

Herbicides in Midwestern Reservoir Outflows, 1992–93



Introduction

Reservoirs are an important resource in the 11 Midwestern States that comprise the upper Mississippi River Basin (see index map) often referred to as the Corn Belt (see map below). Reservoirs impound and store water for such beneficial uses as flood control, hydropower, irrigation, public supply, recreation, and wildlife habitat. However, reservoirs are also repositories for contaminants that are introduced into Midwestern streams. These contaminants, primarily generated from agricultural activities, include nutrients (nitrogen and phosphorus), pesticides (herbicides and insecticides), sediment, and sediment-associated contaminants (U.S. Environmental Protection Agency, 1984; Humenik and others, 1987).

Although most of the sediment entering reservoirs is permanently trapped and deposited along reservoir bottoms, chemicals such as soluble herbicides generally remain in the water column and are stored temporarily until they are flushed from the reservoir. This can substantially affect the water quality downstream from reservoirs. Unregulated

streams in the Midwest generally have high concentrations of herbicides for short periods of time immediately following planting as spring storms wash newly applied herbicides into streams (Wauchope, 1978; Thurman and others, 1991). In contrast, herbicides in streams regulated by reservoirs have smaller peak concentrations that can persist for a much longer period of time (Leung and others, 1982; Stamer and others, 1995).

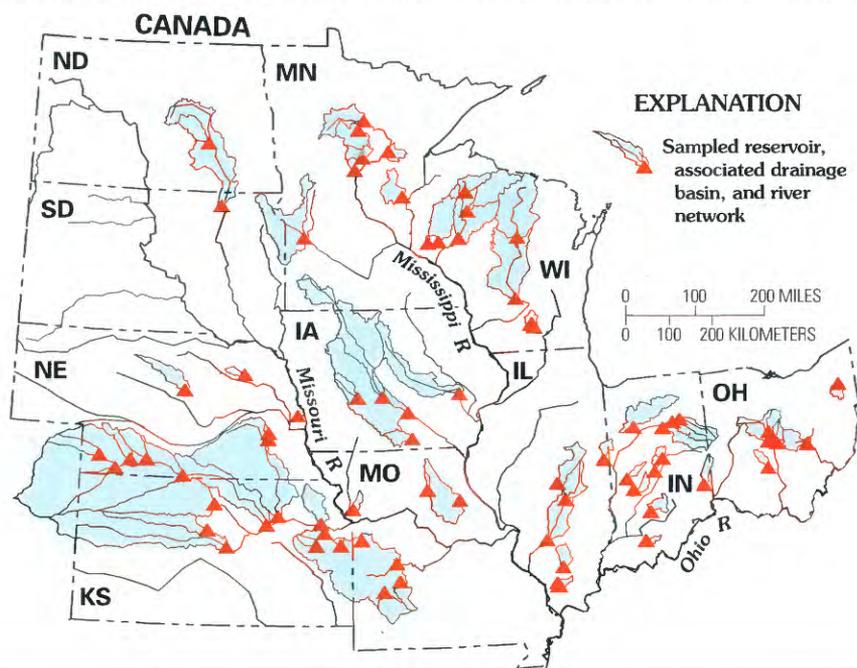
The length of time that reservoirs discharge water with elevated concentrations of herbicides depends on a number of factors. These factors include the time that water remains in a reservoir (residence time), the timing of inflow to the reservoir, the land use and herbicide use in the contributing drainage area, the timing and intensity of rainfall, and the physical and chemical characteristics of the herbicides themselves.

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). The three major row crops in the

Midwest with the highest rates of herbicide use are corn, soybeans, and sorghum. In 1992, use of the herbicides atrazine (21.3 million kilograms), alachlor (20.9 million kilograms), metolachlor (18.6 million kilograms), and cyanazine (11.3 million kilograms) on these three crops in the Corn Belt alone accounted for 25 percent of the 285 million kilograms of herbicides used in the United States (U.S. Department of Agriculture, 1993).

Although herbicides have many benefits, they may also produce a wide range of toxic side effects that may pose a potential hazard to human health and the environment. For instance, the U.S. Environmental Protection Agency (1996) classifies the herbicide alachlor as a human carcinogen, and several other herbicides including atrazine, cyanazine, and metolachlor are classified as possible human carcinogens. In addition, the effects of long-term, low concentrations of herbicides or combinations of herbicides on aquatic ecosystems are largely unknown.

To assess the effects of reservoirs on downstream concentrations of herbicides, 76 reservoirs, out of the more than 500 in the Midwest with a capacity of more than 5,000 acre-feet, were selected for study (see map at left). The purpose of the study was to evaluate the occurrence and temporal distribution of herbicides in Midwestern streams and to relate concentrations to human and natural factors. The drainage-basin areas of the reservoirs ranged from 44 to 64,560 square kilometers with a mean area of 6,140 square kilometers. Basins were highly variable with respect to land use, soil type, and climatic conditions. Cropland represented more than 50 percent of the land area in about 25 percent of the basins. Less than 5 percent of the basins were represented by less than 5 percent cropland. Reservoir outflows were sampled eight times (approximately bimonthly) from April 1992 through September 1993 for a total of 608 samples. The timing and frequency of sampling made it possible to

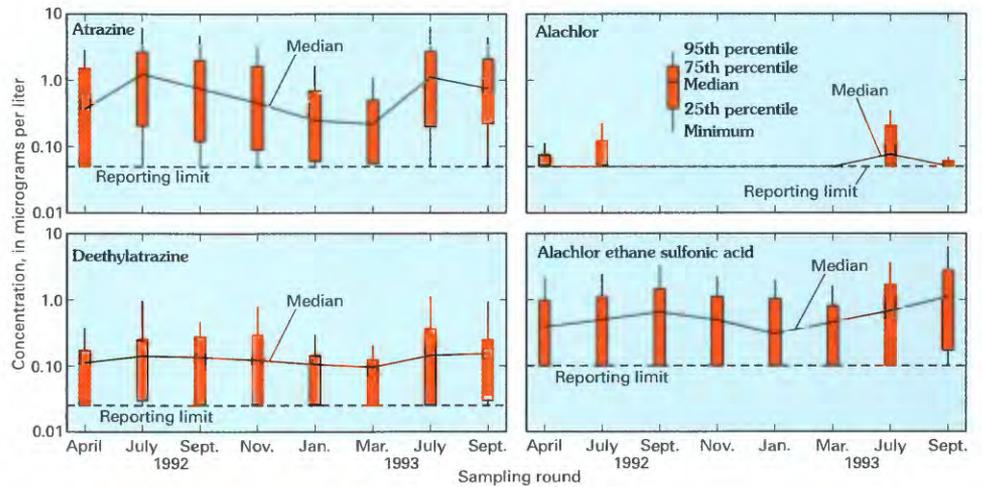


determine approximately when maximum and minimum concentrations of herbicides occurred in the reservoir outflows. All samples were collected using noncontaminating containers and analyzed for 11 herbicides and 6 herbicide metabolites (table 1). A metabolite is a compound that is formed from the breakdown of the parent herbicide.

Results

Most of the reservoirs sampled during this study had detectable concentrations of at least one or more herbicides and (or) metabolites (table 1). Atrazine, its two metabolites, deethylatrazine and deisopropylatrazine, and the alachlor metabolite alachlor ESA were the most frequently detected compounds, all being detected in more than 60 percent of the samples. Cyanazine and metolachlor were also detected in about 50 percent of the samples. The highest herbicide concentration detected was for atrazine [12.4 micrograms per liter ($\mu\text{g/L}$)], and the highest metabolite concentration was for alachlor ESA (19.7 $\mu\text{g/L}$). Of the parent herbicides, atrazine, the most extensively applied herbicide in the Corn Belt, occurred at the highest frequency (82 percent) and in the largest concentration (mean of 1.36 $\mu\text{g/L}$ for samples with detectable concentrations). Alachlor, the second most extensively applied herbicide after atrazine in 1992, was detected less frequently (29.8 percent of samples) and at smaller concentrations (mean of detectable concentrations of 0.27 $\mu\text{g/L}$ than either metolachlor or cyanazine. However, alachlor ESA was detected in a majority of the samples (70.2 percent) and had the highest mean concentration (1.74 $\mu\text{g/L}$) of all of the parent herbicides or metabolites analyzed. Alachlor ESA is more mobile and thought to be less toxic than alachlor, and its higher frequency of detection and larger concentrations in streams as compared to alachlor have been documented in other studies (Thurman and others, 1996; Kalkhoff and others, 1998).

During the 18-month study, the mean sum of the individual concentrations of alachlor and alachlor ESA was 1.9 $\mu\text{g/L}$ when at least one of the two compounds was detected. The mean sum of atrazine and its metabolites was also 1.9 $\mu\text{g/L}$, implying that alachlor and atrazine were used in nearly equal amounts in the study area, a finding consistent with use data (U.S. Department of Agriculture, 1993).



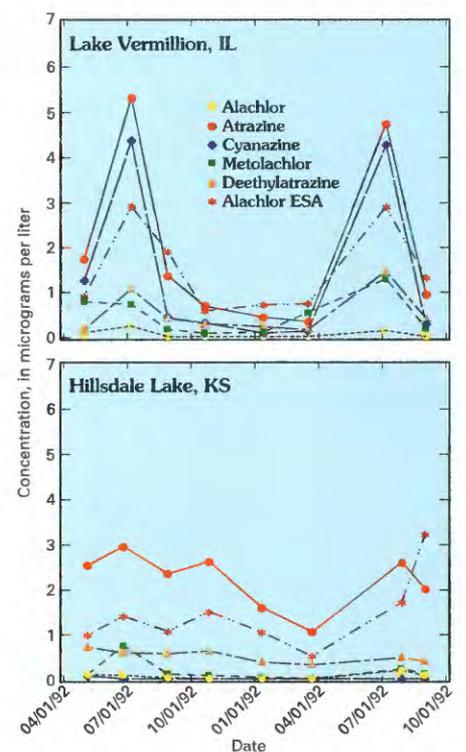
Similarly, the mean sum of the individual concentrations of cyanazine and its metabolites was 1.0 $\mu\text{g/L}$, about one-half the sum for alachlor and atrazine plus their metabolites. This result is also consistent with the fact that cyanazine usage in the study area was about one-half that of atrazine or alachlor.

The temporal variability in the concentrations of two herbicides and two metabolites in reservoir outflows are shown in the graphs above. Concentrations of the parent herbicides, in this case atrazine and alachlor, are generally smallest in the winter and early spring prior to planting. Concentrations of atrazine peaked in the summer gradually decreasing through the fall and winter. Concentrations of alachlor also peaked in the summer and were small or undetectable for the rest of the year. Concentrations of the metabolites deethylatrazine and alachlor ESA also varied seasonally but tended to peak later in the summer and appeared to be less variable as compared to the associated parent herbicides.

The variability in the concentrations of herbicides and metabolites in reservoir outflow is strongly affected by the reservoir residence time. Lake Vermillion in Illinois is a small reservoir with a volume of about 11.4 million cubic meters (9,200 acre-feet) and a relatively short residence time (about 9 days). As a result, water is flushed through the reservoir rapidly, and concentrations of herbicides and associated metabolites exhibit a temporal distribution similar to that of unregulated streams (see graphs at right). During both 1992 and 1993, concentrations of both herbicides and metabolites in Lake Vermillion outflow were low in late April, peaked rapidly in early July, and then decreased rapidly by early October. In contrast to Lake

Vermillion, Hillsdale Lake in Kansas (see photograph) has a much larger volume of about 89 to 160 million cubic meters (72,000-130,000 acre-feet) and a residence time of nearly 8 months. As a result, herbicides and metabolites delivered to Hillsdale Lake in the spring and early summer are stored and subsequently delivered downstream in smaller concentrations and for longer periods of time.

Statistical models were used to estimate mean herbicide concentrations in each reservoir outflow as a function of the physical characteristics of the reservoir, the land and chemical use in the drainage basin, soil characteristics, topographic conditions, and climatic variables. Results from the models indicate that the amount of herbicide used in a drainage basin is the primary process



affecting the concentration of the herbicide in reservoirs. The models also indicate that when drainage basins have steep slopes and poorly drained clay-rich soils, the receiving reservoirs tend to have higher herbicide concentrations. These findings suggest that best-management practices targeted at reducing the use of herbicides and reducing the loss of herbicides to surface- and ground-water systems will be the most successful in lowering herbicide concentrations in reservoirs.

Implications

The presence of herbicides and associated degradation products in reservoirs has implications that could affect the management of public-water supplies in the Midwest. Water from Midwestern reservoirs and streams that receive reservoir outflow are frequently used for public supply. A common characteristic of the 15 herbicides and associated degradation products detected in reservoir outflows during this study is that they are relatively water soluble; thus, they are readily transported in water. Studies have shown that conventional water treatment (coagulation, sand filtration, and chlorination) is ineffective at removing herbicides such as alachlor and atrazine from drinking water and, because of the similar chemical nature, would probably also be ineffective at removing their metabolites. As a result, additional treatment processes such as ozone (Adams and Randtke, 1992) or activated carbon (Najum and others, 1991) need be used to adequately treat herbicide-laden water. Because reservoirs tend to lengthen the period of time that elevated herbicide concentrations are present in the water column, additional treatment may be required during most of the year when the water source is located either in or downstream from a reservoir.

The U.S. Environmental Protection Agency (1996) has established either a Maximum Contaminant Level (MCL) or a Health Advisory Level (HAL) for 9 of the 11 parent herbicides analyzed in this study (table 1). MCLs are legally enforceable drinking-water regulations, whereas HALs are drinking-water criteria and nonenforceable. Because MCLs and HALs are based on annual average concentrations, one or more exceedances of the specified value does not necessarily indicate noncompliance. MCLs or HALs have not been established for any of the six herbicide metabolites

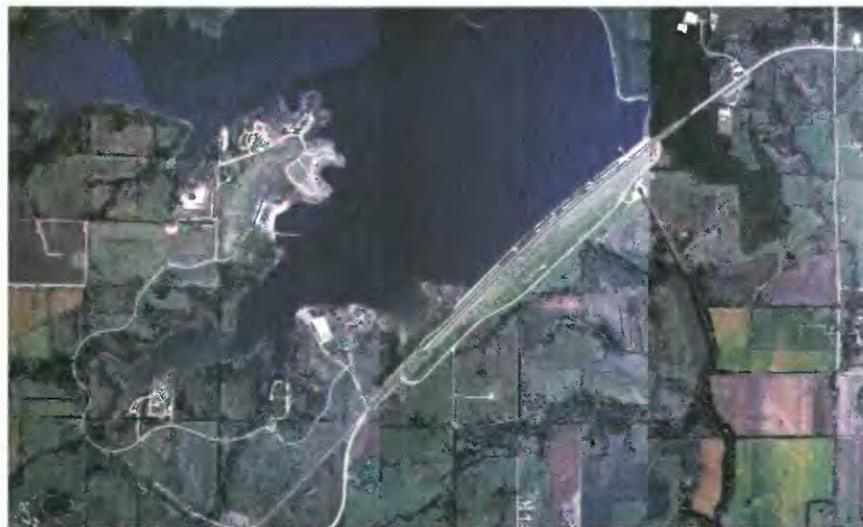


PHOTO COURTESY OF THE MIAMI COUNTY FARM SERVICE AGENCY

Seasonal variations in herbicide concentrations from stream inflow to Hillsdale Lake, a Federally owned multiple-use reservoir in Kansas, appear to be decreased because the volume of water in the lake was large in relation to its outflow.

analyzed during this study or for the combination of the parent herbicides and associated metabolites. However, if the concentrations of the associated metabolites are added to the concentrations of the parent herbicides, the number of reservoirs with mean

annual outflow concentrations that exceeded the parent compound MCL or HAL increases. For example, in 1992, 17 reservoirs would have exceeded the MCL for atrazine on the basis of atrazine and its associated metabolites compared to 6 reservoirs on the basis of atrazine

Table 1. Herbicides and metabolites analyzed in samples collected from 76 Midwestern reservoir outflows, April 1992 through September 1993
[µg/L, micrograms per liter; <, less than]

Herbicide or metabolite	Report- ing limit (µg/L)	Percent of samples with detection ¹	Median concentration ¹ (µg/L)	Mean of samples with detect- able concentrations ¹ (µg/L)	Maximum Contami- nant Level (µg/L)	Health Advisory Level (µg/L)
Herbicides						
Alachlor ²	0.05	29.8	<0.05	0.27	2.0	2.0
Ametryn ²	.05	.7	<.05	.06	---	60
Atrazine ²	.05	82.1	.43	1.36	3.0	3.0
Cyanazine ²	.05	47.2	<.05	.61	---	1.0
Metolachlor ²	.05	53.3	.07	.60	---	70
Metribuzin ²	.05	5.3	<.05	.25	---	100
Prometon ²	.05	9.9	<.05	.12	---	100
Prometryn ²	.05	0	<.05	---	---	---
Propazine ²	.05	4.1	<.05	.10	---	10
Simazine ²	.05	19.7	<.05	.21	4.0	4.0
Terbutryn ²	.05	0	<.05	---	---	---
Herbicide metabolites						
Alachlor ESA ²	.10	70.2	.52	1.74	---	---
Cyanazine amide ³	.05	49.3	<.05	.43	---	---
Deethylatrazine ³	.05	71.6	.17	.39	---	---
Deisopropylatrazine ³	.05	61.8	.08	.26	---	---
Deethylcyanazine ³	.05	25.2	<.05	.14	---	---
Deethylcyanazine amide ³	.05	2.0	<.05	.62	---	---

¹Concentration at or above reporting limits.

²Based on 608 reservoir outflow samples.

³Based on 511 reservoir outflow samples.

only. Similarly, 14 reservoirs would have exceeded the HAL for cyanazine in 1992 on the basis of cyanazine and its associated metabolites compared to 6 reservoirs on the basis of cyanazine only. If alachlor ESA were added to the concentration of alachlor, 11 reservoirs would have exceeded the MCL in 1992, and 16 reservoirs would have exceeded the MCL in 1993. However, unlike the atrazine and cyanazine metabolites, alachlor ESA is a chlorine-free compound upon degradation; thus, it is considered to be less toxic than the parent compound (Baker and others, 1993). Therefore, a comparison of the sum concentration of alachlor plus alachlor ESA to established MCLs for alachlor probably is not valid.

—John K. Stamer, William A. Battaglin, and Donald A. Goolsby

This Fact Sheet is based largely on information contained in the following publications and references cited therein:

Battaglin, W.A., and Goolsby, D.A., 1996, Using GIS and regression to estimate annual herbicide concentrations in outflow from reservoirs in the Midwestern USA, 1992–93, in Hallam, C.A., and others, eds., GIS and water resources, Proceedings: American Water Resources Association Annual Symposium, Fort Lauderdale, Florida, September 22–26, 1996, p. 89–98.

Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W., and Thurman, E.M., 1993, Persistence of herbicides in selected reservoirs in the Midwestern United States—some preliminary result, in Goolsby, D.A., Boyer, L.L., and Mallard, G.E., compilers, Selected papers on agricultural chemicals in water resources of the midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 51–74.

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

Additional References

- Adams, C.D., and Randtke S.J., 1992, Removal of atrazine from drinking water by ozonation: *Journal American Water Works Association*, v. 84, no. 1, p. 91–102.
- Baker, D.B., Bushway, R.J., Adams, S.A., and Macomber, Carol, 1993, Immunoassay screens for alachlor in rural wells—false positives and an alachlor soil metabolite: *Environmental Science & Technology*, v. 27, no. 3, p. 562–564.
- 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.
- Humenik, F.J., Smolen, M.D., and Dressing, S.A., 1987, Pollution from nonpoint sources: *Environmental Science & Technology*, v. 21, no. 8, p. 737–742.
- Kalkhoff, S.J., Kolpin, D.W., Thurman, E.M., Ferrer, Imma, and Barcelo, Damia, 1998, Degradation of chloroacetanilide herbicides—the prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwaters and surface waters: *Environmental Science & Technology*, v. 32, no. 11, p. 1738–1740.
- Leung, S.T., Bulkley, R.V., and Richard, J.J., 1982, Pesticide accumulation in a new impoundment in Iowa: *Water Resources Bulletin*, v. 18, no. 3, p. 485–493.
- Najum, I.N., Snoeyink, V.L., Lykins, B.W., Jr., 1991, Using powdered activated carbon—a critical review: *Journal American Water Works Association*, v. 83, no. 1, p. 65–76.
- Stamer, J.K., Gunderson, K.D., and Ryan, B.J., 1995, Atrazine concentrations in the Delaware River, Kansas: U.S. Geological Survey Fact Sheet FS–001–94, 2 p.
- Thurman, E.M., Goolsby, D.A., Aga, D.S., Pomes, M.L., and Meyer, M.T., 1996, Occurrence of alachlor and its sulfonated metabolite in rivers and reservoirs of the midwestern United States—the importance of sulfonation in the transport of chloroacetanilide herbicides: *Environmental Science & Technology*, v. 30, no. 2, p. 569–574.
- 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, no. 10, p. 1794–1796.
- U.S. Department of Agriculture, 1993, Agricultural chemical usage—1992 field crops summary: U.S. Department of Agriculture, National Agriculture Statistics Service, 118 p.
- U.S. Environmental Protection Agency, 1984, Report to Congress—nonpoint source pollution in the U.S.: Washington, D.C., Office of Water Program Operations, Water Planning Division, unnumbered pages.
- 1996, Drinking water regulations and health advisories: Washington, D.C., EPA–B–96–002, 11 p.
- Wauchope, R.D., 1978, The pesticide content of surface water draining from agricultural fields—a review: *Journal of Environmental Quality*, v. 7, no. 4, p. 459–472.

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

U.S. Geological Survey
Mail Stop 406, Box 25046
Building 53, Room F-1200
Denver Federal Center
Lakewood, CO 80225

Additional information on the Midcontinent Herbicide Project and other USGS programs can be found on the World Wide Web at:

<http://wwwrcolka.cr.usgs.gov/midconherb/index.html>

Additional information on the USGS Toxic Program, which funded this effort, can be found on the World Wide Web at:

<http://toxics.usgs.gov/toxics>