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# Pesticides in Stream Sediment and Aquatic Biota

*Current Understanding of Distribution and Major Influences*

*This report summarizes a comprehensive analysis of existing information on pesticides in bed sediment and aquatic biota of United States rivers and streams: their geographic distribution, sources, trends, environmental fate, and biological significance. 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

About 1 billion pounds of pesticides are used each year in the United States to control weeds, insects, and other organisms. About 80 percent of this quantity is used in agriculture. Although the use of pesticides has resulted in increased crop production and other benefits, it has raised concerns about potential adverse effects on the environment and human health.

In many respects, the greatest potential for unintended adverse effects of pesticides is through contamination of the hydrologic system, which supports aquatic life and related food chains and is used for recreation, drinking water, irrigation, and many other purposes. Water is one of the primary pathways by which pesticides are transported from their application areas to other parts of the environment (see Figure 1).

## Importance of Stream Sediment and Biota

Sediment serves as a habitat for benthic biota (such as insects and clams, which are commonly consumed by fish), as both a source and a removal mechanism for some contaminants to and from the stream, and as a vehicle for contaminant transport downstream. Aquatic biota also are important in the food web of terrestrial organisms, with some aquatic biota, such as fish, being consumed by people and wildlife. Analyzing contaminants in sediment and aquatic biota provides an efficient way to test whether hydrophobic contaminants are present in the stream. Hydrophobic chemicals have little or no affinity for water; such chemicals have a low solubility in water, a high solubility in lipids (fats), and a strong tendency to sorb to organic material in soil and sediment. Many hydrophobic chemicals also are resistant to degradation, so they persist for a long time in the environment. Persistent hydrophobic contaminants in a stream may accumulate in sediment and aquatic biota (Figure 1), even when concentrations in the water are too low to be detected using conventional sampling and analytical methods. Historically, the pesticides of primary concern in sediment and aquatic biota have been the organochlorine insecticides, such as DDT, which were heavily used in agriculture, termite control, and malaria control programs from the mid-1940s to the 1960s or later.

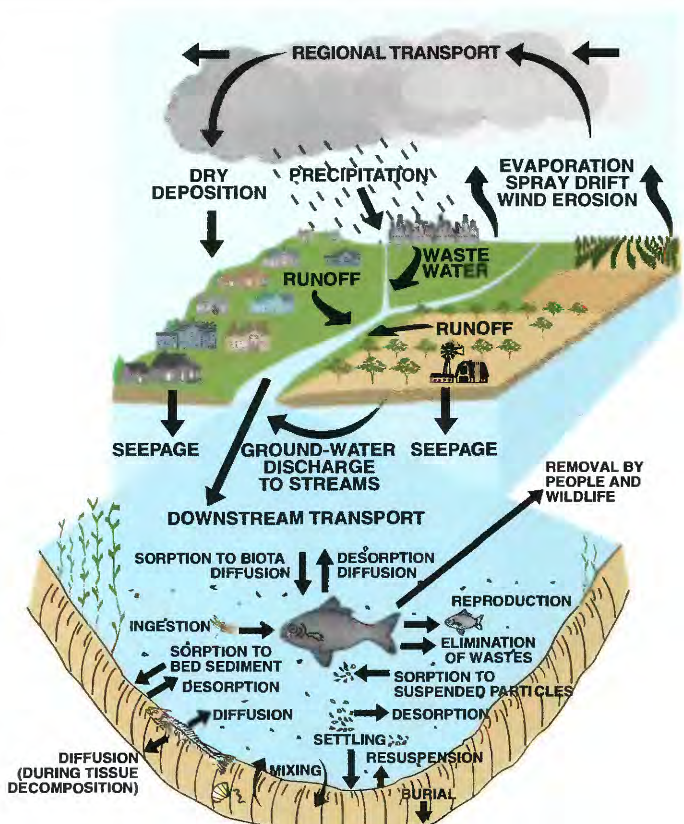


**Figure 1.** Pesticide movement in the hydrologic cycle including pesticide movement to and from sediment and aquatic biotia within the stream. Modified from Majewski and Capel (1995).

## Highlights

- Organochlorine pesticides such as DDT are still detected in many streams today, more than 20 years after their use in agriculture was prohibited.
- DDT, dieldrin, and chlordane are the pesticides most frequently present in sediment and biota at levels that may be toxic to aquatic life, wildlife, or people.
- Nationally, levels of most organochlorine pesticides in whole freshwater fish have declined since the 1960s.
- Organochlorine pesticides continue to enter United States streams from atmospheric deposition and erosion of soils contaminated from past use.
- Pesticides with moderate-to-low water solubility, and moderate-to-high environmental persistence, have the potential to accumulate in sediment and aquatic biota.
- More research is needed on pesticides in urban areas, accumulation of currently used pesticides in sediment and aquatic biota, and the toxic and long-term effects of pesticide mixtures on people and wildlife.

## Historical Study Efforts

During the past 30 years, over 400 scientific studies have looked for pesticides in stream sediment or aquatic biota in the

United States. These include five major national programs that sampled in rivers or estuaries. Most monitoring studies (97 percent) focused on organochlorine insecticides. These studies differed widely in their design features, such as site selection strategy, sample collection methods, and species and tissue type of biota sampled. The study durations ranged from less than one month to 24 years. Fish was the most common type of aquatic biota sampled, followed by mollusks and other invertebrates.

Because of differences among studies in study design and sampling dates, it is difficult to combine data from different studies into an overall national assessment. However, data from individual national programs can be used to assess the occurrence, geographic distribution, and trends of pesticides in fish and, to a lesser extent, sediment from United States rivers.

## Pesticides Found in Sediment and Biota

A large number of pesticides have been detected in stream sediment and aquatic biota in various studies over the last 30 years. Forty-four percent of the pesticides targeted (41 of 93) were detected in sediment, and 64 percent (68 of 106) were detected in aquatic biota (whole fish, edible fish, or mollusks). Most of the compounds detected were organochlorine insecticides or their degradation products. This reflects the hydrophobicity and persistence of these compounds, plus the fact that more monitoring studies looked for organochlorine insecticides (97 percent of studies) than for any other types of pesticides (27 percent). Figure 2 shows the detection frequencies for pesticides most commonly found in sediment and biota (fish and mollusks) by all the monitoring studies reviewed. Because these detection frequencies reflect the study designs and sampling dates of the studies that looked for specific compounds, they are not necessarily representative of all streams in the United States.

The organochlorine insecticides DDT, chlordane, and dieldrin were commonly detected in sediment and aquatic biota (Figure 2), even though their agricultural uses in the United States were discontinued during the 1970s. A few currently used pesticides also were detected in sediment or biota at more than 10 percent of total sites. These include dacthal, 2,4-DB, dicamba, diuron, and trifluralin (herbicides), and chlorpyrifos, dicofol, endosulfan, and lindane (insecticides). These pesticides tend to be intermediate in hydrophobicity and persistence, compared with other pesticides used now or in the past. For most organochlorine pesticides, detection frequencies generally were higher in aquatic biota than in sediment.

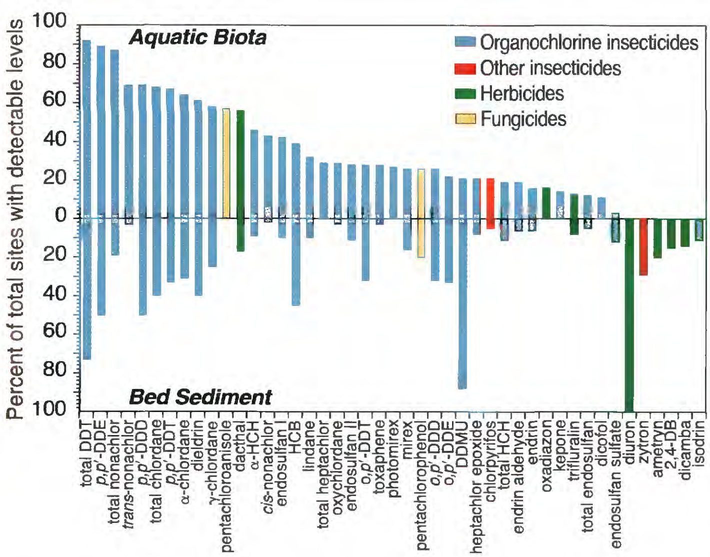


**Figure 2.** Detection frequencies for pesticides in aquatic biota (top) and in bed sediment (bottom) that were targeted at 15 or more sites by the monitoring studies reviewed and that were detected at 10 percent (or more) of total sites.

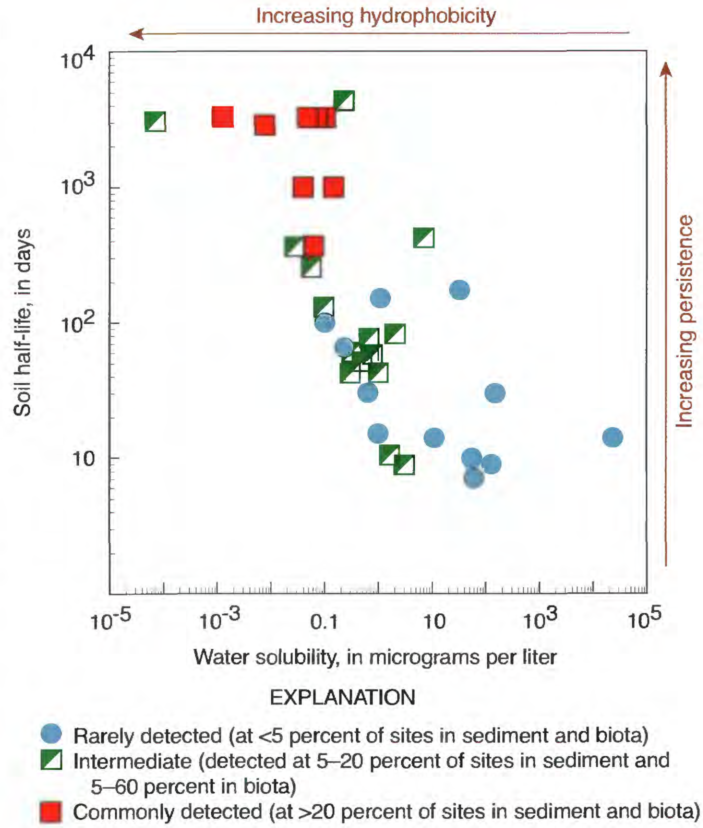


**Figure 3.** The relation between pesticide occurrence in sediment and aquatic biota in past monitoring studies (color symbols) and pesticide properties (water solubility—a measure of hydrophobicity, and soil half-life—a measure of environmental persistence). Only those pesticides targeted at 50 sites or more were included.

## Pesticide Physical and Chemical Properties

Two key properties of pesticides that control their accumulation in sediment and aquatic biota are hydrophobicity and persistence. Historical data were used to develop structure–activity relations between these properties and pesticide occurrence in sediment or aquatic biota (see Figure 3). Generally, pesticides were found to have the potential to accumulate in sediment and aquatic biota if they had (1) a water solubility less than 1 milligram per liter (mg/L) or an octanol-water partition coefficient ($K_{ow}$) greater than 1,000, and (2) a soil half-life greater than 30 days. $K_{ow}$ is an indirect measure of lipid solubility, so that hydrophobic compounds tend to have a high $K_{ow}$ and low water solubility. Soil half-life is the best measure of relative persistence that is available for a large number of pesticides. Each point in Figure 3 represents a different pesticide, color coded according to the frequency with which it was detected in sediment and biota when data were aggregated from past monitoring studies. Figure 3 shows only the effect of hydrophobicity and persistence on pesticide occurrence and does not show the influence of pesticide use. The most commonly detected compounds (red squares) tend to have low water solubility and high persistence. Conversely, most pesticides that are rarely detected in sediment and biota (blue circles) have higher water solubilities and shorter soil half-lives. Several pesticides with intermediate detection frequencies (green–white squares) are moderate in hydrophobicity and persistence. Two pesticides—mirex and endrin (the two uppermost green–white squares)—have lower detection frequencies than predicted from their low water solubilities and long soil half-lives, probably because their use was relatively low.

These structure-activity relations were used to evaluate which currently used pesticides have the potential to accumulate in sediment and aquatic biota. Because most currently used pesticides have relatively high water solubility and short soil half-lives, they are not as likely to accumulate in these media.

However, some currently used pesticides that are intermediate in both hydrophobicity and persistence (see Table 1) are likely to be detected if analyzed in sediment and aquatic biota, although at lower detection frequencies than the very hydrophobic, persistent pesticides such as DDT. It also would be important to consider where, and in what amounts, these pesticides are applied. Studies of the herbicide oxadiazon in California suggest that currently used pesticides that are intermediate in water solubility and persistence may reach fairly high concentrations in sediment and aquatic biota in areas of high pesticide use.

## Geographic Distribution in Relation to Use

The occurrence of a pesticide in a stream depends on the sources of that pesticide in the drainage basin (such as pesticide use), the characteristics of the stream (such as water flow), and the physical and chemical properties of the pesticide (such as water solubility). Organochlorine insecticides are still detected in sediment and biota in many streams because of their environmental persistence and their extensive use in the past.

The occurrence of organochlorine pesticides during the 1980s still showed some association with its use in agriculture 20 years earlier. For example, Figure 4 shows the geographic distribution of total DDT (DDT plus its metabolites DDD and DDE) in freshwater fish from the U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP) in 1986 in relation to regional estimates of agricultural use of DDT plus DDD in 1966, the decade of highest use. In Figure 4, each site is represented by a circle, color coded to represent the quartile in which its median total DDT concentration falls. For example, the red circles correspond to the 75th–100th percentile group. Agricultural land within each region is shaded according to the appropriate quartile of agricultural use of DDT plus DDD.

In 1986, the highest total DDT concentrations in fish were observed in the south, near the Great Lakes, along the northeast Atlantic coast, and at scattered Pacific sites. The southeastern sites correspond to the regions of highest agricultural use in 1966. Higher-than-expected levels of DDT in the Great Lakes and northeast Atlantic areas may be due to nonfarm use, incidental release from chemical manufacturing plants, or atmospheric deposition. High residues at scattered Pacific sites may reflect use on orchards, or proximity to agricultural cropland within the region. Other organochlorine pesticides in fish showed similar associations with land use. Dieldrin concentrations were strongly associated with corn production acreage. High dieldrin levels also occurred at sites in the northeast and Pacific regions, possibly because of urban use and proximity to farmland, respectively.

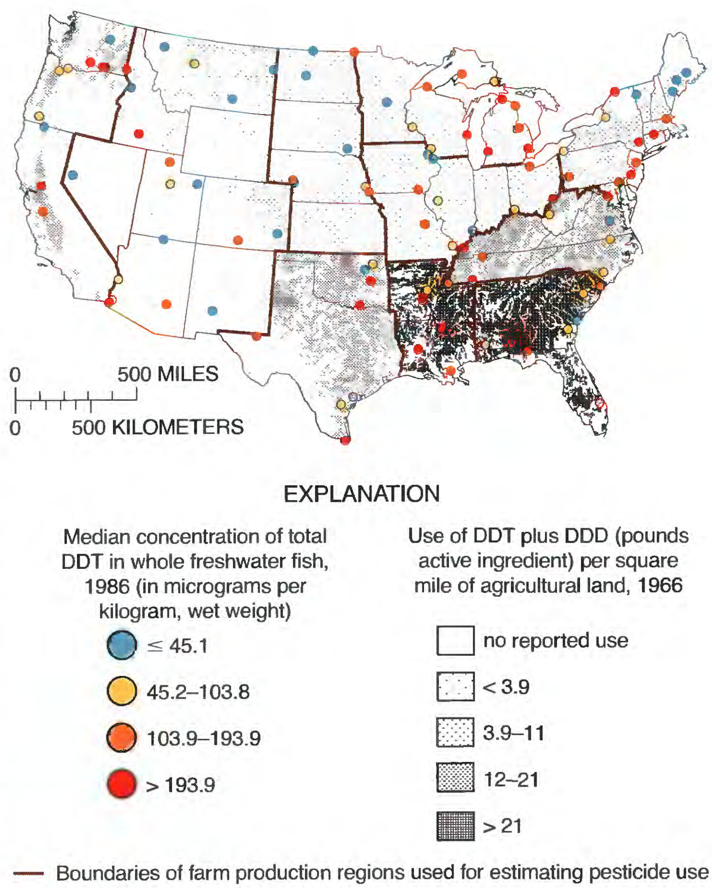


**Figure 4.** Total DDT in whole fish sampled by the National Contaminant Biomonitoring Program in 1986, shown in relation to 1966 agricultural use of DDT plus DDD by farm production region. Data are from U.S. Geological Survey, 1992 (DDT concentrations) and Eichers and others, 1970 (DDT use).

Some currently used pesticides (such as chlorpyrifos, dacthal, and trifluralin) showed an association with recent agricultural use in some studies. Some pesticides were associated with nonagricultural sources in some studies. For example, mirex was found in fish from areas treated for control of red fire ants (the southeast) or near manufacturing sources. Preliminary data from the U.S. Geological Survey's National Water-Quality Assessment Program (1991 to the present) indicate that urban streams have high concentrations and detection frequencies of DDT, chlordane, and dieldrin in sediment and whole fish (see http://water.wr.usgs.gov/pnsp/rep/bst).

**Table 1.** Currently used (1990s) pesticides predicted to have potential to accumulate in sediment and aquatic biota

[Abbreviations: $K_{OW}$, *n*-octanol-water partition coefficient; mg/L, milligram per liter; <, less than; >, greater than]

| Currently used (1990s) pesticides that meet the selection criteria [1] | | |
|---|---|---|
| **Insecticides** | **Herbicides** | **Fungicides or wood preservatives** |
| Chlorpyrifos[2] | Benfluralin | Dichlone |
| Dicofol[2,3] | Bensulide | PCNB[2] |
| Endosulfan[2,3] | Dacthal[2] | Pentachlorophenol[2] |
| Esfenvalerate | Ethalfluralin | |
| Fenthion | Oxadiazon[2] | |
| Fenvalerate[2] | Pendimethalin | |
| Lindane[2,3] | Triallate | |
| Methoxychlor[2,3] | Trifluralin[2] | |
| Permethrin[2] | | |
| Phorate[4] | | |
| Propargite | | |

[1] Selection criteria: (1) water solubility < 1.0 mg/L or log $K_{OW}$ > 3, and (2) soil half-life > 30 days.
[2] Detected in one or more past studies of stream sediment or biota.
[3] Organochlorine insecticide.
[4] Analyzed in >1,000 total samples by past studies, but not detected.

## Long-Term Trends

The existing data for pesticides in stream sediment are not sufficient to assess national long-term trends, but trends in pesticide concentrations in whole freshwater fish can be assessed using NCBP data from 1969 to 1986. Nationally, levels of chlordane, total DDT, dieldrin, endrin, and toxaphene have declined since their agricultural uses were discontinued. An example (DDT trends) is shown in Figure 5. For DDT and dieldrin, data for the 1980s suggest that concentrations may be leveling off, which is consistent with the slow degradation of these pesticides in the environment. For DDT, this trend is supported by changes in the proportional composition of total DDT residues in fish, with the degradation product DDE constituting an increasing percentage of total DDT over time. Organochlorine detection frequencies in the NCBP remain high, with total DDT detected at more than 97 percent of sites, and dieldrin at more than 70 percent of sites, each year.

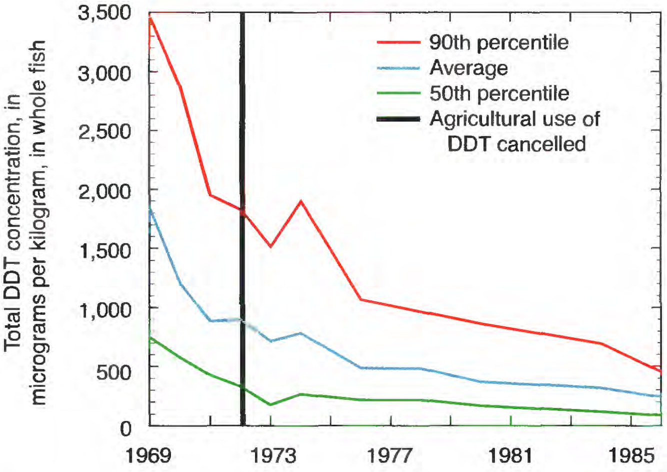


**Figure 5.** Trends in total DDT concentrations in whole fish sampled by the National Contaminant Biomonitoring Program from 1969 to 1986. Data are from U.S. Geological Survey, 1992. For the 90th (or 50th) percentile concentration, 90 (or 50) percent of samples were below the concentration shown.

DDT and other persistent organochlorine pesticides continue to enter surface waters from sources such as atmospheric deposition and erosion of soils that have been contaminated from past use. Field studies indicate that DDT half-lives in soil are on the order of 15 years or longer.

## Significance to Water Quality

Pesticide concentrations measured by the monitoring studies that were reviewed can be used to gauge potential adverse effects at the time the samples were taken. The maximum concentrations measured in each study were compared with guidelines for the protection of aquatic life, fish-eating wildlife, and human health. Because the maximum concentrations from each study were used, these comparisons indicate what percentage of studies may have adverse effects at the most contaminated site in each study, but not what proportion of sites may be affected. Such guidelines generally were based on the results of single-species, single-chemical toxicity tests conducted in the laboratory—therefore, they do not consider more complex issues such as the toxicity of chemical mixtures or the potential for endocrine-disrupting effects on development and reproduction. Also, the monitoring studies reviewed may not be representative of sediment and biota from streams throughout the United States.

The potential effects on aquatic life, fish-eating wildlife, and human health were assessed by comparing the maximum concentrations of pesticides measured by each study in sediment, whole fish, and fish fillets (respectively) with applicable guidelines. Sediment-quality guidelines were selected using procedures developed by the U.S. Environmental Protection Agency (1997). Wildlife guidelines are from the State of New York (Newell and others, 1987), and consider chronic and reproductive toxicity, but not cancer effects. Human-health guidelines are recommended screening values from U.S. Environmental Protection Agency (1995), which consider both chronic toxicity and carcinogenicity.

Even when studies published prior to 1984 were excluded, sediment guidelines were frequently exceeded by maximum concentrations of total DDT (in 52 percent of studies), chlordane (42 percent), and dieldrin (29 percent), indicating a high probability of adverse effects on aquatic life at the most contaminated sites in these studies. New York wildlife guidelines were exceeded for total DDT (77 percent of studies) and dieldrin (25 percent), which indicates potential adverse effects on fish-eating wildlife at the most contaminated sites in these studies. EPA-recommended screening values were exceeded for chlordane, total DDT, dieldrin, and heptachlor epoxide in at least 50 percent of studies. This suggests possible adverse human health effects at the most contaminated sites in these studies, if fish from these sites were consumed at average rates by the general adult population. Adverse health risks may be higher for sport and subsistence fishers, who consume more local fish than the average population.

Human exposure to organochlorine pesticides has been documented by studies detecting these compounds in various human tissues, including breast milk. Consumption of contaminated food (including fish and shellfish) is a major route of human exposure to organochlorine pesticides. Organochlorine concentrations in human blood have been shown to increase after fish consumption and to be correlated with long-term fish consumption rates. Organochlorine compounds tend to be stored in high-fat tissues within the body, but can be mobilized during lactation or starvation. Levels of some organochlorine compounds in human tissues in the United States do not appear to have declined, at least through the early 1980s. Examples include DDT in breast milk and dieldrin in adipose tissue (fat).

The wealth of information on pesticides in bed sediment and aquatic biota in the scientific literature has provided a national perspective on organochlorine pesticides in United States rivers. Nonetheless, significant gaps remain in our understanding of the extent and significance of pesticides in stream sediment and aquatic biota. This analysis suggests a need for additional studies of pesticide occurrence in urban settings, together with more information on urban pesticide use. Also, researchers should look for currently used pesticides with the potential to accumulate in sediment and aquatic biota in areas of high use. Finally, questions remain about the effects of remaining pesticide levels on human and ecosystem health.

### Additional Reading

This Fact Sheet is based on the book by L.H. Nowell, P.D. Capel, and P.D. Dileanis, 1999, Pesticides in Stream Sediment and Aquatic Biota—Distribution, Trends, and Governing Factors: Boca Raton, Fla., CRC Press, Pesticides in the Hydrologic System series, v. 4, 1040 p. (Tel: 1-800-272-7737)

### References

Eichers, T., Andrilenas, P., Blake, H., Jenkins, R., and Fox, A., 1970, Quantities of pesticides used by farmers in 1966: U.S. Department of Agriculture, Economic Research Service, Agricultural Economic Report No. 179, 61 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.

Newell, A.J., Johnson, D.W., and Allen, L.K., 1987, Niagara River Biota Contamination Project: Fish flesh criteria for piscivorous wildlife: New York State Department of Environmental Conservation, Division of Fish and Wildlife, Bureau of Environmental Protection, Technical Report 87-3.

U.S. Environmental Protection Agency, 1995, Guidance for assessing chemical contaminant data for use in fish advisories, v. 1, Fish sampling and analysis, 2nd ed.: U.S. Environmental Protection Agency, EPA 823-R-95-007.

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U.S. Geological Survey, 1992, U.S. Fish and Wildlife Service National Contaminant Biomonitoring Program Fish Data File, 1969–1986: Columbia Environmental Research Center, Columbia, Mo., Lotus and ASCII files.

### 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
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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://water.usgs.gov/nawqa>.