in Midwestern streams, *in* Kenny, J., ed., Ground water/surface water interactions, AWRA Summer Specialty Conference Proceedings: Middleburg, Virginia, American Water Resources Association TPS–02–2, p. 213–218.

Battaglin, W.A., and Goolsby, D.A., 1995, Spatial data in geographic information system format on agricultural chemical use, land use, and cropping practices in the United States: U.S. Geological Survey Open-File Report 94–4176, 87 p.

Battaglin, W.A., and Goolsby, D.A., 1997, Statistical modeling of agricultural chemical occurrence in Midwestern rivers: Journal of Hydrology, v. 196, p. 1–25.

Battaglin, W.A., and Goolsby, D.A., 1998, Regression models of herbicide concentrations in outflow from reservoirs in the midwestern USA, 1992–1993: Journal of the American Water Resources Association, v. 34, p. 1369–1390.

Battaglin, W.A., and Goolsby, D.A., 1999, Are shifts in herbicide use reflected in concentration changes in Midwestern rivers?: Environmental Science & Technology, v. 33, p. 2917–2925.

Battaglin, W.A., Kolpin, D.W., Scribner, E.A., Kuivila, K.M., and Sandstrom, M.W., 2005, Glyphosate, other herbicides, and transformation products in Midwestern streams: Journal of the American Water Resources Association, v. 41, no. 2, p. 323–332.

Battaglin, W.A., Thurman, E.M., Kalkhoff, S.J., and Porter, S.D., 2003, Herbicides and transformation products in surface waters of the Midwestern United States: Journal of the American Water Resources Association, v. 39, p. 743–756.

Becker, R.L., Herzfeld, D., Ostlie, K.R., and Stamm-Katovich, E.J., 1989, Pesticides—surface runoff, leaching, and exposure concerns: Minneapolis, University of Minnesota, Minnesota Extension Service AG–BU–3911, 32 p.

Burkhart, M.R., and Kolpin, D.W., 1993, Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers: Journal of Environmental Quality, v. 22, p. 646–656.

Buxton, H.T., 2000, USGS Toxic Substances Hydrology Program, 2000: U.S. Geological Survey Fact Sheet 0620–00, May 2000, 4 p.

Clark, G.M., and Goolsby, D.A., 2000, Occurrence and load of selected herbicides and metabolites in the lower Mississippi River: The Science of the Total Environment, v. 248, p. 101–113.

Clark, G.M., Goolsby, D.A., and Battaglin, W.A., 1999, Seasonal and annual load of herbicides from the Mississippi River Basin to the Gulf of Mexico: Environmental Science & Technology, v. 33, p. 981–986.

Fallon, J.D., Tierney, D.P., and Thurman, E.M., 2002, Movement of atrazine and deethylatrazine through a Midwestern reservoir: American Water Works Association, v. 94, p. 54–65.

Ferrer, I., Barcelo, D., and Thurman, E.M., 1999, Double-disk solid-phase extraction—simultaneous cleanup and trace enrichment of herbicides and metabolites from environmental samples: Analytical Chemistry, v. 71, p. 1009–1015.

Ferrer, I., Barcelo D., and Tierney, D.P., 2000, First LC/MS determination of cyanazine amide, cyanazine acid, and cyanazine in groundwater samples: Environmental Science & Technology, v. 34, p. 714–718.

Gianessi, L.P., 1992, U.S. pesticide use trends—1966–1989, *in* Gianessi, L.P., ed., Resources for the future: Washington, D.C., Quality of the Environment Division, p. 1–22.

Gianessi, L.P., and Marcelli, M., 2000, Pesticide use in the U.S. crop production, 1997: Washington, D.C., National Summary Report, 101 p.

Goolsby, D.A., and Battaglin, W.A., 1995, Occurrence and distribution of pesticides in streams of the Midwestern United States, *in* Leng, M.L., ed., Agrochemical environmental fate—state of the art: Boca Raton, Florida, Lewis-CRC Press, p. 159–173.

Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W., and Thurman, E.M., 1996, Persistence of herbicides in selected reservoirs in the Midwestern United States—some preliminary results: Iowa Groundwater Quarterly v. 7, p. 11–16.

Goolsby, D.A., Battaglin, W.A., and Thurman, E.M., 1993, Occurrence and transport of agricultural chemicals in the Mississippi River Basin, July through August 1993: U.S. Geological Survey Circular 1120–C, 22 p.

Goolsby, D.A., Coupe, R.H., and Markovchick, D.J., 1991a, Distribution of selected herbicides and nitrate in the Mississippi River and its major tributaries, April through June 1991: U.S. Geological Survey Water-Resources Investigations Report 91–4163, 35 p.

Goolsby, D.A., Scribner, E.A., Thurman, E.M., Meyer, M.T., and Pomes, M.L., 1995, Data on selected herbicides and two triazine metabolites in precipitation in the Midwestern and Northeastern U.S., 1990–91: U.S. Geological Survey Open-File Report 95–469, 341 p.

Goolsby, D.A., Thurman, E.M., and Kolpin, D.W., 1991b, Geographic and temporal distribution of herbicides in surface waters of the upper Midwestern United States, 1989–90: U.S. Geological Survey Water-Resources Investigations Report 91–4034, p. 183–188.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M.T., and Battaglin, W.A., 1997, Herbicides and their metabolites in rainfall—origin, transport, and deposition patterns across the Midwestern and Northeastern United States: Environmental Science & Technology, v. 31, p. 1325–1333.

Hostetler, K.A., and Thurman, E.M., 2000, Determination of chloroacetanilide herbicide metabolites in water using high-performance liquid chromatography-diode array detection and high-performance liquid chromatography/mass spectrometry: The Science of the Total Environment, v. 248, p. 147–156.

Infoplease, 2004, Encyclopedia: Information available on the World Wide Web, accessed December 1, 2004, at URL http://www.infoplease.com/ce6/us/A0813571.html

Kalkhoff, S.J., Lee, K.E., Porter, S.D., Terrio, P.J., and Thurman, E.M., 2003, Herbicides and herbicide degradation products in upper Midwest agricultural streams during August base-flow conditions: Journal of Environmental Quality, v. 32, p. 1025–1035.

Kish, J.L., Thurman, E.M., Scribner, E.A., and Zimmerman, L.R., 2000, Method of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—determination of triazine and chloroacetanilide herbicides in water by solid-phase extraction and capillary column gas chromatography/mass spectrometry with selected ion monitoring: U.S. Geological Survey Open-File Report 00–385, 13 p.

Kolpin, D.W., and Burkart, M.R., 1991, Work plan for regional reconnaissance for selected herbicides and nitrate in ground water of the mid-continental United States, 1991: U.S. Geological Survey Open-File Report 91–59, 18 p.

Kolpin, D.W., and Burkart, M.R., and Thurman, E.M., 1993a, Hydrogeologic, water-quality, and land-use data for the reconnaissance of herbicides and nitrate in near-surface aquifers of the midcontinental United States, 1991: U.S. Geological Survey Open-File Report 93–114, 61 p.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., 1994, Herbicides and nitrate in near-surface aquifers in the midcontinental United States, 1991: U.S. Geological Survey Water-Supply Paper 2413, 34 p.

Kolpin, D.W., Goolsby, D.A., Aga, D.S., Iverson, J.L., and Thurman, E.M, 1993b, Pesticides in near-surface aquifers—results of the Midcontinental United States ground-water reconnaissance, 1991–92, *in* Goolsby, D.A., Boyer, L.L., and Mallard, G.E., eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 26–40.

Kolpin, D.W., Goolsby, D.A., and Thurman, E.M., 1995, Pesticides in near-surface aquifers—an assessment using highly sensitive analytical methods and tritium: Journal of Environmental Quality, v. 24, p. 1125–1132.

Kolpin, D.W., Kalkhoff, S.J., Goolsby, D.A., Sneck-Fahrer, D.A., and Thurman, E.M., 1997, Occurrence of selected herbicides and herbicide degradation products in Iowa's ground water, 1995: Ground Water, v. 35, p. 679–688.

Kolpin, D.W., Schnoebelen, D.J., and Thurman, E.M., 2004, Degradates provide insight to spatial and temporal trends of herbicides in ground water: Ground Water, v. 42, no. 4, p. 601–608.

Kolpin, D.W., and Thurman, E.M., 1995, Postflood occurrence of selected agricultural chemicals and volatile organic compounds in near-surface unconsolidated aquifers in the upper Mississippi River Basin, 1993: U.S. Geological Survey Circular 1120–G, 20 p.

Kolpin, D.W., Thurman, E.M., and Goolsby, D.A., 1996a, Occurrence of selected pesticides and their metabolites in near-surface aquifers of the Midwestern U.S.: Environmental Science & Technolology, v. 30, p. 335–340.

Kolpin, D.W., Thurman, E.M., and Linhart, S.M., 1998, The environmental occurrence of herbicides—the importance of degradates in ground water: Archives of Environmental Contaminant Toxicology, v. 35, p. 1–6.

Kolpin, D.W., Thurman, E.M., and Linhart, S.M., 2000, Finding minimal herbicide concentrations in ground water? Try looking for degradates: Science of Total Environment, v. 248, p. 115–122.

Kolpin, D.W., Thurman, E.M., and Linhart, S.M., 2001, Occurrence of cyanazine compounds in groundwater—degradates more prevalent than the parent compound: Environmental Science & Technology, v. 35, no. 6, p. 1217–1222.

Kolpin, D.W., Zichelle, K.E., and Thurman, E.M., 1996b, Water-quality data for nutrients, pesticides, and volatile organic compounds in near-surface aquifers of the Midcontinental United States, 1992–1994: U.S. Geological Survey Open-File Report 96–435, 47 p.

Lee, E.A., Strahan, A.P., and Thurman, E.M., 2002, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—determination of triazine and phenylurea herbicides and their degradation products in water using solid-phase extraction and liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02–436, 19 p.

Leonard, R.A., 1988, Herbicides in surface water, *in* Grover, R., ed., Environmental chemistry of herbicides, I: Boca Raton, Florida, CRC Press, p. 45–87.

Lerch, R.N., Blanchard, P.E., and Thurman, E.M., 1998, Contribution of hydroxylated atrazine degradation products to the total atrazine load in Midwestern streams: Environmental Science & Technology, v. 32, p. 40–48.

Lerch, R.N., Thurman, E.M., and Kruger, E.L., 1997, Mixed-mode sorption of hydroxylated atrazine degradation products to soil—a mechanism for bound residue: Environmental Science & Technology, v. 31, p. 1539–1546.

Meyer, M.T., 1994, Geochemistry of cyanazine and its metabolites—indicators of contaminant transport in surface water of the Midwestern United States: Lawrence, University of Kansas, Department of Geology, Ph.D. thesis, 362 p.

Meyer, M.T., Mills, M.S., and Thurman, E.M., 1993, Automated solid-phase extraction of herbicides from water for gas chromatographic/mass spectrometric analysis: Chromatography, v. 629, p. 55–59.

Meyer, M.T., and Thurman, E.M., 1996, The transport of cyanazine metabolites in surface water of the Midwestern United States, *in* Morganwalp, D.W., and Aronson, D.S., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20–24, 1993, volume I: U.S. Geological Survey Water-Resources Investigations Report 94–4015, p. 463–470.

Meyer, M.T., Thurman, E.M., and Goolsby, D.A., 1996, Cyanazine, atrazine, and their metabolites as geochemical indicators of contaminant transport in the Mississippi River, *in* Meyer, M.T,. and Thurman, E.M., eds., Herbicide metabolites in surface water and groundwater: American Chemical Society Symposium Series 630, chap. 21, p. 288–303.

Meyer, M.T., Thurman, E.M., and Goolsby, D.A., 2001, Differentiating nonpoint sources of deisopropylatrazine in surface water using discrimination diagrams: Journal of Environmental Quality, v. 30, p. 1836–1843.

Mills, M.S., and Thurman, E.M., 1992, Mixed-mode isolation of triazine metabolites in soil and aquifer sediments using automated solid-phase extraction: Analytical Chemistry, v. 64, p. 1985–1990.

Mills, M.S., and Thurman, E.M., 1994a, Preferential dealkylation reactions of *s*-triazine herbicides in the unsaturated zone: Environmental Science & Technology, v. 28, p. 600–605.

Mills, M.S., and Thurman, E.M., 1994b, Reduction of nonpoint-source contamination of surface water and ground water by starch encapsulation of herbicides: Environmental Science & Technology, v. 28, no. 1, p. 73–79.

Pereira, W.E., and Rostadt, C.E., 1990, Occurrence, distribution, and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries: Environmental Science & Technology, v. 24, p. 1400–1406.

Pomes, M.L., Thurman, E.M., Aga, D.S., and Goolsby, D.A., 1998, Evaluation of microtiter-plate enzyme-linked immunosorbent assay for the analysis of triazine and chloroacetanilide herbicides in rainfall: Environmental Science & Technology, v. 32, p. 163–168.

Pomes, M.L., Thurman, E.M., and Goolsby, D.A., 1996, An evaluation of a microtiter-plate immunoassay assay method for the analysis of triazine and chloroacetanilide herbicides in storm runoff samples, *in* Van Emon, J.M., Gerlach, C.L., and Johnson, J.C., eds., Environmental immunochemical methods: American Chemical Society Symposium Series 646, chap. 16, p. 170–182.

Schnoebelen, D.J., Kalkhoff, S.J., Becher, K.D., and Thurman, E.M., 2003, Water-quality assessment of the Eastern Iowa Basins—selected pesticides and pesticide degradates in streams, 1996–98: U.S. Geological Survey Water-Resources Investigations Report 03–4075, 62 p.

Schraer, S.M., Shaw, D.R., Boyette, Michelle, Coupe, R.H., and Thurman, E.M., 2000, Comparison of enzyme-linked immunosorbent assay and gas chromatography procedures for the detection of cyanazine and metolachlor in surface water samples: Journal of Agricultural and Food Chemistry, v. 48, p. 5881–5886.

Scribner, E.A., Battaglin, W.A., Dietze, D.A., and Thurman, E.M., 2003, Reconnaissance data for glyphosate, other selected herbicides, their degradation products, and antibiotics in 51 streams in nine Midwestern States, 2002: U.S. Geological Survey Open-File Report 03–217, 101 p.

Scribner, E.A., Battaglin,W.A., Goolsby, D.A, and Thurman, E.M., 2000a, Changes in herbicide concentrations in midwestern streams in relation to changes in use: Science of Total Environment, v. 248, p. 255–263.

Scribner, E.A, Goolsby, D.A., Thurman, E.M., and Battaglin,W.A., 1998, A reconnaissance for selected herbicides, metabolites, and nutrients in streams of nine Midwestern States, 1994–95: U.S. Geological Survey Open-File Report 98–181, 44 p.

Scribner, E.A., Goolsby, D.A., Thurman, E.M., Meyer, M.T., and Battaglin, W.A., 1996, Concentrations of selected herbicides, herbicide metabolites, and nutrients in outflow from selected Midwestern reservoirs, April 1992 through September 1993: U.S. Geological Survey Open-File Report 96–393, 128 p.

Scribner, E.A., Goolsby, D.A., Thurman, E.M., Meyer, M.T., and Pomes, M.L., 1994, Concentrations of selected herbicides, two triazine metabolites, and nutrients in storm runoff from nine stream basins in the Midwestern United States, 1990–92: U.S. Geological Survey Open-File Report 94–396, 144 p.

Scribner, E.A., Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., and Pomes, M.L.,1993, Reconnaissance data for selected herbicides, two atrazine metabolites, and nitrate in surface water of the Midwestern United States, 1989–90: U.S. Geological Survey Open-File Report 93–457, 77 p.

Scribner, E.A., Thurman, E.M., and Zimmerman, L.R., 2000b, Analysis of selected herbicide metabolites in surface and ground water of the United States: Science of Total Environment, v. 248, p. 157–168.

Squillace, P.J., and Thurman, E.M., 1992, Herbicide transport in rivers—importance of hydrology and geochemistry in nonpoint-source contamination: Environmental Science & Technology, v. 26, p. 538–545.

Stamer, J.K., Battaglin, W.A., and Goolsby, D.A., 1998a, Herbicides in Midwestern reservoir outflows, 1992–93: U.S. Geological Survey Fact Sheet 134–98, 4 p.

Stamer, J.K., Goolsby, D.A., and Thurman, E.M., 1998b. Herbicides and associated degradation products in rainfall across the Midwestern and Northeastern United States, 1990–91: U.S. Geological Survey Fact Sheet 181–97, 4 p.

Stamer, J.K., and Zelt, R.B., 1992, Distribution of atrazine and similar nitrogen containing herbicides, lower Kansas River Basin: U.S. Geological Survey Yearbook, Fiscal Year 1991, p. 76–79.

Thurman, E.M., Bastian, K.C., and Tony Mollhagan, 2000, Occurrence of cotton herbicides and insecticides in playa lakes of the high plains of west Texas: Science of Total Environment, v. 248, p. 189–200.

Thurman, E.M., and Cromwell, A.E., 2000, Atmospheric transport, deposition, and fate of triazine herbicides and their metabolites in pristine areas at Isle Royale National Park: Environmental Science & Technology, v. 34, p. 3079–3085.

Thurman, E.M., and Fallon, J.D., 1996, The deethylatrazine/atrazine ratio as an indicator of the onset of the spring flush of herbicides into surface water of the Midwestern United States: International Journal of Environmental Analytical Chemists, v. 65, p. 203–214.

Thurman, E.M., Ferrer, Imma, and Barcelo, Damia, 2001, Choosing between atmospheric pressure chemical ionization and electrospray ionization interfaces for the HPLC/MS analysis of pesticides: Analytical Chemistry, v. 73, p. 5441–5449.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface waters of the Midwestern United States—the effect of spring flush: Environmental Science & Technology, v. 25, p. 1794–1796.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern United States using immunoassay and gas chromatography/mass spectrometry: Environmental Science & Technology, v. 26, p. 2440–2447.

Thurman, E.M., Kolpin, D.W., Goolsby, D.A., and Meyer, M.T., 1998, Triazine herbicides risk assessment, *in* Ballantine, L.G., McFarland, J.E., and Hackett, D.S., eds., Source and transport of deethylatrazine and deisopropylatrazine to groundwater of the Midwestern United States: American Chemical Society Symposium Series 683, chap. 17, p. 189–207.

Thurman, E.M., Meyer, M.T., Mills, M.L., Zimmerman, L.R., Perry, C.A., and Goolsby, D.A.,1994, Formation and transport of deethylatrazine and deisopropylatrazine in surface water: Environmental Science & Technology, v. 28, p. 2267–2277.

Thurman, E.M., Meyer, M.T., Pomes, M.L., Perry, C.A., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, p. 2043–2048.

Thurman, E.M., and Mills, M.S., 1998, Solid-phase extraction: New York, John Wiley & Sons, Inc., 344 p.

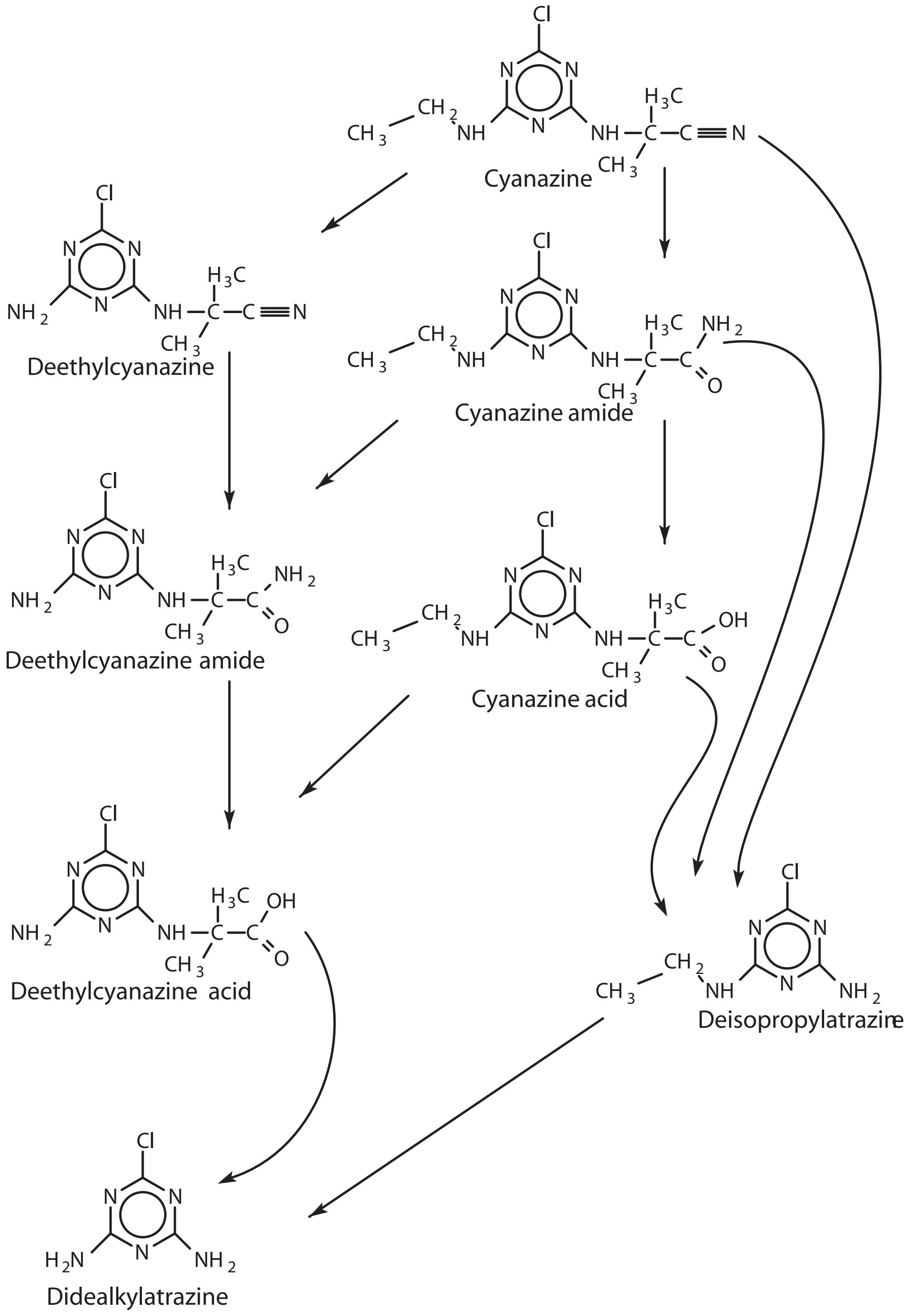
Thurman, E.M., and Snavely, K., 2000, Advances in solid-phase extraction disks for environmental chemistry: Analytical Chemistry, v. 19, p. 18–26.

U.S. Department of Agriculture, 1991–2003, Agricultural chemical usage—1990–2003 field crops summary: Washington, D.C., National Agricultural Statistics Service, published annually, various pagination.

U.S. Environmental Protection Agency, 1998, Propazine—proposed revocation of tolerances: Federal Register, v. 63, no. 52, p. 13156–13158, information available on World Wide Web, accessed April 7, 2005, at URL http://www.epa.gov/fedrgstr/EPA-PEST/1998/March/Day-18/p6979.htm

Wehtje, G.R., Spalding, R.F., Burnside, O.C., Lowry, S.R., and Leavitt, J.R.C., 1983, Biological significance and fate of atrazine under aquifer conditions: Weed Science, v. 31, p. 610–618.

Zimmerman, L.R., and Thurman, E.M., 1999, Method of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—determination of triazine and chloroacetanilide herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 98–634, 21 p.


Cyanazine
Deethylcyanazine
Cyanazine amide
Deethylcyanazine amide
Cyanazine acid
Deethylcyanazine acid
Deisopropylatrazine
Didealkylatrazine