U.S. Department of the Interior
U.S. Geological Survey

Pesticides in Surface Waters

Current Understanding of Distribution and Major Influences

This report summarizes a comprehensive analysis of existing information on national and regional patterns of pesticide occurrence in surface waters of the United States and the major influences on the sources and transport of pesticides. It is one of a four-part series that synthesizes current knowledge and understanding of pesticides in the nation's water resources as part of the National Water Quality Assessment Program.

Pesticides in the Hydrologic System

More than 1.1 billion pounds of pesticides are used each year in the United States. National agricultural use of herbicides, insecticides, and fungicides has grown from 190 million pounds of active ingredient in 1964 to an estimated 811 million pounds in 1993. Although the use of pesticides has resulted in increased crop production and other benefits, concerns about the potential adverse effects of pesticides on environmental and human health have grown steadily. The greatest potential for adverse effects of pesticides, in many respects, is through contamination of the hydrologic system. Water is one of the primary pathways by which pesticides are transported from their application areas to other parts of the environment (Figure 1). Once pesticides reach streams, they can be widely dispersed into other streams, rivers, lakes, reservoirs, and oceans.

Highlights

- Low levels of pesticides have been widespread in the nation's surface waters for several decades.
- Pesticide concentrations in surface waters follow strong seasonal patterns that result from the timing of pesticide applications and runoff conditions.
- Many pesticides are rarely detected in surface waters because of relatively low use, how they are applied, chemical properties, or elevated detection limits.
- In many streams, some pesticides exceed water-quality criteria for seasonal periods each year, but annual average concentrations seldom exceed regulatory standards for drinking water.
- Potential effects of pesticides on humans and aquatic ecosystems are difficult to evaluate because of inadequate information on effects of low-level mixtures, transformation products, and seasonal exposure.
- Improved information is needed on long-term trends, pesticides and transformation products that have not been widely measured, and biological effects of typical exposure patterns.

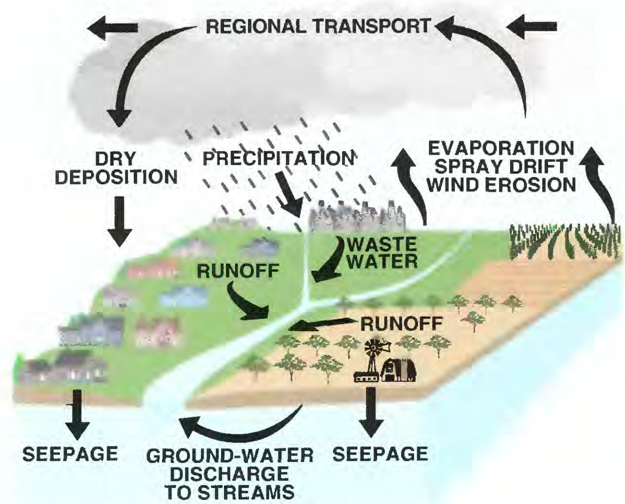

Figure 1. *Pesticide movement in the hydrologic cycle (from Majewski and Capel, 1995).*

Importance of Surface Waters

Streams and reservoirs supply approximately 50 percent of the nation's drinking water, primarily in urban areas. Streams, reservoirs, lakes, and downstream estuaries are also vital aquatic ecosystems that provide important environmental and economic benefits. Surface waters are particularly vulnerable to pesticide contamination because runoff from most agricultural and urban areas, where pesticides are applied, drains into streams. Pesticides may also enter streams through wastewater discharges, atmospheric deposition, spills, and ground water inflow. The uses and ecological significance of surface water, combined with its vulnerability to contamination, make it particularly important to understand the extent and significance of pesticides in this component of the hydrologic system.

Historical Study Efforts

Several large national and multistate studies of pesticides in rivers and streams were conducted between the late 1950's and the mid-1970's. In these and most other studies during this period, the focus was on organochlorine insecticides (such as DDT and dieldrin), a few phenoxy acid herbicides (such as 2,4-D), and organophosphorus insecticides (such as diazinon) in use at the time. Use of organochlorine insecticides declined dramatically after the 1960's, and use of organophosphorus and carbamate insecticides increased. In addition, agricultural use of herbicides has increased dramatically during the last 30 years, from an estimated 84 million pounds in 1964 to more than 500 million pounds in 1992.

In response to the changes in pesticide use, the number of different types of pesticides monitored in surface waters from the mid-1970's to the present has increased (Figure 2). The scale of monitoring studies has changed as well. The national and multistate studies conducted during the 1960's and 1970's have been largely replaced by state and local studies, or by regional studies directed at specific river basins. Recent studies have been relatively short-term and their geographic distribution is highly uneven. Iowa, California, Florida, and the Great Lakes region have been the most frequently studied areas. The most extensive regional studies have been conducted in the Mississippi River Basin. Overall, there has been a steady increase in monitoring of pesticides in surface waters over the last several decades.

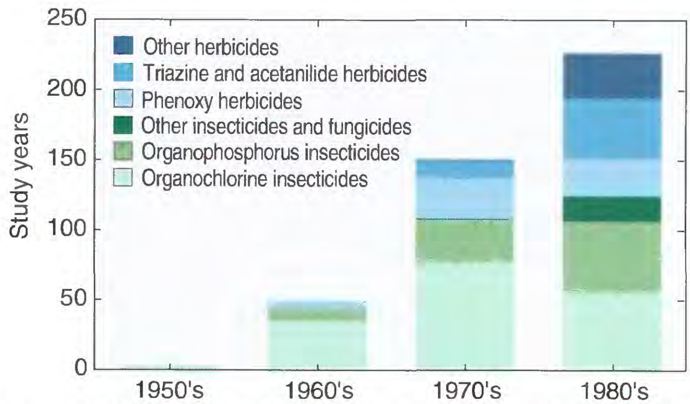

Figure 2. *Distribution of study effort in the studies reviewed, by decade. Each year in which samples were collected in a specific study is defined as one study year regardless of starting month.*

Pesticides Found in Surface Waters

Past studies have detected pesticides in surface waters in all regions of the nation. Of the hundreds of pesticide compounds that have been used in the United States, however, only 98 pesticides and 20 pesticide transformation products were included as analytes in the reviewed studies. Of these 118 compounds, 76 were detected in one or more surface water sites in at least one study. In Figure 3, detection frequencies for herbicides and insecticides are compared with agricultural use. The detection frequencies shown are for compounds targeted at numerous sites in the reviewed studies. Absence of a pesticide in Figure 3 does not necessarily mean that it does not occur in surface waters, but often that it was not studied.

In general, herbicides have been detected more frequently than insecticides, consistent with the greater use of herbicides. The most frequently detected herbicides include several triazines (atrazine, cyanazine, and simazine), acetanilides (metolachlor and alachlor), and 2,4-D. These compounds are among the highest in current agricultural use. Trifluralin and butylate were detected less frequently, despite relatively high use. These are volatile compounds that are usually incorporated into the soil when applied—two factors that reduce the likelihood of transport to surface waters.

Many of the insecticides studied were rarely detected because of low use. Some with relatively high use were rarely detected for other reasons. For example, toxaphene has a high detection limit and aldrin degrades to dieldrin after application. The most frequently detected insecticides that are currently used are carbofuran and diazinon. Some organochlorine compounds that are no longer used were among the most frequently detected insecticides. While many of these detections occurred in studies conducted in the 1960's and 1970's, these compounds have also been detected in surface waters in more recent studies. This results from their storage in the bed sediments of rivers and lakes and their continued inputs from the atmosphere and soil contaminated from past agricultural applications.

While data are sparse in some areas of the nation, pesticide occurrence in surface waters is relatively well documented in the Mississippi River Basin and other parts of the Midwest. Several large regional studies have been conducted recently in this area. These include a 1989-90 survey of 147 streams in the Midwest, a study of the Mississippi River and six major tributaries during 1991-92, and a 1992 study of 76 Midwestern reservoirs. In addition, several Lake Erie tributaries have been monitored from 1983 to the present. All of these studies targeted triazine and acetanilide herbicides, several pesticide transformation products, and insecticides and other herbicides used in the Midwest. Herbicides were detected at nearly all sites in these studies, with atrazine, metolachlor, alachlor, cyanazine, and deethylatrazine (an atrazine transformation product) detected most frequently. Maximum concentrations of these compounds were in the micrograms per liter range, with concentrations generally highest in the smallest rivers. Herbicides of other chemical classes and insecticides were observed less frequently and at much lower concentrations in these studies.

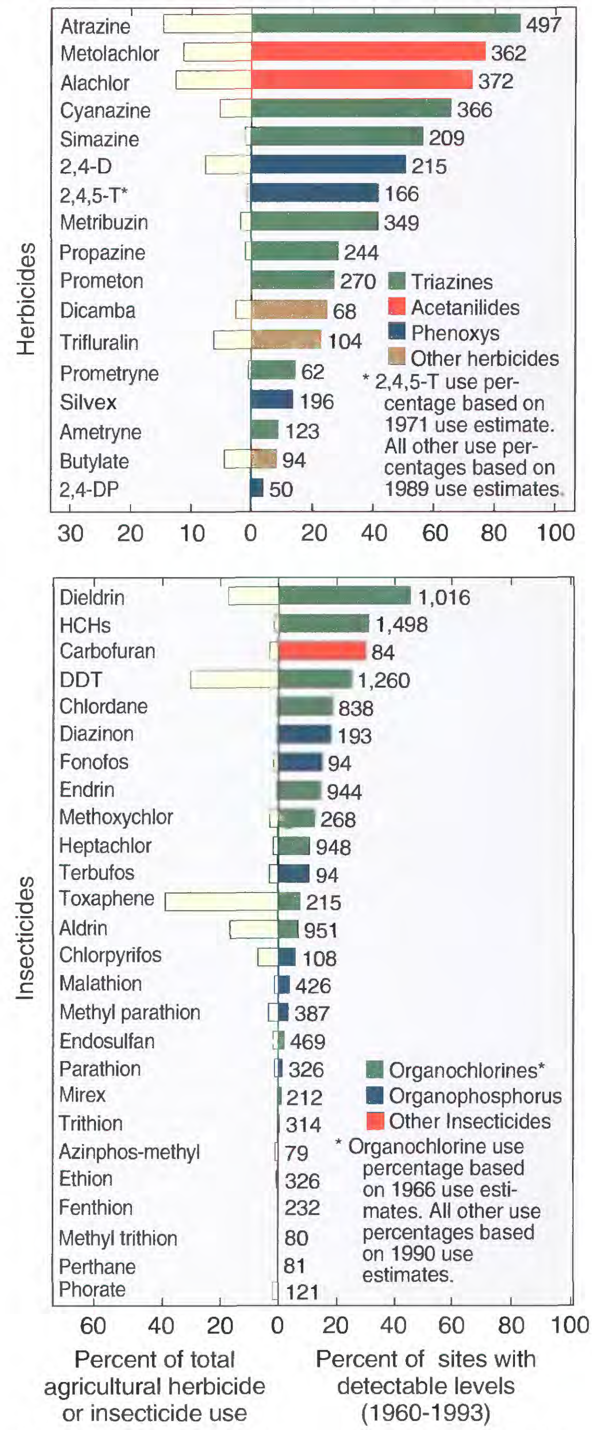

Figure 3. *Detection frequency for pesticides targeted at 50 or more sites in 127 studies conducted between 1958 and 1993. The relative agricultural use of each pesticide is shown in the left half of each graph. Numbers at right of bars represent the number of sites at which chemical was targeted.*

For the most part, the available data are not sufficient to determine any long-term trends in pesticide occurrence in surface waters because of the lack of studies in which the same sites were sampled consistently over a number of years, and to the inherent variability of pesticide concentrations in surface waters. The

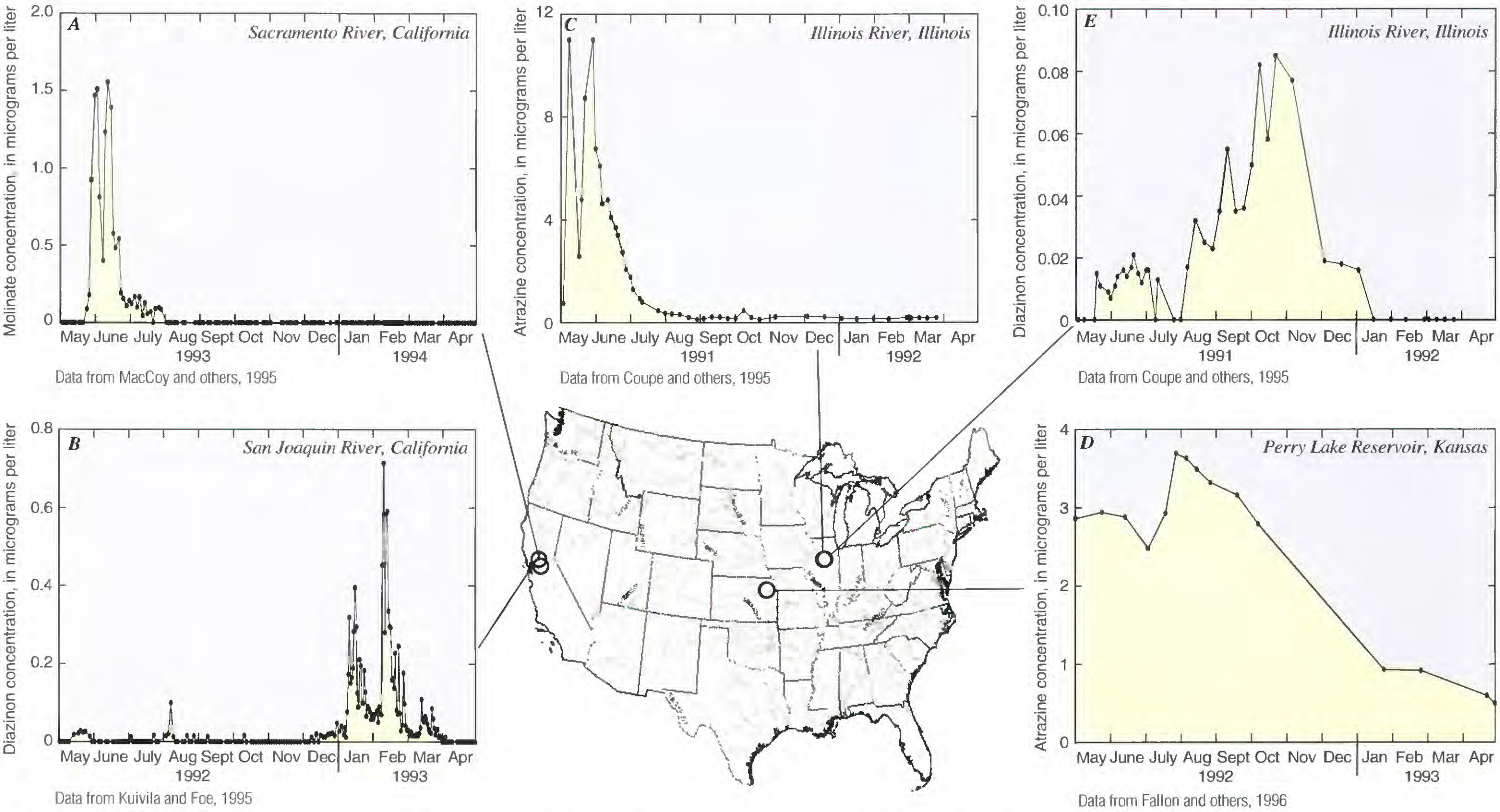

Figure 4. *Seasonal patterns of pesticide occurrence in surface waters in several different regions of the United States.*

increase in detections of triazine and acetanilide herbicides throughout the 1980's and 1990's may be more an indication of a trend toward more targeted monitoring than an actual trend in the occurrence of these compounds in surface waters. In the study of Lake Erie tributaries, for example, concentrations of several triazine and acetanilide herbicides were monitored for eight years in streams draining agricultural areas, with no discernible trend in concentrations over time (Richards and Baker, 1993).

Seasonality of Pesticides in Surface Waters

Seasonal patterns of pesticide occurrence in surface waters vary in different areas of the U.S. In Figure 4, examples of several relatively well-documented seasonal patterns are shown. Herbicides and insecticides used on rice in California have a distinct seasonal concentration pattern in streams because of the release of irrigation water at specific times. This is shown for the herbicide molinate in Figure 4*A*. In streams draining the Central Valley of California, there is a seasonal appearance of diazinon and other organophosphorus insecticides used on orchards in January and February (Figure 4*B*). Rainfall following an application results in movement of the insecticides to surface waters, and pulses of elevated concentrations continue downstream to San Francisco Bay.

In midwestern rivers, the pattern for preemergent herbicides, such as atrazine and alachlor, is relatively well known (Figure 4*C*). Concentrations of some herbicides in streams that drain agricultural areas show a distinct peak in spring and early summer that lasts for a few days to several months, depending on the timing and number of rain events and the size of the drainage basin. By midsummer, transport of herbicides to surface waters diminishes and riverine concentrations decline.

The seasonal cycle of herbicide concentrations in midwestern reservoirs is somewhat different than in rivers. This is shown for atrazine in Figure 4*D*. Reservoirs in the Midwest receive much of their water during the spring runoff period, when concentrations of herbicides in tributary streams are relatively high. Concentrations may remain elevated in reservoirs much longer than in streams, because the herbicides are not flushed from the system as quickly. Relatively high levels of atrazine, cyanazine, metolachlor, and several transformation products of atrazine and alachlor have been observed in reservoirs long after inputs of these compounds from agricultural fields have declined (Goolsby and others, 1993).

The seasonal pattern of diazinon concentrations in the Illinois River (Figure 4*E*) is different from the pattern for the agricultural herbicides. Concentrations in 1991 were elevated throughout the summer and fall, with peak concentrations occurring in the fall. Diazinon is an organophosphorus insecticide used primarily in non-agricultural applications in the Midwest, including lawn care. The Illinois River drains a major urban area (Chicago), and the seasonal pattern is probably the result of applications to lawns by home-owners and commercial applicators.

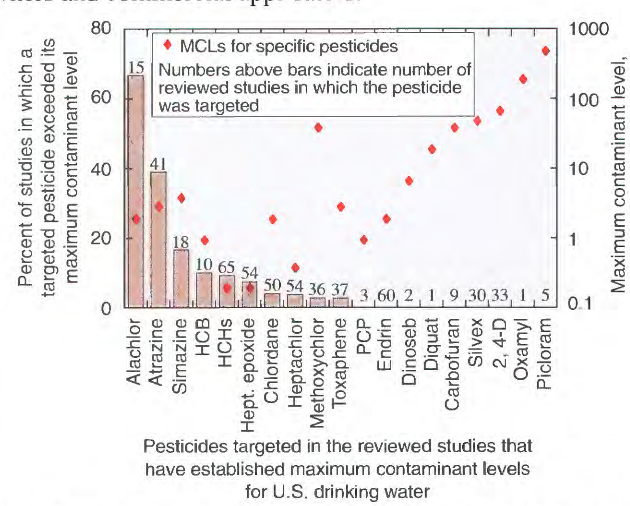

Figure 5. *Percentage of reviewed studies in which a pesticide concentration exceeded a maximum contaminant level (MCL).*

Significance to Water Quality

Under provisions of the Safe Drinking Water Act, the U.S Environmental Protection Agency (EPA) has established maximum contaminant levels (MCLs) for concentrations of certain chemicals in drinking water. Of the currently used pesticides, only nine have established MCLs. Compliance with the Safe Drinking Water Act is determined by the annual average concentration of a specific contaminant in drinking water, based on quarterly sampling. While the MCLs do not directly pertain to concentrations of pesticides in untreated surface waters, they provide benchmark values for comparisons, and they provide perspectives on the significance of the levels observed in surface waters.

The percentage of reviewed studies in which a pesticide exceeded an MCL is shown in Figure 5. Seven of these compounds are organochlorine pesticides or their degradation products, detected primarily in the 1960's and 1970's. In recent years, the herbicides alachlor, atrazine, and simazine have frequently exceeded their MCLs in individual samples. A number of studies have shown that procedures commonly used at most water treatment plants have little effect on concentrations of these herbicides in water. Thus, drinking water derived from some surface water sources in the central United States likely contains concentrations of one or more of these compounds above the MCL for part of the year because of the seasonal pattern described earlier. Annual mean concentrations however, rarely exceed the MCL. A series of exposure assessments done for atrazine, the most commonly detected pesticide, indicate that the majority of people whose drinking water is obtained from surface water sources in the central United States are exposed to annual average concentrations below the MCL (Ciba-Geigy, 1993). The typical situation for a small stream is illustrated in Figure 6, which shows results from eight years of monitoring of alachlor concentrations in Honey Creek, Ohio. Average monthly concentrations of alachlor routinely exceeded the MCL of 2 micrograms per liter during spring and early summer, but the annual average concentration remained below the MCL throughout the 9-year period. In larger rivers, concentrations of herbicides rarely exceeded MCLs. In the Mississippi River, for example, the annual average concentration of atrazine remained below the MCL of 3 micrograms per liter during 15 consecutive years of monitoring at Vicksburg, Mississippi (Ciba-Geigy, 1992).

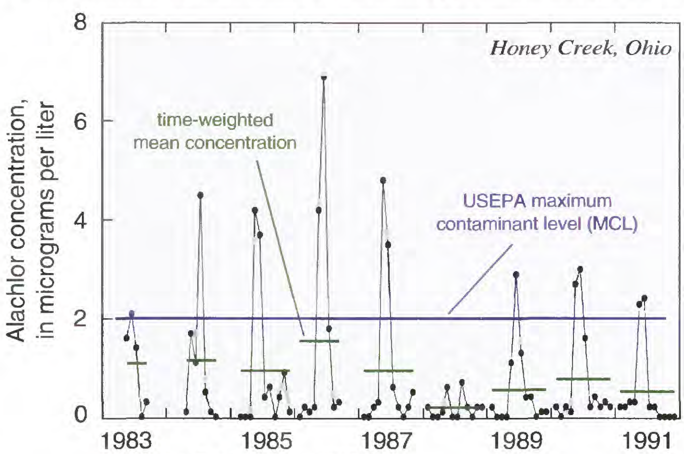

Figure 6. *Comparison of the long-term record of time-weighted mean and average monthly concentrations of alachlor in a small Midwestern stream with maximum contaminant level established for alachlor in drinking water (modified from Richards and Baker, 1993).*

The EPA has established water-quality criteria for the protection of aquatic organisms for short-term (acute) and long-term (chronic) exposures. These guidelines have been established for only 20 of the 118 compounds targeted in the studies reviewed. The National Academies of Sciences and Engineering (NAS/NAE) have recommended criteria concentrations for another 23 of the compounds. All of the organochlorine insecticides targeted in the reviewed studies have exceeded an aquatic-life criterion, if one has been established. Diazinon, an organophosphorus insecticide, has frequently exceeded its NAS/NAE chronic criterion of 0.009 micrograms per liter. No EPA aquatic-life criteria have been established for herbicides, and only 12 have NAS/NAE criteria. Atrazine concentrations often exceed the NAS/NAE criterion of 1 microgram per liter established for protection of marine organisms. NAS/NAE criteria for other herbicides were rarely exceeded. Aquatic-life criteria have not been established for any of the high-use agricultural fungicides.

Our ability to assess the significance of pesticides in surface waters is limited by several factors. First, water-quality criteria have not been established for most pesticides and pesticide transformation products, and existing criteria may be revised as more is learned about the toxicity of these compounds. Second, criteria are based on tests with individual pesticides and do not account for possible cumulative effects if several different pesticides are present. Finally, many pesticides and most transformation products have not been widely monitored in surface waters. These factors, and the lack of data on long-term trends, show significant gaps in our understanding of the extent and significance of pesticide contamination on surface waters. The results of this analysis indicate a need for long-term monitoring studies in which a consistent study design is used and more of the currently used pesticides and their transformation products are targeted.

Additional Reading:

This Fact Sheet is based on the book by S.J. Larson, P.D. Capel, and M.S. Majewski, in press, Pesticides in the Hydrologic System, Vol. 3: Pesticides in Surface Waters, Ann Arbor Press, Inc., Chelsea, Michigan; for more information call 1-800-858-5299.

References:

Ciba-Geigy, 1992, A review of historical surface water monitoring for atrazine in the Mississippi, Missouri, and Ohio Rivers: Ciba-Geigy Corporation, Environmental and Public Affairs Department, Technical Report 6-92, 69 p.

Ciba-Geigy, 1993, Atrazine and drinking water sources: an exposure assessment for populations using the greater Mississippi River system: Ciba-Geigy Corporation, Environmental and Public Affairs Department, Technical Report 2-93, 20 p.

Coupe, R.H., Goolsby, D.A., Iverson, J.L., Markovchick, D.J., and Zaugg, S.D., 1995, Pesticide, nutrient, water-discharge and physical-property data for the Mississippi River and some of its tributaries, April 1991-September 1992: U.S. Geological Survey Open-File Report 93-657, 116 p.

Fallon, J.D. and Thurman, E.M., 1996, Determining the relative age, transport, and three-dimensional distribution of atrazine in a reservoir using immunoassay, *in* Morganwalp, D.W., and Aronson, D.A, eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Colorado Springs, Colorado, September 20-24, 1993: U.S. Geological Survey Water-Resources Investigations Report 94-4015, v. 1, p. 499-504.

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 results: U.S. Geological Survey, Open-File Report 93-418, p. 51-63.

MacCoy, D., Crepeau, K.L., and Kuivila, K.M., 1995, Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-94: U.S. Geological Survey Open-File Report 95-110, 27 p.

Majewski, M.S., and Capel, P.D., 1995, Pesticides in the atmosphere: Distribution, trends, and governing factors, Ann Arbor Press, Inc., Chelsea, Mich., 228 p.

Kuivila, K.M. and Foe, C.G., 1995, Concentrations, transport, and biological effects of dormant spray pesticides in the San Francisco Estuary, California: Journal of Environmental Toxicology and Chemistry, v. 14, no. 7, p. 1141-1150.

Richards, R.P., and Baker, D.B., 1993, Pesticide concentration patterns in agricultural drainage networks in the Lake Erie Basin: Journal of Environmental Toxicology and Chemistry, v. 12, no. 1, p. 13-26.

For more information:

Information on technical reports and hydrologic data related to National Water Quality Assessment (NAWQA) pesticide studies can be obtained from:

Chief, Pesticide National Synthesis
U.S. Geological Survey
Placer Hall
6000 J Street
Sacramento, CA 95819-6129

Additional information on NAWQA and other U.S. Geological Survey programs can be found by accessing the NAWQA home page on the World Wide Web at "http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html."

U.S. Geological Survey Fact Sheet FS-039-97

☆ U.S. GOVERNMENT PRINTING OFFICE: 1997–584–741