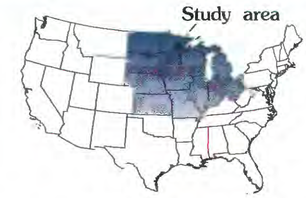
USGS
science for a changing world

Herbicides in Ground Water of the Midwest: A Regional Study of Shallow Aquifers, 1991–94



The intensive herbicide use associated with the "Corn Belt" marks the Midwestern United States as a region where herbicide contamination of ground water could be a problem. To better understand the regional occurrence of herbicides in shallow aquifers of the Midwest, a sampling network of 303 wells across 12 States was developed. The results documented relatively widespread, low-level concentrations of herbicides in the shallow aquifers sampled. The most frequently detected compounds, however, were the transformation products of these herbicides. A relation was determined between herbicide occurrence and the general age of the ground water sampled. Water that recharged ground water within the past 40 years was much more likely to contain herbicides than water recharged earlier.

Background

Parts of 12 Midwestern States (Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin) comprise a region commonly referred to as the "Corn Belt." The Corn Belt is the largest and most intensive crop-producing region of the United States, accounting for about 65 percent of the total harvested cropland and about 60 percent of the herbicide use in the Nation (Battaglin and Goolsby, 1995). This intensive herbicide use marks the Corn Belt as a region where the potential for herbicide contamination of ground water could be significant. Although herbicides have many benefits, they may also produce a wide range of toxic side effects that could pose a potential hazard to human health and the environment.

Previous State and national surveys conducted in the Midwest have produced a wide range in results regarding the detection of herbicides. For example, the reported frequency of detection of atrazine ranged from less than 1 to 47 percent for the 14 State or national studies that analyzed for atrazine (Burkart and Kolpin, 1993). Differences between these studies (such as analytical reporting limits, target population, well-selection criteria, time of sample collection, and objective of study) make interpretations of data collected in prior studies difficult. Differences in the way previous studies were conducted also made it difficult to distinguish between real differences in herbicide distribution in Midwestern ground water caused by natural factors and artificial differences in herbicide distribution attributable to study design.

To better understand the regional occurrence of herbicides in shallow aquifers of the Midwest, the U.S. Geological Survey designed a monitoring network of 303 wells completed in unconsolidated and bedrock aquifers (figs. 1 and 2) located throughout the Corn Belt (Kolpin and Burkart, 1991). Unconsolidated aquifers in the Midwest commonly consist of sand and gravel deposited by glacial meltwater or recent streams. Whereas, bedrock aquifers in the Midwest generally consist of sandstone, limestone, or dolomite. From 1991 to 1994, more than 800 ground-water samples were collected from these wells and analyzed for selected herbicides and herbicide degradation products (degradates) (Kolpin and others, 1993, 1996c). The consistency of this data set allows for a unique investigation of herbicide occurrence in shallow aquifers across the Midwest.

Widespread, Low-Level Occurrence

Detections of herbicides were relatively widespread in shallow aquifers across the Midwest (fig. 1), with one or more compounds being detected at or greater than 0.05 µg/L (microgram per liter, which is equivalent to "part per billion") in 40.3 percent of the 303 wells sampled. The concentrations

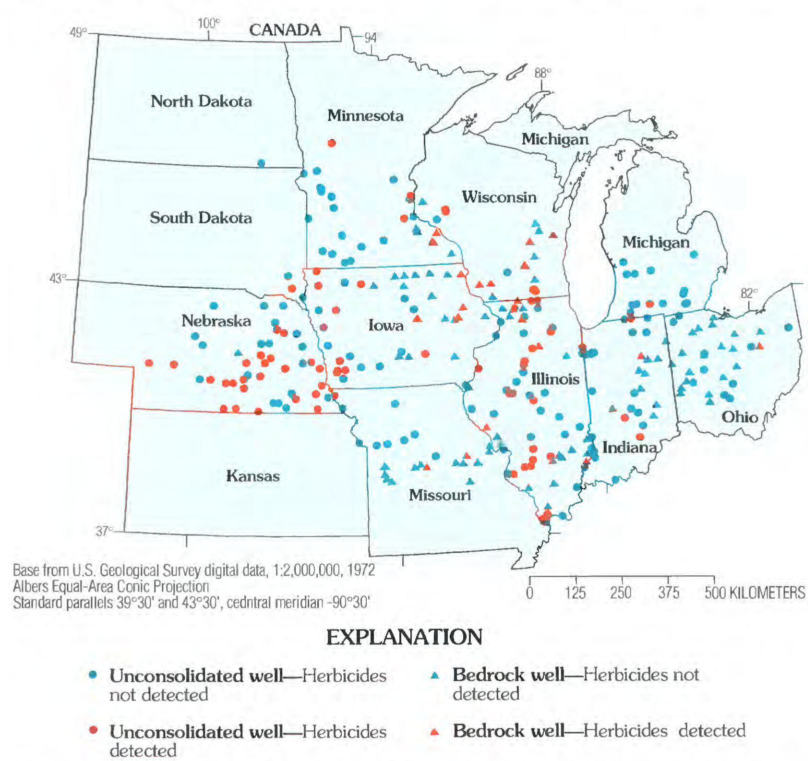


Figure 1. Location of all wells sampled for the study of shallow aquifers in the Midwestern United States and where herbicides were detected in ground water at or greater than 0.05 microgram per liter.

Figure 2. Example of a well sampled for this study.

measured, however, were generally low, with the median total herbicide concentration being approximately 0.5 µg/L. Only one sample had a herbicide concentration (alachlor = 4.3 µg/L) that exceeded a Maximum Contaminant Level (MCL) or Health Advisory Level (HAL) for drinking water (U.S. Environmental Protection Agency, 1995). However, these drinking-water criteria may not answer all questions related to health and environmental risks associated with the presence of herbicides in ground water. First, only 7 of the 13 compounds detected at or greater than 0.05 µg/L have MCLs or HALs established. Second, these criteria only consider the effects of individual pesticides and do not account for possible additive or synergistic toxicity from the presence of more than one compound. The co-occurrence of multiple herbicide compounds in ground-water samples was common during this study (fig. 3). Two or more compounds were present in 60 percent of samples where pesticides were detected. Third, these criteria only consider acute toxic effects and do not consider potential chronic effects such as reproductive, developmental, and neural-behavioral toxicity.

Most Frequently Detected Herbicides—The Importance of Degradates

Although numerous studies have been conducted investigating the occurrence of herbicides in ground water, few have considered the degradates of these herbicides. Degradates (also referred to as metabolites or transformation products) are formed as herbicides break down through chemical and microbial processes to form new compounds in the environment. Degradates were commonly found in shallow aquifers across the Midwest and were four of the five most frequently detected compounds for this study (fig. 4). The frequencies shown have been adjusted to a common detection threshold of 0.05 µg/L to take into account variations in reporting limits among the compounds examined. The frequency of detection for a given herbicide increased substantially when its degradates are considered (fig. 5). Also, a substantial part of the measured concentration for a given herbicide was in the form of its degradates (fig. 6). Consequently, both the overall occurrence (measurement of "how often") and concentration (measurement of "how much") of the herbicides are under-estimated in shallow aquifers if data on herbicide degradates are not considered. Information on degradates is essential to fully understanding the fate and occurrence of the parent herbicides and to determine the complete consequences of a herbicide's use on human health and the environment. Although some degradates appear to be less toxic than their parent compounds (Heydens and others, 1996; Stamper and Tuovinen, 1998), others have been shown to have similar acute (Kaufman and Kearney, 1970; Reddy and others, 1997) and chronic (Babic-Gojmerac and others, 1989; Lang and others, 1997) toxicity as their corresponding parent compounds.

Atrazine was the most frequently detected parent compound in this study (fig. 4). This is likely the result of a comparatively slow rate of atrazine degradation under environmental conditions (Agertved and others, 1992; Widmer and Spalding, 1995) and its long history of extensive use across the Midwest in both agricultural and nonagricultural settings. Indeed, atrazine has been the most frequently detected parent compound in many studies (Kross and others 1990; Holden and others, 1992; Kolpin and others, 1998).

Surprisingly, prometon was the second most frequently detected parent compound (fig. 4). Prometon is used primarily for nonagricultural purposes, such as domestic and commercial applications to driveways, fence lines, lawns, gardens, and as an asphalt additive (Healy, 1996; Pasquarell and Boyer, 1996). A direct association to nonagricultural land and prometon occurrence was found for this study (Burkart and Kolpin, 1993). Thus, agricultural activities are not the only sources of herbicide contamination of ground water, nonagricultural activities (such as urban and suburban use) also contribute to such contamination. The limited information available for prometon suggests that its use is far less than most of the other herbicides examined. What prometon lacks in use may be compensated for by its persistence in the environment, having the longest half-life of the herbicides examined (Wauchope and others, 1992).

Herbicides Found More Often In Young Water

A relation was determined between herbicide occurrence and the general age of the ground water sampled. General age was obtained by measuring the tritium (^3H) concentration in ground water. Tritium is a radioactive isotope of hydrogen (H) that was greatly increased in the atmosphere with the advent of atmospheric testing of nuclear weapons beginning in 1953. Thus, the amount of tritium in a sample can be used as a tracer to determine whether ground water was recharged before or after 1953. As

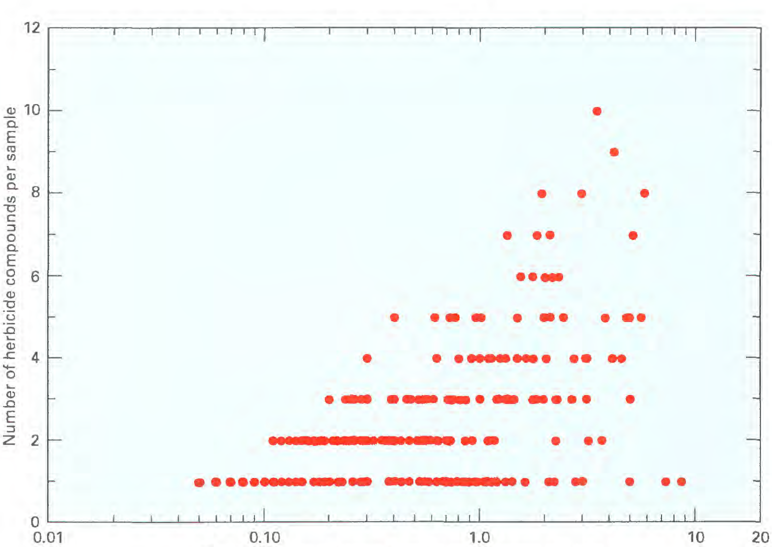


Figure 3. Relation between total herbicide concentration and number of compounds detected that were at or greater than 0.05 microgram per liter during 1991–94.

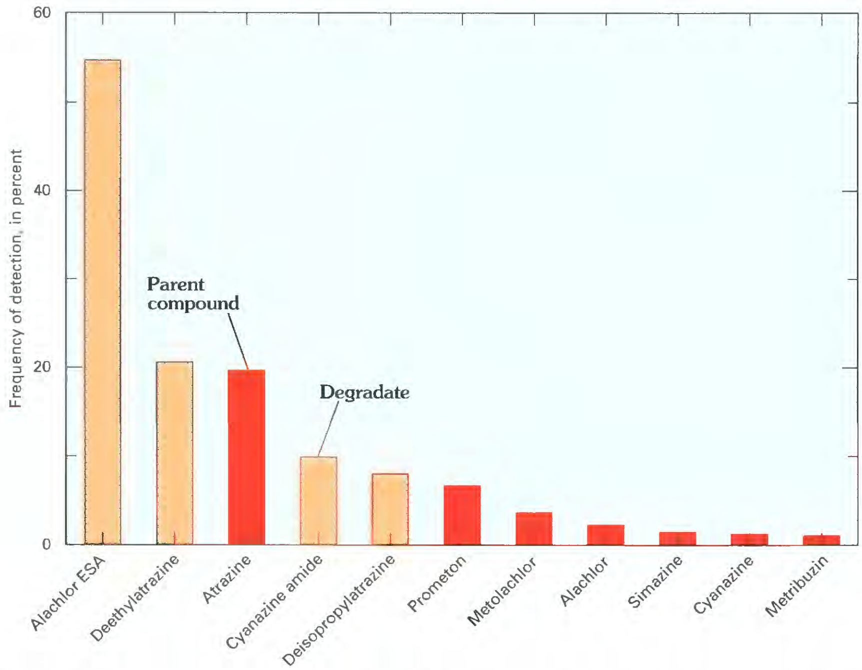


Figure 4. Most frequently detected herbicide compounds (adjusted to a common detection threshold of 0.05 microgram per liter). Alachlor ESA concentrations between the method detection limit (0.05 microgram per liter) and the analytical reporting limit (0.10 microgram per liter) were included in this graph.

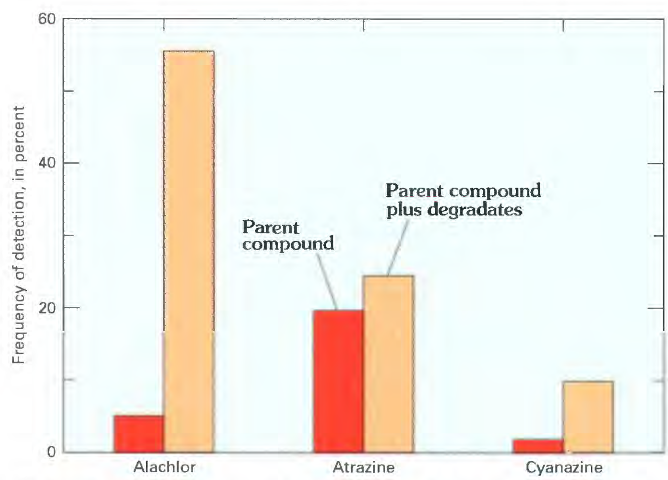


Figure 5. A comparison of the frequency of detection between the parent compound and its corresponding total concentration (parent plus its degradates) for selected herbicides examined during 1991–94.

expected, water that recharged ground water within the past 40 years is more likely to contain herbicides than water recharged earlier (fig. 7). Because the first significant use of herbicides to control weeds in crops also roughly coincides with the start of atmospheric testing of nuclear weapons, ground water determined to be older than 1953 would predate the use of herbicides. The general age of the water does not cause herbicide contamination but simply identifies an aquifer's susceptibility to contamination by indicating the presence of post-1953 recharge water.

Pre-1953 water was much more likely to occur in near-surface bedrock aquifers (47.1 percent, 16 of 34 randomly selected samples) than in near-surface unconsolidated aquifers (7.8 percent, 5 of 64 randomly selected samples). This provides insight as to the reason for the frequency of herbicide detection (using a 0.05-µg/L detection threshold), being substantially less in the bedrock aquifers (21.9 percent, 23 of 105 wells) than in the unconsolidated aquifers (50.0 percent, 99 of 198 wells) sampled.

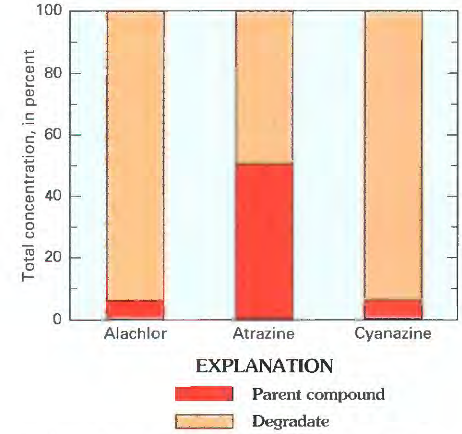


Figure 6. Percentages of measured total concentration derived from the parent compound and that derived from its degradates for selected herbicides, 1991–94.

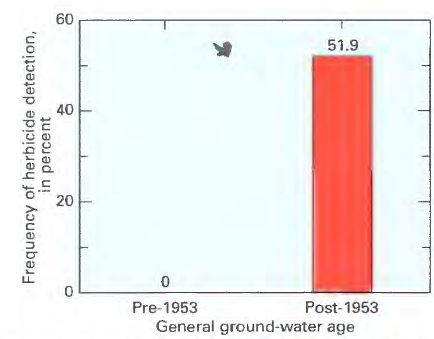


Figure 7. Relation between general age of ground water to frequency of herbicide detection at or greater than 0.05 microgram per liter, 1991–94.

Additional Reading

The results of this study have been published in a variety of publications. Additional reading on this study can be obtained from the following reports: Kolpin and others (1994, 1995, 1996a, 1996b), Kolpin and Thurman (1995), and Kolpin (1997).

—D.W. Kolpin, J.K. Stamer, D.A. Goolsby, and E.M. Thurman

Literature Cited

Agertved, J., Rugge, K., and Baker, J.F., 1992, Transformation of the herbicides MCPP and atrazine under natural aquifer conditions: Ground Water, v. 30, p. 500–506.

Babic-Gojmerac, T., Kneiwald, Z., and Kneiwald, J., 1989, Testosterone metabolism in neuroendocrine organs in male rats under atrazine and deethylatrazine influence: Journal of Steroid Biochemistry, v. 33, p. 141–146.

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 Water-Resources Investigations Report 94–4176, 87 p.

Burkart, 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.

Healy, D.F., 1996, Water-quality assessment of the Rio Grande Valley, Colorado, New Mexico, and Texas—Occurrence and distribution of selected pesticides and nutrients at selected surface-water sites in the Mesilla Valley, 1994–95: U.S. Geological Survey Water-Resources Investigations Report 96–4069, 85 p.

Heydens, W.F., Siglin, J.C., Holson, J.F., and Stegeman, S.D., 1996, Subchronic, developmental, and genetic toxicology studies with the ethane sulfonate metabolite of alachlor: Fundamental and Applied Toxicology, v. 33, p. 173–181.

Holden, L.R., Graham, J.A., Whitmore, R.W., Alexander, W.J., Pratt, R.W., Liddle, S.K., and Piper, L.L., 1992, Results of the National Alachlor Well Water Survey: Environmental Science and Technology, v. 26, no. 5, p. 935–943.

Kaufman, D.D., and Kearney, P.C., 1970, Microbial degradation of *s*-triazine herbicides: Residue Review, v. 32, p. 235–265.

Kolpin, D.W., 1997, Agricultural chemicals in groundwater of the midwestern United States—Relations to land use: Journal of Environmental Quality, v. 26, no. 4, p. 1025–1037.

Kolpin, D.W., Barbash, J.E., and Gilliom, R.J., 1998, Occurrence of pesticides in shallow groundwater of the United States—Initial results from the National Water-Quality Assessment Program: Environmental Science and Technology, v. 32, no. 5, p. 558–566.

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

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

_____1994, Herbicides and nitrate in near-surface aquifers of the Midcontinental United States, 1991: U.S. Geological Survey Water-Supply Paper 2413, 34 p.

Kolpin, D.W., Goolsby, D.A., and Thurman, E.M., 1995, Pesticides in near-surface aquifers—An assessment of highly sensitive analytical techniques and tritium: Journal of Environmental Quality, v. 24, no. 6, p. 1125–1132.

Kolpin, D.W., Nations, B.K, Goolsby, D.A., and Thurman, E.M., 1996b, Acetochlor in the hydrologic system in the Midwestern United States: Environmental Science and Technology, v. 30, no. 5, p. 1459–1464.

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 United States: Environmental Science and Technology, v. 30, no. 1, p. 335–340.

Kolpin, D.W., Zichelle, K.E., and Thurman, E.M., 1996c, 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.

Kross, B.C., Hallberg, G.R., and others, 1990, The Iowa State-wide rural well-water survey—Water-quality data, initial analysis: Iowa Geological Survey Technical Information Series Report 19, 142 p.

Lang, D.H., Rettie, A.E., and Bocker, R.H., 1997, Identification of enzymes involved in the metabolism of atrazine, terbuthylazine, ametryne, and terbutryne in human liver microsomes: Chemistry and Residue Toxicology, v. 10, p. 1037–1044.

Pasquarell, G.C., and Boyer, D.G., 1996, Herbicides in karst groundwater in southeast West Virginia: Journal of Environmental Quality, v. 25, p. 755–765.

Reddy, K.N., Locke, M.A., and Zablotowicz, R.M., 1997, Soil type and tillage effects on sorption of cyanazine and degradation products: Weed Science, v. 45, p. 727–732.

Stamper, D.M., and Tuovinen, O.H., 1998, Biodegradation of the acetanilide herbicides alachlor, metolachlor, and propachlor: Critical Reviews in Microbiology, v. 24, no. 1, p. 1–22.

U.S. Environmental Protection Agency, 1995, Drinking water regulations and health advisories: Washington, D.C., Office of Water.

Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., and Burt, J.P., 1992, The SCS/ARS/CES pesticide properties database for environmental decision-making: Review of Environmental Contamination and Toxicology, v. 123, p. 1–156.

Widmer, S.K., and Spalding, R.F., 1995, A natural gradient transport study of selected herbicides: Journal of Environmental Quality, v. 24, p. 445–453.

For additional information and selected reading about the Midcontinent Herbicide Project, write to:

U.S. Geological Survey
Mail Stop 415, Box 25046
Building 53, Wing F–200
Denver Federal Center
Lakewood, CO 80225

Additional information on the Midcontinent Herbicide Project and other USGS programs can be found by accessing "http://wwwrcolka.cr.usgs.gov/midconherb/index.html" on the World Wide Web.