Potential for Effects on Human Health, Aquatic Life, and Wildlife

The occurrence of pesticides in streams and ground water raises the question—Do pesticides occur at concentrations that may affect human health or stream ecosystems? Comparisons of concentrations measured by NAWQA to water-quality benchmarks provide a screening-level assessment of the potential for adverse effects. Concentrations of pesticides detected in streams and wells were usually lower than human-health benchmarks, indicating that the potential for effects on drinking-water sources probably is limited to a small proportion of source waters. More than half of the wells sampled, but none of the stream sites that were sampled, are current sources of drinking water. Concentrations in streams more frequently exceeded benchmarks for aquatic life and fish-eating wildlife. More than half of all agricultural streams sampled and more than three-quarters of all urban streams had concentrations of pesticides in water that exceeded one or more benchmarks for aquatic life. In addition, organochlorine pesticides—most uses of which were discontinued 15–30 years ago—still exceeded benchmarks for aquatic life and fish-eating wildlife in bed-sediment or fish-tissue samples from many streams.

This chapter examines the potential for pesticides to have adverse effects on human health, aquatic life, and fish-eating wildlife. The potential is assessed by comparing measured concentrations with water-quality benchmarks. The screening-level assessment provides indications of the distribution of potential effects and the pesticides that may cause them, which can be used to prioritize further investigations.

Screening-Level Assessment of Potential Effects

The potential for pesticide concentrations measured by NAWQA to adversely affect human health, aquatic life, or fish-eating wildlife was evaluated by screening-level assessments similar in concept to USEPA screening-level assessments (USEPA, 2004d). The NAWQA screening-level assessments compare site-specific estimates of pesticide exposure (concentration statistics or concentrations determined from measurements of pesticides in various media at NAWQA sampling sites) with water-quality benchmarks derived from standards and guidelines established by USEPA, toxicity values from USEPA pesticide risk assessments, and selected guidelines from other sources. The characteristics and limitations of screening-level assessments are summarized in the accompanying sidebar on page 89. The USEPA standards, guidelines, and toxicity values were developed by USEPA as part of the Federal process for assessing and regulating pesticides, as summarized in the sidebar on page 90.

NAWQA studies were not designed to evaluate specific effects of pesticides on humans, aquatic life, or fish-eating wildlife. The screening-level assessment is not a substitute for either risk assessments, which include many more factors (such as additional avenues of exposure), or site-specific studies of effects. Rather, comparisons of measured concentrations with water-quality benchmarks provide a perspective on the potential for adverse effects, as well as a framework for prioritizing additional investigations that may be warranted. Measured concentrations that exceed a benchmark do not necessarily indicate that adverse effects are occurring—they indicate that adverse effects *may* occur and that sites where benchmarks are exceeded may merit further investigation.

Screening-level assessments should be considered as a first step toward addressing the question of whether or not pesticides are present at concentrations that may affect human health, aquatic life, or wildlife. They provide a perspective on where effects are most likely to occur and what pesticides or degradates may be responsible. As improved data on toxicity and environmental concentrations are developed, benchmarks and exposure estimates can be updated, and the assessments can be improved and expanded. USGS works closely with USEPA to assist them with incorporating NAWQA findings into their risk assessments.

NAWQA screening-level assessments for pesticides are presented in this chapter for human health (concentrations in water), aquatic life (concentrations in water and bed sediment), and fish-eating wildlife (concentrations in whole fish). The selection of benchmarks for each of these assessments is described below along with results and the specific values and sources for benchmarks used are provided in Appendix 3. Each type of benchmark selected for use in the screening-level assessment applies to a specific sampling medium (such as water or bed sediment) and to a specific use of the water resource (such as for drinking water or to support aquatic life). Priority was given to (1) benchmarks based on USEPA standards, guidelines, or toxicity values; (2) benchmarks that are nationally relevant because of the nature or breadth of toxicity data on which they are based; and (3) systematically derived suites of benchmarks that share a common methodology and are available for a large number of NAWQA analytes.

Characteristics and Limitations of the Screening-Level Assessment of Potential Effects

The NAWQA screening-level assessment provides an initial perspective on the potential importance of pesticides to water quality in a national context by comparing measured concentrations with water-quality benchmarks. The screening-level assessment is not a substitute for risk assessment, which includes many more factors, such as additional avenues of exposure. The screening-level results are primarily intended to identify and prioritize needs for further investigation and have the following characteristics and limitations.

- Most benchmarks used in this report are estimates of no-effect levels, such that concentrations below the benchmarks are expected to have a low likelihood of adverse effects and concentrations above a benchmark have a greater likelihood of adverse effects, which generally increases with concentration.
- The presence of pesticides in streams or ground water at concentrations that exceed benchmarks does not indicate that adverse effects are certain to occur. Conversely, concentrations that are below benchmarks do not guarantee that adverse effects will not occur, but indicate that they are expected to be negligible (subject to limitations of measurements and benchmarks described below).
- The potential for adverse effects of pesticides on humans, aquatic life, and fish-eating wildlife can only be partially addressed by NAWQA studies because chemical analyses did not include all pesticides and degradates. In addition, some compounds analyzed by NAWQA do not have benchmarks.
- Most benchmarks used in this report are based on toxicity tests of individual chemicals, whereas NAWQA results indicate that pesticides usually occur as mixtures. Comparisons to single-compound benchmarks may tend to underestimate the potential for adverse effects.
- Water-quality benchmarks for different pesticides and media are not always comparable because they have been derived by a number of different approaches, using a variety of types of toxicity values and test species.
- For some benchmarks, there is substantial uncertainty in underlying estimates of no-effect levels, depending on the methods used to derive them and the quantity and types of toxicity information on which they are based. This is especially true of fish-tissue benchmarks for the protection of fish-eating wildlife, for which there is no consensus on national-scale benchmarks or toxicity values.
- Estimates of pesticide exposure derived from NAWQA concentration measurements are also uncertain—particularly estimates of short-term exposure of aquatic organisms to pesticides in stream water. Generally, short-term average concentrations in stream water, such as 4-day values, are underestimated from NAWQA data.

Screening-Level Assessment for Human Health

NAWQA studies, as emphasized in Chapter 3, characterized the quality of untreated water from streams and ground water, whether or not that water was used as a source of drinking water during the study period. More than half of the wells sampled for ground-water studies, but none of the stream sites that were sampled, were sources of domestic or public water supplies. In this report, measured concentrations of pesticides in all wells and streams sampled, whether or not they were sources of drinking water during the study period, are compared with human-health benchmarks derived from available USEPA drinking-water standards and guidelines as a starting point for understanding the potential importance of pesticides in a human-health context. The benchmarks are described in the accompanying sidebar on page 91 and values are listed in Appendix 3A.

Comparisons of human-health benchmarks to the concentrations observed in NAWQA studies provide a perspective on the potential importance to human health as use of water resources expands, but they are not appropriate for assessing current compliance with drinking-water regulations. A measured concentration or computed annual mean that is greater than a benchmark indicates the potential need for further investigation if such water either is presently used as a drinking-water source, or may be used as a source in the future. A concentration greater than a Maximum Contaminant Level (MCL), even in water that is now a source of drinking water, does not indicate violation of a standard. For water currently used as a drinking-water source, pesticide concentrations in finished water may be lower than those measured in untreated

Federal Regulation of Pesticides in Water

The potential effects of pesticides on humans and the environment are managed under several Federal Acts and regulated through a combination of Federal, State, and Tribal responsibilities. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the Federal Food, Drug and Cosmetic Act (FFDCA), the Food Quality Protection Act (FQPA), the Safe Drinking Water Act (SDWA), and the Clean Water Act (CWA)—all of which are administered by USEPA and partner agencies—provide the regulatory framework that affects the assessment and control of pesticides and their degradates in water resources.

The FIFRA, first enacted in 1947 and amended most recently by the FQPA in 1996, provides the original framework for the Federal pesticide licensing program administered by USEPA and covers the evaluation and registration of pesticides for specific uses. Before a pesticide may be registered it must be shown, among other things, that it will not generally cause "unreasonable adverse effects" to water, air, land, plants, and man and other animals. The FFDCA authorizes USEPA to set maximum residue levels, or tolerances, for pesticides used in or on foods or animal feed, and mandates strong provisions to protect infants and children. Before a pesticide registration may be granted for use on a food commodity, a tolerance must be set or an exemption from a tolerance granted. The FQPA amended the FIFRA and FFDCA to set more stringent safety standards for new and old pesticides. Among its provisions are that (1) human-health assessments must consider aggregate exposures, including all dietary, drinking-water, and nonoccupational exposure; and (2) assessments leading to tolerance decisions must consider, relative to human health, the cumulative effects and common mode of toxicity among related pesticides, the potential for endocrine-disrupting effects, and appropriate safety factors to further protect infants and children. Through application of the FIFRA, FFDCA, and FQPA, USEPA determines the specific conditions under which a pesticide can be legally sold, distributed, and used in the United States, including where, how, and at what application rates pesticides may be used.

The SDWA was originally passed by Congress in 1974 to protect public health by regulating the Nation's public drinking-water supply. The law was amended in 1986 and 1996 and requires protection of drinking water and its sources, including rivers, lakes, reservoirs, springs, and wells (the SDWA does not regulate private wells that serve fewer than 25 individuals). The SDWA authorizes the USEPA to set national health-based standards for drinking water to protect against both naturally occurring and manmade contaminants that may be found in drinking water. The USEPA works with States and water utilities to make sure that these standards are met.

The CWA (originally the Federal Water Pollution Control Act Amendments of 1972, and subsequently amended several times) provides for protection against releases of toxic chemicals. Section 101(a)(3) of the CWA states that "it is national policy that the discharge of toxic pollutants in toxic amounts be prohibited." Section 303(c) of the CWA requires States to develop water-quality standards to protect the public health or welfare, enhance the quality of water, and serve the purposes of the CWA. The control of the discharge of toxic substances is a key objective of the National Pollutant Discharge Elimination System (NPDES) and water-quality standards programs. Section 304(a) of the CWA requires USEPA to develop and publish and, from time to time, revise ambient water-quality criteria for the protection of both human health and aquatic life. When final, these criteria provide USEPA's recommendations to States and authorized Tribes as they develop their own water-quality standards. USEPA-recommended criteria are not regulations, and they do not impose legally binding requirements on USEPA, States, authorized Tribes, or the regulated community. However, USEPA-recommended criteria may form the basis for State or Tribal water-quality standards and become enforceable through NPDES permits or other environmental programs. USEPA's role in this process, in addition to providing criteria recommendations, is to review and approve the water-quality standards developed by States and Tribes.

water (depending on whether and how the water is treated), because some drinking-water treatment processes reduce pesticide concentrations. In addition, NAWQA sampling methods were not designed to meet the specific sampling and analytical requirements for determining compliance with an MCL.

Streams

Annual mean concentrations of pesticides in the 186 streams sampled by NAWQA were seldom greater than human-health benchmarks during 1992–2001, and most exceedances were in streams draining agricultural and urban watersheds (fig. 6–1). Specifically, pesticide concentrations exceeded one or more human-health benchmarks in about 10 percent of agricultural streams, 7 percent of urban streams, and in 1 of the 65 mixed-land-use streams sampled by NAWQA. No benchmarks were exceeded in the eight undeveloped streams that were sampled.

The streams sampled by NAWQA that had concentrations of a pesticide greater than a human-health benchmark were clustered in a few regions. Specifically, 6 agricultural streams and 1 mixed-land-use stream with concentrations greater than one or more benchmarks (5 of 7 streams for atrazine and 4 of 7 for cyanazine) were in the Corn Belt or southern Mississippi River Basin, where atrazine and cyanazine use was high during the study period (fig. 6–2). Two agricultural streams, 1 in California and 1 in Washington, had concentrations of dieldrin that were greater than its benchmark. The 2 urban streams in which benchmarks were exceeded are in Texas (diazinon) and Hawaii (dieldrin).

A new analysis of atrazine's potential risks has been developed by USEPA as part of the reregistration process (USEPA, 2003a). The analysis is based on the concentrations of atrazine and three of its chlorinated degradates, referred to, collectively, as "total atrazine." The human-health benchmarks from this new analysis are 37.5 µg/L for the 90-day moving average if the monitoring frequency is at least weekly and 12.5 µg/L if monitoring is less frequent. Comparison of these benchmark values to 90-day moving averages determined from NAWQA data for the sum of atrazine and deethylatrazine (NAWQA did not measure the 2 other chlorinated degradates) indicates that 4 of the 5 sites that exceeded the MCL-based benchmark also had 90-day averages that exceeded the 12.5 µg/L level. Of these 4 sites, however, 3 had at least weekly sampling frequencies during the high-concentration period of the year and concentrations would thus be compared with the 37.5 µg/L benchmark. Of the 3 sites with at least weekly sampling, 1 exceeded the 37.5 µg/L benchmark. Use of benchmarks from the new risk analysis would, therefore, result in screening-level exceedances for 2 sites instead of 5 sites, although inclusion of the other chlorinated degradates could increase the number of sites with exceedances. Further analysis of the distribution of atrazine concentrations in streams nationwide is presented in Chapter 7.

Human-Health Benchmarks for Pesticides in Water

Benchmarks for assessing the potential for pesticides in water to affect human health were derived from three types of USEPA drinking-water standards and guidelines developed by USEPA's Office of Water (USEPA, 2004c, 2005e). One or more drinking-water standards or guidelines are available for 47 of the 83 pesticides and degradates analyzed by NAWQA (Appendix 3A).

Maximum Contaminant Level (MCL)—The maximum permissible concentration of a contaminant in water that is delivered to any user of a public water system. This is an enforceable standard issued by USEPA under the Safe Drinking Water Act and established on the basis of health effects and other factors (analytical and treatment technologies, and cost).

Lifetime Health Advisory (HA-L)—The concentration of a chemical in drinking water that is not expected to cause any adverse, noncarcinogenic effects over a lifetime exposure. A health advisory is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, Tribal and local officials. The HA-L is based on toxicity (dose-response) information for the chemical. It assumes lifetime consumption of 2 liters (L) of water per day by a 70-kilogram (kg) adult, and that 20 percent of total exposure to the contaminant comes from drinking water (80 percent is assumed to come from other sources).

10^{-6} Cancer Risk Concentration—The concentration of a chemical in drinking water corresponding to an excess estimated lifetime cancer risk of 1 in 1 million (10^{-6}). These values are calculated from the estimated cancer potency, which is derived using a conservative (protective) model of carcinogenesis, so that the cancer risk is an upper-limit estimate. The definition of "acceptable" level of cancer risk is a policy issue, not a scientific one. USEPA reviews individual State and Tribal policies on cancer risk levels as part of its oversight of water-quality standards under the Clean Water Act. USEPA's policy is to accept measures adopted by States to limit cancer risk to the range of 10^{-6} to 10^{-4} (USEPA, 1992a). The concentration corresponding to a cancer risk of 10^{-6} was used as the benchmark for the NAWQA screening-level assessment, consistent with the conservative (protective) nature of such assessments.

Application of Human-Health Benchmarks for Water

If available, the MCL was used as the human-health benchmark for a given pesticide. For pesticides with no MCL, the lower of the HA-L and the 10^{-6} cancer risk concentration was used. Human-health benchmarks were compared with time-weighted annual mean concentrations of pesticides in streams, as well as with concentrations measured in individual wells for ground water.

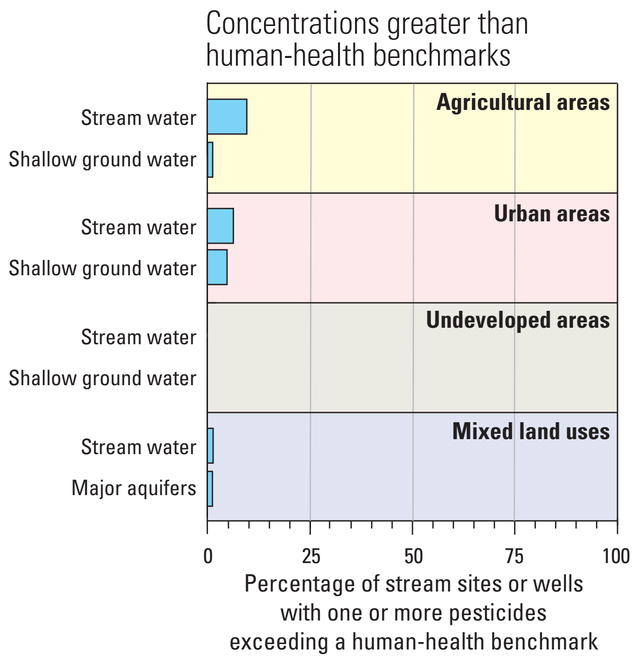


Figure 6–1. Annual mean concentrations of one or more pesticides were greater than a human-health benchmark in about 10 percent of agricultural streams and about 7 percent of urban streams that were sampled. No streams draining undeveloped watersheds, and only 1 stream with mixed land uses in its watershed, had concentrations greater than a benchmark. About 1 percent of all domestic and public-supply wells sampled had concentrations greater than a benchmark. More than half of the wells sampled for ground-water studies, but none of the stream sites sampled, were sources of domestic or public water supplies during the study period.

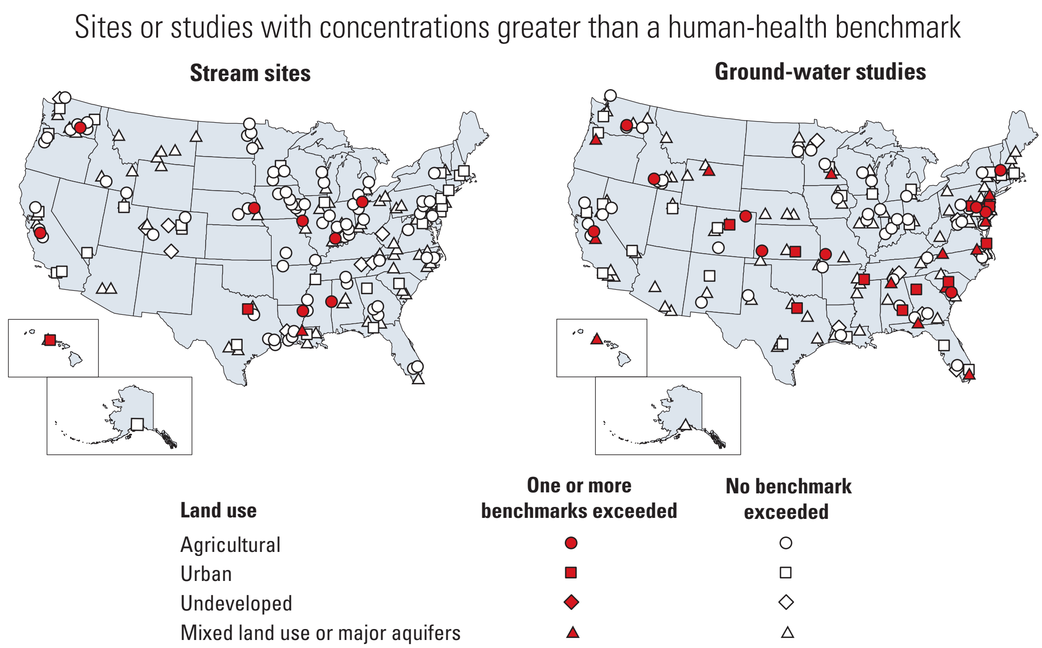


Figure 6–2. Most streams sampled by NAWQA that had concentrations of a pesticide greater than a human-health benchmark were agricultural streams in the Corn Belt and lower Mississippi River Basin, where atrazine and cyanazine accounted for the exceedances. Two urban streams in Texas and Hawaii had concentrations greater than benchmarks for diazinon and dieldrin, respectively. Wells with concentrations greater than benchmarks were widely scattered among 36 of the 187 ground-water study areas, with the highest proportion in urban areas. Dieldrin accounted for most benchmark exceedances in ground water. Streams are indicated if the annual mean concentration of one or more pesticides was greater than a benchmark, and ground-water studies are indicated if one or more wells had a concentration greater than a benchmark.

Although NAWQA findings for streams are not directly applicable to drinking-water supplies because no NAWQA stream sites were located at water-supply intakes, a perspective on potential significance to human health is provided by comparing streams sampled by NAWQA with streams that serve as sources of drinking water and that have similar land uses in their watersheds. The Nation's 1,679 public water-supply intakes on streams were classified using NAWQA's land-use definitions (table 3–1 and fig. 3–1). The stream sites where intakes are located are composed of 12 percent agricultural streams (194 intakes); 1 percent urban streams (22 intakes); 55 percent undeveloped streams (926 intakes); and 32 percent streams that drain watersheds with mixed land use (537 intakes). As a group, however, agricultural streams with drinking-water intakes have proportionally less agricultural land in their watersheds than do the agricultural streams sampled by NAWQA (see Chapter 3). Thus, the finding that 10 percent of agricultural streams sampled by NAWQA had concentrations of pesticides greater than one or more benchmarks indicates that probably fewer than 10 percent of the 194 drinking-water intakes on agricultural streams used source waters with concentrations greater than human-health benchmarks during the study period. In addition, source water may be treated or mixed with other water sources to reduce pesticide concentrations prior to consumption.

Overall, the human-health screening-level assessment for streams sampled by NAWQA during the study period indicates that few of the drinking-water intakes that currently withdraw water from streams are likely to be located on streams with pesticide concentrations greater than a benchmark. This broad finding is derived from combined data from multiple sites sampled in different sampling periods from 1993 to 2000. In addition, there are sufficient NAWQA stream sites with primary sampling years distributed throughout the study period to assess changes over time in benchmark exceedances for agricultural streams in the corn-and-soybeans crop setting (fig. 4–6) and for urban streams. Although there were too few exceedances of human-health benchmarks at urban sites for meaningful assessment of trends, agricultural streams in the corn-and-soybeans crop setting had the highest frequencies of benchmark exceedances by atrazine and cyanazine. In this agricultural setting, the changes in percentages of stream sites that had concentrations that exceeded a benchmark were different for the two herbicides (fig. 6–3). Observations about changes shown in figure 6–3, however, are preliminary because they are based on different groups of sites for each sampling period and site-to-site variability in conditions may distort actual trends. There was no clear pattern of change through the study period for atrazine, but the highest proportion of sites with exceedances by atrazine occurred near the end of the study period, during 1998–2000. In contrast, there was a consistent decrease in exceedances for cyanazine during the study period, with none during 1998–2000. Data on the agricultural use of these two pesticides in the Corn Belt show that these changes in frequencies of benchmark exceedances are consistent with their use (fig. 6–3).

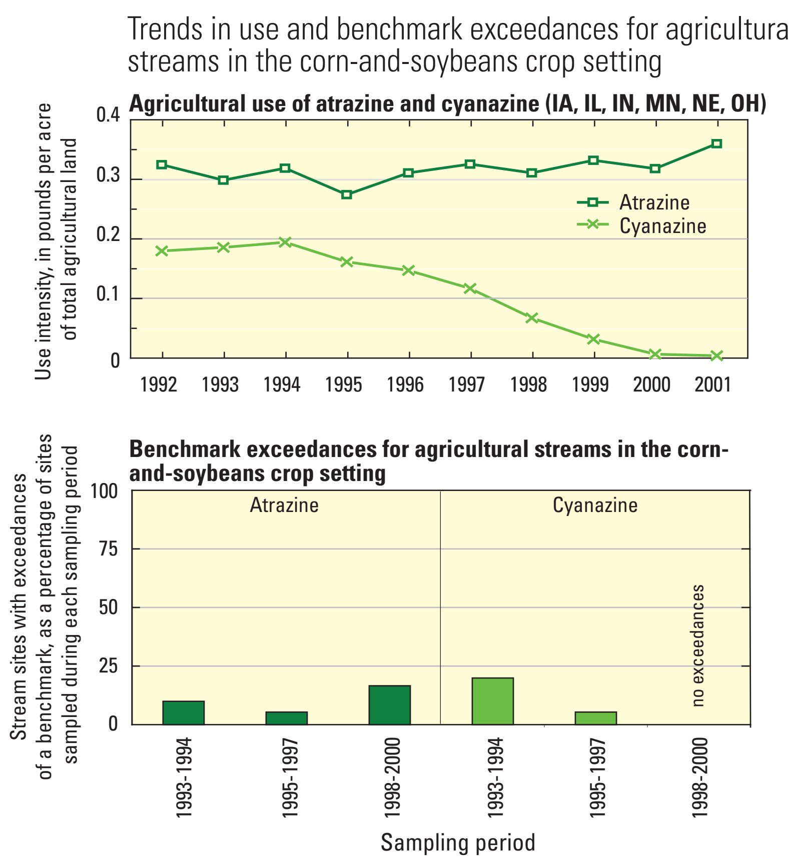


Figure 6–3. Changes over time in the percentage of agricultural stream sites in the corn-and-soybeans crop setting that had exceedances of human-health benchmarks for atrazine and cyanazine generally followed trends in use. Sites were grouped according to the year of sampling. The 1993–1994 sampling period included 10 sites, the 1995–1997 period included 19 sites, and the 1998–2000 period included 6 sites.

Potential Effects of Fish Consumption on Human Health

In addition to drinking water, humans also can be exposed to pesticides through consumption of contaminated fish. When persistent, hydrophobic compounds, such as organochlorine pesticides, enter a stream, they tend to bioaccumulate in fish and other aquatic organisms. Because USEPA sets tolerances only for currently registered pesticides, there are no tolerances for the cancelled organochlorine pesticides in fish. However, 48 States, the District of Columbia, American Samoa, and three Tribes have issued active fish-consumption advisories and safe-eating guidelines to inform people about the recommended level of consumption for fish caught in local waters. Fish advisories are advice to limit or avoid eating certain fish. USEPA has published guidance to States, Territories, Tribes, and local governments to use in establishing fish-consumption advisories (USEPA, 2000a). As of 2004, there were a total of 79 active fish-consumption advisories for chlordane, 67 advisories for DDT and its degradation products DDE and DDD, and 22 for dieldrin (USEPA, 2005f,g). Although some advisories for organochlorine pesticides have been rescinded in recent years, as residues of these pesticides continue to degrade slowly in the environment (see chapter 8), new advisories were issued in 2004 for DDT, toxaphene, mirex, and chlorinated pesticides (USEPA, 2005f).

USEPA guidelines include recommended screening values, which are "concentrations of target analytes in fish or shellfish tissue that are of potential public health concern and that are used as threshold values against which levels of contamination in similar tissue collected from the ambient environment can be compared" (USEPA, 2000a). Screening values were derived separately for carcinogenic and noncarcinogenic effects, and USEPA recommends that the lower of the two screening values be used for pesticides that have both types of effects. USEPA screening values are intended to protect the majority of the United States population and are based on average fish and shellfish consumption rates by recreational fishers. For potential carcinogens, the recommended screening value is based on a maximum acceptable cancer risk of 10^{-5} (1 in 100,000). USEPA screening values are available for 9 of the 12 organochlorine pesticides and pesticide groups (such as total chlordane) measured by NAWQA in whole fish.

Comparisons of concentrations of organochlorine pesticide compounds measured in NAWQA fish samples with USEPA screening values are limited in two ways. First, NAWQA analyzes contaminants in whole fish, whereas USEPA screening values apply to edible fish tissue. Organochlorine compounds have high affinities for the lipid (fat) in fish and other biota. Whole fish generally have higher lipid content and, therefore, may have higher organochlorine concentrations than the part of the fish that is consumed (fillets). Thus, comparisons of NAWQA measurements with USEPA screening values are probably, in this sense, worst-case assessments. Second, most fish sampled by NAWQA are bottom-feeding species, such as carp and white sucker, which are not consumed as frequently as game fish. Depending on the compound, however, the difference between game-fish fillets and the whole bodies of bottom-feeders may not be significant. For example, in a national study of bioaccumulative chemicals in fish, the USEPA (1992b) found that some organochlorine compounds (including dieldrin, oxychlordane, and DDE) were roughly similar in average concentrations in game-fish fillets and whole-fish samples of bottom-feeders, whereas other compounds (including chlordane, nonachlor, and heptachlor epoxide) had higher average concentrations in whole-fish samples of bottom feeders than in game-fish fillets.

NAWQA results for whole fish, with these caveats considered, may be useful for screening-level assessment of streams for which there are no data specifically on edible tissue of fish commonly consumed in that area. If pesticide concentrations measured in a whole-fish sample are less than a screening value for edible tissue, then residues in the edible portion of the fish are likely to be less than the screening value, suggesting low human-health concern. On the other hand, if a concentration in whole fish exceeds the screening value, the level in edible tissue may not exceed the value, but additional sampling and analysis of fillets for species that are commonly consumed may be warranted to determine whether or not the concentration in edible fish tissue exceeds the screening value.

The NAWQA analysis provides the following general perspective:

- Organochlorine concentrations measured by NAWQA in whole fish exceeded USEPA screening values most often in agricultural and urban streams (67 percent of sites), followed by streams draining areas of mixed land use (55 percent).
- Concentrations greater than screening values in agricultural streams were dominated by dieldrin, total DDT, and heptachlor epoxide, whereas these same compounds plus total chlordane accounted for most concentrations greater than screening values in urban streams.
- If people commonly consume fish from a stream where screening values were exceeded by NAWQA-measured concentrations in whole fish, and no prior monitoring of the commonly consumed fish has been done, then further investigation of organochlorine pesticide compounds in edible fish tissue may be warranted.

Ground Water

Concentrations of one or more pesticides were greater than human-health benchmarks in about 1 percent of sampled wells that are used for drinking water—including 17 of 2,356 domestic wells and 8 of 364 public-supply wells (table 6–1). Many public-supply wells have some level of water treatment, which may or may not affect pesticide concentrations, whereas domestic wells generally have no treatment, so that samples usually represent the actual quality of water consumed. Shallow ground water in urban areas had the greatest proportion of sampled wells with concentrations of pesticides that were greater than one or more benchmarks, including 1 of 9 public-supply wells, 3 of 17 domestic wells, and 37 of 835 observation wells, for a total of about 5 percent. About 1 percent of wells sampled in agricultural areas and about 1 percent of wells sampled in major aquifers had concentrations greater than one or more benchmarks. Wells with concentrations greater than benchmarks were widely scattered among 36 of the 187 ground-water studies across the Nation, including 11 of 33 urban land-use studies, 10 of 53 agricultural land-use studies, and 15 of 92 major aquifer studies (fig. 6–2). Most of these studies with one or more benchmark exceedances had only 1 or 2 wells with exceedances. All concentrations greater than benchmarks were accounted for by dieldrin (72 wells) and four other pesticides: dinoseb (4 wells), atrazine (4), lindane (2), and diazinon (1).

Human-health benchmarks were seldom exceeded in domestic and public-supply wells.

Of the pesticides analyzed by NAWQA, dieldrin is the primary pesticide identified by the screening-level assessment for further consideration regarding ground water. Of the 72 wells with dieldrin concentrations greater than its screening-level benchmark, 39 were shallow wells in urban areas (including 3 domestic wells and 1 public-supply well), 12 were shallow wells in agricultural areas (including 5 domestic wells), and 21 were wells in major aquifers (including 7 domestic and 6 public-supply wells). Although aldrin (which transforms to dieldrin) and dieldrin are no longer used in the United States, the screening-level assessment indicates that some wells may still be affected by dieldrin from historical uses.

Table 6–1. Most wells sampled for agricultural and urban land-use studies were shallow observation wells that are not used for drinking water, but about 29 percent of wells sampled in agricultural areas were domestic wells. Most wells sampled for the major aquifer studies are used for drinking water; about 13 percent were public-supply wells, and 71 percent were domestic wells. Overall, about 1 percent of all domestic and public-supply wells had concentrations of a pesticide greater than a human-health benchmark.

Type of ground-water study	Public-supply wells		Domestic wells		Observation wells	
	Number sampled	Percentage of samples exceeding a benchmark	Number sampled	Percentage of samples exceeding a benchmark	Number sampled	Percentage of samples exceeding a benchmark
Agricultural land use	1	0.0	406	1.2	1,005	1.1
Urban land use	9	11	17	18	835	4.4
Major aquifers	354	2.0	1,933	0.5	453	2.0

Screening-Level Assessment for Aquatic Life in Streams

The potential for pesticides to adversely affect aquatic life in streams was evaluated by comparing measured concentrations in water and bed sediment with their respective water-quality benchmarks. The benchmarks are described in the accompanying sidebars (p. 97 and 105) and benchmark values are listed in Appendix 3.

Water

NAWQA findings indicate that pesticides detected in stream water, most of which were in use during the study period, had the potential to adversely affect aquatic life in many of the streams sampled. Of 186 stream sites sampled nationwide, 57 percent of 83 agricultural streams, 83 percent of 30 urban streams, and 42 percent of 65 streams with mixed-land-use watersheds had concentrations of at least one pesticide that exceeded one or more aquatic-life benchmarks during the selected year of sampling (fig. 6–4). One of 8 undeveloped streams that were sampled for pesticides in water had concentrations that were greater than an aquatic-life benchmark. Concentrations greater than benchmarks occurred throughout the study period. Agricultural streams had benchmark exceedances at 68 percent of sites sampled during 1993–1994, 43 percent during 1995–1997, and 50 percent during 1998–2000. Urban streams had benchmark exceedances at 90 percent of sites sampled during 1993–1994, 100 percent during 1995–1997, and 64 percent during 1998–2000. Streams with mixed land uses in their watersheds had benchmark exceedances at 38 percent of sites sampled during 1993–1994, 40 percent during 1995–1997, and 46 percent during 1998–2000.

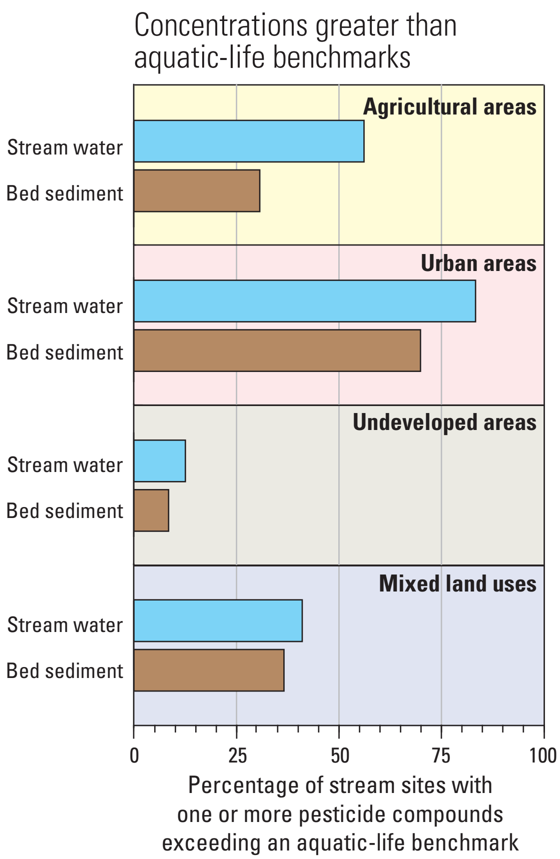


Figure 6–4. Pesticides have the potential to adversely affect aquatic life in many streams, particularly in urban areas, as indicated by the relatively high proportions of sites with measured concentrations greater than aquatic-life benchmarks for both water and bed sediment.

Streams in which one or more pesticides exceeded an aquatic-life benchmark for water are distributed throughout the country in agricultural, urban, and mixed-land-use settings (fig. 6–5). Most concentrations that exceeded benchmarks, particularly by the greatest amounts, occurred during seasonal periods of high concentrations, as illustrated by results for diazinon in Arcade Creek, an urban stream in the Sacramento River Basin (fig. 6–6). The number, type, and degree of benchmark exceedances vary widely among sites indicated in figure 6–5 and meaningful generalizations are difficult. Some streams, such as Arcade Creek (fig. 6–6), exceeded one or more benchmarks by substantial margins for a sustained period during the year. Other sites briefly exceeded a benchmark for one pesticide. Of the 100 sites with one or more benchmark exceedances, 46 sites exeeded 1 benchmark to varying degrees and frequencies, and 30 sites exceeded 3 or more different benchmarks to varying degrees and frequencies. Because of this variability and the complexity of translating exceedances of screening-level benchmarks into specific potential for effects, the screening-level results, as noted earlier should be used as the starting point for further site-specific investigation. Streams in which concentrations did not exceed a benchmark included most undeveloped streams, plus streams in agricultural and mixed-land-use settings in regions where pesticide use was low, such as the Yellowstone River Basin and the Ozark Plateaus.

Aquatic-Life Benchmarks for Pesticides in Water

Benchmarks for assessing the potential for pesticides in stream water to adversely affect aquatic life were of two general types: (1) ambient water-quality criteria for the protection of aquatic life (AWQC-AL), which were developed by USEPA's Office of Water (OW), and (2) benchmarks derived from toxicity values obtained from registration and risk-assessment documents developed by USEPA's Office of Pesticide Programs (OPP). Toxicity data from OPP documents were used to supplement OW criteria to expand the coverage of pesticides and to incorporate the most recent toxicity information used by USEPA. AWQC-AL are available for 7 of the 83 pesticides and degradates analyzed by NAWQA. One or more toxicity values from OPP documents are available for 60 of the 83 NAWQA analytes, including 5 of the 7 that have AWQC-AL. A total of 62 of the pesticide compounds analyzed in water by NAWQA have one or more aquatic-life benchmarks (Appendix 3A).

Ambient Water-Quality Criteria for Aquatic Organisms

USEPA's OW derives both acute and chronic criteria, each of which specifies a threshold concentration for unacceptable potential for effects, an averaging period, and an acceptable frequency of exceedances.

Acute AWQC-AL—The highest concentration of a chemical to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. Except where a locally important species is very sensitive, aquatic organisms should not be unacceptably affected if the 1-hour average concentration does not exceed the acute criterion more than once every 3 years, on average. The intent is to protect 95 percent of a diverse group of organisms (USEPA, 2004d).

Chronic AWQC-AL—The highest concentration of a chemical to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. Except where a locally important species is very sensitive, aquatic organisms should not be unacceptably affected if the 4-day average concentration does not exceed the chronic criterion more than once every 3 years, on average. The intent is to protect 95 percent of a diverse group of organisms (USEPA, 2004d).

Toxicity Values from Risk Assessments

Seven types of aquatic toxicity values were compiled from OPP's registration and risk-assessment documents. The OPP toxicity values are for specific types of organisms. Acute and chronic values were compiled for fish and invertebrates, and acute values for vascular and nonvascular plants. A value for aquatic-community effects was available only for atrazine. The types and amounts of toxicity data available for different pesticides were highly variable. USEPA estimates the toxicity or hazard of a pesticide by selecting the most sensitive endpoints from multiple acute and chronic laboratory and field studies. For many pesticides, USEPA has completed a screening-level ecological risk assessment, which includes acute and chronic assessments for both fish and invertebrates. For some pesticides, acute assessments have also been completed for nontarget aquatic plants. NAWQA derived benchmarks from OPP toxicity values, generally following OPP procedures (USEPA, 2005h).

In recent years, USEPA has developed methods for conducting refined risk assessments, in which probabilistic tools and methods are incorporated to predict the magnitude of the expected impact of pesticide use on nontarget organisms, as well as the uncertainty and variability involved in these estimates. The screening-level benchmarks used in NAWQA analysis and summarized below were derived from the toxicity values reported in USEPA registration and risk-assessment documents.

In the few cases where refined assessments were available, these were given preference. In deriving a benchmark for a given type of organism (such as fish) and a given exposure duration (acute or chronic), the lowest of the available toxicity values was selected for each benchmark, unless a preferred toxicity value was specified in a refined risk assessment—in which case that preferred toxicity value was used instead. For two of the benchmarks—acute-fish and acute-invertebrates—the selected toxicity values were multiplied by the USEPA level of concern (LOC) of 0.5, so that the benchmark for NAWQA screening corresponds to the acute risk level defined by USEPA (2005h).

Six benchmarks were based directly on toxicity endpoints used in OPP screening-level assessments (USEPA, 2005i):

Acute fish—The lowest tested 50-percent lethal concentration (LC_{50}) for acute (typically 96-hour) toxicity tests with freshwater fish, multiplied by the LOC of 0.5.

Acute invertebrate—The lowest tested LC_{50} or 50-percent effect concentration (EC_{50}) for acute (typically 48 or 96-hour) toxicity tests with freshwater invertebrates, multiplied by the LOC of 0.5.

Acute vascular plant—The lowest tested EC_{50} for freshwater vascular plants in acute toxicity tests (typically < 10 days).

Acute nonvascular plant—The lowest tested EC_{50} for freshwater nonvascular plants (algae) in acute toxicity tests (typically < 10 days).

Chronic fish—The lowest no-observed-adverse-effects concentration (NOAEC), or the lowest-observed-adverse-effects concentration (LOAEC) if a NOAEC is not available, for freshwater fish in early lifestage or full life-cycle tests.

Chronic invertebrate—The lowest NOAEC, or LOAEC if a NOAEC is not available, for freshwater invertebrates in life-cycle tests.

One additional benchmark, a benchmark for aquatic-community effects, was derived from the refined risk assessment for atrazine. This endpoint for atrazine incorporates community-level effects on aquatic plants and indirect effects on fish and aquatic invertebrates that could result from disturbance of the plant community (USEPA, 2003b).

Application of Aquatic-Life Benchmarks for Water

Acute AWQC-AL values and all acute benchmarks were compared with each measured concentration for the most complete year of data for each NAWQA stream site. Chronic AWQC-AL values were compared with 4-day moving average concentrations. This approach matches the time periods in the definitions of acute and chronic AWQC-AL, which are 1-hour average and 4-day average concentrations, respectively (Stephan and others, 1985). Chronic benchmarks for invertebrates were compared with 21-day moving averages, and chronic benchmarks for fish and the aquatic-community benchmark for atrazine were compared with 60-day moving averages. These time periods are those used or recommended by USEPA in OPP risk assessments (USEPA, 2003b; USEPA, 2005g). Moving average concentrations for 4-, 21-, and 60-day periods were computed for each day of the year for each stream site from hourly concentration estimates determined by straight-line interpolation between samples. This method was tested using data on pesticide concentrations in Ohio streams studied by Richards and Baker (1993) and Richards and others (1996), using an approach similar to that used by Crawford (2004). Results indicate that all three averages, but particularly the 4-day averages, are consistently underestimated when computed from data collected at frequencies similar to the NAWQA sampling design (indicating a tendency to also underestimate the potential for toxicity to aquatic life in this respect).

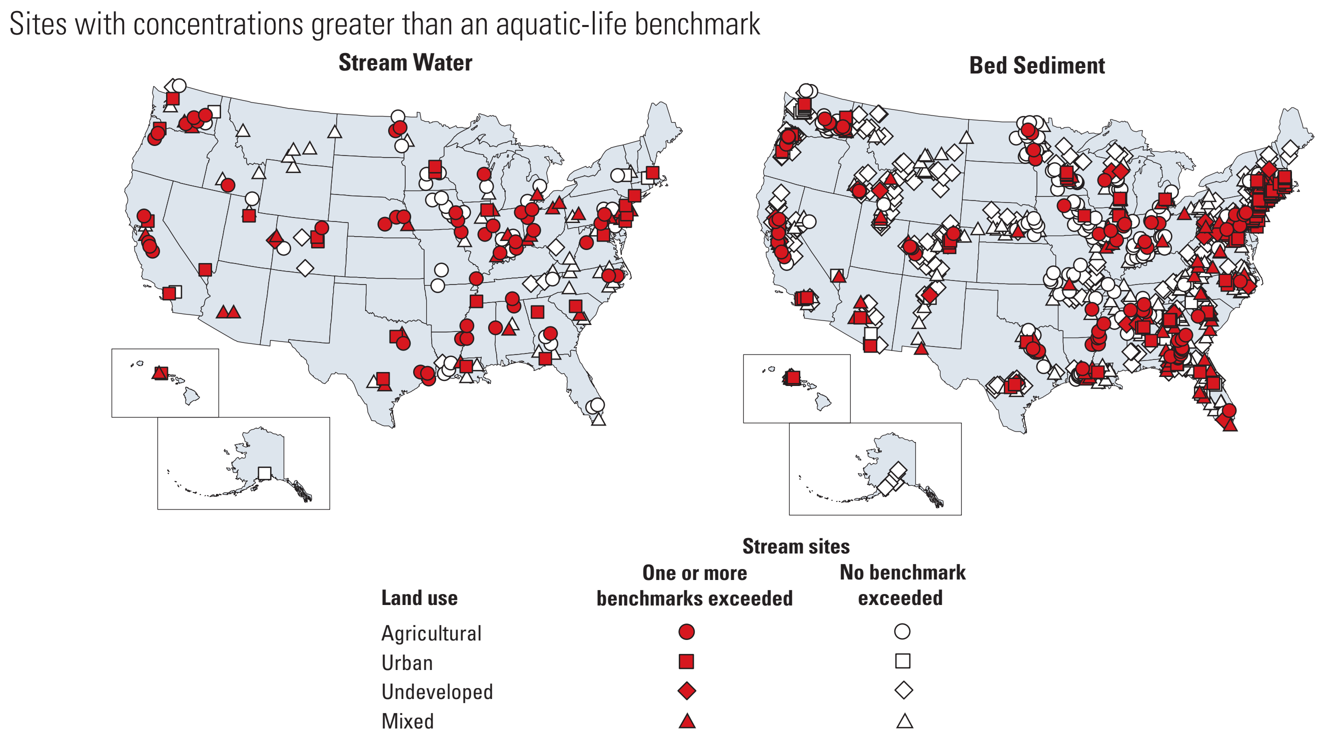
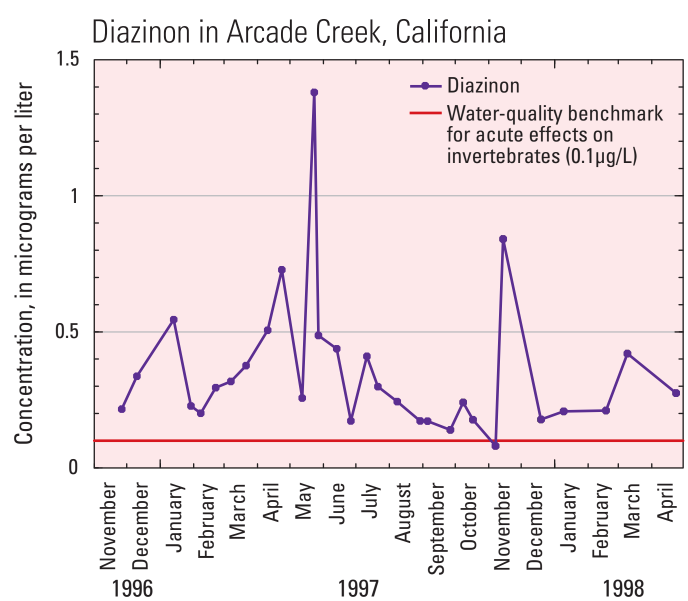


Figure 6–5. Aquatic-life benchmarks for pesticides in water and bed sediment were exceeded by concentrations measured in many agricultural, urban, and mixed-land-use streams throughout the Nation.

Figure 6–6. Concentrations of diazinon in Arcade Creek, an urban creek in Sacramento, California (Sacramento River Basin), exceeded the aquatic-life benchmark for acute effects on invertebrates (0.10 µg/L) by the greatest amounts during seasonal pulses of high concentrations in the winter and spring. (Modified from Domagalski and others, 2000.)



The insecticides diazinon, chlorpyrifos, and malathion accounted for most concentrations that were greater than aquatic-life benchmarks in water from urban streams, whereas chlorpyrifos, azinphos-methyl, atrazine, *p,p′*-DDE, and alachlor accounted for most concentrations greater than benchmarks in water from agricultural streams (fig. 6–7). Streams draining watersheds with mixed land uses reflected a combination of urban and agricultural influences. Generally, the types of benchmarks most frequently exceeded by the herbicides atrazine and alachlor were those for acute effects on either vascular or nonvascular plants, whereas the insecticides diazinon, chlorpyrifos, malathion, azinphos-methyl, and carbaryl most frequently exceeded acute or chronic benchmarks for invertebrates or benchmarks based on chronic ambient water-quality criteria.

The geographic distributions of benchmark exceedances for atrazine (fig. 6–8), diazinon (fig. 6–9), and chlorpyrifos (fig. 6–10) illustrate the varying distributions and types of potential effects on aquatic life. Concentrations of atrazine were greater than one or more aquatic-life benchmarks in 18 percent of agricultural streams, but in only one stream with a predominantly nonagricultural watershed. As discussed in Chapter 4, concentrations of atrazine in agricultural streams matched the geographic distribution of corn cultivation, where applications are greatest (fig. 4–9). As noted above, the atrazine benchmarks most frequently exceeded were the acute benchmarks for vascular and nonvascular plants, although the benchmark for aquatic community effects and the chronic benchmark for invertebrates also were exceeded at about 35 and 12 percent, respectively, of the sites where one or more atrazine benchmarks were exceeded (fig. 6–8).

Diazinon concentrations were greater than one or more aquatic-life benchmarks in 73 percent of the urban streams that were sampled, compared with 37 percent for chlorpyrifos (fig. 6–7). The urban stream sites where diazinon exceeded a benchmark were distributed throughout the country (fig. 6–9). Benchmarks for both of these insecticides were exceeded in smaller proportions of agricultural streams, although chlorpyrifos exceeded one or more of its benchmarks in 21 percent of the agricultural streams. The highest concentrations of chlorpyrifos in agricultural streams, as discussed in Chapter 4, were in streams within the corn-growing areas of the central United States; in the lower Mississippi River Basin, where both corn and cotton are grown; and in streams draining agricultural areas in the West, where fruits, nuts, and vegetables are grown.

The diazinon benchmarks most frequently exceeded (fig. 6–9) were the acute and chronic benchmarks for invertebrates reported by USEPA (USEPA, 2004e). As shown in figure 6–10, the chlorpyrifos benchmarks most frequently exceeded were the acute and chronic benchmarks for invertebrates and also the acute and chronic ambient aquatic-life criteria (Appendix 3A). While none currently exists, USEPA is drafting ambient aquatic-life criteria for diazinon. During

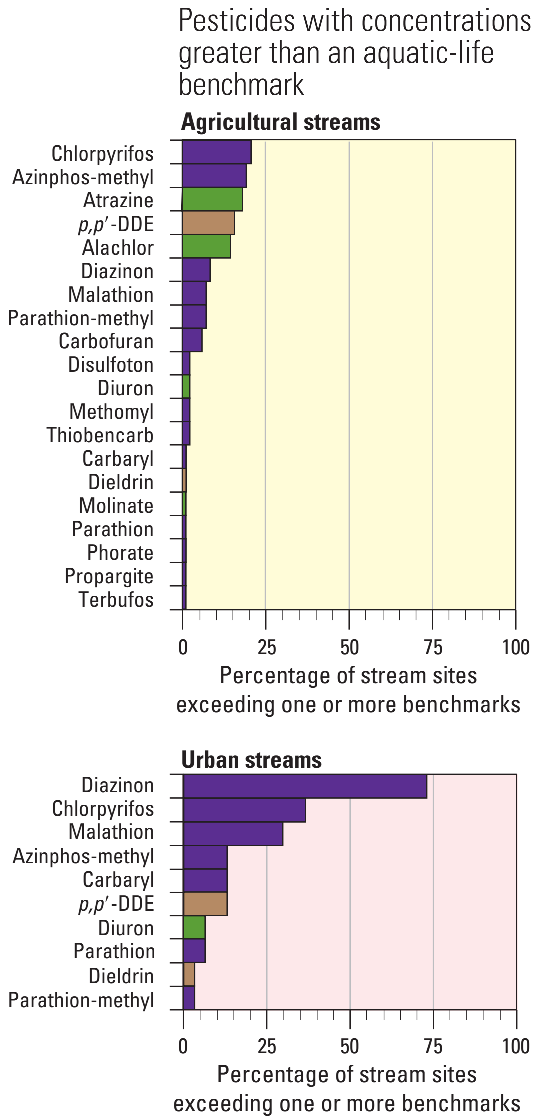


Figure 6–7. Contributions of individual pesticides to exceedances of aquatic-life benchmarks for water show the significance of insecticides in urban streams, particularly diazinon, chlorpyrifos, and malathion during the 1992–2001 study period. In agricultural streams, most exceedances of benchmarks were by chlorpyrifos, azinphos-methyl, atrazine, *p,p′*-DDE, and alachlor. Water-quality benchmarks are provided in Appendix 3A.

Chapter 6

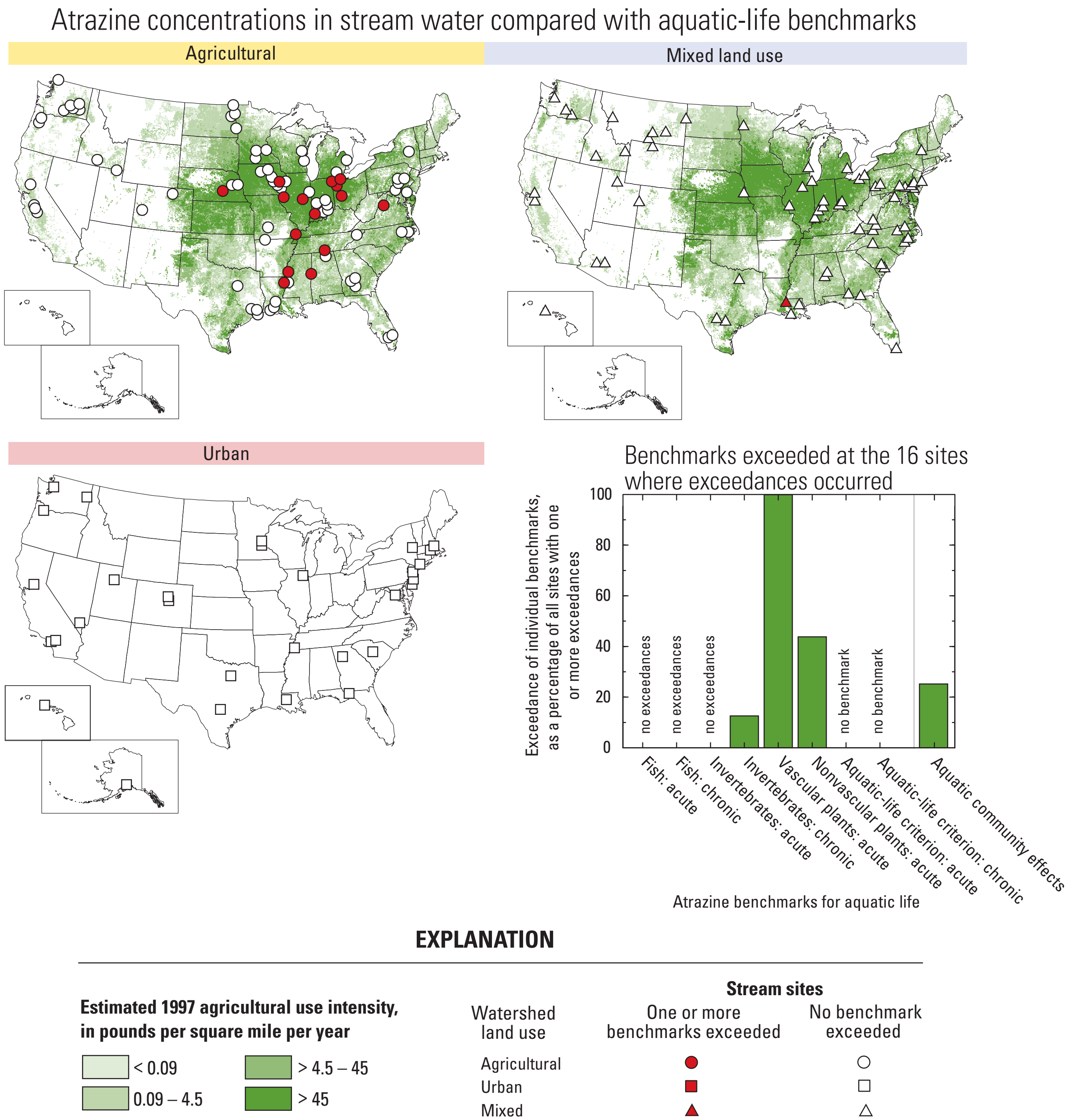


Figure 6–8. Streams in which atrazine concentrations were greater than at least one of its aquatic-life benchmarks were predominantly agricultural streams in areas where applications were greatest. The aquatic-life benchmarks most frequently exceeded by atrazine concentrations were those for vascular and nonvascular plants. Water-quality benchmarks are provided in Appendix 3A.

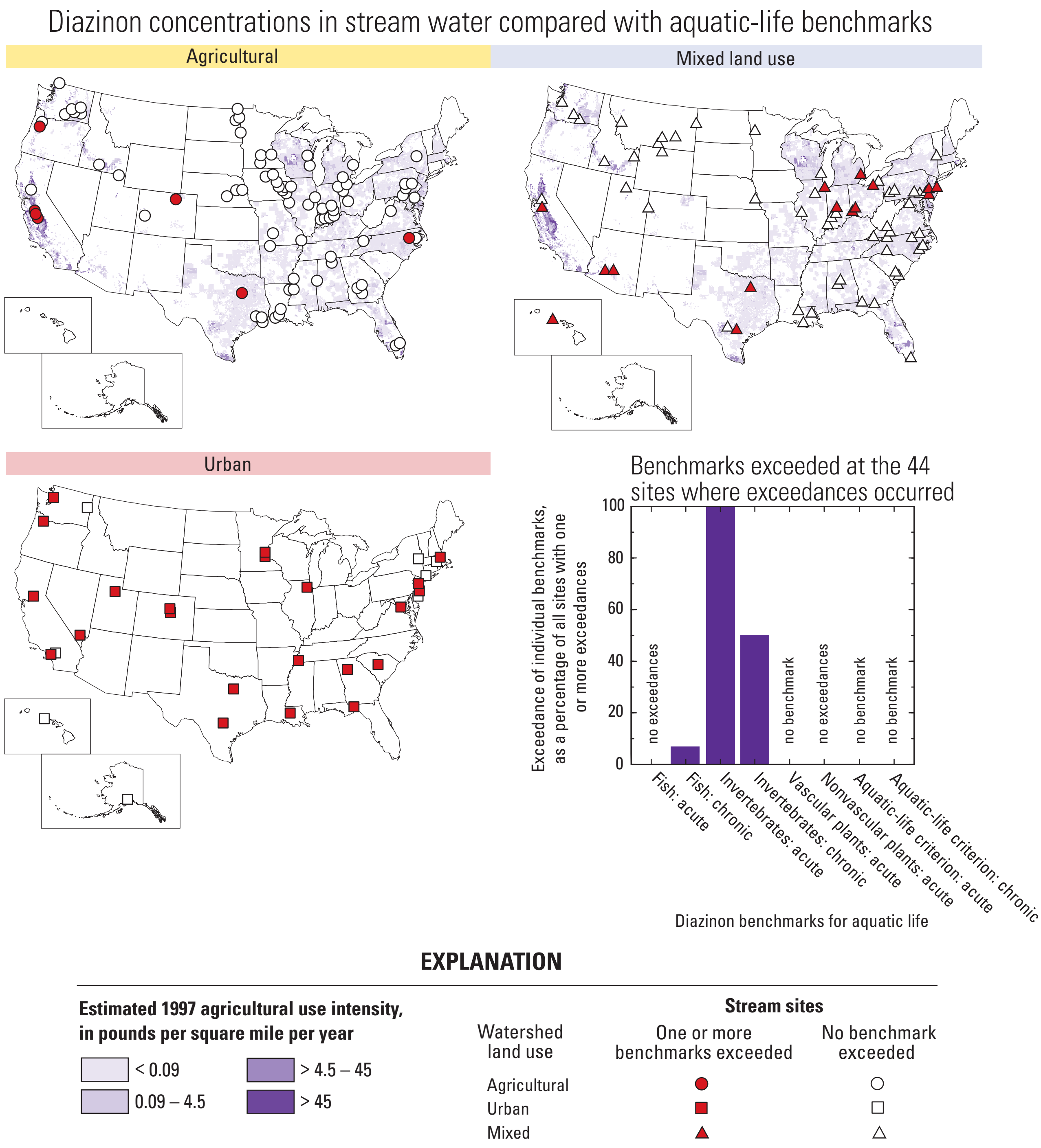


Figure 6–9. Most streams in which diazinon concentrations were greater than at least one aquatic-life benchmark were urban streams, but concentrations in some agricultural streams in areas where applications were greatest also exceeded a benchmark. The aquatic-life benchmarks most frequently exceeded by diazinon were those for invertebrates. Water-quality benchmarks are provided in Appendix 3A.

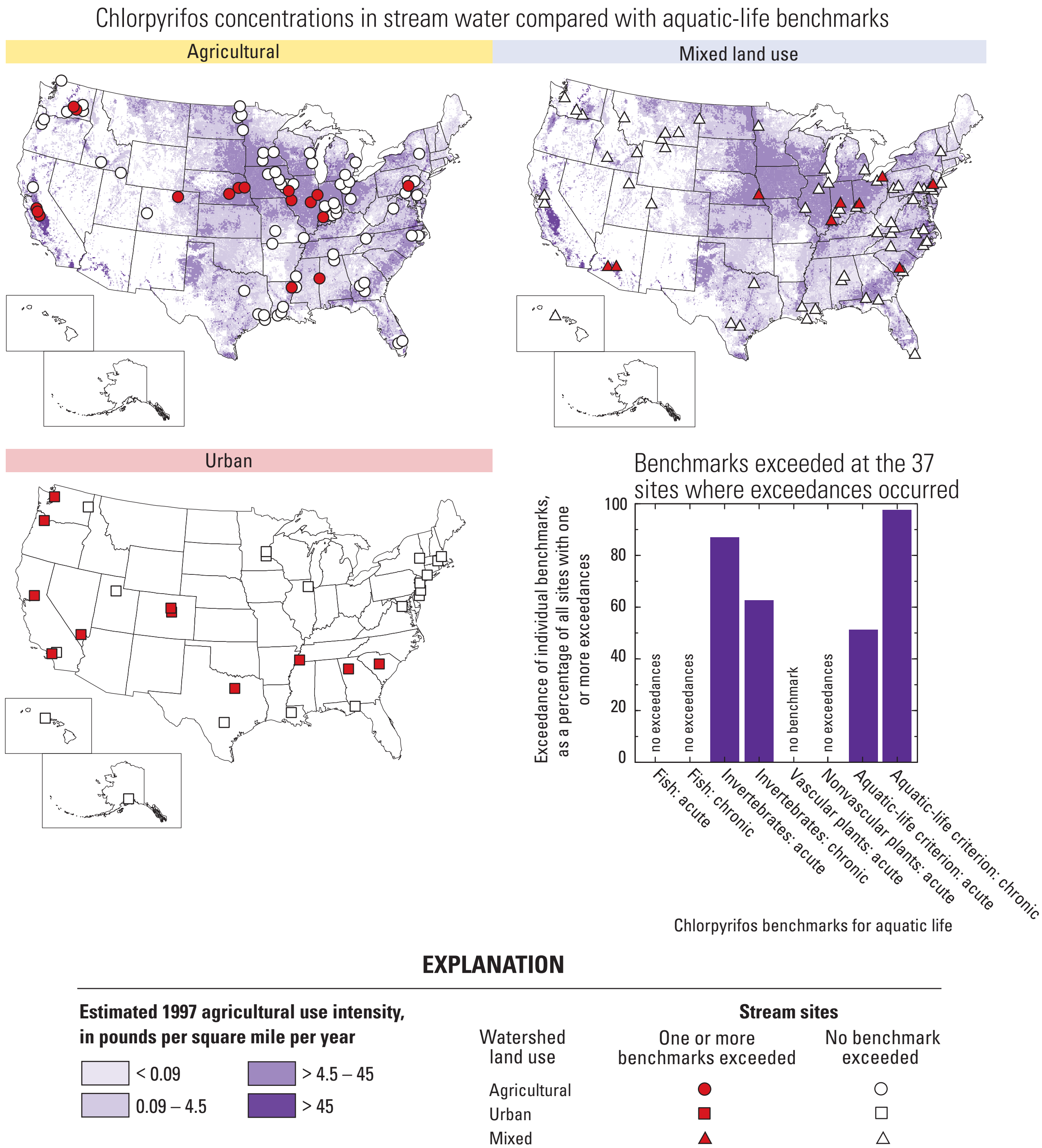


Figure 6–10. Most streams in which chlorpyrifos concentrations were greater than at least one aquatic-life benchmark were agricultural streams in areas where applications were greatest, or urban streams. The aquatic-life benchmark most frequently exceeded by chlorpyrifos was the USEPA chronic aquatic-life criterion. Chlorpyrifos concentrations also frequently exceeded acute and chronic benchmarks for invertebrates at the same sites where the chronic aquatic-life criterion was exceeded. Water-quality benchmarks are provided in Appendix 3A.

this development process, and in response to USEPA's diazinon risk assessment, public comment noted an atypical distribution of the acute toxicity data for invertebrates. If data from the second most sensitive study were used (USEPA, 2000b), rather than the most sensitive study, then the calculated acute invertebrate benchmark for diazinon would change from its original 0.1 μg/L to a value of 0.4 μg/L. The result of using a benchmark of 0.4 μg/L would be a reduction in the proportions of sites with diazinon exceedances from 73 to 40 percent for urban streams and from 8 to 6 percent for agricultural streams.

Overall, the screening-level assessment for potential effects of pesticides in stream water on aquatic life indicates that 56 percent of the 178 sampled streams that have watersheds dominated by urban, agricultural, or mixed land uses had concentrations of one or more pesticides that exceeded an aquatic-life benchmark during the study period. Pesticide use and occurrence were not constant during 1992–2001, however, and NAWQA data can be used, as for human-health benchmarks, to characterize changes that may have occurred for some pesticides in the land-use settings for which there are adequate data.

As noted for analysis of human-health benchmarks, there are sufficient NAWQA data for limited analysis of changes over time in benchmark exceedances for urban streams and for agricultural streams in the corn-and-soybeans crop setting. When grouped by sampling period, the percentages of urban stream sites that had concentrations of diazinon, chlorpyrifos, or malathion that exceeded a benchmark were lowest for urban sites sampled during the last part of the study (fig. 6–11). Observations about changes shown in figures 6–11 and 6–12, however, are preliminary because they are based on different groups of sites for each sampling period and site-to-site variability in conditions may distort actual trends. Although there are no consistent data available on the trends in the urban use of these pesticides during the study period, these results indicate the possibility that some reductions in urban use may have occurred. As mentioned earlier and discussed in Chapter 8, nonagricultural uses and some agricultural uses of diazinon and chlorpyrifos have declined since 2001 because of use restrictions initiated by USEPA. If concentrations of these insecticides are, in fact, declining in urban streams, the potential for effects on aquatic life in urban streams likely will also decline if their uses are replaced with pesticides that reach streams in less toxic amounts (or with alternative approaches to pest control).

In agricultural streams, most exceedances of aquatic-life benchmarks were by chlorpyrifos, azinphos-methyl, atrazine, *p,p′*-DDE, and alachlor (fig. 6–7). The greatest potential for effects on aquatic life was generally in areas where one or more of these pesticides were intensively used, or in the case of *p,p′*-DDE, where its parent compounds were intensively used in the past. For the purpose of characterizing changes over time in benchmark exceedances, there were sufficient agricultural stream sites with sampling years distributed throughout the study period only for streams in the corn-and-soybeans crop setting (fig. 4–6). This agricultural setting had the highest use during the study period of chlorpyrifos, atrazine, and alachlor. The changes in the percentages of stream sites in this setting that had concentrations exceeding benchmarks were different for the three pesticides during the study period (fig. 6–12). There was no clear trend for chlorpyrifos, an increasing number of exceedances for atrazine, and a decrease in exceedances for alachlor (with none during 1998–2000). Data on the agricultural use of these three pesticides from 1992 to 2001 in the Corn Belt show that these changes over time in benchmark exceedances are consistent with changes in their use (fig. 6–12).

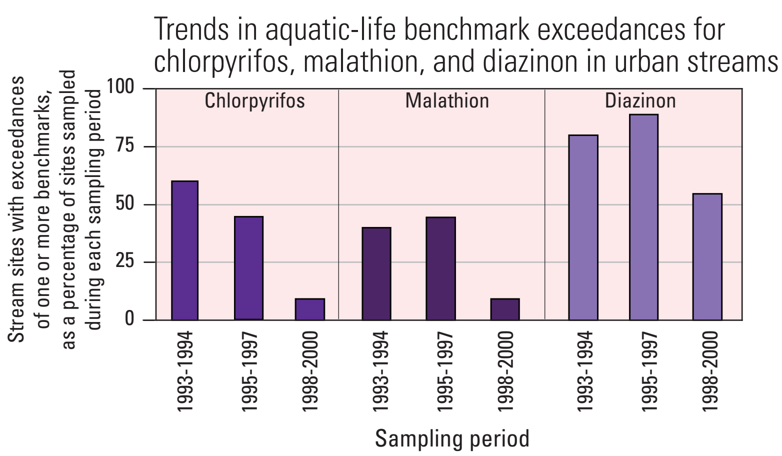


Figure 6–11. The percentages of urban streams that had exceedances of aquatic-life benchmarks for chlorpyrifos, malathion, and diazinon were lowest for each insecticide during the last sampling period. Sites were grouped according to the year of sampling. The 1993–1994 sampling period included 10 sites, the 1995–1997 period included 9 sites, and the 1998–2000 period included 11 sites.

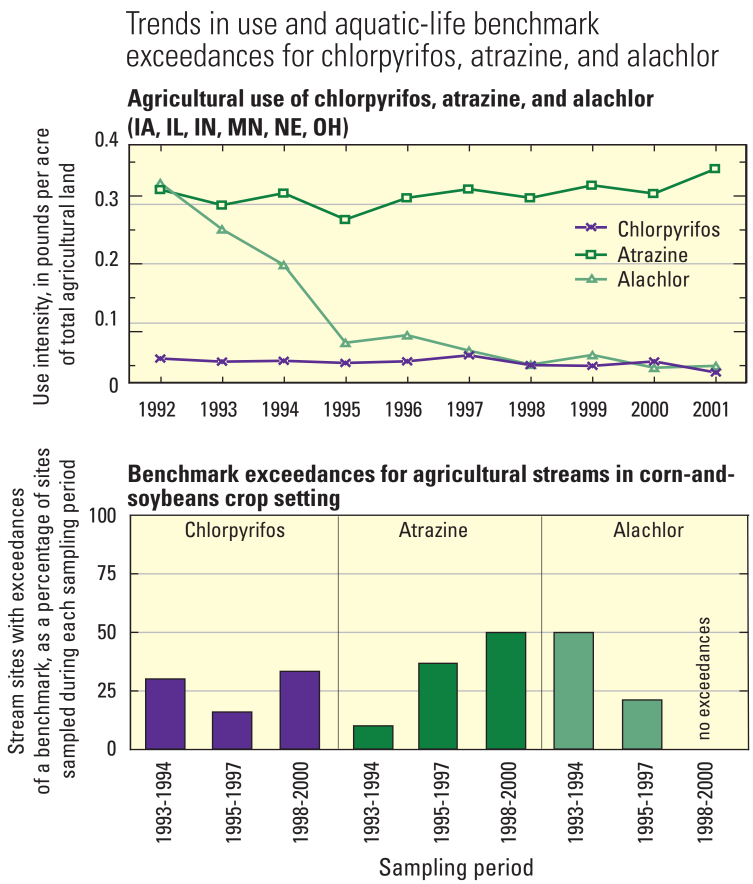


Figure 6–12. Changes over time in the percentage of agricultural stream sites in the corn-and-soybeans crop setting that had exceedances of aquatic-life benchmarks for chlorpyrifos, atrazine, and alachlor generally followed trends in use. Sites were grouped according to the year of sampling. The 1993–1994 sampling period included 10 sites, the 1995–1997 period included 19 sites, and the 1998–2000 period included 6 sites.

Bed Sediment

Concentrations of organochlorine pesticide compounds measured in bed sediment were greater than one or more aquatic-life benchmarks at 70 percent of urban sites, 31 percent of agricultural sites, 36 percent of mixed-land-use sites and 8 percent of undeveloped sites (fig. 6–4). The geographic distribution of sites where aquatic-life benchmarks for bed sediment were exceeded is similar to findings for water in many respects, including urban streams distributed throughout the country and many agricultural and mixed-land-use streams in the Southeast, East, and irrigated areas of the West (fig. 6–5).

In urban streams, concentrations of DDT or one or more of its degradates or by-products were greater than benchmarks at 58 percent of sampled sites, total chlordane at 57 percent of sites, and dieldrin at 26 percent of sites (fig. 6–13). In agricultural streams, compounds in the DDT group exceeded benchmarks at 28 percent of sites and dieldrin at 8 percent of sites.

The geographic distributions of concentrations that were greater than benchmarks are different for DDT compounds (fig. 6–14) compared with dieldrin (fig. 6–15), following their historical use patterns. Concentrations of one or more DDT compounds were greater than benchmarks for aquatic life in 58 percent of urban streams and about 28 percent of agricultural and mixed-land-use streams that were sampled. As discussed in Chapter 4, historical use of DDT for agriculture was highest in the Southeast, where cotton, tobacco, and peanuts were grown, and in a number of areas of the Nation where orchard crops, potatoes, vegetables, or specialty crops were grown. Dieldrin concentrations did not exceed its aquatic-life benchmark as frequently as DDT compounds, with 26 percent of urban streams

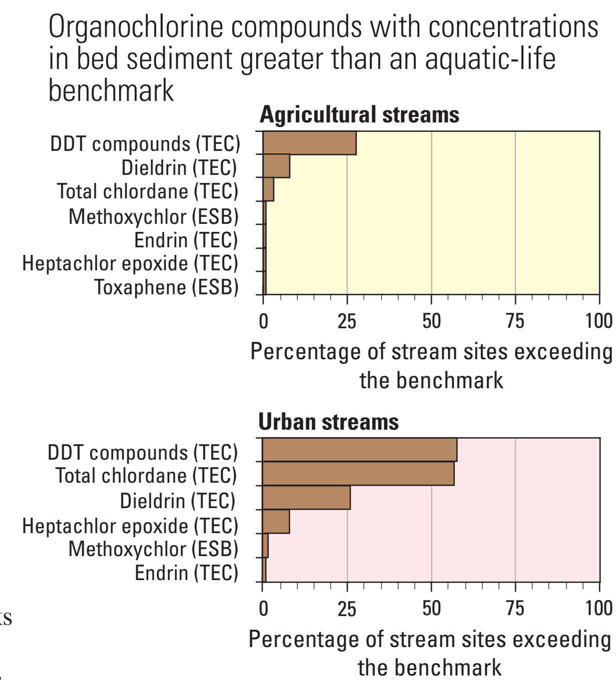


Figure 6–13. Contributions of individual pesticide compounds and groups to exceedances of aquatic-life benchmarks for bed sediment show the importance of historically used insecticides in urban streams, particularly DDT compounds, chlordane, and dieldrin. In agricultural streams, DDT compounds and dieldrin accounted for most exceedances of benchmarks. The type of benchmark is listed after each compound name as ESB for equilibrium partitioning sediment benchmark, or as TEC for threshold effect concentration. Water-quality benchmarks are provided in Appendix 3B.

Aquatic-Life Benchmarks for Organochlorine Compounds in Bed Sediment

Benchmarks for assessing the potential for organochlorine pesticides compounds in bed sediment to adversely affect aquatic life were selected from consensus-based sediment-quality guidelines developed for sediment-dwelling aquatic organisms (MacDonald and others, 2000). These benchmarks are available for 6 of the 16 individual organochlorine pesticide compounds and compound groups (such as total chlordane) measured in sediment, including all of the most commonly detected ones. Threshold effect concentrations (TEC), which are concentrations below which harmful effects on sediment-dwelling organisms are not expected, were used as the primary screening-level benchmarks. In NAWQA's analysis, the TEC benchmarks were supplemented by USEPA equilibrium partitioning sediment benchmarks (ESB), which are available for 6 of the 16 organochlorine pesticide compounds and groups measured (USEPA, 2003c,d,e). Although ESBs are not available for some of the most commonly detected pesticides in sediment (DDT and chlordane), the 6 compounds with ESBs include 3 pesticides that do not have TEC benchmarks—toxaphene, methoxychlor, and endosulfan (Appendix 3B). Therefore, sediment benchmarks are available for a total of 9 of the 16 organochlorine pesticides or pesticide groups analyzed by NAWQA.

The two types of sediment benchmarks are quite different from one another. The TECs are empirically derived and are effective predictors of toxicity (or nontoxicity) in field-collected sediment, but they cannot be used to infer cause and effect related to individual contaminants. The TEC was selected as the primary benchmark because it meets the objectives of a screening-level assessment. The ESB is mechanistically based and is not designed to predict toxicity in field-collected sediment that contains multiple contaminants. A concentration greater than an ESB indicates a high likelihood of toxicity resulting from the specific contaminant. ESBs were used to provide some information on potential toxicity for pesticides that do not have TEC benchmarks.

Consensus-based threshold effect concentration (TEC)—The concentration of sediment-associated contaminants below which adverse effects on sediment-dwelling organisms are not expected to occur. The consensus-based TEC benchmarks are empirically based and indicate the likelihood that field-collected samples containing a given pesticide concentration will be toxic or nontoxic, but they do not necessarily indicate cause-and-effect. The particular pesticide upon which the benchmark is based is not necessarily the source of the toxicity because sediment may contain multiple contaminants. Validation data showed that 15–29 percent of sediment samples, depending on the pesticide, had measurable toxicity at organochlorine pesticide concentrations below their respective TECs (MacDonald and others, 2000). The incidence of toxicity above the TEC was consistently higher, with 40 percent of samples for one pesticide (endrin), and 70–100 percent for the rest, showing measurable toxicity above their respective TECs.

Equilibrium partitioning sediment benchmark (ESB)—The concentration of a chemical in sediment that USEPA expects will not adversely affect most benthic organisms. ESBs are mechanistic benchmarks based on the equilibrium partitioning model, which assumes that the toxicity of an organic contaminant in sediment is causally related to bioavailability and that bioavailability is controlled by contaminant sorption to sediment organic carbon. ESBs further assume that the contaminant is in equilibrium with sediment particles and sediment pore water. In the natural environment, including areas with highly erosional or depositional bed sediment, contaminants may not attain equilibrium. Each ESB is designed to predict toxicity caused by a specific contaminant (or group) only, and it is not expected to correctly predict toxicity when other contaminants are present in toxic amounts, such as may occur in field-collected samples containing contaminant mixtures. Thus, when a contaminant concentration exceeds its ESB in field-collected sediment, the sediment is predicted to be toxic because of the presence of that contaminant.

Application of Aquatic-Life Benchmarks for Bed Sediment

Aquatic-life benchmarks for sediment, both TECs and ESBs, were compared with pesticide concentrations measured by NAWQA in composite bed-sediment samples collected from depositional areas in streams (one sample per site). TECs, which are expressed on a total sediment basis, were compared directly with NAWQA-measured pesticide concentrations in sediment. Because ESBs are in units of micrograms of contaminant per gram of sediment organic carbon, NAWQA-measured pesticide concentrations (micrograms of contaminant per kilogram of total sediment) were first divided by the measured organic carbon content (grams of organic carbon per kilogram of total sediment) of the sediment sample, before comparison with ESBs.

and 8 percent of agricultural and mixed-land-use streams having concentrations greater than the benchmark. For dieldrin, a cluster of agricultural sites with concentrations greater than the benchmark is located in the Corn Belt, where use of aldrin and dieldrin on corn was most intensive. In urban areas, these pesticides were used for such purposes as mosquito and termite control.

The screening-level assessment for organochlorine compounds in bed sediment indicates that most urban streams sampled by NAWQA (70 percent), and about one-third of sampled streams with watersheds dominated by agricultural or mixed land uses, had concentrations of organochlorine compounds that exceeded one or more aquatic-life benchmarks during the study period. Although DDT, aldrin, dieldrin, and chlordane are no longer used in the United States, the screening-level assessment indicates that these compounds and their degradates continue to be present at levels in bed sediment that may have adverse effects on aquatic life in some streams.

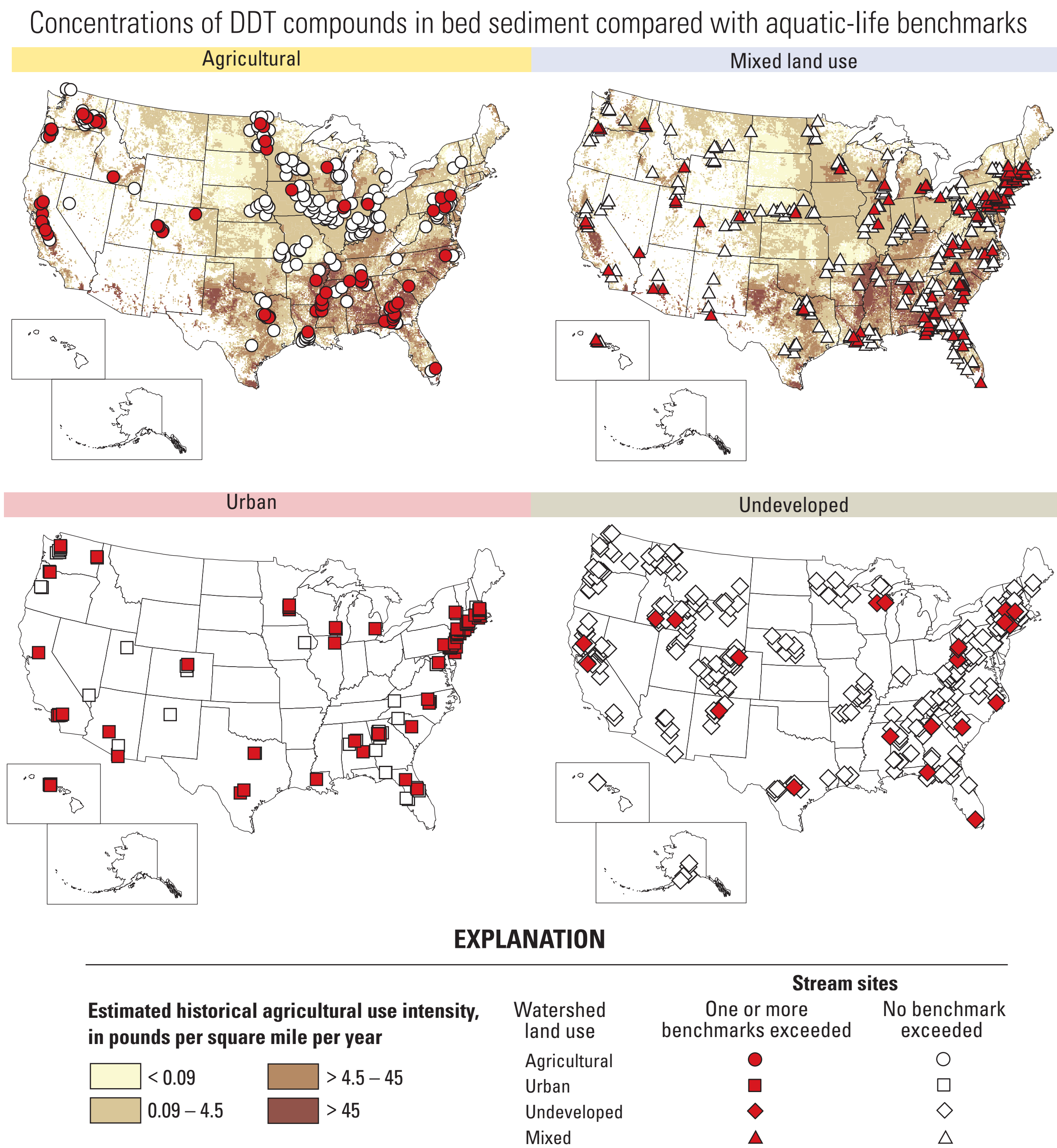


Figure 6–14. Streams in which concentrations of one or more DDT compounds in bed sediment exceeded an aquatic-life benchmark were predominantly urban streams, or agricultural and mixed-land-use streams in areas where historical use of DDT plus DDD was greatest. Water-quality benchmarks are provided in Appendix 3B.

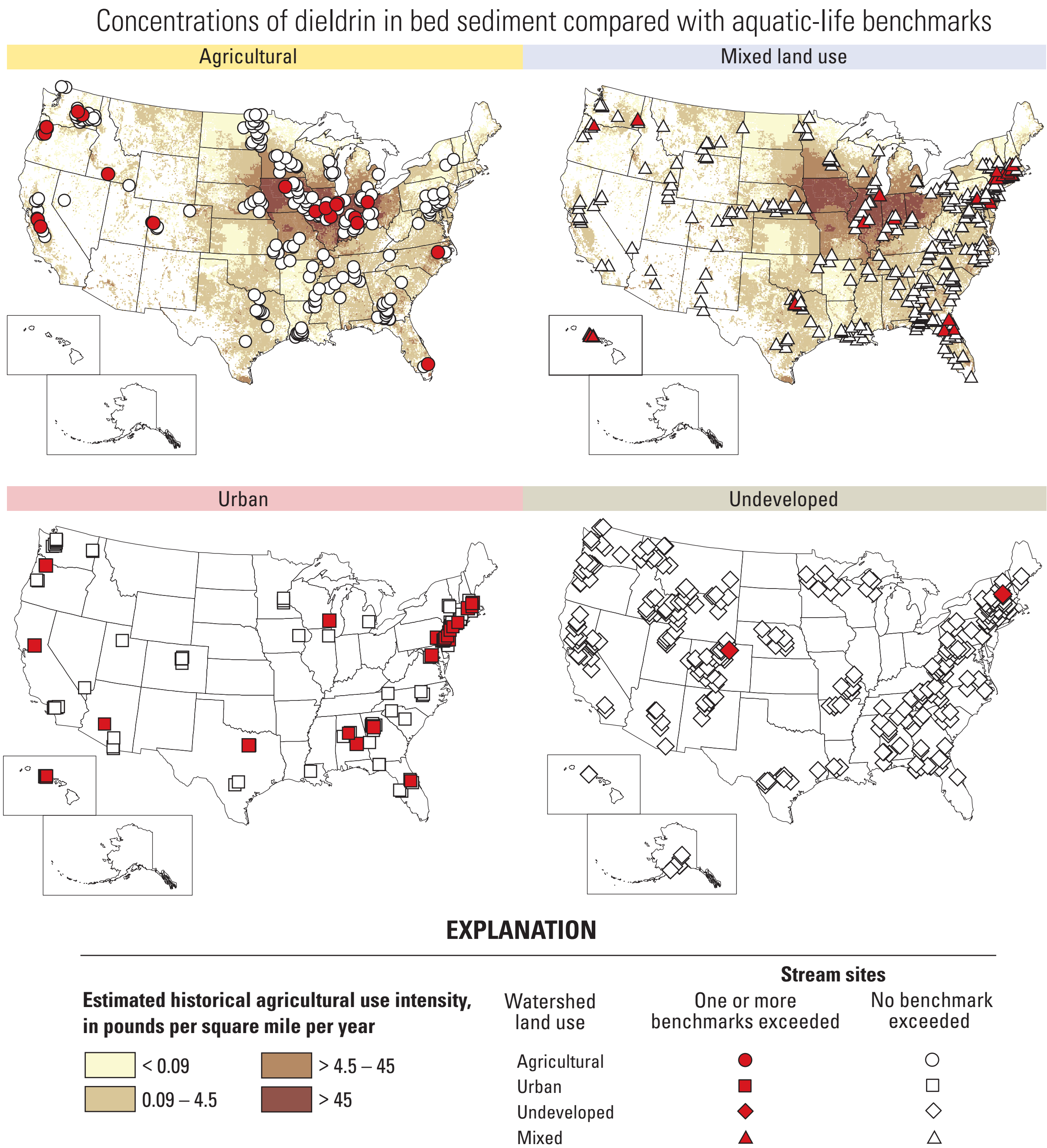


Figure 6–15. Streams in which dieldrin concentrations in bed sediment exceeded its aquatic-life benchmark were predominantly urban streams or agricultural and mixed-land-use streams in areas where historical use of aldrin plus dieldrin was greatest. Water-quality benchmarks are provided in Appendix 3B.

Screening-Level Assessment for Fish-Eating Wildlife

NAWQA data on pesticides in whole fish were compared with both the low and high values of the range in available benchmarks, because there is no consensus on a national-scale suite of wildlife benchmarks (see accompanying sidebar, p. 109). Comparisons of measured concentrations of organochlorine pesticide compounds in whole-fish tissue with wildlife benchmarks indicate a correspondingly wide range of potential for effects, depending on whether the low or high benchmark values are used (fig. 6–16). The high benchmarks for fish tissue were exceeded most frequently in streams in the populous Northeast; in high-use agricultural areas in the upper and lower Mississippi River Basin; in high-use irrigated agricultural areas of the West, such as eastern Washington and the Central Valley of California; and in urban streams distributed throughout the country (fig. 6–17). Few fish samples were analyzed in the Southeast. The low (more protective) benchmarks generally show an expanded proportion of sites in the same regions and land uses.

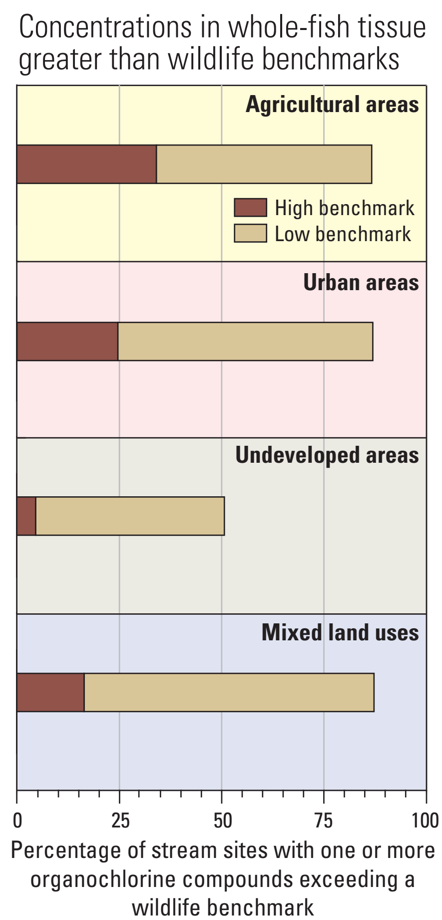


Figure 6–16. Wildlife benchmarks for concentrations of organochlorine pesticides in fish tissue were often exceeded, but the range of results for high and low benchmark values indicates that there is considerable uncertainty in wildlife benchmark values. Water-quality benchmarks are provided in Appendix 3B.

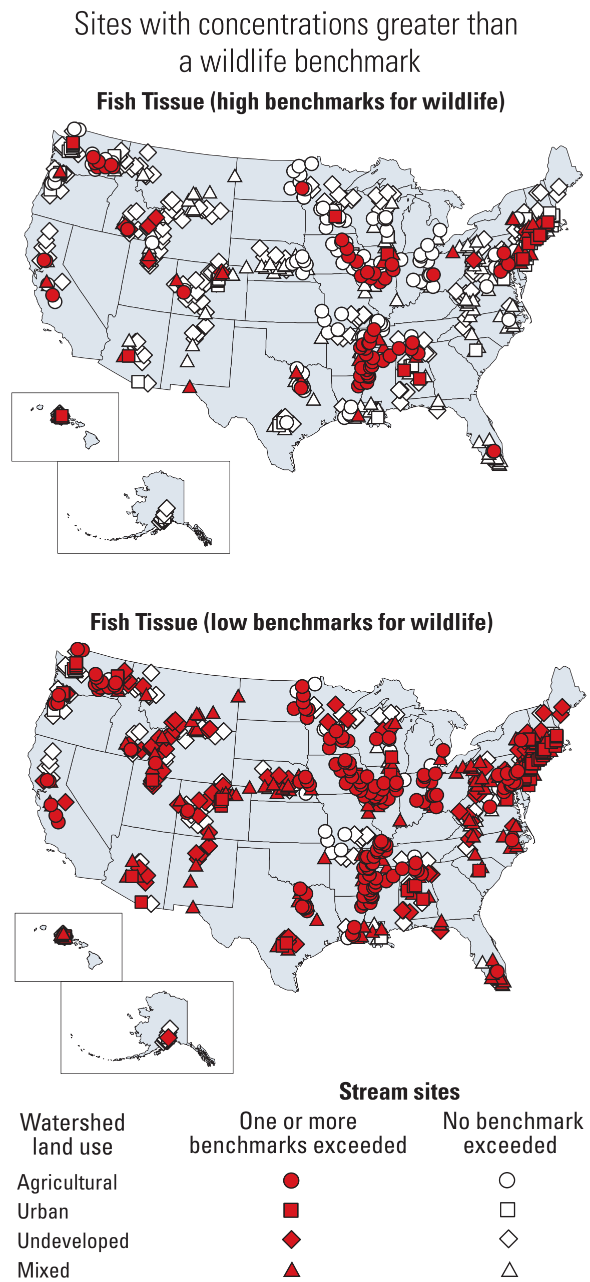


Figure 6–17. Wildlife benchmarks were exceeded by organochlorine pesticide compounds in whole fish most frequently in urban and mixed-land-use streams in the populous Northeast, in agricultural streams in areas with high historical use, and in urban streams distributed throughout the country. Water-quality benchmarks are provided in Appendix 3B.

Wildlife Benchmarks for Pesticides in Whole Fish

Benchmarks for assessing the potential for organochlorine pesticide compounds in fish tissue to adversely affect wildlife that consume either fish or other fish-eating wildlife were selected from several sources (Appendix 3B). USEPA is developing tissue-based criteria for bioaccumulative contaminants, but the process is not complete (USEPA, 2005i).

Currently, there is no broad consensus on a single system of national-scale, fish-tissue benchmarks for wildlife. Relatively few tissue-based wildlife benchmarks are available, some of which were developed for State or regional applications. Most available benchmarks have, however, been derived using similar methodologies (based on the same USEPA methodology for using laboratory animal test data to develop human-health benchmarks). First, a no-observed-adverse-effects level (NOAEL) for wildlife is estimated from the NOAEL for the most sensitive test species. Then the concentration of a contaminant in food that would result in a dose equivalent to the NOAEL (assuming no exposure through other environmental media) is calculated from estimates of the food consumption rate and body weight for multiple representative wildlife species. Calculations usually are done for both mammalian and avian species, and the lowest is commonly selected as a screening-level benchmark. Benchmark values from different sources vary considerably for a given compound, despite similar methodologies. The extreme case is total DDT, for which tissue-based wildlife benchmarks range from 6 to 200 µg/kg wet weight. Different values for a particular pesticide may result from the use of different test species in toxicity tests, the use of different uncertainty factors to account for interspecies differences, and differences in the duration of exposure or test endpoints measured. In addition, results may be extrapolated to different representative wildlife species, which typically are selected to reflect the geographic location and objectives of the program or organization setting the benchmarks.

Because of the lack of consensus on tissue-based benchmarks for protection of wildlife, whole-fish concentrations measured by NAWQA were compared with a range of available benchmark values for each compound. First, systematically derived wildlife benchmarks were compiled, resulting in four sets of wildlife benchmarks (described below). Second, the lowest and highest benchmark values for each organochlorine pesticide or group were selected and used in two separate analyses of NAWQA fish data. Each wildlife benchmark used in this report represents the concentration of a pesticide or group in fish, below which adverse effects on fish-eating wildlife are not expected to occur (100 percent of exposure to the pesticide is assumed to be from consumption of fish). One or more fish-eating wildlife benchmarks were available for 10 of the 12 organochlorine pesticides and groups measured by NAWQA in fish tissue.

NOAEL-based toxicological benchmark for fish-eating wildlife—This benchmark is the NOAEL-equivalent concentration in food derived for the most sensitive fish-eating wildlife species for which data are available. NOAEL-equivalent concentrations in food were derived for a variety of wildlife species by Sample and others (1996) for the Department of Energy, Oak Ridge National Laboratory, for use in ecological risk assessments at waste sites. Endpoints such as reproductive and developmental toxicity and reduced survival were used whenever possible, but for some contaminants, data were limited and other endpoints (such as organ-specific toxic effects) were used. The representative wildlife species used by Sample and others (1996) represent a wide range of diets and body weights and have wide geographic distributions within the United States. These include several fish-eating species: mink, river otter, belted kingfisher, osprey, and great blue heron. For this report, the lowest value was selected from the available NOAEL-equivalent concentrations in food that were derived for fish-eating species and used as the benchmark for each compound. These benchmarks are available for 8 of the 12 organochlorine pesticides and pesticide groups measured by NAWQA in fish.

Canadian Tissue Residue Guideline (TRG)—This benchmark is designed to protect all life stages of all wildlife during a lifetime exposure to a substance present as a contaminant in aquatic food sources (CCME, 1998). TRGs are calculated from the most sensitive of the available toxicity tests and applied to the Canadian wildlife species with the highest food intake/body weight ratio (CCME, 1998). TRGs are available for two organochlorine pesticides (DDT and toxaphene), which were derived using Wilson's storm petrel and the mink as representative wildlife species (CCME, 1999a,b).

New York fish flesh criteria (FFC) for protection of piscivorous wildlife, noncancer values—These are intended to protect specific wildlife species from adverse effects other than cancer, such as mortality, reproductive impairment, and organ damage (Newell and others, 1987). The New York State Department of Environmental Conservation (NYSDEC) derived these criteria using the same extensive laboratory animal toxicology database that is used to derive criteria for the protection of human health. Instead of extrapolating from laboratory animals to humans, the NYSDEC extrapolated from laboratory animals to wildlife. To represent birds and mammals, the NYSDEC selected a generic bird (with a body weight of 1 kg and a food consumption rate of 0.2 kg/day) and the mink. New York FFC are available for 8 of the 12 organochlorine pesticides and pesticide groups measured by NAWQA in fish.

Proposed criteria from the Contaminant Hazard Review series—Proposed tissue-based criteria for wildlife are included among recommendations for protection of natural resources in the Contaminant Hazard Review series developed by the U.S. Fish and Wildlife Service. Proposed criteria are available from this series for two organochlorine pesticides, toxaphene and chlordane. For chlordane (Eisler, 1990), the criterion is based on birds only—Eisler noted that criteria for protection of mammalian wildlife were lacking, and criteria for birds were incomplete and still required NOAELs from lifetime exposures. Wildlife benchmarks for toxaphene (Eisler and Jacknow, 1985) are based on criteria for human-health protection (ranging in various foods from 0.1 to 7.0 mg/kg), which are expected to protect sensitive species of wildlife.

Application of Fish-eating Wildlife Benchmarks for Fish

Fish-eating wildlife benchmarks for fish tissue were compared with concentrations of organochlorine pesticide compounds or groups measured by NAWQA in composite samples of whole fish (one sample per site). Concentrations measured by NAWQA were compared with both the lowest and the highest benchmark values available for each pesticide compound and group. The analysis thus reflects the degree of uncertainty in estimating the potential for adverse effects on wildlife.

Most of the concentrations that exceeded a benchmark, as well as most of the variance between high and low benchmarks, were due to total DDT. Using the high and low ends of the range of benchmark values available for different pesticides (or pesticide groups), wildlife benchmarks were exceeded at 11 to 88 percent of urban stream sites for total DDT, 15 to 18 percent for dieldrin, and 0 to 10 percent for total chlordane. In agricultural streams, total DDT exceeded wildlife benchmarks at 29 to 87 percent of sites, dieldrin at 7 to 11 percent, and toxaphene at 0 to 9 percent (fig. 6–18).

The wildlife screening-level assessment for organochlorine compounds in fish tissue indicates that these compounds still occur at some sites at concentrations that have the potential to adversely affect fish-eating wildlife. Although there is relatively high uncertainty in benchmark values, total DDT and dieldrin accounted for most benchmark exceedances, and there were 34 percent of agricultural sites and 25 percent of urban sites with concentrations that exceeded both low and high benchmark values for one or more pesticide compounds or groups.

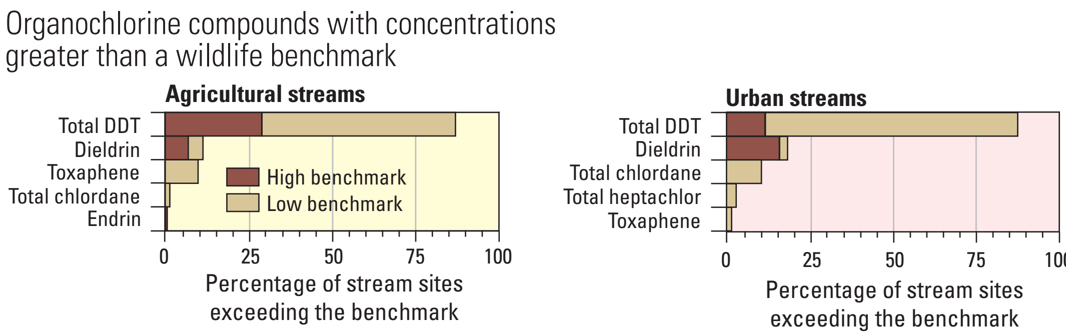
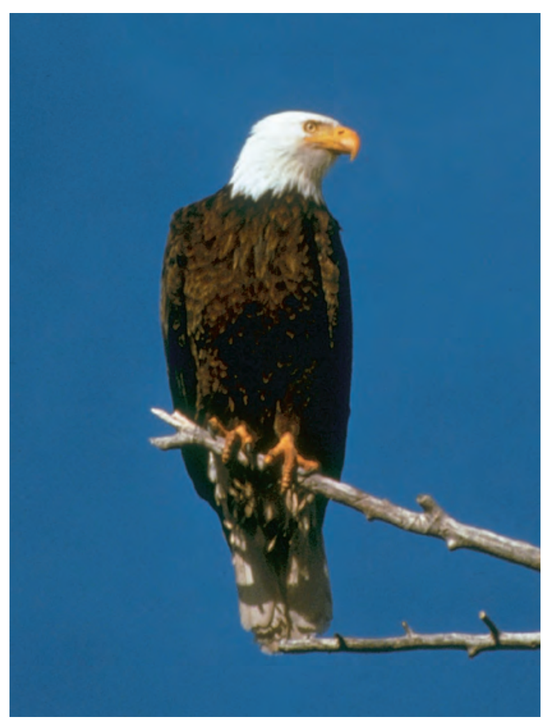


Figure 6–18. Contributions of individual organochlorine pesticide compounds or groups to exceedances of whole-fish tissue benchmarks for fish-eating wildlife show the potential significance of total DDT and dieldrin. Water-quality benchmarks are provided in Appendix 3B.



Organochlorine compounds from historical pesticide use are still a concern for fish-eating wildlife in some streams (Photograph by W.H. Mullins © 1974).

Emerging Issues for Assessment of Pesticide Effects

Although pesticides are among the most intensively studied of environmental contaminants, and many studies of fate and effects are required to register a pesticide for use, comprehensive assessment of their potential effects continues to present challenges. Two issues receiving particular attention by the scientific and regulatory communities are the potential effects of pesticide mixtures, the occurrence of which was examined in Chapter 5, and the potential effects of pesticides on endocrine systems.

Approaches for Assessing Potential Effects of Pesticide Mixtures on Humans and Aquatic Life

Understanding the potential effects of chemical mixtures on humans and the environment is one of the most complex problems facing scientists and regulatory agencies. USEPA identified this issue as a priority in its research strategy for 2000 and beyond (USEPA, 2000b). Although guidelines and detailed procedures for evaluating potential effects from exposure to chemical mixtures have been provided by USEPA (USEPA, 1986, 2000b) and other agencies (ATSDR, 2004b), implementation has been difficult because of the complexity of mixtures that occur in the environment and the inadequacy of data on the toxicity of the mixtures. Most toxicological testing is performed on single chemicals—usually at high exposure levels—whereas most human and ecological exposures are to chemical mixtures at relatively low doses (USEPA, 2000b; ATSDR, 2004b).

Humans can be exposed to mixtures of pesticides and their degradates that occur in streams and ground water if such water is used as a source of drinking water and if treatment does not eliminate the pesticide compounds. Aquatic organisms are exposed to mixtures that occur in streams. Pesticide mixtures may be derived from common sources (such as point sources) or from multiple nonpoint sources, and may include several different types of pesticide compounds with different mechanisms of toxicity. Although a review of recent research on the effects of pesticide mixtures is beyond the scope of this report, the present approaches taken by USEPA and other agencies for regulating and assessing pesticide mixtures provide an indication of present knowledge and information gaps.

Evaluation and management of potential risks to humans of pesticide mixtures that may occur in drinking water are primarily addressed at the Federal level by USEPA and the Agency for Toxic Substances and Disease Registry (ATSDR). Much of the attention to potential effects of chemical mixtures on human health has been associated with risk assessments required for hazardous waste sites as part of implementing the Comprehensive Environmental Recovery, Compensation, and Liability Act (CERCLA), but specific assessment of pesticide mixtures is also now occurring to meet requirements of the Food Quality Protection Act (FQPA) of 1996. Under the FQPA, USEPA must assess the cumulative risks of pesticides that share a common mechanism of toxicity, or act the same way in the body. These cumulative assessments consider exposures from food, drinking water, and residential sources. USEPA also incorporates regional exposures from residential and drinking-water sources to account for the considerable variation in potential exposures across the country. To date, USEPA has determined that within each of four different chemical classes (organophosphates, N-methyl carbamates, triazines, and chloroacetanilides), several specific pesticide compounds have a common mechanism of toxicity and require cumulative risk assessments to better define the potential effects of exposure of humans to multiple pesticides within each class.

The potential effects of chemical mixtures on aquatic life have not received as much attention as for human health, although USEPA's Office of Research and Development, National Center for Environmental Assessment, has completed ecological risk-assessment guidelines that support the cumulative risk-assessment approach (USEPA, 2003f). The pesticide registration and reregistration processes require ecological risk assessment, which includes evaluation by USEPA of the likelihood that exposure to more than one pesticide and its degradates may cause harmful ecological effects.

Potential effects of pesticide mixtures on aquatic life also may be considered as part of assessments for National Pollutant Discharge Elimination System (NPDES) permits or hazardous waste sites. Procedures developed by USEPA for conducting assessments for NPDES permits involve a battery of tests, referred to as "whole effluent toxicity" (WET) tests, for both effluents and receiving waters. The WET tests are toxicity tests applied to actual or simulated effluent and receiving water and, therefore, assess the combined toxicity to aquatic life of all contaminants present in water (USEPA, 2004f). Although the WET test procedures provide a methodology for directly testing ambient waters that contain mixtures, they have not yet been applied more broadly to assess mixtures of pesticides from nonpoint sources that do not involve NPDES permits. Similarly, the risk-assessment methods developed for mixtures that occur at hazardous waste sites (USEPA, 2003f) provide a systematic approach to assessing potential effects of pesticide mixtures on aquatic life, but they are generally not applied to ambient water-quality conditions.

In addition to these various approaches to addressing mixtures as part of the regulatory process, researchers are studying the effects of specific mixtures of pesticides and degradates and relating the occurrence of mixtures to their potential effects on aquatic ecosystems. The accompanying sidebar by Lydy and Belden (p. 114) provides a perspective on current understanding and the status of research regarding the potential effects of pesticide mixtures on aquatic life. NAWQA has begun to examine relations between biological measures of stream quality and the range of stresses introduced by agricultural and urban activities, including exposure to pesticides. The accompanying sidebar on the Pesticide Toxicity Index (p. 116) summarizes how the index is used by NAWQA as a relative indication of the potential toxicity of a mixture to aquatic life and illustrates its applications with examples from NAWQA studies.

Although an array of approaches has been developed for assessing the potential effects of mixtures using the best available data on exposure and effects, progress toward understanding the potential effects of pesticide mixtures on humans and aquatic life has been hampered, in part, by sparse data on the composition and concentrations of mixtures that actually occur in streams and ground water. As examined in Chapter 5, pesticide degradates are potentially important components of pesticide mixtures that need to be considered when evaluating potential effects. Improved data on the occurrence and composition of mixtures from NAWQA and other studies can help to characterize the potential exposure of humans, aquatic life, and wildlife to mixtures and provide a basis for systematically prioritizing mixtures that may occur in streams and ground water.

Endocrine Disruption and Pesticides

Endocrine systems are present in mammals, birds, fish, and other organisms. They are comprised of glands that produce hormones, which act as chemical messengers, and receptors in various organs and tissues that recognize and respond to the hormones. The endocrine system regulates all body functions from conception through adulthood, including the development of the brain and nervous system, the growth and function of the reproductive system, and metabolism and blood-sugar levels. Disruption of the endocrine system by a contaminant can occur in a number of ways, such as by mimicking a natural hormone, blocking the effects of a hormone, or causing overproduction or underproduction of hormones (Gross and others, 2003).

More than 50 synthetic chemical compounds, including a number of pesticides, have been identified as potential endocrine disruptors in various studies over the past several years (National Academy of Sciences, 1999). The studies include bioassays demonstrating estrogenic or anti-estrogenic activity and field studies correlating contaminants with hormone-related effects. Examples of such field studies include feminization of gull embryos linked to elevated DDT (Fry and Toone, 1981), population declines of alligators in some Florida Lakes with elevated concentrations of organochlorine pesticides (including DDT) (Guillette and others, 1994), and feminization of fish in water bodies receiving municipal discharges or industrial effluents (Purdom and others, 1994).

In 1994, the NAWQA Program investigated the potential influence of contaminants on sex steroid hormones and other biomarkers in common carp (Goodbred and others, 1997). Abnormal ratios of sex steroid hormones in both male and female carp were found at some sites, and the ratio of estrogen to testosterone, an indicator of potential abnormalities in the endocrine system, was significantly lower at sites where some of the highest pesticide concentrations were detected (fig. 6–19). Further investigation is needed to determine whether (1) reduced hormone ratios are caused by pesticides, and (2) the reduced hormone ratios are associated with significant effects on fish populations.

The 1996 Food Quality Protection Act requires USEPA to screen and assess pesticides and other environmental contaminants for potential effects on human endocrine systems, an assessment which USEPA is extending to wildlife as well. A review of NAWQA pesticide data compared with a list of potential endocrine disrupting compounds (Keith, 1997) indicates that 17 pesticides measured by NAWQA in water are possible endocrine disruptors (USEPA has not yet designated pesticides that it considers to be potential endocrine disruptors). Eleven of these pesticides were among those most frequently found in NAWQA stream samples (fig. 6–20).

Research on the effects of chemicals on endocrine systems is in its relatively early stages. Several important aspects are still unclear, including the degree to which such effects occur in the environment; whether effects on individual organisms translate to effects on populations and communities; and at what concentrations effects on populations become significant. There is considerable scientific uncertainty about the causes of reported effects (Kavlock and others, 1996). A major effort is underway by USEPA and other agencies to systematically identify and better understand endocrine disruptors (USEPA, 1998).

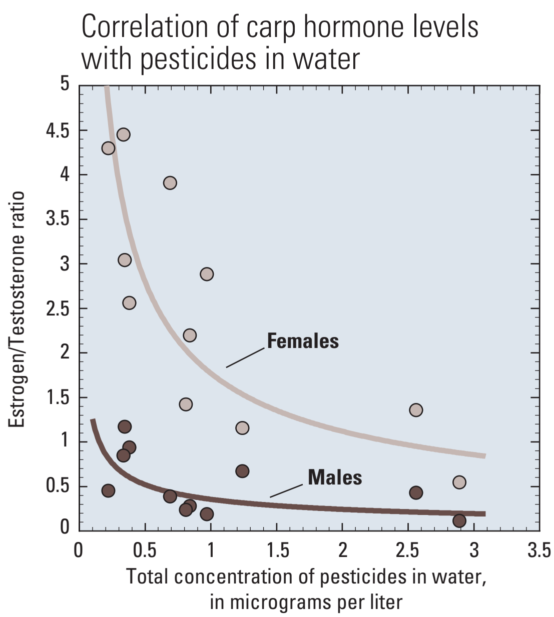


Figure 6–19. Ratios of estrogen-to-testosterone in carp from 11 streams sampled by NAWQA in 1994 were inversely correlated with pesticide concentrations. Low ratios indicate potential abnormalities in carp endocrine systems (Goodbred and others, 1997).

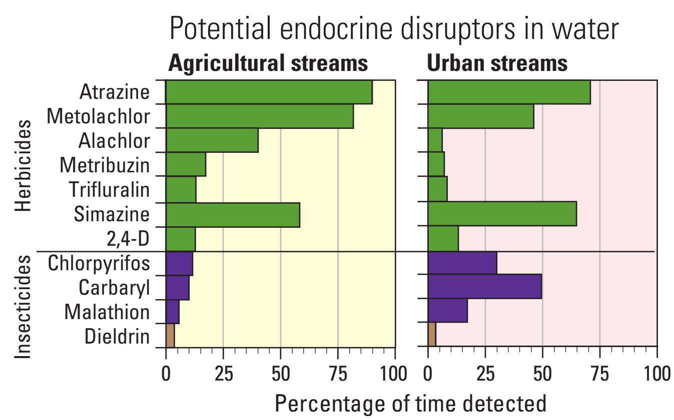


Figure 6–20. Eleven pesticides that have been identified as potential endocrine disruptors (Keith, 1997) were among the pesticides most frequently detected in NAWQA water samples from agricultural and urban streams.

Assessing Potential Effects of Pesticide Mixtures

Michael J. Lydy and Jason B. Belden
Fisheries and Illinois Aquaculture Center and Department of Zoology
Southern Illinois University

NAWQA studies show that the most common form of pesticide exposure for aquatic organisms is simultaneous exposure to multiple pesticides. More than 50 percent of all stream samples contained five or more pesticides. Yet, most pesticide research, historically and currently, has evaluated the effects of individual pesticides as if they occurred alone. Scientists and risk assessors are only in the beginning stages of developing the knowledge base and procedures for evaluating the potential environmental effects of pesticide mixtures in aquatic ecosystems.

Conceptual Models of Mixture Effects

Research on mixtures indicates that a wide array of possible interactions among pesticides may occur, but they all fall into one of four categories:

Independent—Co-occurring pesticides act independently of one another, with each causing the degree of effects on a population as would be expected from its individual concentration. This might occur for pesticides with different target organs and modes of action.

Additive—Co-occurring pesticides act in an additive manner, with effects on a population as would be expected by summing the toxicity-normalized concentrations of multiple individual pesticides that are present. This might be expected for pesticides with similar chemical structures and a common mode of action.

Antagonistic—Co-occurring pesticides have a combined toxicity that is less than that predicted from the additive model.

Synergistic—Co-occurring pesticides have a combined toxicity that is greater than that predicted from the additive model.

The additive model, also called the Concentration Addition Model, is the most common baseline used for assessing effects of pesticide mixtures, although not all mixtures strictly follow it. In a 2-compound mixture, the concentration of chemical A and the concentration of chemical B would be normalized (weighted) by toxicity as follows: the concentration of each chemical present in the sample is divided by its toxicity value (usually the concentration needed to cause a 50-percent effect in a population) and the toxicity-weighted concentrations are then added together. The effect expected would then be based on this normalized total concentration. For example, if two pesticides that have the same toxicity are each present in a stream at 10 μg/L, then the expected effect would be the same as the effect of 20 μg/L of either one of the compounds alone.

Experimentally, additive toxicity has been observed for several groups of mixtures, including 2-compound mixtures of the s-triazine herbicides atrazine and cyanazine in reproductive tests with the green alga *Chlorella fusca* (Faust and others, 1993) and 2-compound mixtures of several organophosphate insecticides, including chlorpyrifos, diazinon, and azinphos methyl, in tests with midges (Lydy and Austin, 2004). In addition, the organophosphate insecticides chlorpyrifos and diazinon were strictly additive in their toxicity to the cladoceran, *Ceriodaphnia dubia*, in toxicity studies performed in natural, storm, and laboratory waters (Bailey and others, 1996, 1997, 2000).

Several studies have shown that pesticide interaction can result in less (antagonistic) or more (synergistic) toxicity than predicted by the Concentration Addition Model. For example, researchers have demonstrated that simultaneous exposure to esfenvalerate (a pyrethroid insecticide) and diazinon (an organophosphate insecticide) resulted in greater than additive toxicity to fathead minnows (Denton and others, 2003). The likely reason for this synergism is that diazinon inhibits the esterase enzymes, thus reducing the organism's capability to detoxify pyrethroids. Other studies have shown that the herbicide atrazine, when present at concentrations above 40 μg/L, increases the toxicity of the organophosphate insecticides chlorpyrifos (fig. 6–21) and diazinon to aquatic invertebrates (Belden and Lydy, 2000; Anderson and Lydy, 2002). Note that atrazine itself is not acutely toxic to these invertebrates, even at high concentrations in water. In this case, the reason for the increased toxicity is that atrazine induces (increases production of) specific oxidative enzymes, resulting in a higher transformation rate of chlorpyrifos into a more toxic metabolic product (Belden and Lydy, 2000). In both of these examples, one contaminant changed the organism's capacity to metabolize the other contaminant, thus increasing or decreasing the amount of pesticide or pesticide breakdown products within the organism, and leading to large changes in the degree of toxicity.

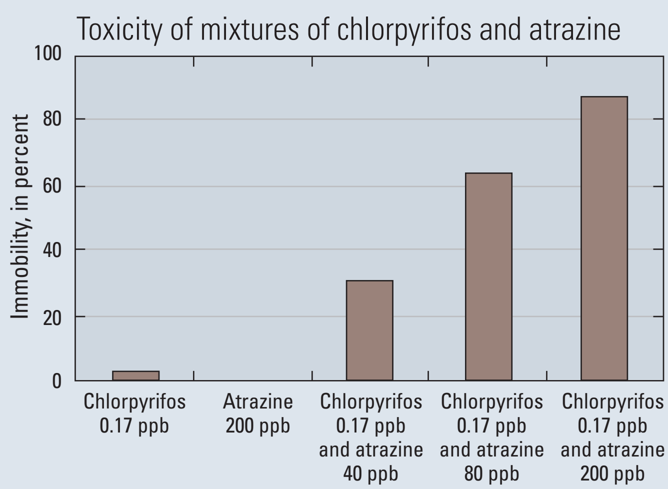


Figure 6–21. Although atrazine itself was not acutely toxic to the aquatic invertebrates tested in this study (chironomids), an increase in atrazine concentration caused an increase in the toxicity observed for chlorpyrifos (a synergistic interaction), as indicated by increased immobility (Belden and Lydy, 2000). (Concentrations are shown in ppb [parts per billion] as in the original report, which is equivalent to micrograms per liter.)

Studies of the toxicity of pesticide mixtures have resulted in the full spectrum of additive, synergistic, and antagonistic responses. Generally, pesticides within the same pesticide class and that have similar structures and a common mode of action (for example, organophosphate insecticides) are more likely to follow the additive model, while pesticides from different classes (for example, herbicides and insecticides) have more varied effects. Table 6–2 summarizes the results from selected studies of mixtures containing the organophosphate insecticide diazinon. Because of the complexity of the modes of action and chemical transformations that occur for each pesticide, the toxicity of most pesticide mixtures will deviate from the simple additive model. It is not known how likely such deviations from additivity are, nor is there consensus on how large a deviation from the model is significant. In many cases, this deviation may be smaller than that obtained from testing the organisms under slightly different conditions (intraspecies toxicity testing), indicating that other sources of uncertainty may be more significant than errors in mixture models. However, until a more thorough understanding of pesticide interactions is achieved, the possibility of pesticide combinations resulting in greater toxicity than predicted by the additive model needs to be considered.

Implications

In most situations, a mixture of pesticides presents a greater risk to aquatic organisms than do any of the individual components of the mixture. The ecological effects caused by mixtures of pesticides, however, are highly uncertain and are in the relatively early stages of investigation. Further research must be conducted before the possible impacts that pesticide mixtures may have on the environment can be determined. The large numbers of chemicals and varying exposure routes that occur in the environment make testing every possible exposure scenario impossible. For example, in a mixture of 20 compounds, there are 190 pairs of compounds, and more than a million possible combinations (pairs, triples, and so on). Thus, it makes sense for researchers assessing mixture effects to prioritize and test those combinations with a high probability of environmental occurrence and those that are useful in developing refined models to predict the toxicity of similar pesticide mixtures.

Ultimately, aquatic toxicologists need to understand the dynamic world that organisms encounter. Besides pesticides, organisms are exposed to other types of chemical contaminants (such as metals and industrial contaminants) and also biological and physical stressors (such as changes in flow rate, temperature, habitat, food availability, and predation) simultaneously. It is likely that these stressors interact. However, until we better understand the biology of aquatic systems, from the molecular to the ecosystem level, we will continue to struggle in predicting the existence and significance of chemical interactions.

Table 6–2. Selected studies of pesticide mixtures containing diazinon illustrate the spectrum of possible responses for such mixtures. The types of compounds included are two organophosphate insecticides (OP), a pyrethroid insecticide (P), a triazine herbicide (T), and a nutrient.

Mixture	Type of compound	Species tested	Result	Deviation from concentration addition	Reference
Diazinon and chlorpyrifos	OP OP	Midges (aquatic invertebrate)	Additive	None	Lydy and Austin (2004)
Diazinon and chlorpyrifos	OP OP	*Ceriodaphnia dubia* (aquatic invertebrate)	Additive	None	Bailey and others (1996, 1997)
Diazinon and esfenvalerate	OP P	Fathead minnows	Synergistic	140 to 170 percent greater toxicity	Denton and others (2003)
Diazinon and atrazine	OP T	Midges, amphipods (aquatic invertebrates)	Synergistic	Up to 400 percent greater toxicity	Anderson and Lydy (2002); Belden and Lydy (2000)
Diazinon and ammonia	OP Nutrient	*Ceriodaphnia dubia* (aquatic invertebrate)	Antagonistic	27 to 32 percent less toxic	Bailey and others (2001)

Pesticide Toxicity Index

To expand the assessment of potential effects of pesticides in stream water on aquatic life, NAWQA developed a Pesticide Toxicity Index (Munn and Gilliom, 2001). The Pesticide Toxicity Index (PTI) accounts for multiple pesticides in a sample, including pesticides without established benchmarks for aquatic life. The PTI combines information on exposure of aquatic biota to pesticides (measured concentrations of pesticides in stream water) with toxicity estimates (results from laboratory toxicity studies) to produce a relative index value for a sample or stream. The PTI value is computed for each sample of stream water by summing the toxicity quotients for all pesticides detected in the sample. The toxicity quotient is the measured concentration of a pesticide divided by its toxicity concentration from bioassays (such as an LC_{50} or EC_{50}). For each sample, separate PTI values are computed for fish and benthic invertebrates. This approach follows the Concentration Addition Model of toxicity described by Lydy and Belden (accompanying sidebar, p 114). Although simple additivity is unlikely to strictly apply for complex mixtures of pesticides from different classes and with different effects and modes of action, the PTI is still useful as a relative index. Deneer (2000) reported that "for more than 90 percent of 202 mixtures in 26 studies, concentration addition was found to predict effect concentrations correctly within a factor of two." While the PTI does not indicate whether water in a sample is toxic, its value can be used to rank or compare the relative potential toxicity of different samples or different streams.

The PTI provides a means to rank different stream sites compared with each other and is a tool for investigating relationships between pesticide levels and the quality of aquatic ecosystems. For example, pesticides were commonly detected in agricultural streams and drains throughout the Yakima River Basin, often at concentrations exceeding one or more aquatic-life benchmarks for individual pesticides (Fuhrer and others, 2004). Data for 24 stream sites in the Yakima River Basin showed that the number of pollution-tolerant

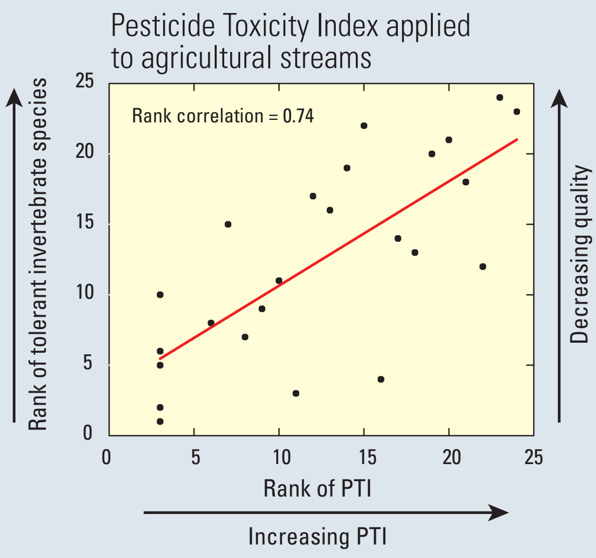


Figure 6–22. Streams and drains in the Yakima River Basin with the highest PTI values tended to have the highest numbers of pollution-tolerant benthic invertebrates, indicating lower water quality. The ranks were significantly correlated at a 95-percent confidence level. (Modified from Fuhrer and others, 2004.)

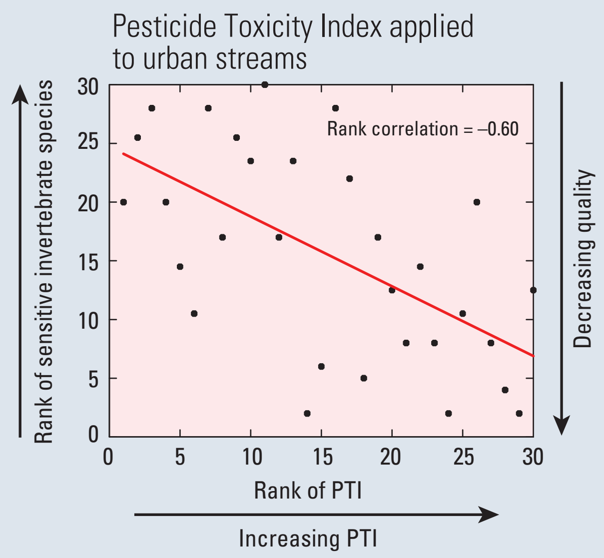


Figure 6–23. Streams in the Dayton and Cincinnati, Ohio areas with the highest PTI values tended to have the lowest numbers of sensitive invertebrate species, indicating lower water quality. The ranks were significantly inversely correlated at a 95-percent confidence level. (Modified from Rowe and others, 2004.)

benthic invertebrates (higher numbers indicate a stressed ecosystem) significantly increased with the rank of PTI values (fig. 6–22). Pesticides, however, are only one of many factors that may affect aquatic communities—other factors include physical habitat quality, food availability, and the presence of other contaminants. Detailed studies are required to distinguish the relative roles of different chemical and physical factors.

Another example is for streams in the Dayton and Cincinnati, Ohio, urban areas, which were studied in the Great and Little Miami River Basins (Rowe and others, 2004). Results for 30 streams with varying degrees of urban land use in their watersheds indicated that the number of sensitive invertebrates (lower numbers indicate a stressed ecosystem) significantly decreased with increasing PTI values (fig. 6–23). As with the Yakima River Basin example, this correlation does not demonstrate a cause-and-effect relationship between pesticides and the benthic invertebrate community. The PTI was one of several factors found to correlate with degree of urbanization—which also included chloride levels in water and synthetic chemicals in bed sediment—that may affect benthic invertebrates (Rowe and others, 2004).

For a national-level perspective, the PTI was used to rank NAWQA stream sites by the potential toxicity of measured pesticide concentrations to fish and benthic invertebrates. Invertebrate PTI values generally were more than 10 times higher than those for fish, as shown by frequency distributions of the 95th percentile PTI values for streams in all land-use settings (fig. 6–24). The higher toxicity values for invertebrates reflect greater sensitivity of invertebrates compared with fish, particularly to insecticides. A large proportion of benthic invertebrates are insects, which explains the high relative toxicity of insecticides to this taxonomic group. PTI values for both fish and invertebrates are highest for samples collected from agricultural and urban streams, lowest for undeveloped streams, and intermediate for mixed-land-use streams. These results are consistent with the results of the screening-level assessment (using aquatic-life benchmarks) of the potential effects of pesticides in water on aquatic life.

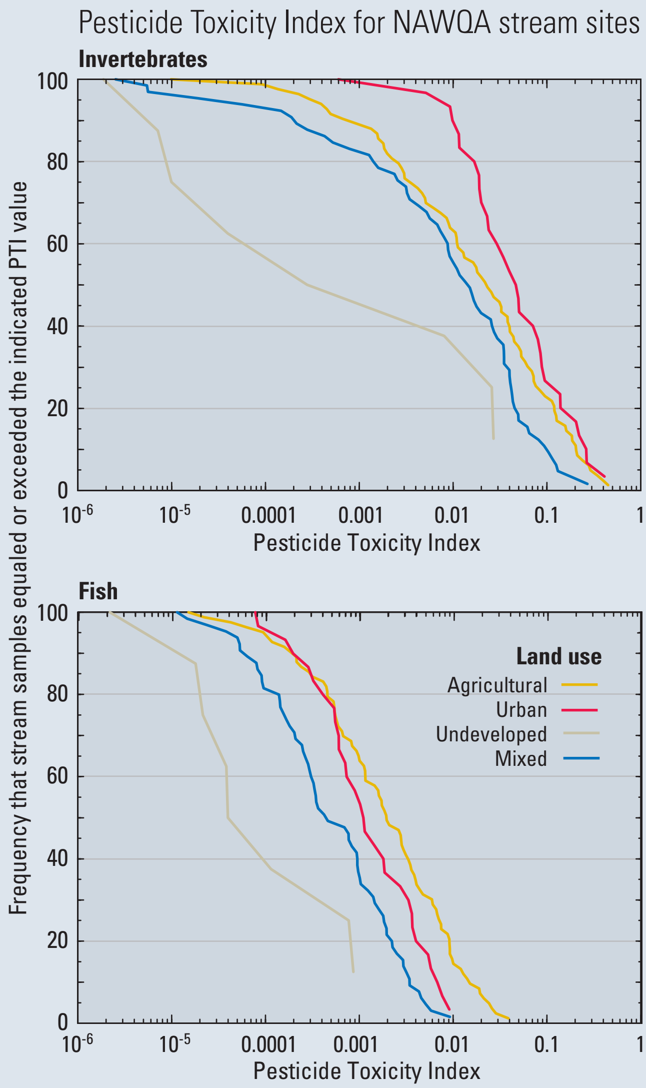


Figure 6–24. Invertebrate PTI values for all land-use categories were more than 10 times higher than fish PTI values. Urban and agricultural streams had the highest PTI values. This analysis is based on the 95th percentile PTI value for each site, which is an estimate of the PTI value that was exceeded by 5 percent of samples at the site.