



W.H. Mullins ©



Kevin J. Breen



Dennis A. Wentz

**Pesticides used to control weeds, insects, and other pests on farms and in urban areas can be harmful to humans and the environment if they contaminate our water resources**



W.H. Mullins © 1974



Gregg Patterson

# Pesticides

Results of NAWQA studies show that pesticides are widespread in streams and ground water sampled within agricultural and urban areas of the Nation. As expected, the most heavily used compounds are found most often, occurring in geographic and seasonal patterns that mainly correspond to distributions of land use and associated pesticide use.

The frequency of pesticide contamination, however, is greater than expected. At least one pesticide was found in almost every water and fish sample collected from streams and in about one-half of all wells sampled. Moreover, individual pesticides seldom were found alone— almost every water and fish sample from streams and about one-half of samples from wells with a detected pesticide contained two or more pesticides.

For individual pesticides in drinking water, NAWQA results are generally good news relative to current water-quality standards and guidelines. Average concentrations in streams and wells rarely exceeded standards and guidelines established to protect human health. For aquatic life and wildlife, however, NAWQA results indicate a high potential for problems in many streams, particularly in urban areas, where concentrations of more than one pesticide often approached or exceeded established water-quality guidelines.

Important questions remain unanswered about potential risks of pesticide contamination to humans and the environment. Currently, standards and guidelines are available only for a limited number of individual pesticides, do not account for mixtures of pesticides or for pesticide breakdown products, and are based on tests that have assessed a limited range of potential health and ecological effects. Long-term exposure to low-level mixtures of pesticide compounds, punctuated with seasonal pulses of higher concentrations, is the most common pattern of exposure, but the effects of this pattern are not yet well understood.

The uncertainty about whether present-day levels of pesticide contamination are a threat to human health or the environment makes it imperative that we document and understand the nature of pesticide exposure, the causes of contamination, and the actions we can take to reduce pesticide levels in streams and ground water. ►

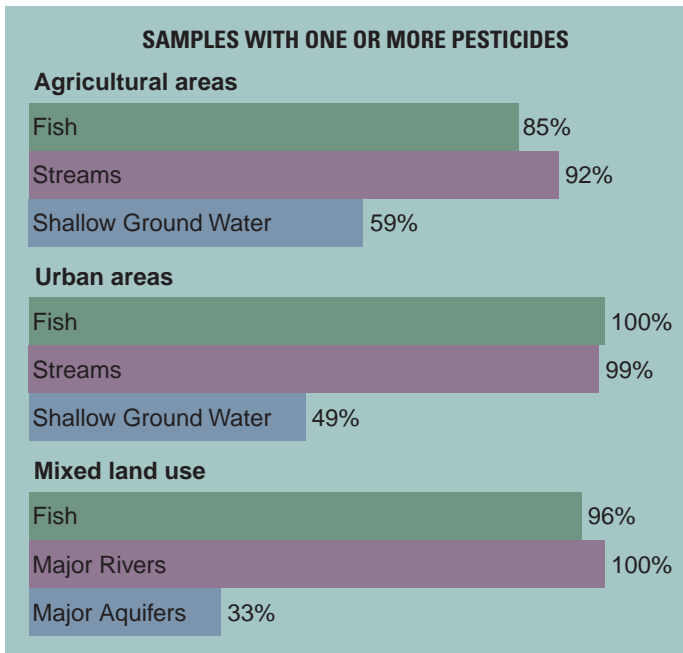
# Decades of pesticide use have resulted in their widespread occurrence in streams and ground water

More than 90 percent of water and fish samples from all streams contained one or, more often, several pesticides. Pesticides found in water were primarily those that are currently used, whereas those found in fish and sediment are organochlorine insecticides, such as DDT, that were heavily used decades ago. Most of the pesticides in use today are more water soluble and break down faster in the natural environment than the long-lived organochlorine insecticides of the past.<sup>(31)</sup>

About 50 percent of the wells sampled contained one or more pesticides, with the highest detection frequencies in shallow ground water beneath agricultural and urban areas and the lowest frequencies in major aquifers, which generally are deeper. Ground water has a lower incidence of pesticide contamination than streams because water infiltrating the land surface moves

slowly through soil and rock formations on its way to ground water and through the aquifer. This contact with soil and rock and the slow rate of flow allow greater opportunity for sorption and degradation of pesticides, and varied flow pathways mean that some wells do not tap ground water that originated from places or times affected by pesticide use.

Although streams and rivers are more vulnerable than ground water to rapid and widespread contamination, ground-water contamination is extremely difficult to reverse because of the slow rate of ground-water flow. **Management practices that reduce the transport of pesticides to streams can yield rapid improvements in water quality. Ground water, on the other hand, will respond slowly to changing practices—sometimes taking many years or even decades to recover.**



## WHAT WAS MEASURED...

Many of the Nation's most heavily used agricultural and urban pesticides were measured in the NAWQA Program. The 83 target compounds analyzed in water include 76 pesticides and 7 selected breakdown products and account for about 75 percent of the Nation's agricultural use of synthetic pesticides. They include 17 of the top 20 herbicides and 15 of the top 20 insecticides.

Historically used organochlorine insecticides, like DDT, were measured in bed sediment and fish, where they accumulate and persist for decades. The 32 organochlorine compounds analyzed in bed sediment or fish consist of 8 individual parent compounds, 1 individual breakdown product, and 7 groups of parent compounds plus related breakdown products or chemical impurities in the manufactured product. These compounds account for more than 90 percent of the Nation's historical use of organochlorine insecticides in agriculture.

## WHAT WAS NOT...

Many important pesticide compounds were not measured because of analytical and budget constraints. The top 20 herbicides not measured were glyphosate (ranked 10), MSMA (14), and propazine (17). The top 20 insecticides not measured were cryolite (12), acephate (13), dimethoate (14), methomyl (15), and thiodicarb (18). Other pesticides not measured include inorganic pesticides, such as sulfur and copper, oil, and biological pesticides. Important omissions also include numerous pesticide breakdown products and carrier agents that may affect water quality.

Although NAWQA studies are targeting the broadest and most complete range of pesticides ever measured in a single assessment, these omissions are important to keep in mind and must temper conclusions.

Further information on pesticides measured is available via the World Wide Web at <<http://water.usgs.gov/lookup/get?nawqapest>>.



# Pesticides are a potential concern for human health and aquatic life

Most pesticides are manufactured compounds that are designed to kill specific pests, such as weeds and insects. Many pesticides have the potential to harm nontarget organisms, especially if the organisms are exposed to high levels or for a long period of time. In the early 1960s, Rachel Carson's widely publicized book "Silent Spring"<sup>(32)</sup> described the ecological impacts of DDT and other pesticides. Concerns about the unintended effects of pesticides continue to this day, and evaluation of the risk to humans and the environment from present-day levels of pesticide exposure remains highly controversial.

A difficult aspect of evaluating potential effects of pesticides is determining what may occur as a result of varying types and durations of exposure. Exposure is complicated by pesticide mixtures, breakdown products, strong seasonal concentration pulses, and high concentrations during stormflows. In contrast, most toxicity assessments are based on controlled experiments with a single contaminant over a limited range of concentrations.

Although uncertainties remain, water-quality standards and guidelines have been developed for many pesticides in order to protect human health and aquatic life, and they are used in this report to signal potential problem areas. Concentrations that exceed a standard or guideline, however, may not be a problem at some sites. Conversely, the absence of an exceedance does not ensure that there is no problem.

Some people believe that any presence of pesticides in their drinking water is too much, whereas others feel that the standards and guidelines established for many of the major pesticides provide adequate protection. Which of these perspectives is closest to the truth remains unclear, but certainly the effects of common patterns of pesticide exposure found in NAWQA studies have not yet been fully evaluated.

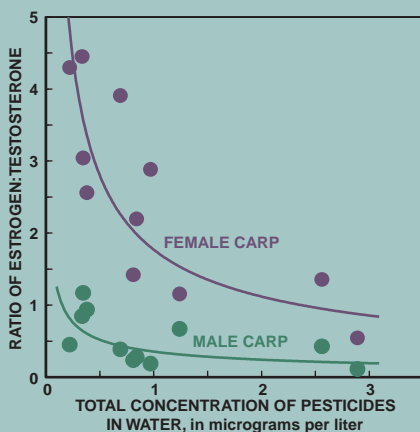
The uncertainty in whether or not present-day levels of pesticide contamination are a threat to human health or aquatic life makes it imperative that we understand the nature of exposure, the causes of contamination, and the actions we can take to reduce pesticide levels in streams and ground water. Only by accurately characterizing the nature and causes of environmental exposure can we develop effective strategies to minimize exposure and reliably evaluate relations between exposure and effects.

## STANDARDS AND GUIDELINES FOR PROTECTING WATER QUALITY

Water-quality standards and guidelines generally are maximum acceptable concentrations of pesticides for protecting humans, aquatic life, or wildlife. They are established by the United States and other nations, international organizations, and some States and tribes. For this report, precedence was given to standards and guidelines established by the USEPA and then to those established by Canada or the International Joint Commission for the Great Lakes, although some states may have different standards and guidelines that take priority for particular water bodies.<sup>(25)</sup>

Drinking-water standards or guidelines have been established for 43 of the 76 pesticides analyzed, and aquatic-life guidelines have been established for 28 of the 76 pesticides. Aquatic-life or wildlife guidelines are available for 8 of the 16 pesticides (compounds or groups) analyzed in bed sediment or fish.

Current standards and guidelines do not completely eliminate risks because: (1) values are not established for many pesticides, (2) mixtures and breakdown products are not considered, (3) the effects of seasonal exposure to high concentrations have not been evaluated, and (4) some types of potential effects, such as endocrine disruption and unique responses of sensitive individuals, have not yet been assessed.



## HORMONE LEVELS IN FISH SHOW SIGNS OF POSSIBLE ENDOCRINE DISRUPTION

A reconnaissance study of sex hormones in carp collected at 11 NAWQA stream sites indicates that pesticides may be affecting the ratio of estrogen to testosterone in both males and females.<sup>(33)</sup> The hormone ratio, which is sometimes used as an indicator of potential abnormalities in the endocrine system, was significantly lower at sites with the highest pesticide concentrations. Although the lower hormone ratios may not be associated with measurable effects on fish populations, they are a signal that further investigation is needed.



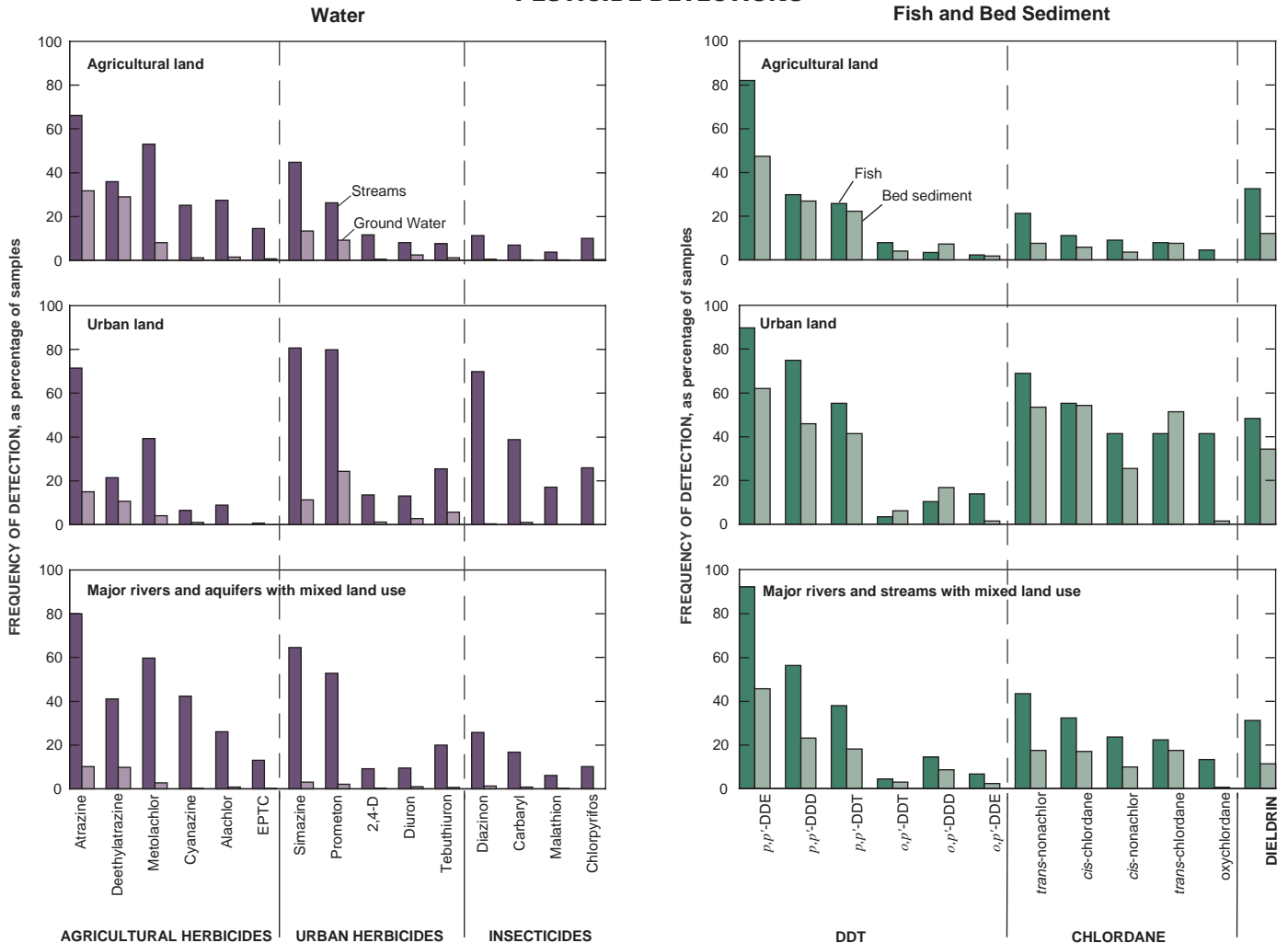
Charles G. Crawford

# The most frequently detected pesticides are those most heavily used...now or in the past

Not surprisingly, the top 15 pesticide compounds found in water are among those with the highest current use. They include five of the most heavily used agricultural herbicides and one degradation product, five herbicides that are extensively used in urban areas, and four of the most commonly used insecticides.

The pesticide compounds found most often in fish and bed sediment are related to three major groups of insecticides that were heavily used in the 1960s. Organochlorine compounds related to DDT and dieldrin were widely used in both agricultural and urban areas, and chlordane was mainly used in urban areas.

## PESTICIDE DETECTIONS



## Different pesticides dominate in different land-use areas

The occurrence of pesticides in streams and ground water follows broad patterns in land use and associated pesticide use. The patterns are complex, however, and differ between streams and ground water because of the wide range of use practices and processes that govern the movement of pesticides in the hydrologic environment.

### AGRICULTURAL AREAS

Herbicides are the most common type of pesticide found in streams and ground water within agricultural areas. The most common herbicides in agricultural streams were atrazine and its breakdown product



Dennis A. Wentz

deethylatrazine (DEA), metolachlor, cyanazine, alachlor, and EPTC. All 5 of the parent compounds rank in the top 10 in national use. Atrazine was found in about two-thirds of all samples from agricultural streams, often occurring year-round.

Similar to streams, the most common compounds found in shallow ground water were atrazine and DEA, but only about one-third of the samples had detectable levels. The lower rates of atrazine and DEA detection in ground water compared to streams result from longer travel times, greater opportunity for

sorption or breakdown, and greater variability of source water in wells.

One of the most striking results for shallow ground water in agricultural areas, compared with streams, is the low rate of detection for several high-use herbicides other than atrazine. This is probably because these herbicides break down faster in the natural environment compared to atrazine. Studies show that breakdown products of metolachlor, alachlor, and cyanazine are much more commonly found in ground water than are the parent compounds.<sup>(34)</sup>

Compared to herbicides, currently used insecticides were less frequently found in most agricultural streams. But some streams in agricultural areas with particularly high use of specific insecticides, such as diazinon in the San Joaquin-Tulare Basins, had among the highest concentrations measured. Insecticides were rarely detected in ground water in agricultural areas. **The less frequent occurrence of currently used insecticides in streams compared with herbicides, and their infrequent occurrence in ground water, result from their relatively low application rates and rapid breakdown in the environment.**



Dennis A. Wentz

In contrast to currently used insecticides, the organochlorine insecticides of the past still persist in agricultural streams because of their extreme resistance to breakdown in the environment. DDT was the most



Jana S. Stewart

commonly detected organochlorine group—found in almost every fish sample—followed by dieldrin and chlordane. DDT and aldrin (which breaks down rapidly to dieldrin in the environment) were two of the top three insecticides used for agriculture in the 1960s.



## URBAN AREAS

The most distinct differences between pesticides found in urban and agricultural areas are the greater prevalence of insecticides in urban streams and the relatively frequent occurrence of urban herbicides in both streams and shallow ground water. Insecticides were found more often, and usually at higher concentrations, in urban streams than in agricultural streams. Diazinon, carbaryl, chlorpyrifos, and malathion, which nationally rank 1, 8, 4, and 13 among insecticides used for homes and gardens, accounted for most detections in water. Historically used insecticides also were found more frequently in urban streams. Urban streams had the highest detection frequencies of DDT, chlordane, and



Peter E. Hughes

**Insecticides in urban streams are a concern for aquatic life, for downstream water supplies, and possibly for recreational users. Effective management will likely require a combination of reducing current home, garden, and commercial use and controlling sediment sources to streams.**

Similar to agricultural areas, insecticides were seldom detected in ground water in urban areas. Interestingly, however, the most commonly detected insecticide in shallow ground water was dieldrin, which was found in about 3 percent of the wells sampled. Although dieldrin is not very mobile in water, its

highest frequencies of urban use. Of the urban herbicides, 2,4-D, simazine, and diuron also have substantial agricultural use, ranking in the top 25 nationally. Diuron and 2,4-D were not detected as frequently as other compounds with similar use, probably because the analytical method for these two compounds is less sensitive and resulted in fewer detections than for other compounds, even when concentrations were similar. As in streams, the most frequently found herbicides in shallow ground water in urban areas were atrazine, DEA, simazine, and prometon. Unlike streams, however, metolachlor was seldom detected, probably because of its lower urban use and lower persistence in the environment compared to the other herbicides.



Kevin J. Breen

dieldrin in fish and bed sediment, and the highest concentrations of chlordane and dieldrin. Chlordane and aldrin were widely used for termite control until the mid-1980s, although their agricultural uses were restricted during the 1970s.<sup>(35, 36)</sup> Much more chlordane was used for termite control than for agriculture.

environmental persistence and the heavy historical use of dieldrin and aldrin have combined to yield contamination of some wells.

The herbicides most commonly found in urban streams, in addition to atrazine and metolachlor, are simazine, prometon, 2,4-D, diuron, and tebuthiuron, all of which are commonly used in nonagricultural settings for maintenance of roadsides, commercial areas, lawns, and gardens. Prometon and 2,4-D have among the



Barbara J. Dawson



Peter A. Steeves

## Pesticides found in major rivers and aquifers reflect contributions from both agricultural and urban areas

Major rivers and streams draining areas of mixed land use contain pesticides from both agricultural and urban sources and from both past and present use. In water that comes mainly from agricultural areas, the most commonly found pesticides are the major herbicides atrazine (and DEA), metolachlor, cyanazine, and alachlor. In water that comes mainly from urban areas, the most common pesticides are the herbicides simazine and prometon and the insecticides diazinon and carbaryl.

Like water, the fish and bed sediment of major rivers and streams with mixed land-use influences contain mixtures of organochlorine insecticides from agricultural and urban areas. Detection frequencies and concentrations of DDT, dieldrin, and chlordane were generally intermediate between those of agricultural and urban streams.

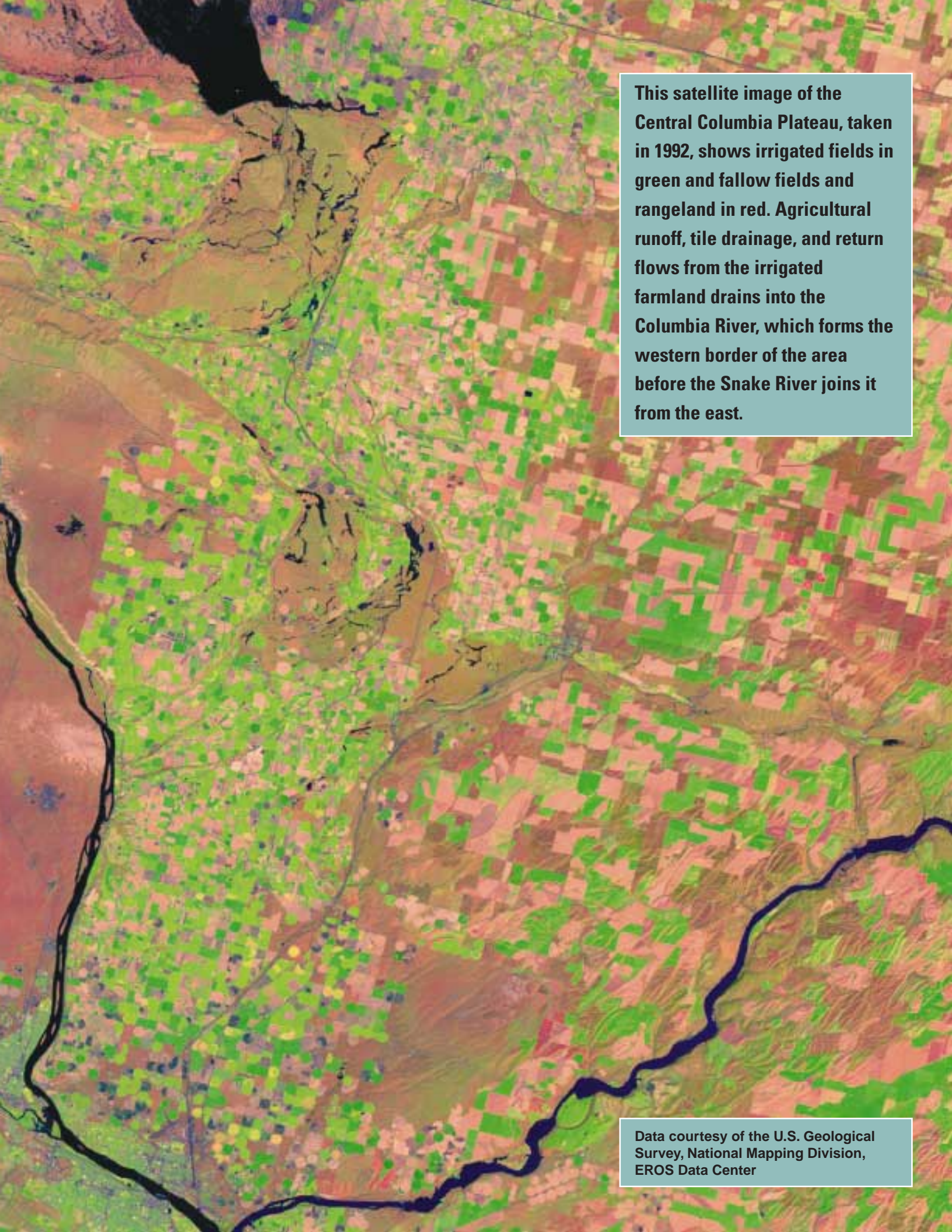
Many large rivers with mixed land-use influences tend to have lower concentrations of pesticides compared with agricultural and urban streams because of a larger influence of undeveloped land. Some rivers in intensive agricultural regions, however, have concentrations that are similar to those in agricultural streams, although they are less variable over time. Rivers with mixed land uses almost always contain detectable pesticides that reflect the diversity of sources present.

In contrast, ground water in major aquifers has a substantially lower frequency of pesticide occurrence than shallow ground water in agricultural and urban areas. This difference results from the generally deeper wells sampled in major aquifers and the greater influence of undeveloped areas. Additionally, owing to the slow rate of ground-

water flow, much of the water sampled in the major aquifers may have infiltrated into the ground before pesticides were applied. The two most frequently detected compounds in major aquifers were atrazine and DEA, resulting from the high and extensive use of atrazine, the greater extent of agricultural land compared to urban land affecting most major aquifers sampled, and the high mobility and long-lived nature of atrazine and DEA.

**Because the pesticides found in major rivers and aquifers reflect contributions from both agricultural and urban land uses, efforts to improve the quality of these water resources will require management of nonpoint sources in both agricultural and urban areas.**





This satellite image of the Central Columbia Plateau, taken in 1992, shows irrigated fields in green and fallow fields and rangeland in red. Agricultural runoff, tile drainage, and return flows from the irrigated farmland drains into the Columbia River, which forms the western border of the area before the Snake River joins it from the east.

Data courtesy of the U.S. Geological Survey, National Mapping Division, EROS Data Center



# Geographic distributions of pesticides follow patterns in land use and pesticide use

**An essential step toward understanding and managing the effects of pesticides on water quality is to examine the geographic distribution of pesticide levels in relation to land use and pesticide use and to determine areas of the Nation and environmental settings that merit the greatest concern and attention.**

The geographic distribution of pesticide levels is summarized in a series of maps that show results for herbicides and insecticides in streams and ground water for agricultural, urban, and mixed land uses, the latter including major rivers and aquifers. To identify potential water-quality problems, pesticide concentrations in water and bed sediment from streams are compared to aquatic-life guidelines because most streams sampled are not directly used as drinking-water sources. Pesticide concentrations in shallow ground water and water from major aquifers are compared to drinking-water standards and guidelines for human health. Most of the major aquifers, and shallow ground water in about one-half of the study areas, are sources of drinking water. Methods used to construct the maps are explained on page 31.

The national maps show national and regional patterns, or in some cases the apparent lack of pattern, in pesticide levels. They cannot, however, show important aspects of local variability in pesticide levels—for this, the reader is referred to the individual reports available for each NAWQA Study Unit (see page 80).



A.C. Haralson, Arkansas Department of Parks and Tourism

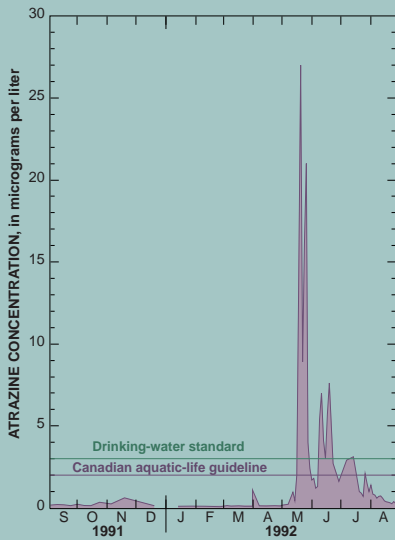


Alan R. Wycheck, Harrisburg Hershey Carlisle Tourism and Convention Bureau



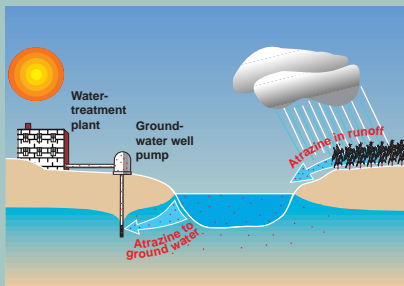
Phil Schofield ©

### HERBICIDES EXCEEDED WATER-QUALITY STANDARDS OR GUIDELINES IN SOME STREAMS IN THE CORN BELT



The heavy use of herbicides on corn in the Central Nebraska Basins is reflected in high atrazine concentrations in the Platte River during runoff from rainfall following spring herbicide applications. Low-level atrazine concentrations were found throughout much of the year, punctuated by seasonal pulses of high concentrations that exceeded the drinking-water standard (MCL) and the Canadian aquatic-life guideline. The annual average concentration, however, did not exceed the drinking-water standard.

Lincoln, Omaha, and smaller cities along the Platte River withdraw drinking water from an aquifer adjacent to the river. Much of the ground water that is pumped from the sand and gravel portions of this aquifer is vulnerable to contamination from atrazine in the Platte River. This is a concern to water providers



because studies have shown that conventional water treatment is ineffective in removing herbicides like atrazine from the treated water supplied to households.<sup>(38)</sup>

## Herbicides in streams and major rivers were highest in the most intensively farmed agricultural regions

Total herbicide concentrations consistently ranked highest in agricultural streams and major rivers of the White River Basin and Central Nebraska Basins, which are on the eastern and western margins of the Corn Belt, respectively. The Corn Belt has the highest herbicide use in the Nation. The high concentrations measured in the White River Basin and Central Nebraska Basins are consistent with other studies in the Mississippi River Basin, which show broad-scale herbicide contamination of streams and rivers, including the Mississippi River.<sup>(37)</sup>

All seven agricultural streams and the two major rivers sampled in the White River Basin and Central Nebraska Basins frequently had concentrations of one or more herbicides that exceeded a Canadian aquatic-life guideline. Atrazine exceeded its guideline of 2 µg/L at all sites, and cyanazine exceeded its guideline of 2 µg/L at four sites. At this time, there are no national aquatic-life guidelines for these compounds in the United States, and individual States have varying guidelines.

**Given the regional extent of intensive herbicide use and elevated levels of herbicides in streams within the Corn Belt, management strategies that are successful in reducing use and runoff of herbicides that are applied for corn and soybean production will likely lead to regional-scale improvements in water quality.**

Other streams ranking high in herbicide concentrations were agricultural streams that drain intensively farmed areas in the Willamette Basin, San Joaquin-Tulare Basins, South Platte River Basin, and Trinity River Basin. A diverse group of herbicides, including trifluralin, metolachlor, and 2,4-D, in addition to atrazine and cyanazine, exceeded aquatic-life guidelines in one or more of these streams.

Most streams with low herbicide concentrations were agricultural streams in areas with low to moderate herbicide use in their drainage basins. Exceptions to this are low concentrations of herbicides in agricultural streams of the Red River of the North Basin and in the Southeast, even though use is moderate to high. One possible reason for the low concentrations in the Red River of the North Basin is a higher retention of herbicides in the soil because of particularly high levels of organic matter.

Among urban sites, only Las Vegas Wash in Las Vegas had relatively high herbicide concentrations compared to other streams. Only Little Buck Creek in the Indianapolis area had concentrations that exceeded a Canadian aquatic-life guideline, and that was in a small percentage of samples because of atrazine use on agricultural land in its watershed.



## A national ranking of **HERBICIDES** in streams

### Sum of herbicide concentrations

- Highest 25 percent of streams
- Middle 50 percent
- Lowest 25 percent

### Aquatic-life guidelines

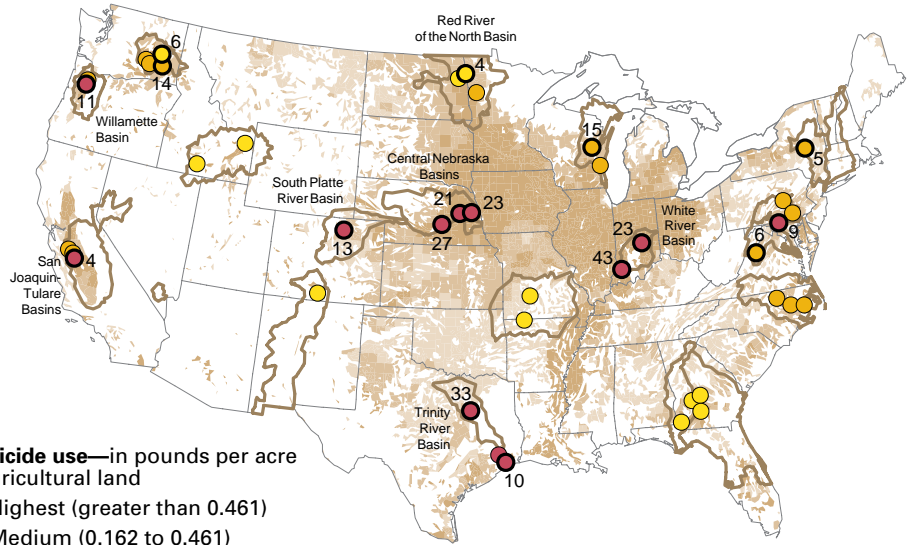
- <sup>9</sup> Bold outline indicates exceedance by one or more herbicides. Number is percentage of samples that exceeded a guideline

### Agricultural streams

Concentrations were highest and most often exceeded aquatic-life guidelines in streams in the White River Basin and Central Nebraska Basins in the Corn Belt, where herbicide use is among the highest reported nationwide.

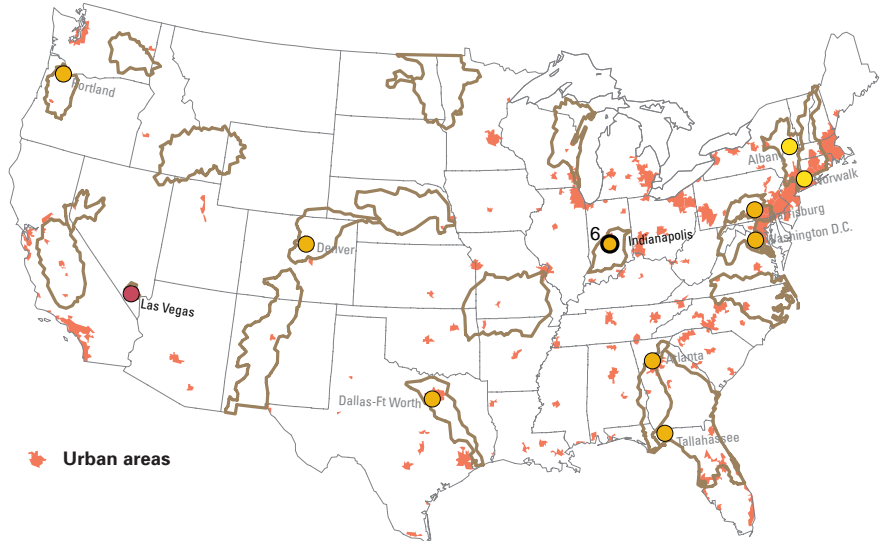
### Herbicide use—in pounds per acre of agricultural land

- Highest (greater than 0.461)
- Medium (0.162 to 0.461)
- Lowest (less than 0.162)
- No reported use



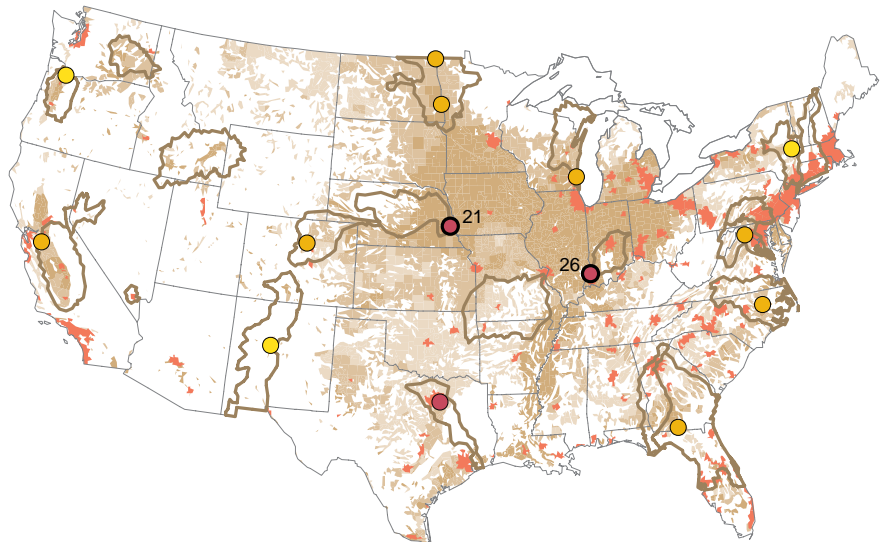
### Urban streams

Most urban streams had moderate or low herbicide concentrations compared to streams in agricultural and mixed land-use settings.



### Rivers and streams with mixed land use

Aquatic-life guidelines were exceeded in about one fourth of the samples from the two major rivers sampled in the Corn Belt, but most major rivers had moderate herbicide concentrations.



See p. 31 for more information about these maps

# Insecticides in streams were highest in urban areas

Most urban streams sampled, plus two major rivers dominated by urban influences—the South Platte River downstream from Denver and the Trinity River downstream from Dallas-Fort Worth—had among the highest insecticide concentrations of all streams and rivers sampled. Nine of 11 urban streams and both rivers had concentrations that exceeded aquatic-life guidelines, usually in more than 20 percent of the samples. The most common insecticides to exceed guidelines were diazinon, chlorpyrifos, and malathion. Chlorpyrifos and malathion have USEPA aquatic-life criteria of 0.041 µg/L and 0.100 µg/L, respectively, and diazinon has a guideline of 0.080 µg/L established by the International Joint Commission for the Great Lakes.

**Insecticides in urban streams, largely from use around homes and in gardens, parks, and commercial areas, frequently occur at levels of concern for aquatic life and may be a significant obstacle for restoring urban streams.**

Most agricultural streams had moderate or low concentrations of insecticides but, as for herbicides, several streams that drain intensively farmed areas that are irrigated had among the highest insecticide levels. Although

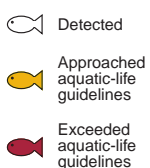
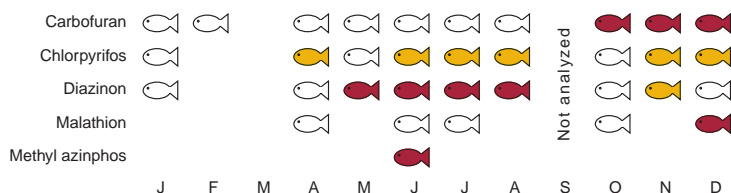
concentrations of insecticides in agricultural streams tended to be low compared to urban streams, concentrations above aquatic-life guidelines were common. For about one-half of the agricultural streams, samples exceeded a guideline for one or more insecticides. In addition to diazinon and chlorpyrifos, an insecticide that frequently exceeded its guideline in agricultural streams was methyl azinphos, which has a USEPA aquatic-life criterion of 0.010 µg/L.

Insecticide concentrations in most major rivers usually were lower than those measured in urban streams and exceeded aquatic-life guidelines in relatively few samples. Exceptions are the San Joaquin River, which drains farmlands with some of the heaviest insecticide use in the Nation, and the South Platte and Trinity Rivers, which are affected by both point and nonpoint sources from urban areas.



INSECTICIDES DETECTED IN WATER IN ZOLLNER CREEK, OREGON, 1993 AND 94

Dennis A. Wentz



Zollner Creek in the Willamette Basin receives agricultural runoff from intensively irrigated crops, including row crops, grass, wheat, hops, nurseries, and orchards. A wide variety of insecticides was applied to these crops; the insecticides were transported to the creek by irrigation and stormwater runoff. One or more insecticides were found in most water samples collected during the 2-year period, and several approached or exceeded concentrations that may be harmful to aquatic life, sometimes occurring as mixtures.

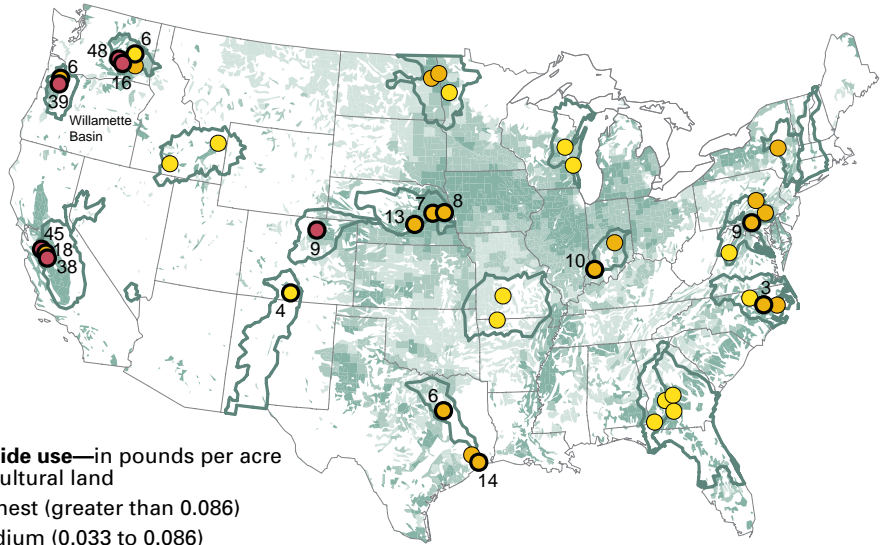
## A national ranking of **INSECTICIDES** in streams

### Sum of insecticide concentrations

- Highest 25 percent
- Middle 50 percent
- Lowest 25 percent

### Aquatic-life guidelines

- <sup>9</sup> Bold outline indicates exceedance by one or more insecticides. Number is percentage of samples that exceeded a guideline



### Insecticide use—in pounds per acre of agricultural land

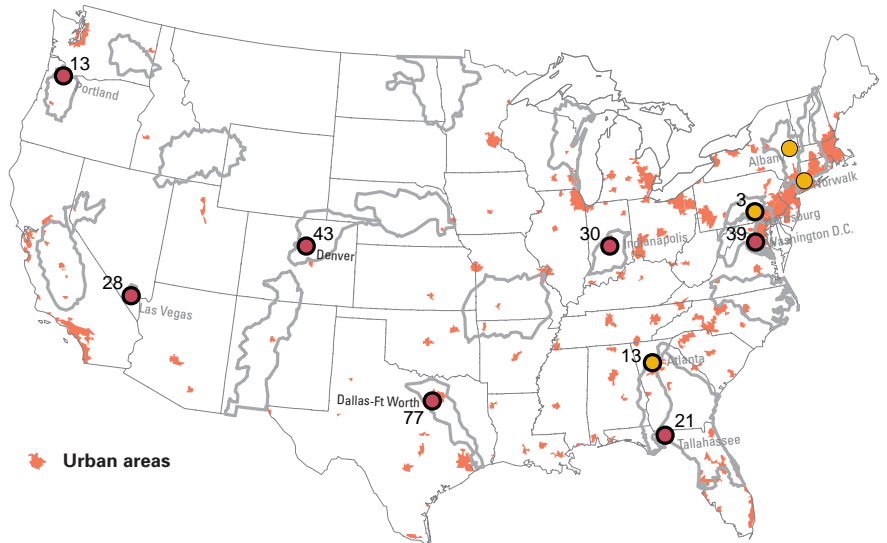
- Highest (greater than 0.086)
- Medium (0.033 to 0.086)
- Lowest (less than 0.033)
- No reported use

## Agricultural streams

Most streams had moderate or low concentrations, but several in irrigated areas of the West had among the highest concentrations. About one-half of the agricultural streams had concentrations that exceeded an aquatic-life guideline.

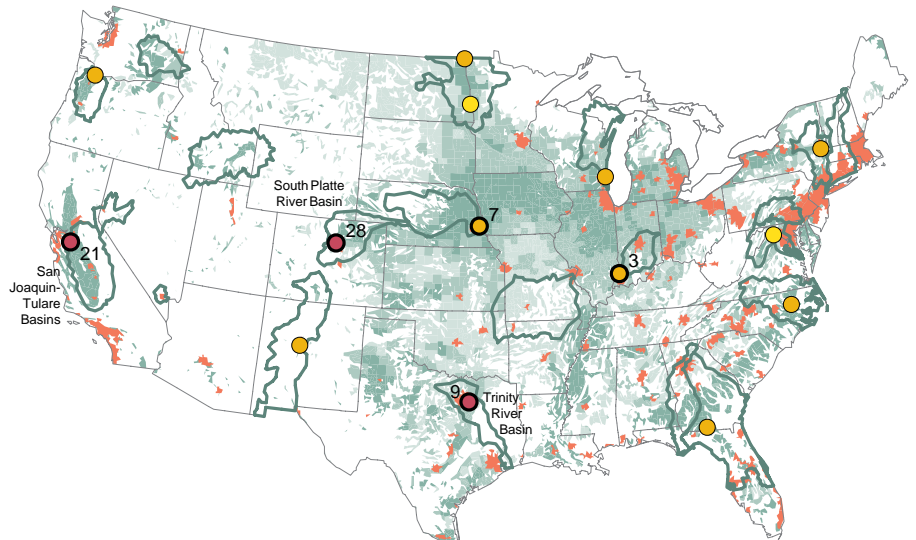
## Urban streams

Most streams had among the highest concentrations. Typically, 10 to 40 percent of samples had concentrations that exceeded one or more aquatic-life guidelines.



## Rivers and streams with mixed land use

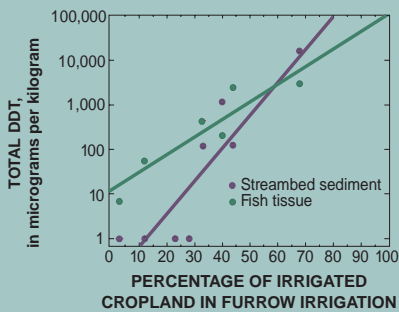
Concentrations were low to moderate except for the urban-affected South Platte and Trinity Rivers, and the San Joaquin River, which drains farmlands with some of the most intensive insecticide use in the Nation.



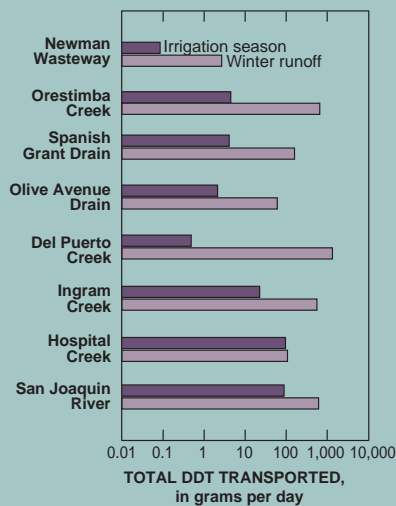


## CONTROL OF SOIL EROSION IS KEY TO REDUCING ORGANOCHLORINE INSECTICIDES

Organochlorine insecticides bind strongly to soils and are carried with eroded soils to streams by runoff from irrigation and rainfall. In streams, the soil-bound insecticides may dissolve in water, remain suspended, or settle to the streambed. They also accumulate in fish. Understanding and managing soil erosion is a key to reducing organochlorine contamination.



For example, furrow irrigation causes more erosion than sprinkler or drip irrigation. In the Central Columbia Plateau, DDT concentrations in streambed sediment and fish increased as the percentage of furrow irrigation in the basin increased.



In the San Joaquin-Tulare Basins, the amount of DDT transported with suspended sediment in the San Joaquin River and tributaries generally was greater during winter runoff than during the irrigation season. Controlling irrigation-induced soil erosion would reduce but not eliminate DDT in the streams because large quantities are transported during infrequent storms.

## Organochlorine insecticides were highest in urban streams and where historical agricultural use was greatest

Concentrations of organochlorine insecticides in bed sediment and fish correspond to land use and past application rates. Although most uses of organochlorine insecticides ended 10 to 25 years ago, they remain a significant water-quality issue for many streams. Overall, 14 percent of bed-sediment samples had concentrations that exceeded sediment-quality guidelines for protection of aquatic life,<sup>(39)</sup> and 19 percent of sites had concentrations in fish that exceeded New York guidelines for protection of fish-eating wildlife.<sup>(40)</sup> Compounds that most often exceeded guidelines were DDT and chlordane in bed sediment and DDT and dieldrin in fish.

Almost all urban streams had high or medium concentrations of the organochlorine insecticides compared with other sites. Sediment-quality guidelines were exceeded at 37 percent of urban sites, with several sites each in urbanized areas of the Connecticut, Housatonic, and Thames River Basins, Hudson River Basin, Trinity River Basin, and Georgia-Florida Coastal Plain. Concentrations in whole fish exceeded guidelines for the protection of fish-eating wildlife at 21 percent of urban sites.

In agricultural streams, concentrations of organochlorine insecticides were highest in areas of high past use. High concentrations were most common for streams in the Central Columbia Plateau, Georgia-Florida Coastal Plain, and Trinity River Basin. One or more sediment-quality guidelines were exceeded at 15 percent of agricultural sites, and concentrations in whole fish exceeded wildlife guidelines at 20 percent of sites.

Many streams and rivers with mixed land-use influences also had high concentrations in bed sediment, particularly in basins with extensive agricultural areas where past use was high, such as in the Southeast and the irrigated West, and in basins with high population density, such as in the Northeast. Sediment-quality guidelines were exceeded at 11 percent of these sites, and wildlife guidelines were exceeded in whole fish at 24 percent of these sites. In undeveloped areas, organochlorine concentrations generally were low and did not exceed sediment-quality guidelines.

A significant health concern in some regions is consumption of fish with high levels of organochlorine insecticides in their flesh. Human-health guidelines for edible fish tissue<sup>(41)</sup> are not directly applicable to NAWQA results, which are based on whole-fish analysis of mostly carp and suckers. Nevertheless, the NAWQA fish data provide a relative indication of potential concern. **At about 30 percent of NAWQA sites, insecticide concentrations in whole fish exceeded human-health guidelines for edible fish tissue.<sup>(41)</sup> For any of these streams that are active fisheries, additional assessment of fillets of edible species is advisable if this has not already been done.**

## A national ranking of **ORGANOCHLORINES** in bed sediment

### Sum of organochlorine insecticide concentrations

- Highest 25 percent
- Second highest 25 percent
- Lowest 50 percent (all with no detections)

### Aquatic-life guidelines

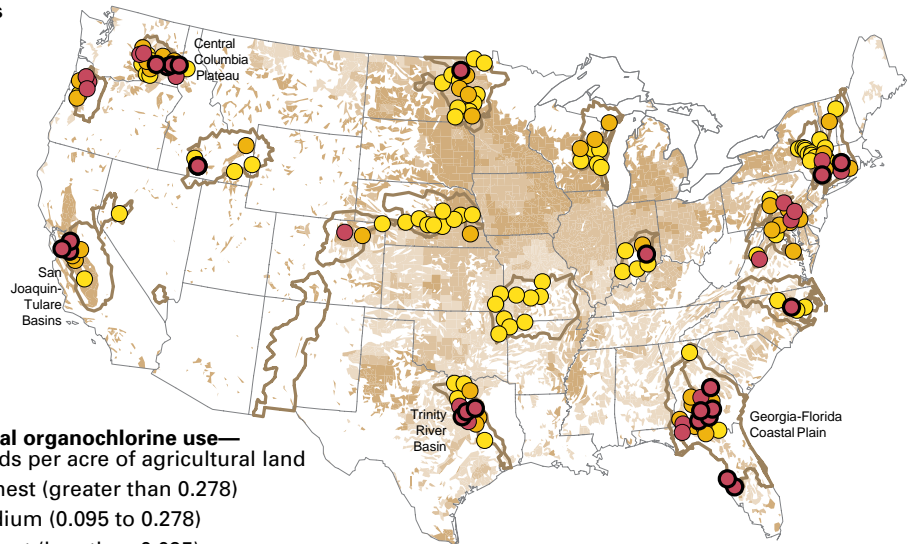
- Bold outline indicates exceedance by one or more organochlorine insecticides

### Agricultural streams

Highest concentrations occurred where historical use was highest on crops such as cotton, peanuts, orchards, and vegetables.

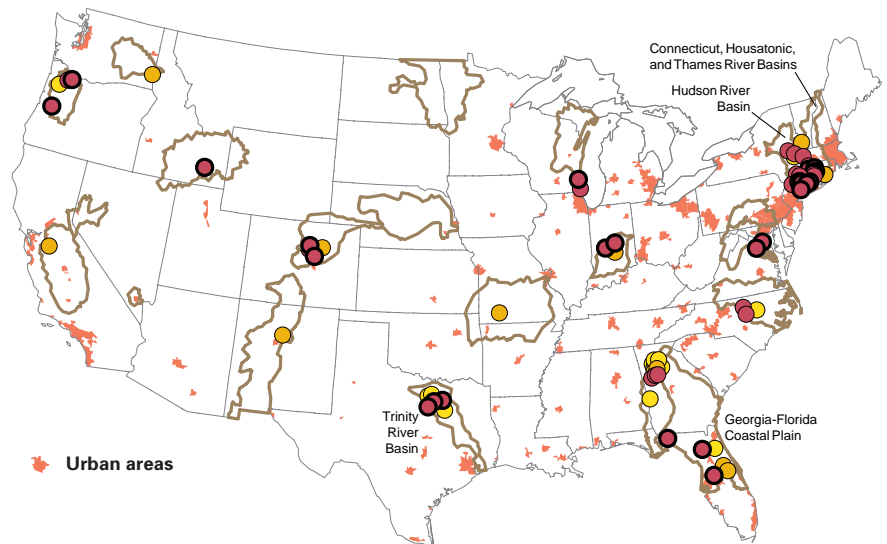
### Historical organochlorine use— in pounds per acre of agricultural land

- Highest (greater than 0.278)
- Medium (0.095 to 0.278)
- Lowest (less than 0.095)
- No reported use



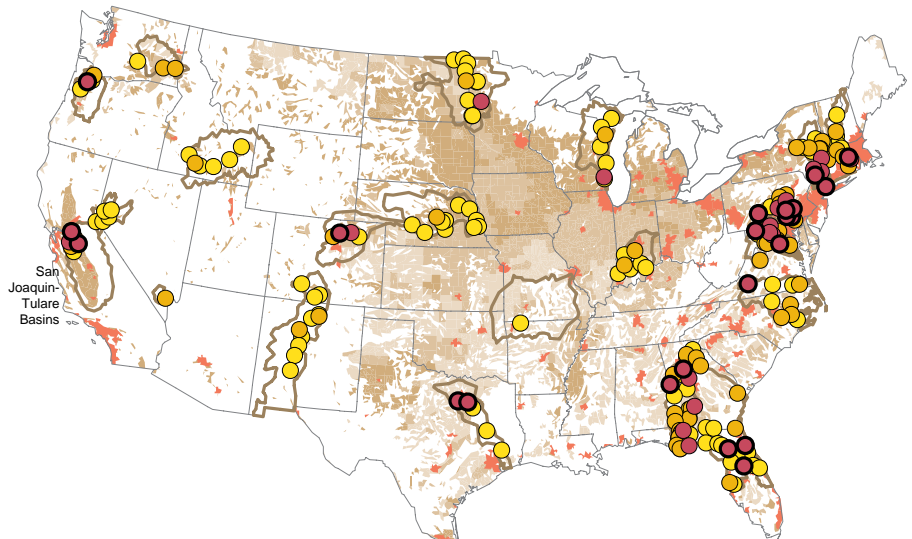
### Urban streams

Most urban streams had higher concentrations than the majority of agricultural streams, and concentrations exceeded sediment-quality guidelines at almost 40 percent of the sites.



### Rivers and streams with mixed land use

Concentrations followed the patterns in contributing agricultural and urban areas, with the highest concentrations in areas of high population densities or intensive historical use in agriculture.



See p. 31 for more information about these maps

# Herbicides in shallow ground water were most common beneath agricultural areas

The highest frequencies of detection for pesticides in ground water were for herbicides in shallow ground water beneath agricultural areas. In these areas where herbicide use was moderate to high, soil and geologic conditions favored rapid movement of herbicides to the ground water. Most studies of shallow ground water in agricultural areas detected herbicides in more than 50 percent of wells sampled.

Compared to streams, ground-water detections were dominated by fewer compounds—mainly those that have the combination of relatively high mobility and chemical stability that allows them to move and persist in the flow system long enough to reach a well. Only atrazine, its breakdown product DEA, metolachlor, prometon, and simazine were found in more than 5 percent of all wells.

Of the 36 studies of shallow ground water in agricultural areas, which included more than 1,000 wells, only one well in an unused shallow ground-water area in the Connecticut, Housatonic, and Thames

River Basins had an atrazine concentration that exceeded the drinking-water standard of 3 µg/L.

Herbicides were moderately common in shallow ground water beneath urban areas. In an urban area of the Albemarle-Pamlico Drainage, a shallow aquifer used for drinking-water supply had one monitoring well where an atrazine concentration exceeded the drinking-water standard.

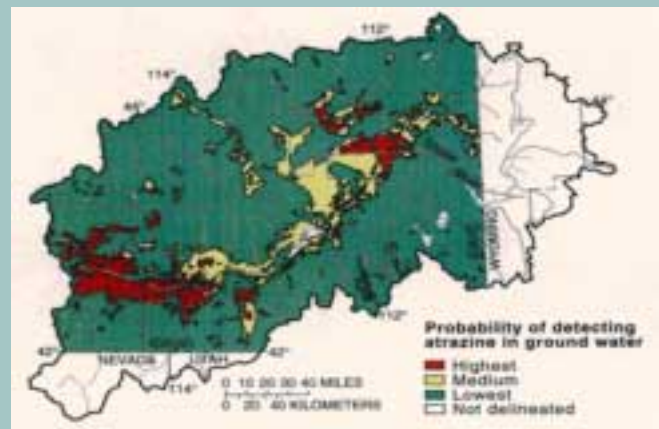
Major aquifers, all of which are drinking-water sources, are generally deeper than the shallow ground water studied and had distinctly lower detection frequencies of herbicides. Only 3 of 33 aquifers sampled had among the highest ranked detection frequencies, and none of the wells sampled in major aquifers had herbicide concentrations that exceeded drinking-water standards or guidelines.

Ground-water contamination, compared to stream contamination, is more strongly governed by soil and geologic conditions, and each well is uniquely affected by sources of pesticides and flow conditions in its immediate vicinity. Local variability

in these conditions can result in degradation of water quality in one or a few wells, even if most wells are not affected. The greatest frequencies of herbicide detection in major aquifers occurred in vulnerable settings. The three aquifers with the highest frequencies of detection were (1) the Platte River Alluvial aquifer in the Central Nebraska Basins, which is shallow and overlain by permeable sandy soils, (2) the Upper Floridan aquifer in the Appalachian-Chattahoochee-Flint River Basin, which is a limestone formation where flow rates are high, and (3) a shallow limestone aquifer in the Lower Susquehanna River Basin.

## PREDICTING ATRAZINE CONTAMINATION IN GROUND WATER

As part of Idaho's State Pesticide Management plans for herbicides, maps have been developed to portray the potential for atrazine contamination in ground water in southeastern Idaho.<sup>(42)</sup> Atrazine data from the NAWQA Program in the Upper Snake River Basin were used to calibrate and verify predictive models. Significant factors used to successfully predict atrazine concentrations in ground water were atrazine use, land use, precipitation, soil type, and depth to ground water. Continued development of these types of modeling tools will aid in designing cost-effective programs for monitoring and protecting ground-water resources across the Nation.





## A national ranking of **HERBICIDES** in ground water

**Herbicide detection frequency**—Each circle represents a ground-water study

- Highest 25 percent
- Middle 50 percent
- Lowest 25 percent

**Drinking-water standards or guidelines**

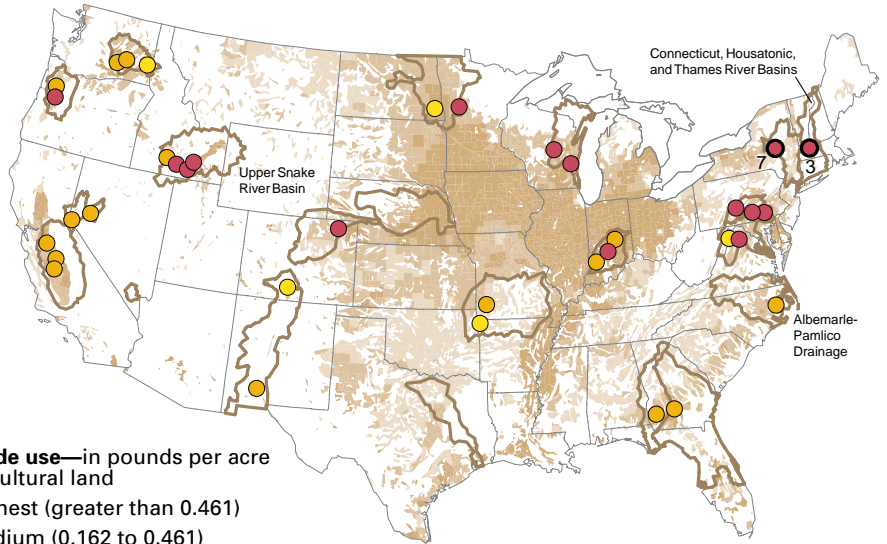
- <sup>3</sup> Bold outline indicates exceedance by one or more herbicides. Number is percentage of wells that exceeded a standard or guideline

### Shallow ground water in agricultural areas

The highest detection frequencies occurred where use is moderate to high and where soil and geologic conditions promote rapid infiltration.

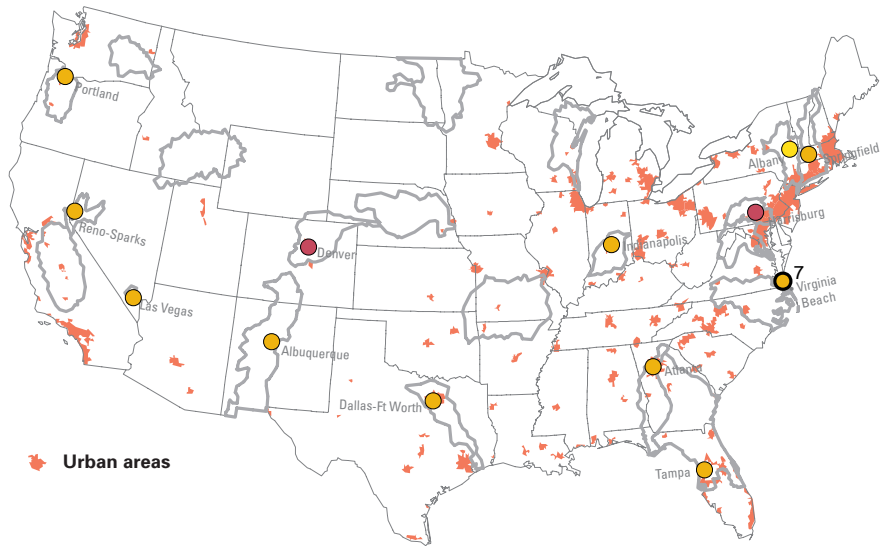
**Herbicide use**—in pounds per acre of agricultural land

- Highest (greater than 0.461)
- Medium (0.162 to 0.461)
- Lowest (less than 0.162)
- No reported use



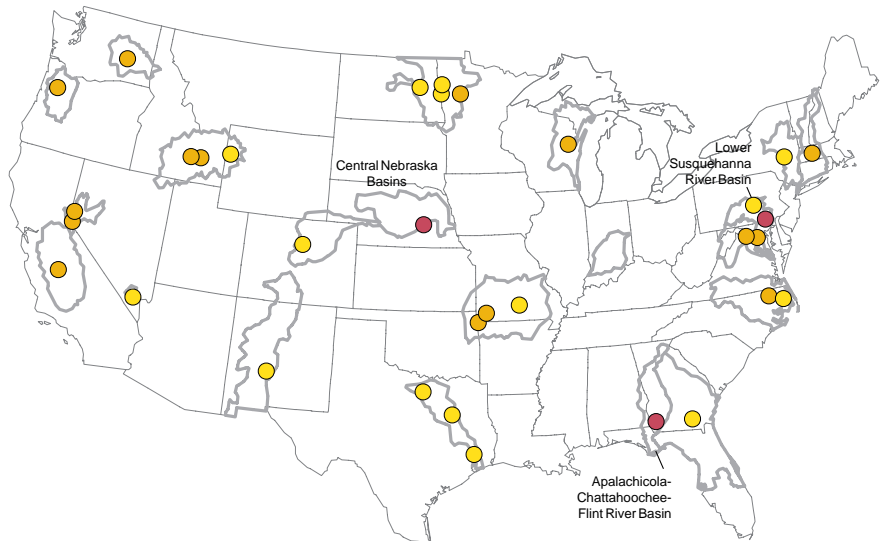
### Shallow ground water in urban areas

Only two urban areas had detection frequencies in the highest 25 percent of all ground-water studies.



### Major aquifers

Detections were infrequent, except for a few aquifers in vulnerable settings—shallow aquifers with permeable sandy soils or limestone formations.



See p. 31 for more information about these maps

## Insecticides were seldom found in ground water but may be a concern in some areas

Insecticides, in contrast to herbicides, were not detected in a number of ground-water studies and, where detected, were usually found in less than 10 percent of wells. The most frequently detected insecticides in ground water were dieldrin and diazinon, although each was found in only 1 to 2 percent of all wells. The relative abundance of dieldrin was unexpected because of its low mobility in water compared with many currently used pesticides. Dieldrin, however, is one of the more mobile compounds within the historically used organochlorine group. Moreover, it is long-lived in the environment, which results in its great persistence in the ground-water flow system.

**Although insecticides were much less common than herbicides in ground water, they exceeded drinking-water standards or guidelines more often.** In all but one well where exceedances occurred, dieldrin was the insecticide that exceeded the guideline. The guideline used for dieldrin is a USEPA Risk Specific Dose of 0.02 µg/L, which corresponds to a cancer risk level of 1 in 100,000. The wells that exceeded the Risk Specific Dose for dieldrin were mainly wells tapping shallow ground water that is not used for human consumption.

The infrequent but potentially important occurrences of dieldrin in some wells may be the result of local contamination of individual wells. The combination of relatively shallow ground water and pesticide use in the vicinity of wells increases the likelihood that some wells will have flow pathways that allow pesticides to move from the land surface to the well, sometimes down the borehole itself.



Daniel J. Hippe

### DIELDRIN PERSISTS IN SHALLOW URBAN GROUND WATER

In the Apalachicola-Chattahoochee-Flint River Basin, insecticide concentrations in ground-water samples generally were less than current drinking-water standards or guidelines. However, dieldrin concentrations in water samples collected during 1994–95 from 5 of 37 shallow wells and springs in Metropolitan Atlanta exceeded the USEPA Risk Specific Dose of 0.02 µg/L, which corresponds to a cancer risk level of 1 in 100,000. Dieldrin and aldrin, which breaks down to dieldrin in the environment, had been used on agricultural land prior to 1975 and for structural termite control until 1987.<sup>(36)</sup> Although this ground water is not used as a source of drinking water, the presence of dieldrin in ground-water samples collected several years after being banned is indicative of the compound's persistence in soils and ground water and its potential to be a problem in some wells.

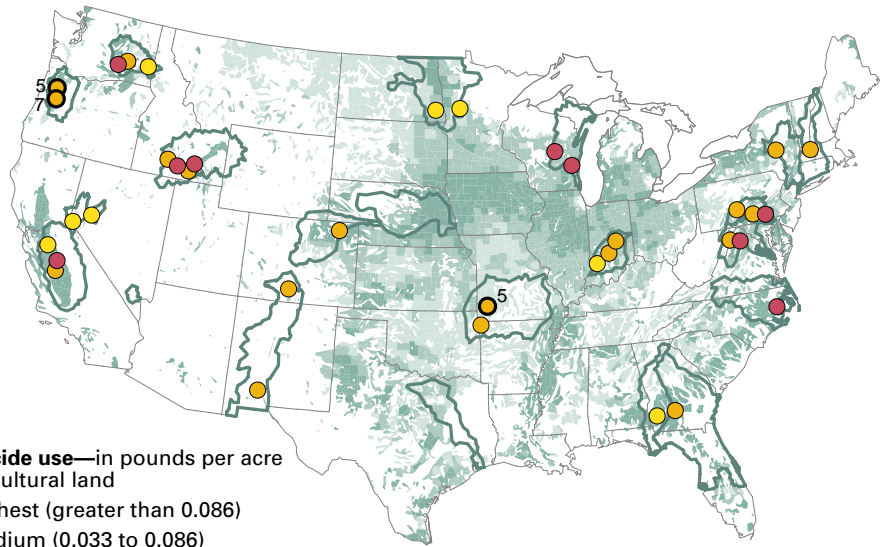
## A national ranking of **INSECTICIDES** in ground water

**Insecticide detection frequency**—Each circle represents a ground-water study or major aquifer

- Highest 25 percent
- Middle 46 percent
- Lowest 29 percent (all with no detections)

**Drinking-water standards or guidelines**

- <sup>5</sup> Bold outline indicates exceedance by one or more insecticides. Number is percentage of wells that exceeded a standard or guideline



**Insecticide use**—in pounds per acre of agricultural land

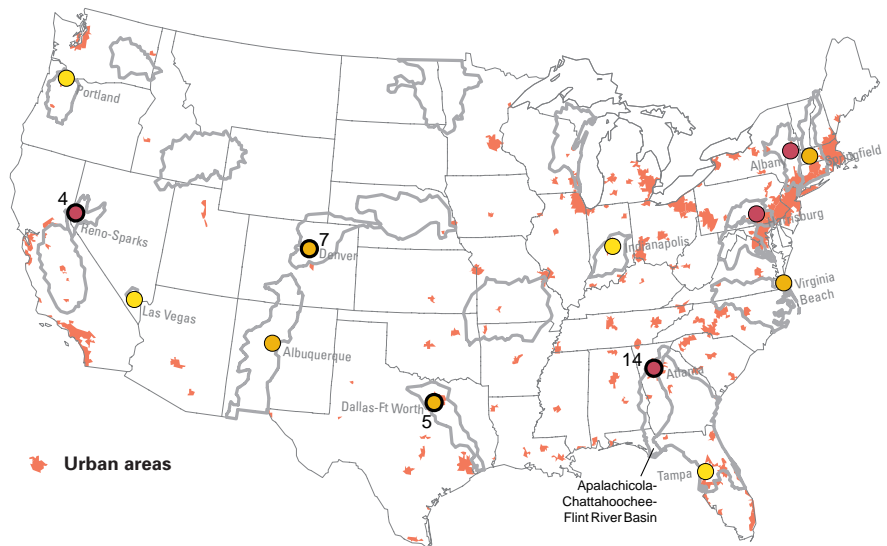
- Highest (greater than 0.086)
- Medium (0.033 to 0.086)
- Lowest (less than 0.033)
- No reported use

### Shallow ground water in agricultural areas

Detection frequencies ranked low to moderate in most studies.

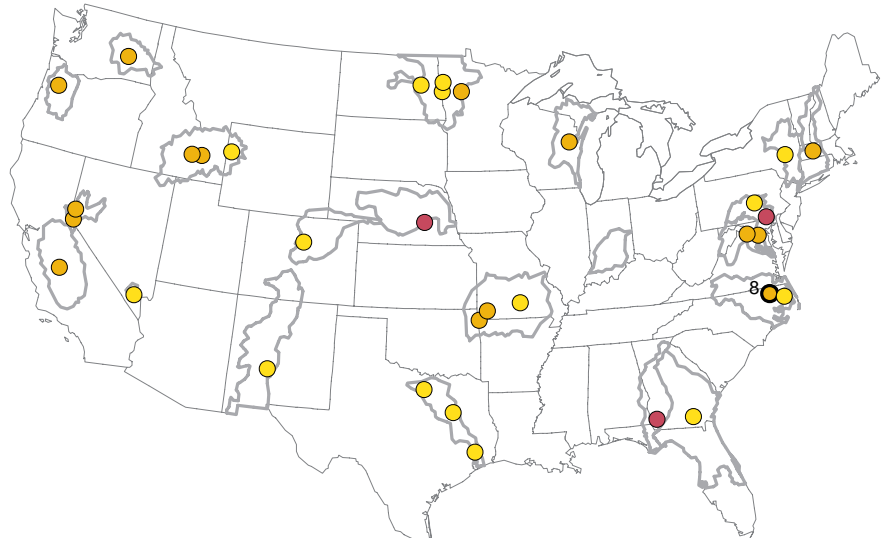
### Shallow ground water in urban areas

Detection frequencies ranked high in urban areas compared with other study areas but still were low compared to herbicides. Although aldrin and dieldrin have not been used for years, dieldrin was the most frequently detected insecticide.



### Major aquifers

Most major aquifers ranked low to moderate in detection frequency and, only one well exceeded a drinking-water standard or guideline (dieldrin).





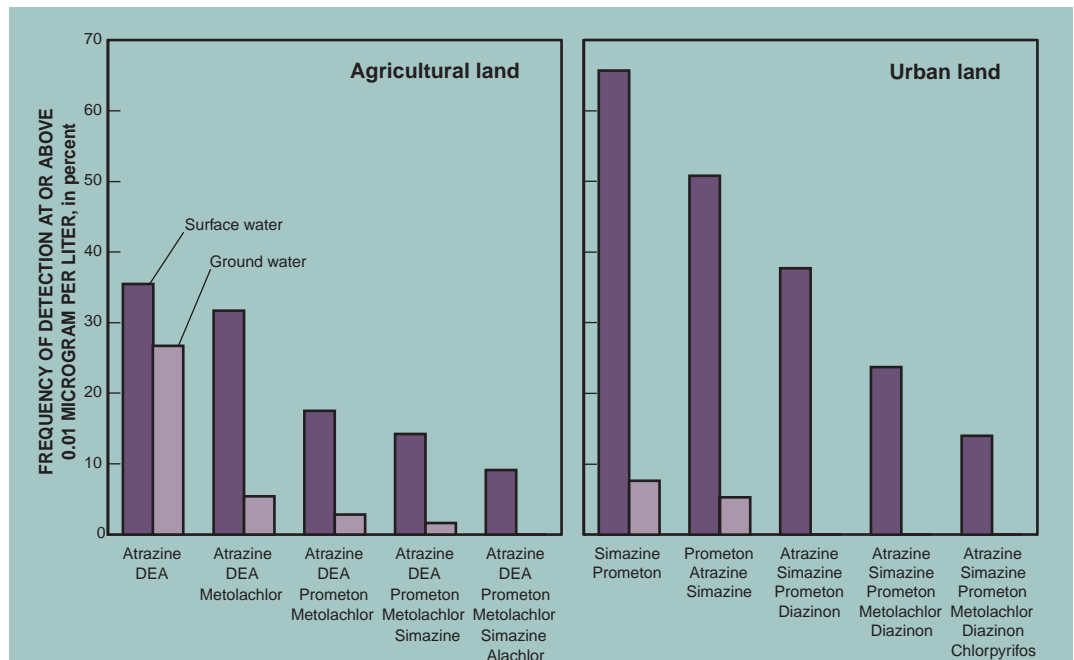
# Differences in occurrence and behavior of pesticides complicate evaluation of potential effects

## PESTICIDES USUALLY OCCUR AS MIXTURES

Pesticides usually occur in mixtures of several compounds rather than individually, but most of our experience and research on environmental effects is based on exposure to individual compounds. **Therefore, it is vital that we understand and document the occurrence and composition of common low-level mixtures and begin to evaluate their effects.**

More than 50 percent of all stream samples contained five or more pesticides, and nearly 25 percent of ground-water samples contained two or more pesticides. In the Central Columbia Plateau, for example, 66 percent of ground-water samples with detections contained more than one pesticide, most commonly in shallow monitoring wells. The most common mixtures were found more than twice as frequently in streams than in ground water, except for the atrazine-DEA combination.

Mixtures of currently used pesticides in stream water may occur in combination with mixtures of organochlorine insecticides in bed sediment and fish. Moreover, about 50 percent of bed-sediment and fish samples with pesticide detections contained compounds from two or more of the major organochlorine groups.



### COMMON PESTICIDE MIXTURES IN WATER

The composition of the most common pesticide mixtures differs between urban and agricultural areas and between agricultural areas with different crops and pests. In urban areas, simazine and prometon were the most common pesticides found together, whereas atrazine, DEA (deethyl-atrazine), and metolachlor were the most common compounds found in mixtures from agricultural areas. Mixtures containing both herbicides and insecticides were a common occurrence in urban streams. More than 10 percent of urban stream samples contained a mixture of at least 4 herbicides plus the insecticides diazinon and chlorpyrifos.

## BREAKDOWN PRODUCTS CAN BE IMPORTANT

Once released into the environment, pesticides undergo a series of chemical and biological reactions whereby the original pesticide breaks down into intermediate compounds, and eventually into carbon dioxide and other harmless compounds. Some breakdown products are short-lived, whereas others persist for years or decades. Little is known about the occurrence of many pesticide breakdown products, and even less is known about their effects on human health and aquatic life.

**Of the thousands of possible breakdown products, few have been looked for in streams or ground water.**<sup>(6,43)</sup> Some are less toxic than their parent compounds, whereas others have been found to have similar or even greater toxicities.

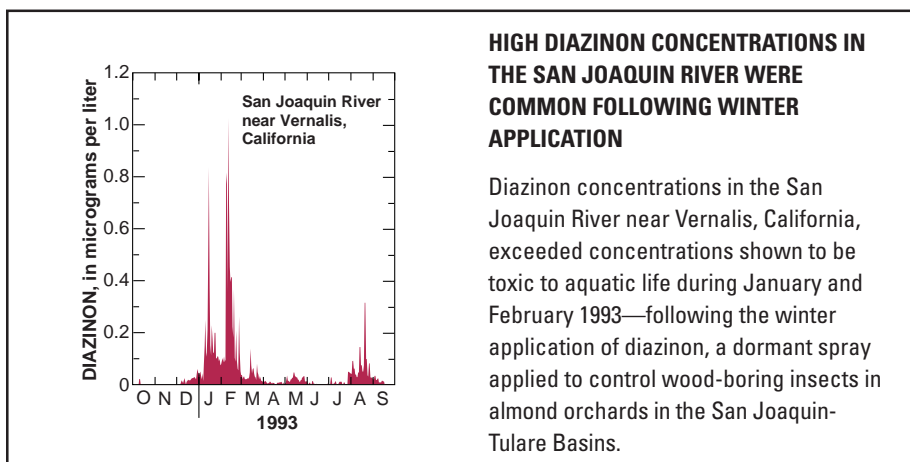
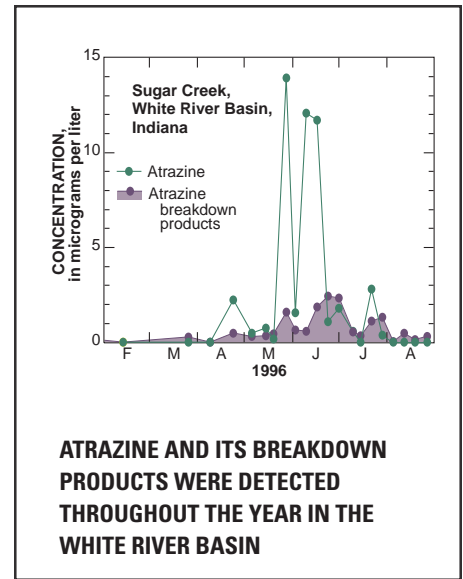
Only seven breakdown products were analyzed in water samples from the first 20 Study Units: 2,6-diethyl-aniline (parent pesticide, alachlor), 3-hydroxy-carbofuran (carbofuran), aldicarb sulfone and aldicarb sulfoxide (aldicarb), DDE (DDT), alpha-HCH (lindane), and DEA (atrazine). Of the parent pesticides, atrazine is the most heavily used, and both it and DEA were widespread in streams and ground water across the Nation. The two were found together

in about 35 percent of stream samples and about 25 percent of ground-water samples from agricultural areas.

With few exceptions, most of the other breakdown products were found in fewer than 1 percent of samples in each of the Study Units. However, several breakdown products of alachlor and metolachlor have been frequently found in other studies, often at much higher concentrations than the parent pesticide.<sup>(34, 44)</sup> As NAWQA evolves, more complete analyses of breakdown products are being added as analytical methods and budget constraints allow.

## CONCENTRATIONS IN STREAMS FOLLOW STRONG SEASONAL PATTERNS

Seasonal patterns in concentrations and occurrences of pesticides in agricultural streams, which tend to repeat each year, correspond to patterns in use and streamflow, including contributions from ground water. Generally, the number and concentrations of herbicides found in most agricultural streams were highest from April through July, whereas insecticides occurred more variably throughout the summer. The spring herbicide pulse was commonly observed in corn-growing areas and other agricultural areas shortly after



herbicide application, when herbicides were transported to streams in runoff induced by spring rain and irrigation. In some parts of the Nation, other patterns can occur. For example, some insecticides, such as diazinon in the San Joaquin-Tulare Basins, have patterns of high concentrations during the winter, resulting from the use of dormant sprays on orchards. Differences in patterns also may result from local water-management practices, including the timing of reservoir storage and water use, the timing of runoff from agricultural fields due to irrigation or storms, or ground-water contributions during periods of low streamflow. **Seasonal patterns need to be characterized and understood because they dictate the timing of high concentrations in drinking-water supplies and the times when aquatic organisms may be exposed to high concentrations during critical stages of their life cycle.** For example, some water suppliers reduce their use of certain surface-water supplies during spring runoff.

# Trends in pesticide concentrations follow changes in use

Pesticides in streams and ground water change over time as the types and amounts of chemicals in use change. With the exception of organochlorine insecticides, however, consistent data that are adequate for assessing long-term trends have not been widely collected. Examples for the organochlorine insecticides and recent changes in herbicide use illustrate the importance of tracking such trends.

## ORGANOCHLORINE INSECTICIDES HAVE DECREASED

**A striking historical trend is the reduction in concentrations of organochlorine insecticides in sediment and fish following restrictions on their use, yet they continue to occur at levels of concern.** This trend is evident in sediment cores from lakes and reservoirs and by comparison of NAWQA findings to historical concentrations in fish measured by the U.S. Fish and Wildlife Service (USFWS).

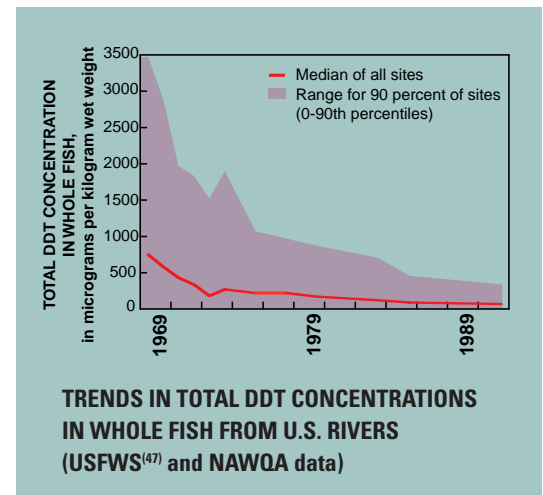
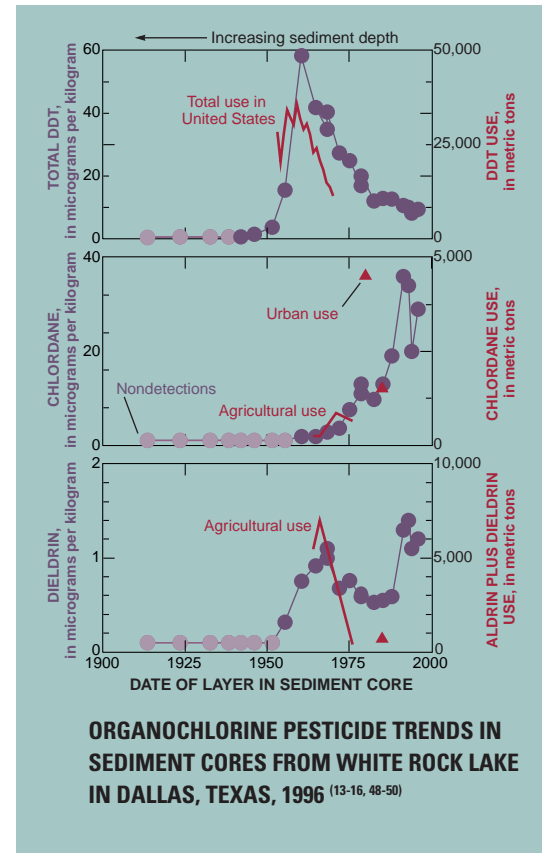
As sediment erodes from the land surface over time, it is deposited in layers on the bottom of lakes and reservoirs. Age-dated sediment cores that penetrate these layered deposits can be used to track trends in sediment-associated contaminants within the drainage basin.

Concentrations of total DDT (DDT plus breakdown products DDE and DDD) in sediment cores from lakes and reservoirs reflect high historical use of DDT followed by a ban in 1972. DDT concentrations peaked during the 1960s, which coincides with its peak use as an insecticide. Total DDT concentrations in sediment have decreased since 1972 in all sampled lakes and reservoirs that drain urban and agricultural areas within the United States.<sup>(45)</sup>

Unlike DDT, aldrin and chlordane were used for termite control until the late 1980s, long after their agricultural uses were cancelled in the early 1970s. Chlordane and dieldrin concentrations peaked in many agricultural areas during the 1970s, and decreased thereafter. In some urban lakes and reservoirs, however, such as White Rock Lake in the Trinity River Basin, chlordane and dieldrin peaked much later, probably as a result of continued urban use during the 1980s. This watershed is dominated by new (post-1960) urbanization.<sup>(46)</sup>

Concentrations of DDT, chlordane, and dieldrin in whole fish have declined nationally since the 1970s. To assess trends in DDT concentrations, NAWQA data for streams and rivers with mixed land influences were compared with similar data from 1969 to 1986 collected by the USFWS National Contaminant Biomonitoring Program.<sup>(47)</sup> Total DDT concentrations in fish declined markedly from 1969 to the present. The declines were greatest during the early 1970s, with concentrations since the mid-1980s showing a slower decline or even a plateau.

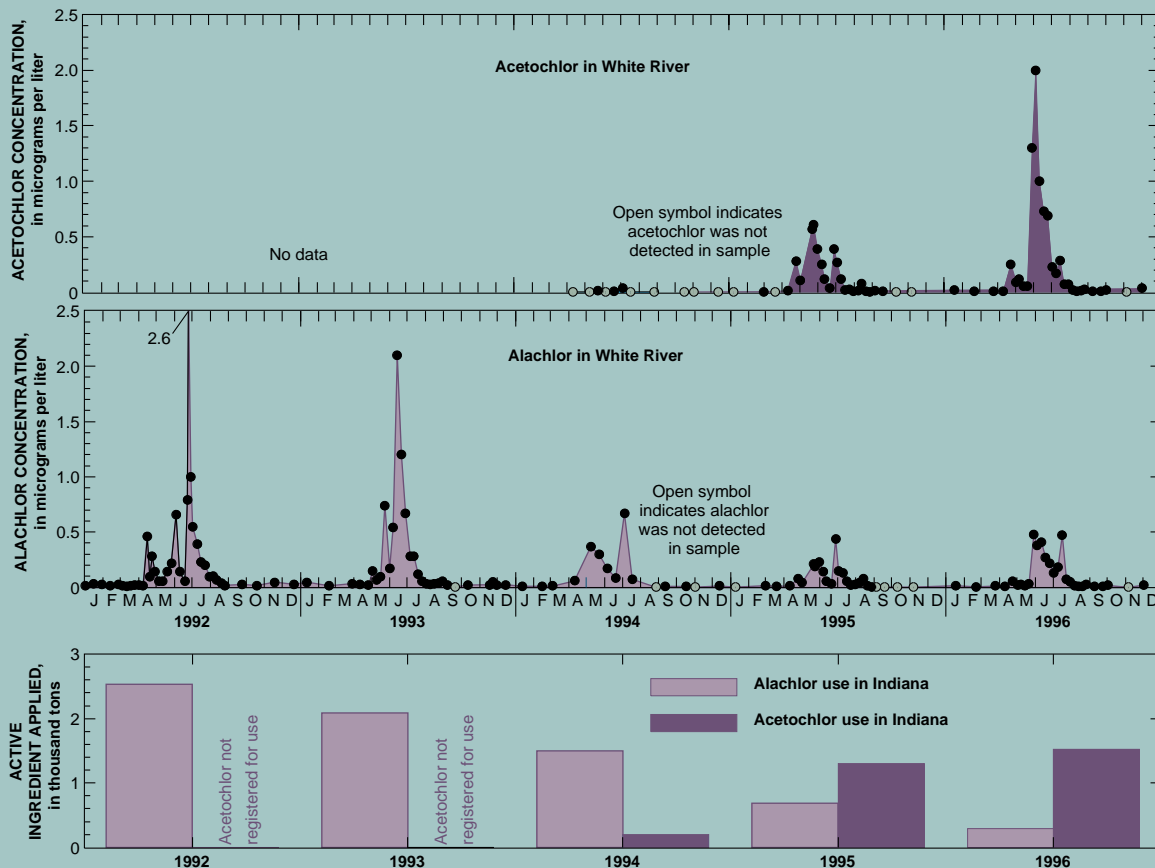
Despite the observed national decline in total DDT concentrations, the detection frequency for total DDT in whole fish from major rivers remains high (94 percent in the 1990s), and locally contaminated areas persist. This is probably caused by the presence of total DDT in the streambed and continued inputs of total DDT to hydrologic systems as contaminated soils erode into streams.





## RECENT CHANGES IN HERBICIDE USE HAVE BEEN RAPIDLY REFLECTED IN STREAMS

Few studies have documented long-term trends in water concentrations of currently used pesticides with sufficient consistency in locations, timing, and methods to be conclusive. Recently, however, a major change has occurred in herbicide use patterns for corn and soybeans, with a new compound, acetochlor, partially replacing alachlor beginning in 1994. The increase in acetochlor concentrations and decrease in alachlor concentrations in the White River from 1994 through 1996 illustrate the direct connection between chemical use and concentrations in streams and in the major rivers into which they flow.



**TRENDS IN HERBICIDE USE WITH TIME ARE REFLECTED IN STREAM QUALITY**

Alachlor concentrations in streams in the White River steadily declined from 1992 through 1996 and corresponded with a decline in alachlor use in the basin. Application of acetochlor, a corn herbicide registered for use in 1994, has partially replaced the use of alachlor in the basin. Acetochlor was detected at only trace concentrations during the 1994 growing season. By 1996, acetochlor was commonly detected in the White River, where a peak concentration of about 2 µg/L was measured.

## STREAMS AND GROUND WATER RESPOND DIFFERENTLY TO CHANGE

Generally, as pesticide use in a basin changes, concentrations in streams quickly reflect these changes. In ground water, however, responses to trends in pesticide-use patterns will be highly variable depending on the nature of the flow system and variability in flow pathways, well depth, and other factors. For the most part, changes in concentrations of pesticides in ground water are much slower than in streams, and responses of ground water to changing use can be delayed for years or decades in some systems.