4 Occurrence and Distribution in Streams and Ground Water

Pesticides were found at detectable concentrations in streams and ground water within most areas sampled that have substantial agricultural or urban land uses. Pesticides were detected in almost every water sample from streams, but were less common in ground water. Organochlorine pesticide compounds were detectable in fish andwom most streams, despite the fact that most of the parent pesticides have not been used in the United States for years. Although more than 100 pesticide compounds were analyzed in water, fish, or sediment, less than 40 of these compounds accounted for most of the detections. The distributions of the most prevalent pesticides in streams and ground water largely follow geographic patterns in land use and associated present or past pesticide use.

Photograph by Eric Hatch Photography, Loveland, Ohio

This chapter summarizes NAWQA results from 1992 to 2001, focusing on the pesticides that were most frequently detected in streams and ground water. Pesticide detections are assessed in relation to land use, pesticide use, hydrologic settings, and the properties of the pesticides themselves. More detailed examination of seasonal patterns, pesticide mixtures, and degradates is included in Chapter 5, and a screening-level assessment of the potential significance of pesticides to human health, aquatic life, and wildlife is provided in Chapter 6.

Overview of Pesticide Occurrence

NAWQA results show that pesticides occurred at detectable concentrations in streams and ground water within most areas that have substantial agricultural or urban land uses. These findings build upon an extensive body of previous research, demonstrating that pesticides and their degradates are present in ground water (for example, Barbash and Resek, 1996; Kolpin and others, 1996), surface waters (for example, Larson and others, 1997; Battaglin and others, 2003), and stream sediments and aquatic biota (for example, Nowell and others, 1999; Seiler and others, 2003) in a wide variety of hydrologic, ecological, and land-use settings across the United States.

In streams sampled by NAWQA, at least one pesticide or degradate was detected more than 90 percent of the time in water, in more than 80 percent of fish samples, and in more than 50 percent of bed-sediment samples collected during 1992–2001 (fig. 4–1). Pesticides analyzed in water were primarily those that are currently used, whereas those analyzed in fish and sediment were predominantly pesticides (or their degradates and by-products) that are no longer used in the United States, such as DDT and other organochlorine pesticides. Detections in stream water were evaluated on a time-weighted basis and results are expressed as the percentage of time that concentrations were detectable. For both fish tissue and bed sediment, one sample was analyzed per site and detections are expressed as a percentage of samples or sites analyzed. Detectable concentrations occurred in water more than 90 percent of the time for streams draining watersheds with agricultural, urban, and mixed land use. Similarly, organochlorine pesticide compounds were detected in more than 90 percent of fish-tissue samples and in more than 50 percent of bed-sediment samples from streams in watersheds with agricultural, urban, and mixed land use. In water, fish tissue, and bed sediment, detections were the least frequent, but not absent, for streams draining undeveloped watersheds—where pesticide use is lowest.

Pesticides were detected distinctly less often in ground water than in streams (fig. 4–1). Detections in ground water are based on one sample per well. Streams are generally more vulnerable to contamination than ground water because of the direct and relatively rapid overland transport of pesticides that occurs with surface runoff (see Chapter 2). Ground water in most areas is less vulnerable because water infiltrates the land surface and moves slowly through soil and aquifer materials before reaching most wells. This extended travel time allows more opportunities for the concentrations of pesticides in water to

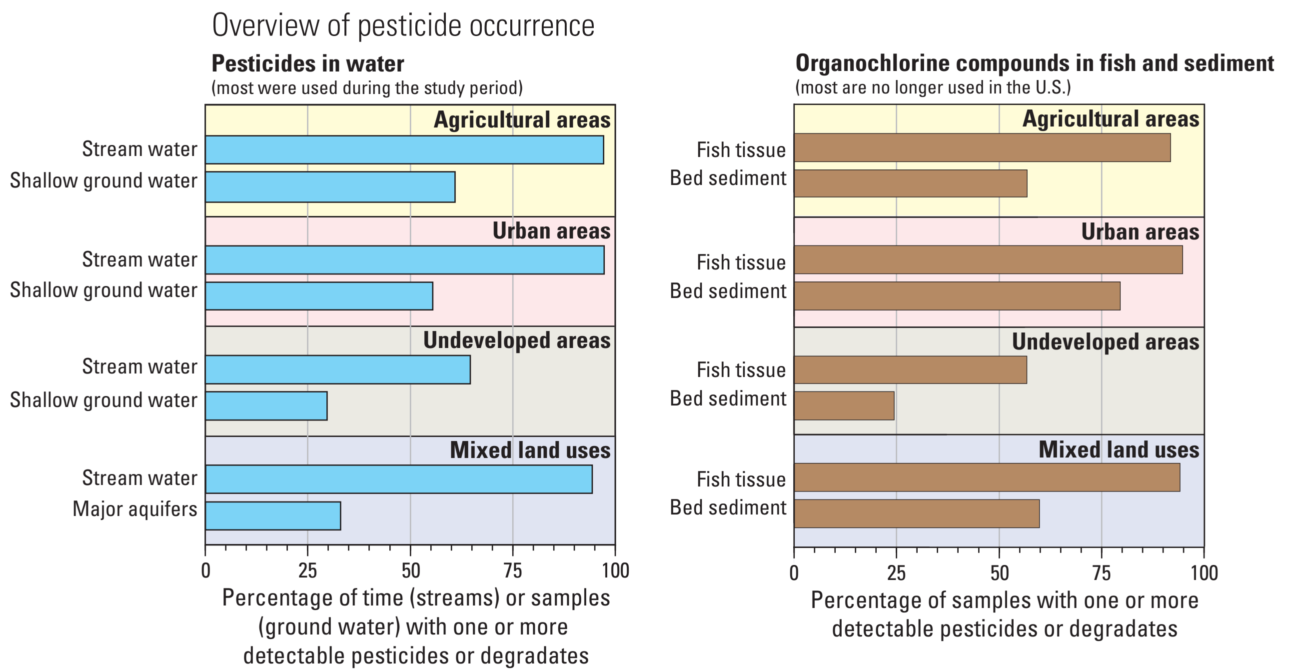

Figure 4–1. Considering all streams sampled across all land uses, one or more pesticides or their degradates were detectable more than 90 percent of the time in water, and were detected in more than 80 percent of fish samples and in more than 50 percent of bed-sediment samples. Less than half of all ground-water samples contained one or more detected pesticides or their degradates, with the most frequent detections occurring in shallow ground water beneath agricultural and urban areas.

be reduced from the combined action of sorption, dispersion, dilution, and transformation. The slow movement of water and solutes through the subsurface, however, also makes contamination of ground water more difficult to reverse once it occurs. The highest frequencies of detection were in shallow ground water beneath agricultural and urban areas, where almost 60 percent of samples had detections of one or more pesticides or degradates. The lowest frequencies of detection were found in shallow ground water beneath undeveloped areas and in deeper ground water in major aquifers. Samples from major aquifers generally represent older ground water that originated as recharge in areas of mixed land use, sometimes before the current land uses were present.

Pesticides Detected Most Frequently

About 40 pesticide compounds, of the more than 100 examined by NAWQA, accounted for most detections in water, fish, or bed sediment. Understanding the occurrence and distribution of these most prevalent pesticides—both spatially and temporally—in relation to their use and properties, land use, and hydrologic settings is critical for evaluating the potential significance of pesticides to water quality.

Water

Twenty-five pesticide compounds, including 24 pesticides and 1 degradate, were each detected more than 10 percent of the time in streams in agricultural, urban, or mixed-land-use settings, or in more than 2 percent of wells in agricultural or urban settings (fig. 4–2). These 25 pesticide compounds include 11 of the herbicides used most heavily in agriculture during the study period (plus the atrazine degradate, deethylatrazine)—hereinafter referred to collectively as agricultural herbicides; 7 herbicides used extensively (though not exclusively) for nonagricultural purposes—referred to as urban herbicides; and 6 insecticides used in both agricultural and urban settings, but most intensively in urban settings (fig. 4–3).

The broad patterns of pesticide occurrence in streams generally corresponded to land use and pesticide use. For example, major agricultural herbicides, such as atrazine and metolachlor, were found most often in agricultural settings, whereas herbicides frequently used in urban areas, such as simazine and prometon, were found most often in urban settings. Urban herbicides also were detected in some agricultural areas, either because of agricultural uses (such as for simazine), or their use for nonagricultural weed control (such as for prometon). Insecticides were generally found most often in urban settings where, with the exception of carbofuran, they are used more intensively than in most agricultural settings. Patterns of detection in ground water also generally corresponded with patterns of land use, although not as closely as for streams. For example, atrazine and metolachlor were among the pesticides detected most frequently in both streams and shallow ground water in agricultural areas.

Pesticides were detected least often in streams and shallow ground water in undeveloped areas. The occurrence of atrazine, deethylatrazine, and metolachlor in undeveloped streams was likely caused by one or more of several factors: (1) most undeveloped watersheds include small areas of agricultural or urban land; (2) pesticides are used in many undeveloped areas for a variety of purposes, such as pest control in forest lands or weed control along utility and roadside rights-of-way; and (3) pesticides can be transported in the atmosphere from other areas.

Not surprisingly, the pesticides that were most commonly detected in streams draining watersheds with mixed land use reflected multiple sources from agricultural and urban applications. The overall frequency of pesticide occurrence in mixed-land-use streams was similar to those observed in both agricultural and urban streams. Likewise, the pesticides detected in major aquifers indicate the influences of both agricultural and urban sources, but overall detection frequencies were lower in major aquifers than in shallow ground water in agricultural and urban areas.

The pesticide detected most frequently in streams and ground water was atrazine, an herbicide used to control weeds in corn fields.

Chapter 4

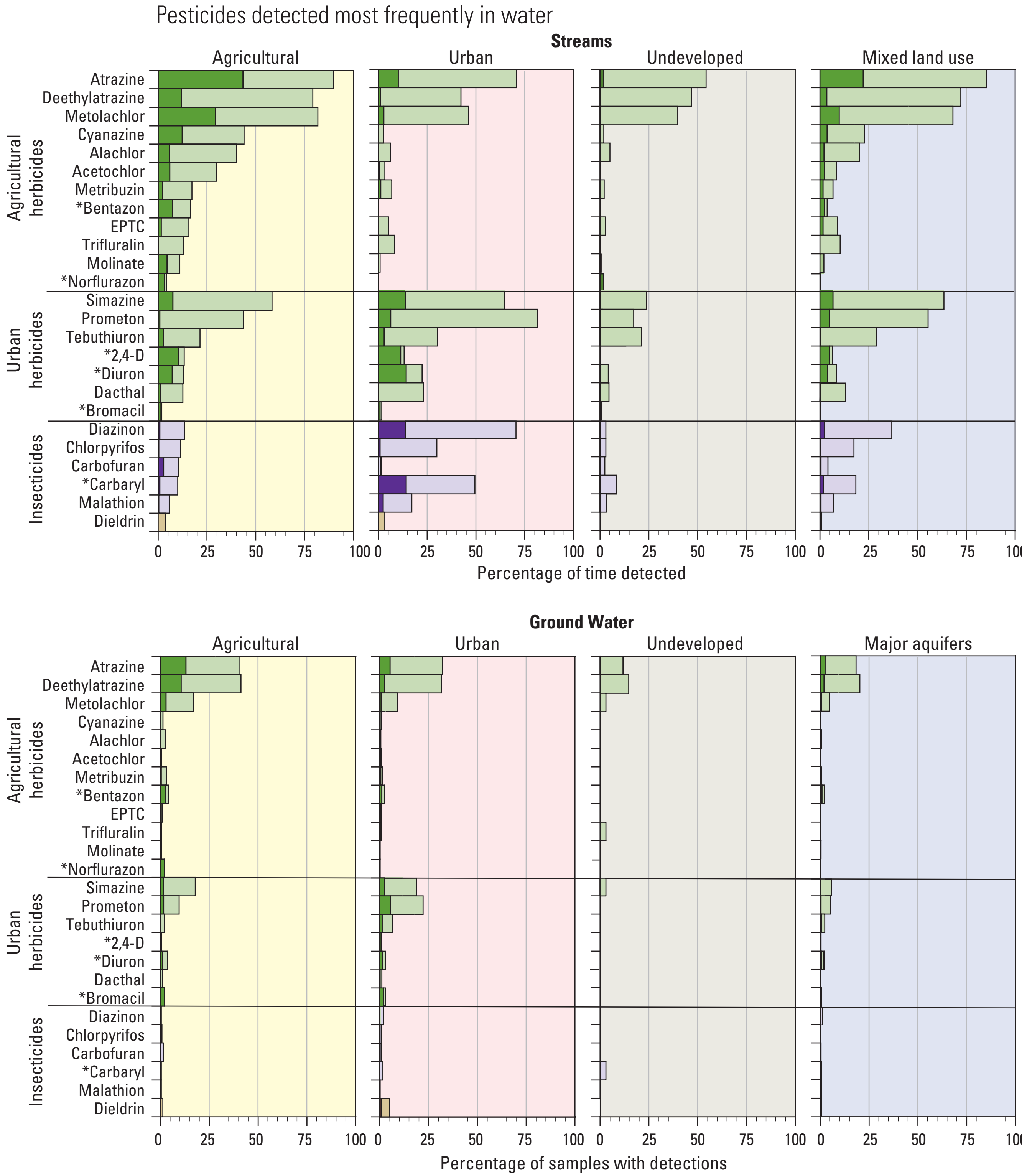

Figure 4–2. Consistent with their patterns of use during the study period, agricultural herbicides—most commonly atrazine (and its degradate deethylatrazine), metolachlor, cyanazine, alachlor, and acetochlor—were detected more frequently in agricultural areas than in urban areas; urban herbicides were found most often in urban areas; and most insecticides, such as diazinon and carbaryl, were detected more frequently in urban streams than in agricultural streams. Two different detection levels are used in this analysis. The dark portion of each bar indicates detections at concentrations greater than or equal to 0.1 µg/L , the light portion indicates detections less than 0.1µg/L*, and the end of each bar is the total for all detections.

*The pesticides 2,4-D, bentazon, bromacil, carbaryl, diuron, and norflurazon could not be detected reliably at concentrations less than 0.1 µg/L; consequently, the reported frequencies below this level for these compounds are minimum estimates.

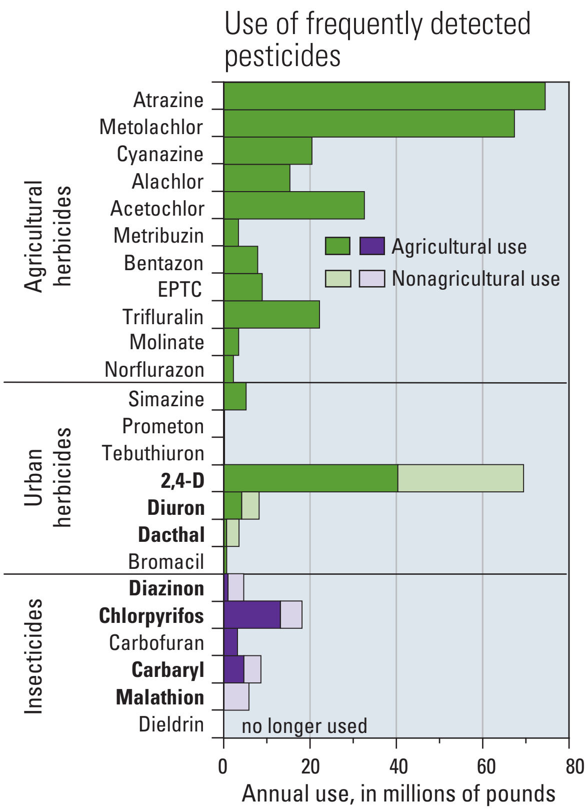

Figure 4–3. The pesticides detected most frequently in water include 11 of the herbicides used most heavily for agriculture during the study period, 7 herbicides used extensively for nonagricultural purposes (mostly in urban areas, but with some agricultural applications), and 6 insecticides. (Agricultural-use estimates are from Gianessi and Marcelli [2000] for 1997; nonagricultural-use estimates are from Kiely and others [2004] for 1999, but were available only for 2,4-D, carbaryl, chlorpyrifos, dacthal, diazinon, diuron, and malathion—indicated by bold type.)

Understanding the Occurrence Assessment

The overview described in this chapter serves as a broad first step toward understanding the distribution and importance of pesticides that were detected in streams and ground water. As explained in Chapter 3, the NAWQA assessment did not include samples from all parts of the Nation or include all pesticides currently used. To provide a national perspective, the occurrence of pesticide compounds in streams and ground water is summarized by land use, environmental medium and component of the hydrologic system sampled, and detection level—all of which have important influences on how results are interpreted.

- **Land use**—Grouping results by land use follows the NAWQA design by combining data from sites expected to have similar influences of land use on water quality (see Chapter 3). Within each general land-use setting, however, there can be substantial variability among sampling sites in specific land-use conditions and pesticide use, as well as hydrologic settings. A pesticide that is common in agricultural streams as a national group, such as a corn herbicide, may never occur in some particular agricultural streams, whereas another pesticide that is uncommon nationally, such as a rice herbicide, may be frequently detected in a few particular streams.

- **Media and hydrologic component sampled**—Grouping results by the different environmental media that were sampled from streams clearly separates organochlorine compounds—which were derived primarily from past use and which, because of their hydrophobic nature, were assessed by their occurrence in fish tissue and bed sediment—from predominantly water-soluble pesticides, most of which were in use during the study period and were measured in water. Grouping results by hydrologic component further distinguishes between streams and ground water for analysis of pesticides in water. The occurrence and concentration results for stream water, unless noted otherwise, were evaluated on a time-weighted basis for each site to eliminate biases caused by more frequent sampling during high-use seasons. Ground-water results are based on one sample per well, and bed-sediment and fish-tissue results are based on one composite sample per site.

- **Detection level**—Analyses of pesticide occurrence in this chapter are based on two different detection levels: (1) detection at any concentration—as low as 0.001 µg/L in water—referred to as total detection frequency, and (2) detections greater than or equal to a common detection level for all compounds in a particular medium—0.1 µg/L for water, 5 micrograms per kilogram (µg/kg) wet weight for fish tissue, and 2 µg/kg dry weight for bed sediment. Two detection levels are necessary for certain data analyses because variations in analytical sensitivity result in differences in minimum detectable concentrations among different compounds. Consequently, direct comparisons of detection frequencies among compounds should be based on a common detection level. For example, of the 25 pesticide compounds most frequently detected in water, 2,4-D, bentazon, bromacil, carbaryl, diuron, and norflurazon could not be reliably detected at concentrations less than about 0.1 µg/L, whereas the other 19 compounds were detectable at levels substantially less than 0.1 µg/L. The reported total detection frequencies of the 6 less-detectable pesticides are thus underestimates of occurrence compared with the total frequencies for the other 19 compounds. Variations in detection sensitivity must be carefully considered when interpreting data on occurrence—the absence of detections does not indicate with certainty that pesticides are not present.

Fish Tissue and Bed Sediment

Thirteen organochlorine pesticide compounds, including historically used parent pesticides and their degradates and by-products, were each found in more than 10 percent of fish or bed-sediment samples from streams draining watersheds with either agricultural, urban, or mixed land use. Figure 4–4 summarizes findings for these 13 compounds, as well as for 2 additional compounds derived from DDT use—*o,p′*-DDT and its degradate, *o,p′*-DDE, which were detected less frequently than the others. The fish and bed-sediment data for organochlorine compounds provide complementary types of information for understanding the presence of these compounds in streams.

The 15 organochlorine pesticide compounds included in figure 4–4 are derived from 8 parent pesticides. The parent pesticides applied were the insecticides DDT, DDD (also known as TDE), dieldrin, aldrin, chlordane, and heptachlor—each of which had all agricultural and nonagricultural uses cancelled by 1988 or earlier, and the fungicides hexachlorobenzene and pentachlorophenol—most uses of which were discontinued by the mid 1980s or before. DDT and chlordane were applied as technical mixtures containing the parent pesticides and other compounds. For example, technical DDT was typically composed

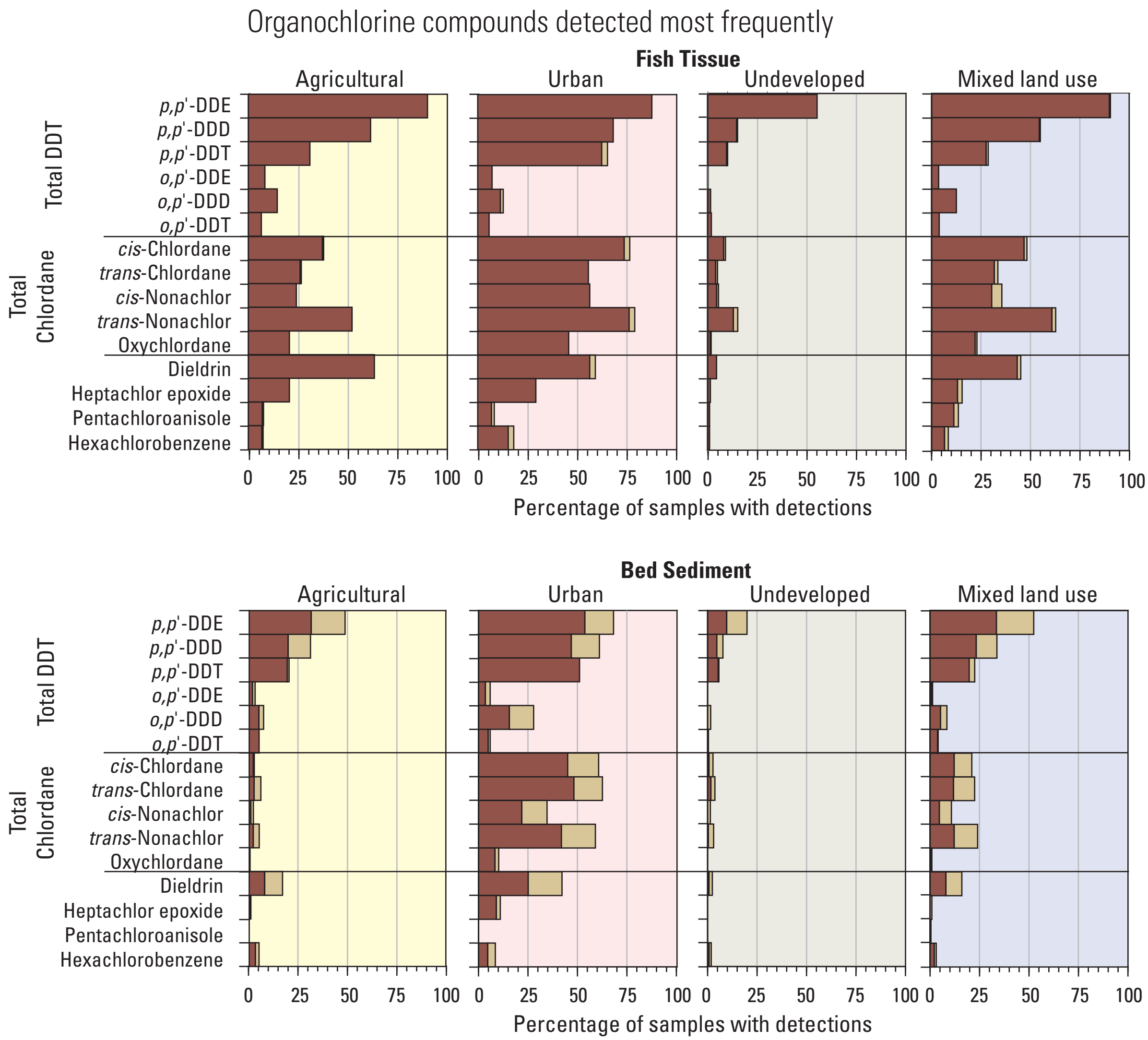

Figure 4–4. Historically used organochlorine pesticides and their degradates were generally detected more frequently in whole fish and bed sediment in urban streams than in agricultural streams, thus matching the pattern found for currently used insecticides in water. DDT and chlordane compounds, as well as dieldrin, were relatively widespread. The dark portion of each bar indicates detections at concentrations greater than or equal to 5 µg/kg (wet weight) for fish tissue and 2 µg/kg (dry weight) for bed sediment, the light portion indicates detections at concentrations less than these levels, and the end of each bar is the total for all detections.

of about 80 percent *p,p′*-DDT (the active ingredient) and 20 percent *o,p′*-DDT (*o,p′* and *p,p′* indicate different isomers of DDT). Furthermore, in addition to being applied as pesticides, DDD and dieldrin are also formed in the environment from the transformation of DDT and aldrin, respectively. Dieldrin that originated from the application of aldrin could not be distinguished from dieldrin applied as dieldrin. Thus, for the purposes of certain data analyses, parent pesticide compounds were grouped together with their corresponding degradates and by-products, reflecting their common or indistinguishable origins.

Six compounds were analyzed in the DDT group (the *p,p′* and *o,p′* isomers of DDT, DDE, and DDD). The sum of the concentrations of these compounds is referred to as the total DDT concentration. Five compounds were analyzed in the chlordane group, with total chlordane concentration calculated as the sum of concentrations of the *cis* and *trans* isomers of chlordane and nonachlor, plus the chlordane degradate oxychlordane. Additional individual compounds frequently found in streams included dieldrin; pentachloroanisole, a degradate of pentachlorophenol; heptachlor epoxide, a degradate of heptachlor; and hexachlorobenzene. Historically, DDT, DDD, aldrin, and dieldrin were used widely in both agricultural and urban areas, whereas chlordane use for urban applications was greater than its agricultural use. As shown in figure 4–5, the agricultural uses of DDT plus DDD, and of dieldrin plus aldrin, were higher than the uses of heptachlor and chlordane. Most organochlorine insecticides had their agricultural uses discontinued in the 1970s, whereas some urban applications (including termite control) were permitted until the late 1980s.

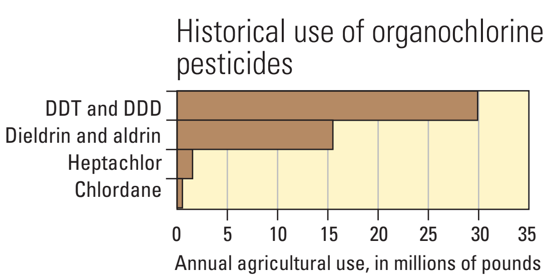

Figure 4–5. In 1966, the agricultural uses of DDT plus DDD (mostly as DDT), and of dieldrin plus aldrin (mostly as aldrin), were greater than the present-day agricultural use of any individual insecticide. Heptachlor and chlordane had much lower agricultural use. (Use estimates are from Eichers and others, 1970.)

Results for fish tissue and bed sediment show generally similar patterns of detection among the organochlorine pesticide compounds (fig. 4–4), but detections were more frequent in fish tissue because these compounds typically accumulate to higher concentrations in biological tissues (wet-weight concentrations) than in sediment (dry-weight concentrations). Patterns of occurrence of organochlorine compounds in fish and bed sediment generally match the patterns in relation to land use that are evident for currently used insecticides in water. Frequencies of detection were higher for most organochlorine pesticide compounds in urban streams than in agricultural streams. The most frequently detected compounds were those composing the DDT group, the chlordane group, and dieldrin.

Streams with undeveloped watersheds had the lowest frequencies of detection of organochlorine compounds in either fish or bed sediment, yet more than half of the fish-tissue samples from these streams had detectable levels of *p,p′*-DDE, a principal degradate of DDT. The frequent presence of *p,p′*-DDE in fish from undeveloped streams may be explained by factors similar to those believed to result in the presence of currently used pesticides in water from undeveloped streams: (1) past use in small areas of developed land within their watersheds, (2) past use for control of insects in undeveloped areas (such as for forest management), and (3) atmospheric transport from other areas.

Fish and bed sediment from streams draining watersheds with mixed land use had frequencies of detection of DDT, dieldrin, and chlordane that generally reflected a mixture of agricultural and urban influences, and were higher than in undeveloped streams (fig. 4–4).

Influence of Land Use

The preceding overviews of detection frequencies clearly show that pesticide occurrence in streams and ground water is strongly influenced by land use and associated pesticide use. These relations are explored in more detail below, focusing on the occurrence of some of the pesticides that were detected most frequently in agricultural and urban settings.

Agricultural Areas

The pesticides detected most often in water from agricultural streams (fig. 4–2) were among the agricultural herbicides used most heavily during the study period (figs. 4–3 and 3–5). The top five, from highest to lowest frequency of detection at concentrations at or above 0.1 µg/L, were atrazine (ranked 1st in national agricultural use; deethylatrazine was also frequently detected), metolachlor (2nd in use), cyanazine (8th in use), 2,4-D (3rd in use), and simazine (18th in use). Prometon was detected frequently at low levels (rarely at concentrations greater than 0.1 µg/L) and ranked only behind atrazine, metolachlor, simazine, and cyanazine in total detection frequency. Prometon is not registered for use on crops, but is used for weed control around fences, buildings, and roads within agricultural areas.

As with streams, the pesticides most commonly found in shallow ground water within agricultural areas were atrazine (and deethylatrazine) and metolachlor, the two herbicides used most heavily for agriculture during the study period. Although atrazine and metolachlor had about the same total use, atrazine and deethylatrazine were found in ground water more than twice as often as metolachlor, probably because atrazine is considerably more persistent than metolachlor (as discussed in more detail later in this chapter). Deethylatrazine was detected in ground water about as frequently as atrazine, whereas in streams it was found less often than atrazine and usually at lower levels. The greater proportional occurrence of deethylatrazine in ground water reflects the greater opportunity for atrazine degradation over the longer periods of time that water in the subsurface spends in contact with microbes, especially in the soil zone (as discussed further in Chapter 5). Cyanazine, alachlor, and acetochlor—which are used on corn and other crops, but in less than half the amounts of atrazine and metolachlor—were seldom detected in ground water, most likely because of their lower use and relatively low persistence (Appendix 2). In contrast, simazine and prometon were among the pesticides found most often in ground water, despite even lower agricultural use than cyanazine, alachlor, or acetochlor. Simazine and prometon are more persistent in soil than these other herbicides, and thus have greater opportunities for transport to ground water.

Currently used insecticides were found less frequently than herbicides in most agricultural streams and were rarely found in ground water. This finding results from their relatively low application rates in most agricultural settings, compared with herbicides (fig. 3–5), and their generally lower mobility and persistence in the environment (Appendix 2). The insecticide used most heavily for agricultural purposes during the study period was chlorpyrifos. Yet, annual use of chlorpyrifos was only about 20 percent that of atrazine use, and chlorpyrifos is also less mobile in the hydrologic system. Although the annual agricultural use of each of the other four major insecticides examined—diazinon, carbofuran, carbaryl, and malathion—was less than half that of chlorpyrifos during the study period, the total detection frequencies of all five insecticides in agricultural streams were notably similar.

Historically used organochlorine pesticides and their degradates and by-products remained a common occurrence in fish and bed sediment in agricultural streams, although most were detected less frequently in samples from agricultural streams than from urban streams—especially in sediment (fig. 4–4). The compounds found most commonly in agricultural streams were those in the DDT group, followed by dieldrin and the chlordane group. Relative frequencies of detection corresponded to their rankings of historical use in agriculture (fig. 4–5). The frequency of occurrence of compounds in the chlordane group in agricultural streams was higher than expected from its low historical agricultural use compared with DDT plus DDD and dieldrin plus aldrin—possibly because of extensive nonagricultural applications in agricultural areas (such as termite control). In addition, chlordane was a minor component (10–20 percent) of technical-grade heptachlor, which was also used extensively both in agriculture and as a termiticide (IARC, 2001).

Although these broad patterns in pesticide occurrence across all agricultural areas that were sampled provide a useful national perspective, the aggregated results obscure many substantial differences among different agricultural settings in the types and levels of pesticides that were detected. The many diverse agricultural settings of the United States that were sampled—each with its own unique combination of climate, crops, and pests—have distinctive patterns in pesticide use that resulted in different patterns of pesticide occurrence. These patterns of occurrence are complex because of the wide ranges of different use practices, pesticide properties, and hydrologic processes that govern the sources, movement, and persistence of pesticides in streams and ground water.

Comparisons of patterns in pesticide occurrence among three of the Nation's major crop-group settings illustrate the variability among settings. Classification of the Nation's agricultural areas for the NAWQA water-quality studies identified 21 major crop-group settings of varying areal extent (Gilliom and Thelin, 1997). This classification is based on combinations of one to three crops that account for most of the harvested acreage in each of the Nation's counties. Three crop-group settings were selected as examples for comparison in this report: "corn and soybeans," "wheat and alfalfa," and "rice." Each crop-group setting has a different geographic distribution and extent (fig. 4–6). Other crops are also present to varying degrees in each of the three settings; thus, the estimated use of a pesticide in a particular crop setting may also include its estimated use for other crops in the same area.

Estimates of pesticide use intensity, expressed as an annual average rate of application on all cropland in each crop-group setting, show clear differences between the settings (fig. 4–7). Overall rates of use were highest in the corn-and-soybeans setting and lowest in the wheat-and-alfalfa setting. Use in each setting is dominated by the particular herbicides and insecticides needed to control the pests specific to the crops grown in that setting. For example, atrazine and metolachlor dominated herbicide use in the corn-and-soybeans setting; 2,4-D was the top herbicide used in the wheat-and-alfalfa setting

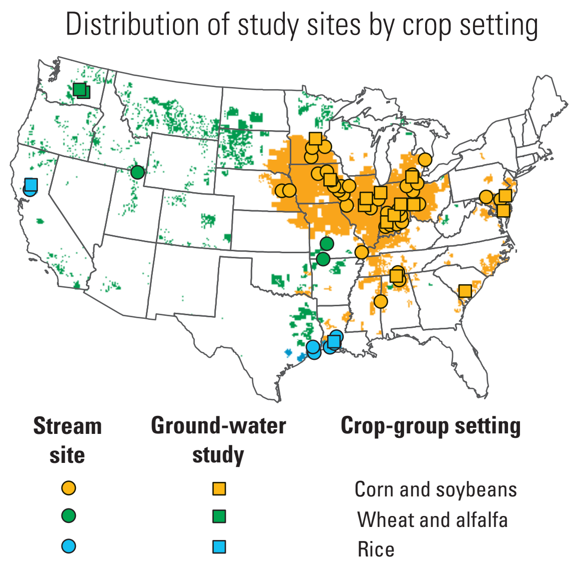

Figure 4–6. The distributions of crop-group settings and study sites for the corn-and-soybeans, wheat-and-alfalfa, and rice crop groups show distinct differences in the locations and extent of the three agricultural settings. (Crop groups are from Gilliom and Thelin, 1997.)

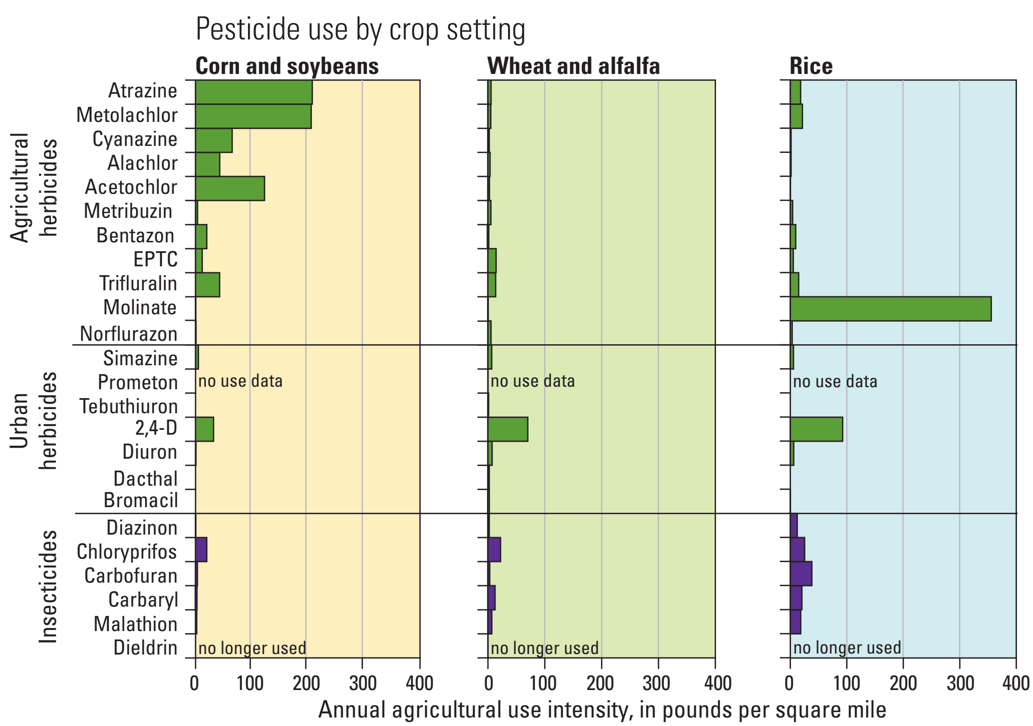

Figure 4–7. Different pesticides dominated use in each of the crop-group settings, as illustrated by the estimated 1997 agricultural use. The herbicides atrazine, metolachlor, acetochlor, and cyanazine were the most intensively used pesticides in the corn-and-soybeans setting; molinate, 2,4-D, and several insecticides were most intensively used in the rice setting; and 2,4-D and chlorpyrifos were the most intensively used pesticides in the wheat-and-alfalfa setting, where overall use was least.

Chapter 4

(but at less than half the intensity of atrazine and metolachlor use in the corn-and-soybeans setting); and molinate was the top herbicide used in the rice setting (with use intensity that was 70 percent greater than that of either atrazine or metolachlor in the corn-and-soybeans setting).

The occurrence of pesticides in streams and ground water within these three crop settings (fig. 4–8) corresponded to the estimated agricultural-use patterns in many respects (fig. 4–7), but also showed some unexpected results, as summarized below. These examples of results for specific crop-group settings illustrate both the degree of predictability and the complexity of pesticide occurrence and transport in the hydrologic system. Each crop setting has unique characteristics, and each specific study area within a crop setting is unique as well, resulting in variability within crop-group settings as well as among them. Nonetheless, organizing the assessment of pesticides by crop-group setting can help to link the occurrence of pesticides in streams and ground water with specific management practices and can provide the foundation for customizing pesticide management to individual settings.

Photographs by Don Brennemen, University of Minnesota Agricultural Extension Service (middle), and © 2003 Corbis (top).

Expected results:

- *Corn and soybeans*—The two herbicides used most heavily for corn and soybeans—atrazine and metolachlor—were those detected most frequently in streams and ground water. In addition, deethylatrazine was detected at about the same frequency as atrazine in both streams and ground water within this setting. Chlorpyrifos was both the most frequently detected and the most heavily used insecticide.
- *Wheat and alfalfa*—Overall detection frequencies were low in the wheat-and-alfalfa setting, consistent with relatively low pesticide use. The herbicide used most heavily in the wheat-and-alfalfa setting, 2,4-D, was one of the most frequently detected pesticides in streams at concentrations at or above 0.1 µg/L.
- *Rice*—Molinate, the herbicide used most heavily on rice, was among those detected most frequently in streams. Detections of molinate were far more frequent in the rice setting than in the other agricultural settings. The insecticide used most intensively on rice, carbofuran, was the one detected most frequently at or above 0.1 µg/L in both streams and ground water. Carbofuran and the other four insecticides used mostly in the rice setting were detected more frequently in the rice setting than in the other two crop-group settings, where their use was less intensive.

Unexpected results:

- *Corn and soybeans*—Simazine and prometon were found more frequently than was expected from their low agricultural use, indicating relatively substantial use of these herbicides for noncrop purposes within agricultural areas (although most concentrations were low).
- *Wheat and alfalfa*—Atrazine and prometon were the herbicides detected most frequently in streams and ground water, despite little (atrazine) or no (prometon) agricultural use on either wheat or alfalfa (although most concentrations were low).
- *Rice*—Low-use pesticides, including atrazine (and deethylatrazine), metolachlor, and tebuthiuron, were frequently detected, probably because of noncrop uses within this setting. Bentazon was frequently detected in streams and particularly in ground water. Bentazon was detected most frequently in the rice-growing area of California, where it was used heavily until it was banned in 1989.

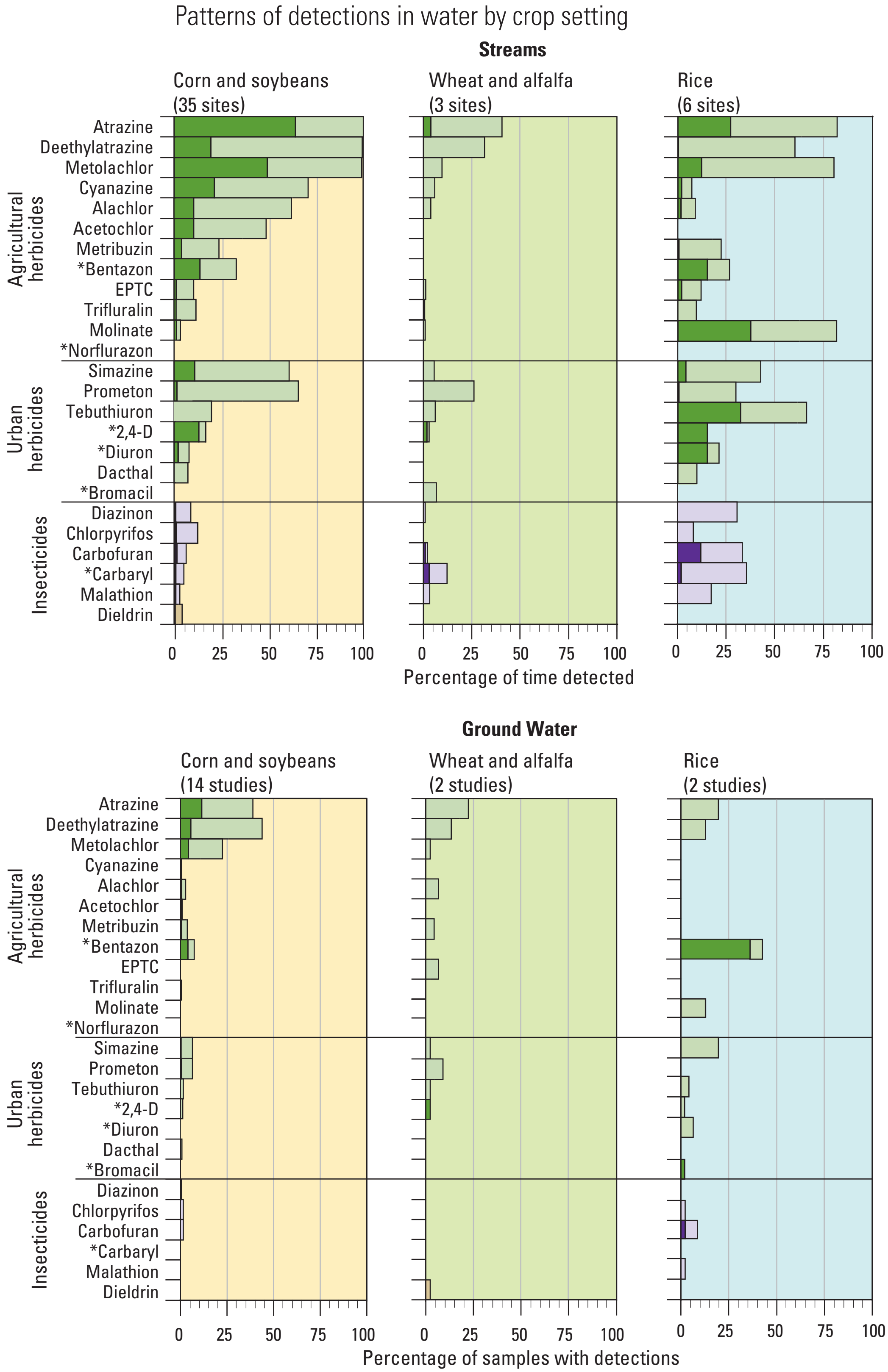

Figure 4–8. The occurrence of pesticides in streams and ground water sampled within the corn-and-soybeans, wheat-and-alfalfa, and rice crop-group settings corresponded to the patterns of estimated agricultural use in many respects (see fig. 4–7), but nonagricultural uses also influence occurrence. The dark portion of each bar indicates detections at concentrations greater than or equal to 0.1 µg/L , the light portion indicates detections less than 0.1µg/L*, and the end of each bar is the total for all detections (see sidebar on p. 45.)

*The pesticides 2,4-D, bentazon, bromacil, carbaryl, diuron, and norflurazon could not be detected reliably at concentrations less than 0.1 µg/L, and the reported frequencies below this level for these compounds are minimum estimates.

Urban Areas

The most distinct differences between pesticides found in urban and agricultural areas were the more frequent detections and higher concentrations of insecticides in urban streams, and the frequent detections of urban herbicides in streams and shallow ground water sampled in urban areas.

Diazinon, chlorpyrifos, carbaryl, and malathion, which nationally ranked 2nd, 4th, 8th, and 15th among pesticides in frequencies of outdoor applications for home-and-garden use at the beginning of the study period (Whitmore and others, 1992), accounted for most detections of insecticides in urban streams (fig. 4–2). Diazinon and carbaryl were by far the most frequently detected and were found at frequencies and levels comparable to those for the common herbicides. The use of diazinon and chlorpyrifos has been substantially curtailed since the end of the study period, and analysis of recent data for diazinon (Chapter 8) shows that concentrations in some streams have now declined as well. Historically used insecticides also were found most frequently in fish and bed sediment from urban streams, which had among the highest detection frequencies for chlordane compounds, DDT compounds, and dieldrin (fig. 4–4). Urban streams also had the highest concentrations of total chlordane and dieldrin in both sediment and fish tissue. Chlordane and aldrin were widely used for termite control until the mid-to-late 1980s, although their agricultural uses were restricted during the 1970s.

Insecticides were seldom detected in ground water beneath urban areas (fig. 4–2). The most commonly detected insecticide in shallow ground water in urban areas, however, was dieldrin, which was found in about 5 percent of the wells sampled. Although dieldrin is not very mobile in water, its environmental persistence and the extensive historical use of dieldrin and aldrin have apparently combined to yield detectable concentrations in some wells 5 to 15 years after all uses of dieldrin and aldrin were discontinued.

The most frequently detected herbicides in streams and shallow ground water in urban areas were atrazine (and deethylatrazine), simazine, prometon, and metolachlor, although metolachlor was seldom detected in ground water—probably because of its lower urban use and lower persistence compared with the other herbicides. Considering only detections at or above 0.1 µg/L, however, the herbicides detected most frequently in urban streams were diuron (14 percent of the time), simazine (14 percent), 2,4-D (11 percent), and atrazine (10 percent).

The herbicides found more often in urban areas than in most agricultural areas—considering detections at all concentrations—were simazine, prometon, diuron, 2,4-D, tebuthiuron, and dacthal. The use of 2,4-D and prometon ranked 1st and 14th among herbicides in frequency of outdoor home-and-garden applications at the beginning of the study period (Whitmore and others, 1992). Although 2,4-D, simazine, and diuron also ranked 3rd, 18th, and 23rd among herbicides in national use for agriculture, no agricultural use was reported for prometon or tebuthiuron.

Pesticides are used extensively in residential areas and associated recreational and commercial areas, including golf courses.

Geographic Distribution

The geographic distribution of each pesticide in streams and ground water is governed by the intensity and distribution of its use, its chemical and physical properties, and the characteristics of the hydrologic system. The interactions among these factors are illustrated by comparing the findings for several different pesticides in relation to their uses and properties. Results for five pairs of the most frequently detected pesticides are presented—atrazine and metolachlor; simazine and prometon; acetochlor and 2,4-D; diazinon and chlorpyrifos; and total DDT and dieldrin—representing a wide range of use patterns and properties (figs. 4–9 to 4–16). These comparative stories provide insights about some of the most important pesticides, while also illustrating the types and magnitudes of influences that affect all pesticides.

Methods and Statistics for Assessing Geographic Distributions of Pesticides

Consistent measures and scales are used to represent concentration levels appropriate to each medium in the comparisons of geographic distributions among pesticides (figs. 4–9 to 4–16):

- For pesticides in stream water, maps in this chapter are based on the time-weighted 95th-percentile concentration at each site for the selected year of data, which is the concentration exceeded about 5 percent of the time, or about 18 days per year (generally not consecutive). Use of the 95th percentile for comparisons reduces the influence of different detection levels among compounds because it is usually higher than the lowest detectable concentration.

- For pesticides in ground water, maps in this chapter are based on the frequency of detections at or above 0.01 µg/L within each study area. Evaluation of each of the pesticides using only detections at or above the detection level of 0.01 µg/L yields results that are directly comparable among all pesticides mapped for ground water. Symbols representing ground-water studies are shown at the centroid of each study area.

- For total DDT and dieldrin in streams, data for bed sediment are used because fish were not collected in all parts of the country. One composite bed-sediment sample was collected at each site—maps are based on the concentration in each individual sample.

- For all maps, the distribution of agricultural use for each pesticide is shown by a consistent set of categories of 1997 use intensity—or historical use intensity for total DDT and dieldrin—so that maps can be directly compared among the 10 pesticides. Use was estimated for 1997 by combining the 1997 state-level use data reported by Gianessi and Marcelli (2000) with county crop acreages from the 1997 Census of Agriculture (U.S. Department of Agriculture, 1999), using methods described by Thelin and Gianessi (2000). Use intensity was mapped for agricultural land using land-cover data from the early 1990s (Vogelmann and others, 2001) as described by Nakagaki and Wolock (2005). Historical use of DDT (including DDD) and dieldrin (including aldrin) was estimated by a similar approach, but using regional use estimates for 1966 (Eichers and others, 1970) and 1971 (Andrilenas, 1974), and the 1964 and 1969 Censuses of Agriculture for crop distributions (Nowell and others, 2006). Use intensity was mapped for agricultural land using land-cover data from the mid-1970s (Fegeas and others, 1983).

- Chemical and physical properties that help explain observed patterns were introduced in Chapter 2 and are tabulated in Appendix 2. The properties emphasized are environmental persistence (soil half-life) and mobility in water (represented by the soil organic carbon-water partition coefficient, or K_{oc}). The higher the K_{oc} value, the greater the affinity of the compound for soil organic matter, suspended particles, and bed sediment—and, thus, a lower tendency to be transported in water.

Atrazine and Metolachlor—

The two most heavily used herbicides occurred at similar levels in streams, but atrazine was more prevalent than metolachlor in ground water, probably because of its greater persistence.

Atrazine and metolachlor were the two most heavily used herbicides in the United States during the 1990s. Most of their agricultural use was associated with corn production—about 85 percent of 75 million lb/yr for atrazine and 75 percent of 67 million lb/yr for metolachlor (fig. 4–3). Both herbicides also have relatively low and poorly quantified nonagricultural use—atrazine is estimated at less than 1 million lb/yr (USEPA, 2003a). Uses of metolachlor include turf, nurseries, fence rows, and landscaping, and uses of atrazine include conifer forestry, Christmas tree farms, sod, golf courses, and residential lawns (particularly in the South). Both atrazine and metolachlor are highly soluble and mobile in water, but atrazine is more persistent than metolachlor, with a soil half-life of 146 days, compared with 26 days for metolachlor (Appendix 2).

Concentrations of both atrazine and metolachlor in agricultural streams closely matched the geographic distribution of corn cultivation, where applications are greatest (fig. 4–9). Both atrazine and metolachlor were also frequently detected in urban streams, but at substantially lower concentrations compared with agricultural streams in high-use areas, except in parts of the South where atrazine is used on turf grasses. Concentrations in streams draining watersheds with mixed land use most closely resembled those in agricultural streams, in large part because many of these streams have watersheds with relatively high proportions of agricultural land.

In contrast to their similarity in streams, patterns of atrazine and metolachlor were different from each other in ground water (fig. 4–10). Metolachlor was detected less frequently than atrazine, regardless of land use or depth of ground water. This difference probably occurs because metolachlor transforms more quickly in soil than does atrazine. Metolachlor, therefore, is less likely to be transported to ground water, although the opposite may be true for some of its degradates that appear to be more persistent than the parent compound (Kalkhoff and others, 1998). Neither metolachlor nor atrazine was detected at the highest frequencies (> 25 percent) in ground water underlying large areas of Illinois, Indiana, and Ohio, despite their high use in this region. This distinct regional pattern, which has been noted by several previous studies (Hallberg, 1989; Burkart and Kolpin, 1993; Baker and others, 1994), is most likely a consequence of the widespread use of subsurface drainage systems in this area (which move shallow ground water rapidly to streams and reduce transport to deeper ground water), as well as the presence of low-permeability glacial till.

Atrazine and metolachlor were heavily used on cropland throughout the Corn Belt during the study period.

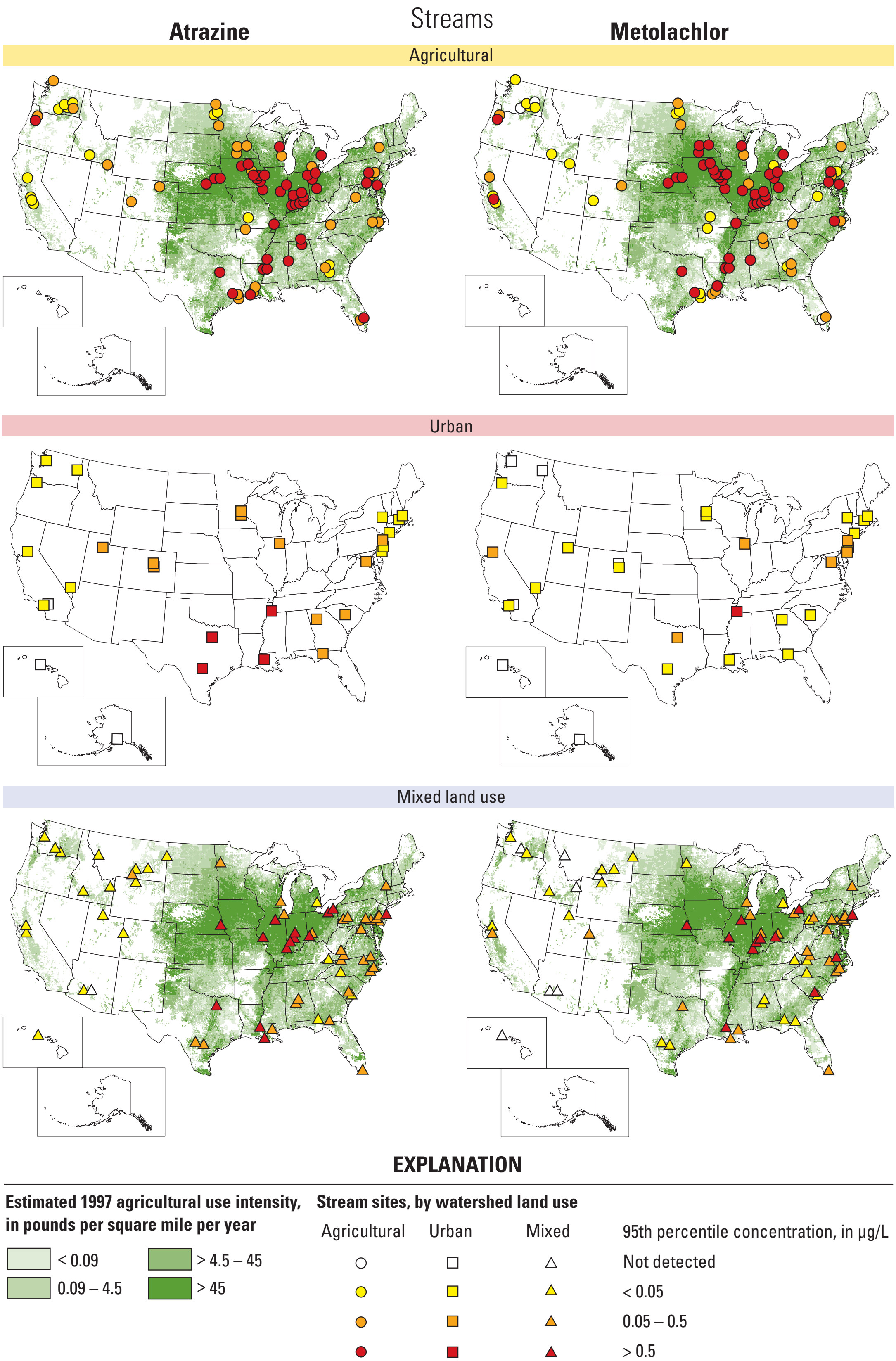

Figure 4–9. Concentrations of both atrazine and metolachlor in agricultural streams closely matched the geographic distribution of their use on crops. Both atrazine and metolachlor were also often found in urban streams, but at substantially lower concentrations compared with most agricultural streams. An exception is atrazine in some urban streams in parts of the South where atrazine was used on turf grasses. Agricultural use for 1997 was estimated as described in the “Methods” sidebar on p. 53.

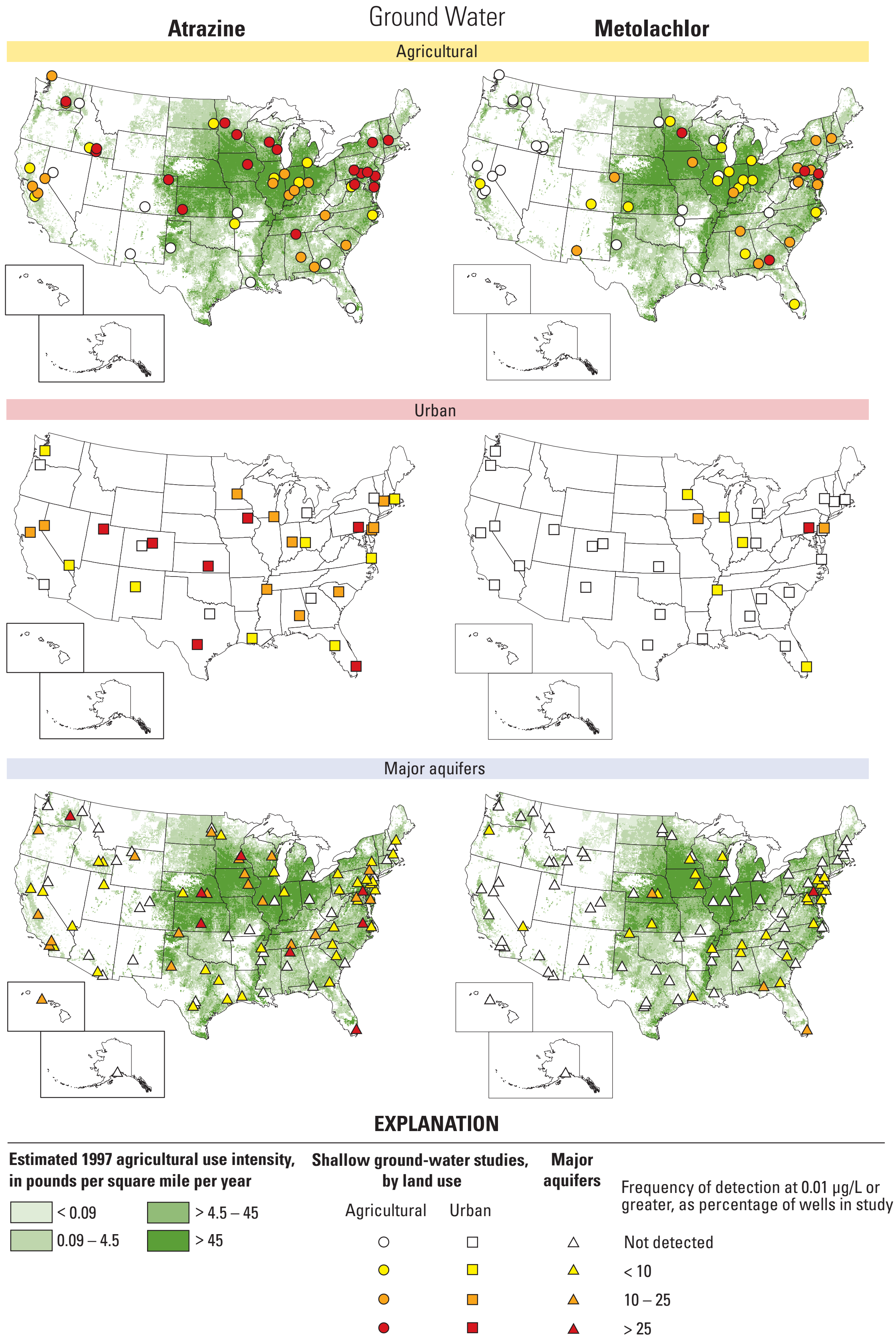

Figure 4–10. Patterns of atrazine and metolachlor detections were different from each other in ground water, although both were detected less frequently than expected in the central Corn Belt where the intensity of use was greatest. Metolachlor was detected less frequently than atrazine, regardless of land use or depth of ground water, probably because metolachlor is less persistent in soil than atrazine. Agricultural use for 1997 was estimated as described in the “Methods” sidebar on p. 53.

Simazine and Prometon—

Although prometon is not registered for agricultural use, it frequently occurred in agricultural streams and ground water, probably because of use for nonagricultural purposes in those areas and its high persistence.

Simazine and prometon are commonly used herbicides that, compared with atrazine and metolachlor, had lower total use and higher proportions of nonagricultural use during the study period. About 5 million lb/yr of simazine were applied for agricultural purposes nationwide (fig. 4–3), compared with about 75 and 67 million lb/yr of atrazine and metolachlor, respectively. Relative to atrazine and metolachlor, simazine is used on a wider variety of crops—including corn (about 40 percent of total use), citrus orchards (about 35 percent), and other orchards and vineyards (about 20 percent). Nonagricultural uses of simazine include applications to turf grasses and lawns, roadsides and other rights-of-way, and nurseries. Prometon is not registered for agricultural use, but is applied for nonagricultural purposes—albeit in small amounts—for bare-ground weed control around buildings, storage areas and fences, as well as along roadways, railroads, and other rights-of-way. Both simazine and prometon are highly soluble and mobile in water, but prometon is more persistent than simazine, with a soil half-life of 932 days, compared with 91 days for simazine (Appendix 2).

The occurrence of simazine in agricultural and urban streams was consistent with its geographic patterns of use (fig. 4–11), particularly in comparison to the more heavily used atrazine (fig. 4–9). For example, concentrations of simazine in agricultural streams in the Corn Belt were notably lower than concentrations of atrazine, reflecting the lower use of simazine on corn. On the other hand, detection frequencies and concentrations of simazine in urban streams were nearly identical to those of atrazine, reflecting generally similar nonagricultural use. Prometon was detected less frequently than simazine in agricultural streams, at lower concentrations, and without the geographic patterns that follow use on crops. The prometon detections in agricultural areas probably result from nonagricultural applications in these areas. In urban streams, prometon was detected at frequencies similar to those observed for simazine, atrazine, and diazinon—although at somewhat lower concentrations (see figs. 4–11, 4–9, and 4–14, respectively). The most likely explanation for the frequent occurrence of prometon is that its high persistence (10 times that of simazine and more than 5 times that of atrazine) results in its prolonged presence in watersheds.

The occurrence and concentrations of simazine in ground water (fig. 4–12) were consistent with patterns observed for atrazine and metolachlor (fig. 4–10). Like atrazine and metolachlor, detection frequencies were relatively low in shallow ground water beneath agricultural areas in Illinois, Indiana, and Ohio relative to other high use areas—probably because of the common use of subsurface drainage systems and widespread presence of glacial till in this region (noted earlier). Simazine was generally detected more frequently than atrazine and metolachlor in Florida and California, which is consistent with its higher use in orchards and vineyards in those areas. Prometon, consistent with its lack of registered agricultural uses, was detected less frequently than simazine in shallow ground water in agricultural areas. In most urban study areas, prometon was detected at similar or greater frequencies than simazine in shallow ground water.

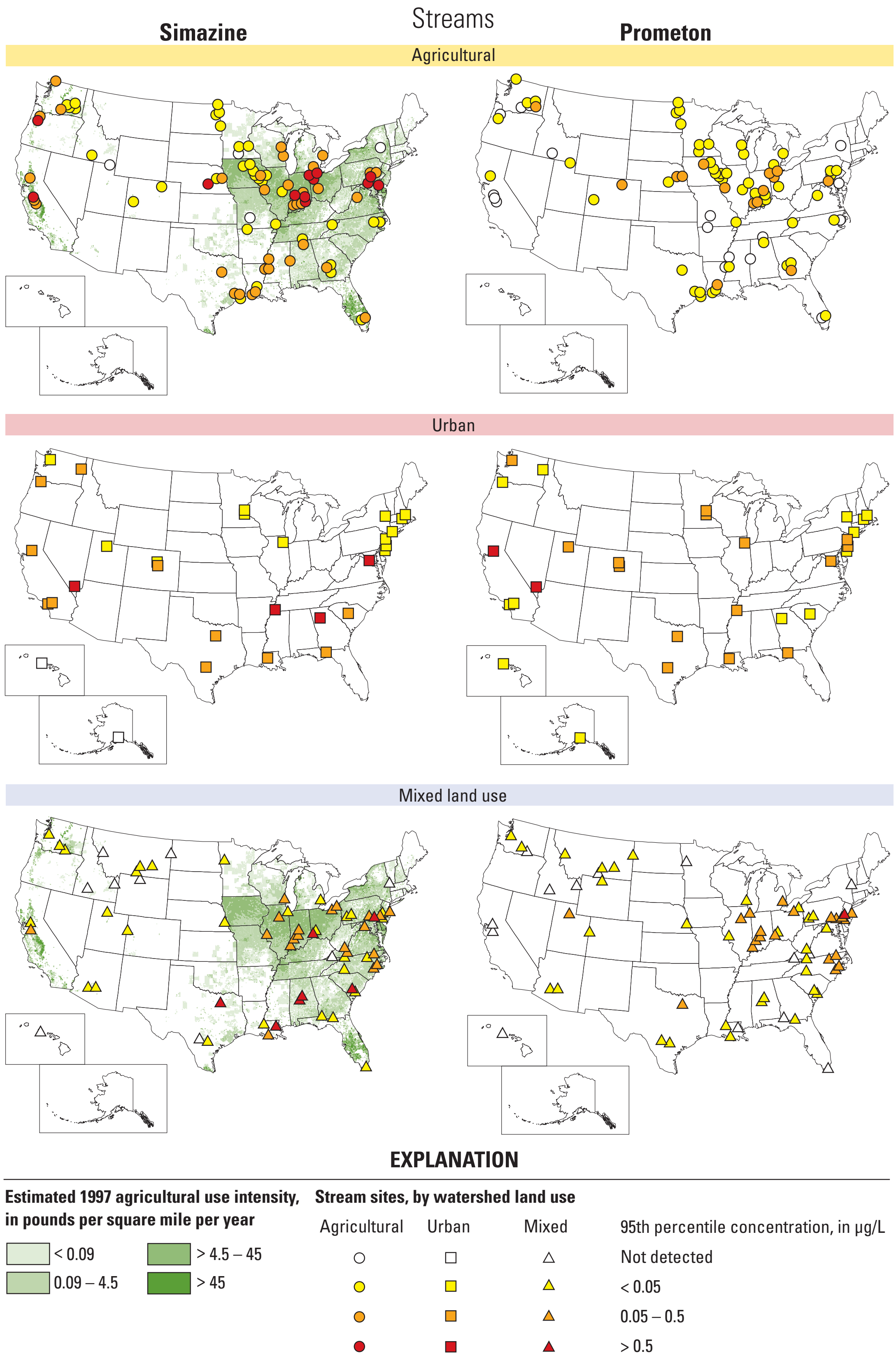

Figure 4–11. The occurrence and concentrations of simazine in agricultural and urban streams were consistent with its use, particularly in comparison with the more heavily used atrazine (fig. 4–9.) Prometon was detected less frequently than simazine in agricultural streams, at lower concentrations, and without the geographic patterns that follow use on specific crops. Prometon is not registered for agricultural use and no estimates of agricultural use are shown. Agricultural use of simazine for 1997 was estimated as described in the "Methods" sidebar on p. 53.

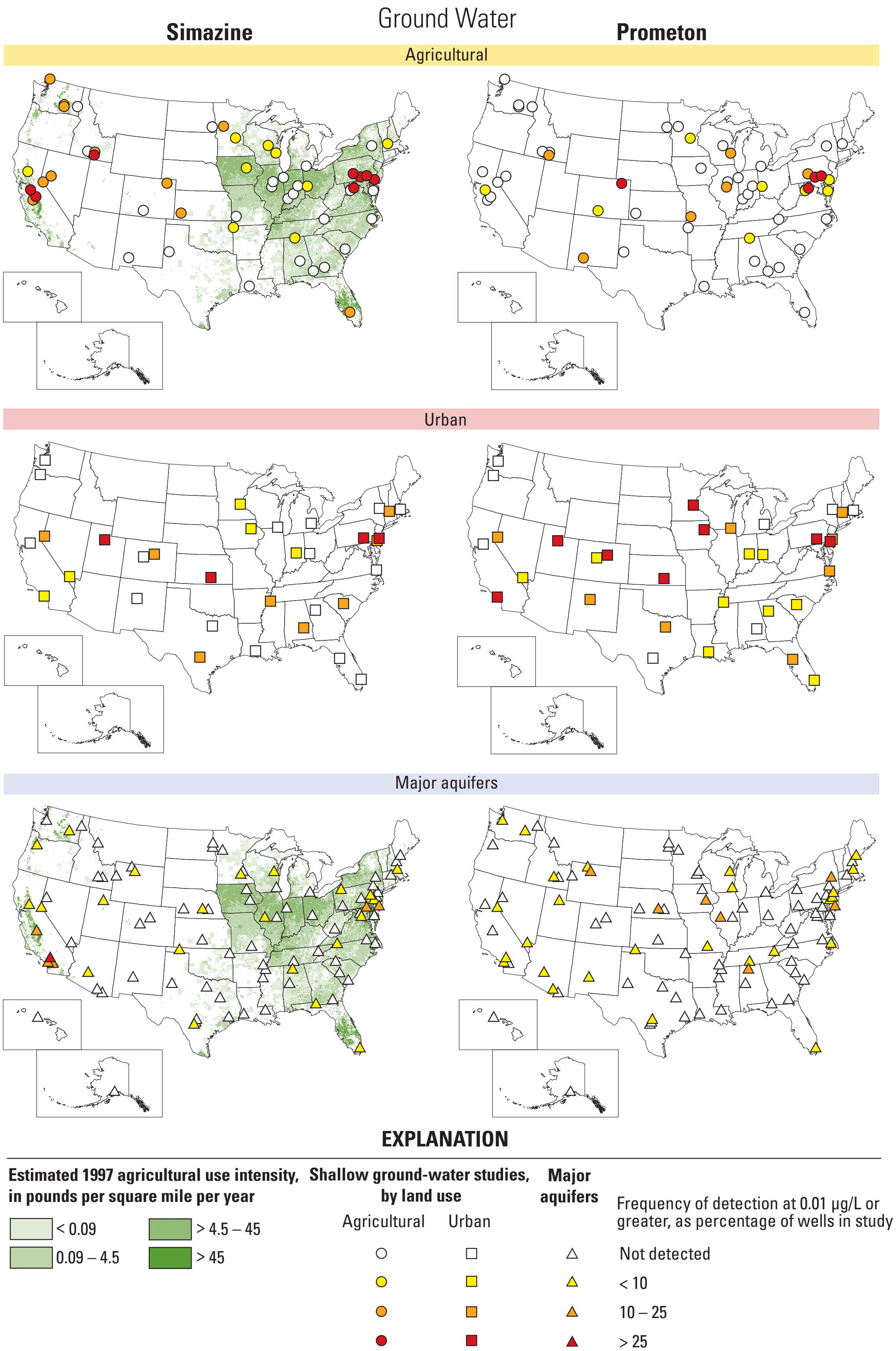

Figure 4–12. The occurrence of simazine in ground water was less frequent than atrazine and metolachlor (fig. 4–10), but the relative patterns were similar, including relatively low detection frequencies in shallow ground water beneath agricultural areas in Illinois, Indiana, and Ohio, compared with other high-use areas around the Nation. Prometon was detected less frequently than simazine in shallow ground water within agricultural areas. Prometon is not registered for agricultural use and no estimates of agricultural use are shown. Agricultural use of simazine for 1997 was estimated as described in the "Methods" sidebar on p. 53.

2,4-D and Acetochlor—

These two herbicides, which have relatively similar chemical and physical properties, have different geographic patterns of occurrence in streams because of their different use patterns.

The herbicides 2,4-D and acetochlor ranked 3rd and 5th in national agricultural use during the study period (about 41 and 33 million lb/yr, respectively, in 1997; fig. 4–3), but their use is distributed differently. Acetochlor, which is a relatively new pesticide introduced in 1994, is used only on corn, whereas 2,4-D is widely applied for multiple agricultural purposes, including weed control for pasture (accounting for about 40 percent of use), wheat (20 percent), corn and soybeans (17 percent), as well as other crops and fallow land. In addition, 2,4-D has the highest documented nonagricultural use of any pesticide (nearly 30 million lb/yr; fig. 4–3). Both 2,4-D and acetochlor are relatively soluble and mobile in water and neither is particularly persistent, with soil half-lives of 7 and 14 days, respectively.

The occurrence and concentrations of these two compounds in agricultural and urban streams were generally consistent with their patterns of use (fig. 4–13). Specifically, relatively high concentrations of 2,4-D occurred in agricultural streams across the Nation in various high-use areas, whereas the highest concentrations of acetochlor were generally in the heart of the Corn Belt and in other corn-growing areas. Also consistent with their use patterns, 2,4-D concentrations were higher in urban streams than concentrations of acetochlor. Infrequent low-level detections of acetochlor in some urban streams may result from relatively minor agricultural use within the predominantly urban watersheds or atmospheric transport from nearby agricultural areas.

Geographic results for 2,4-D and acetochlor are not presented for ground water because both pesticides were detected in less than 1 percent of the wells sampled (fig. 4–2). Their infrequent occurrence in ground water is probably a result of their low persistence. For acetochlor, this hypothesis is supported by the more frequent detection of at least two of its degradates in ground water—relative to acetochlor itself—in some studies (for example, Kalkhoff and others, 1998; Groschen and others, 2004).

2,4-D was a commonly used herbicide during the study period on croplands where wheat is grown (Photograph copyright by Phil Schofield).

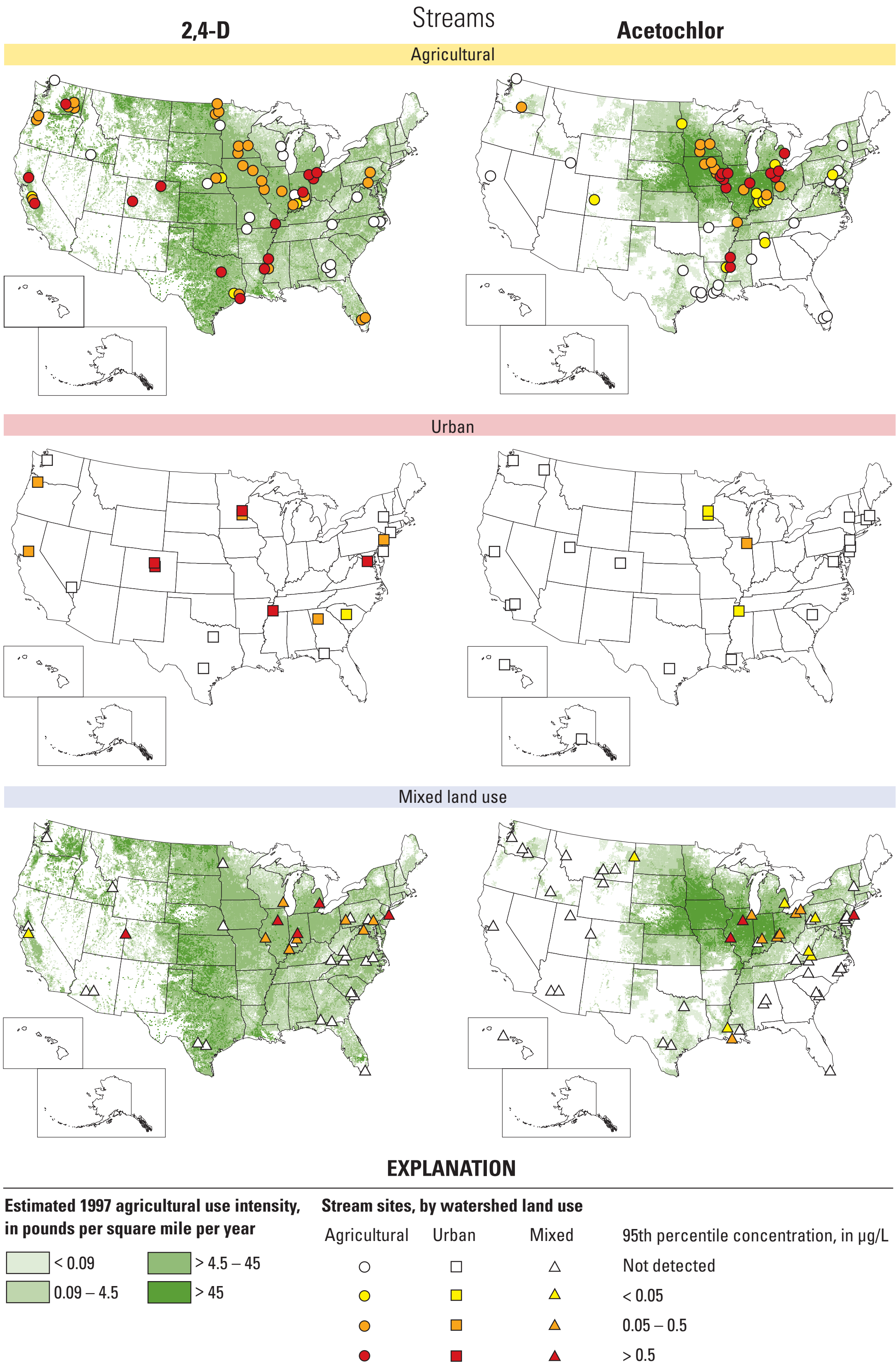

Figure 4–13. The occurrence and concentrations of 2,4-D and acetochlor in agricultural streams were generally consistent with their patterns of use. Relatively high concentrations of 2,4-D were observed in agricultural streams across the Nation, whereas elevated concentrations of acetochlor were generally observed in the heart of the Corn Belt and in other corn-growing areas. In urban streams, 2,4-D concentrations were generally higher than those of acetochlor. Agricultural use for 1997 was estimated as described in the "Methods" sidebar on p. 53.

Chlorpyrifos and Diazinon—

Despite greater use, chlorpyrifos was found less frequently than diazinon in water, probably because of its greater affinity for particles and resulting lower mobility in water.

Chlorpyrifos and diazinon are insecticides that were commonly used in both agricultural and urban areas during the study period. About 13 million lb of chlorpyrifos were applied to crops in 1997, mostly on corn and cotton (accounting for more than 50 percent of national use), with the remainder on alfalfa, peanuts, wheat, tobacco, and orchards. Less diazinon was used for agriculture (about 1 million lb in 1997), mostly for a wide variety of fruits, nuts, and vegetables (fig. 4–3). Nonagricultural uses of chlorpyrifos and diazinon totaled about 5 million and 4 million lb/yr in 2001, respectively (fig. 4–3). Both diazinon and chlorpyrifos are substantially less mobile in water than the six herbicides just discussed, but chlorpyrifos has a greater affinity for soil organic matter and particles (higher K_{oc}) than diazinon and, thus, a lower solubility and mobility in water. Both pesticides have similar half-lives in soil—39 days for diazinon and 31 days for chlorpyrifos (Appendix 2).

The geographic distributions of these insecticides in agricultural and urban streams were consistent with their patterns of use (fig. 4–14). Of agricultural streams, the highest concentrations of chlorpyrifos were in streams draining the corn-growing areas of the central United States and the lower Mississippi River Basin, where both corn and cotton are grown, and in streams draining orchard areas in the West. Concentrations of diazinon in agricultural streams were highest in parts of the West where it is intensively used on fruits, nuts, and vegetables. For both insecticides, concentrations in most urban streams were higher than in most agricultural streams, and were similar to those found in agricultural areas with the greatest intensities of use.

In urban streams, diazinon was detected about 75 percent of the time, compared with about 30 percent for chlorpyrifos (fig. 4–2), even though their nonagricultural use was similar. In addition, 95th-percentile concentrations equaled or exceeded 0.05 µg/L in 23 of 30 urban streams for diazinon, compared with only 3 streams for chlorpyrifos. In agricultural streams, both chlorpyrifos and diazinon were found at relatively similar frequencies and concentrations, despite the 10-fold higher use of chlorpyrifos. The markedly greater occurrence of diazinon in proportion to use, compared with chlorpyrifos, may be explained by the greater solubility and mobility of diazinon in water. Because chlorpyrifos has a greater affinity for organic matter than diazinon, however, there may have been substantial occurrence and transport of chlorpyrifos in suspended sediment in streams that was not observed. As discussed in Chapter 3, all NAWQA stream-water samples were filtered prior to analysis.

Chlorpyrifos and diazinon were rarely detected in ground water (less than 1 percent of samples; fig. 4–2), so their geographic distributions are not shown. This infrequent occurrence is explained by their relatively low persistence and low water solubility, as well as their low use compared with the major herbicides.

Chlorpyrifos was commonly used on cotton during the study period.

Both chlorpyrifos and diazinon were used on apples and other orchard crops during the study period.

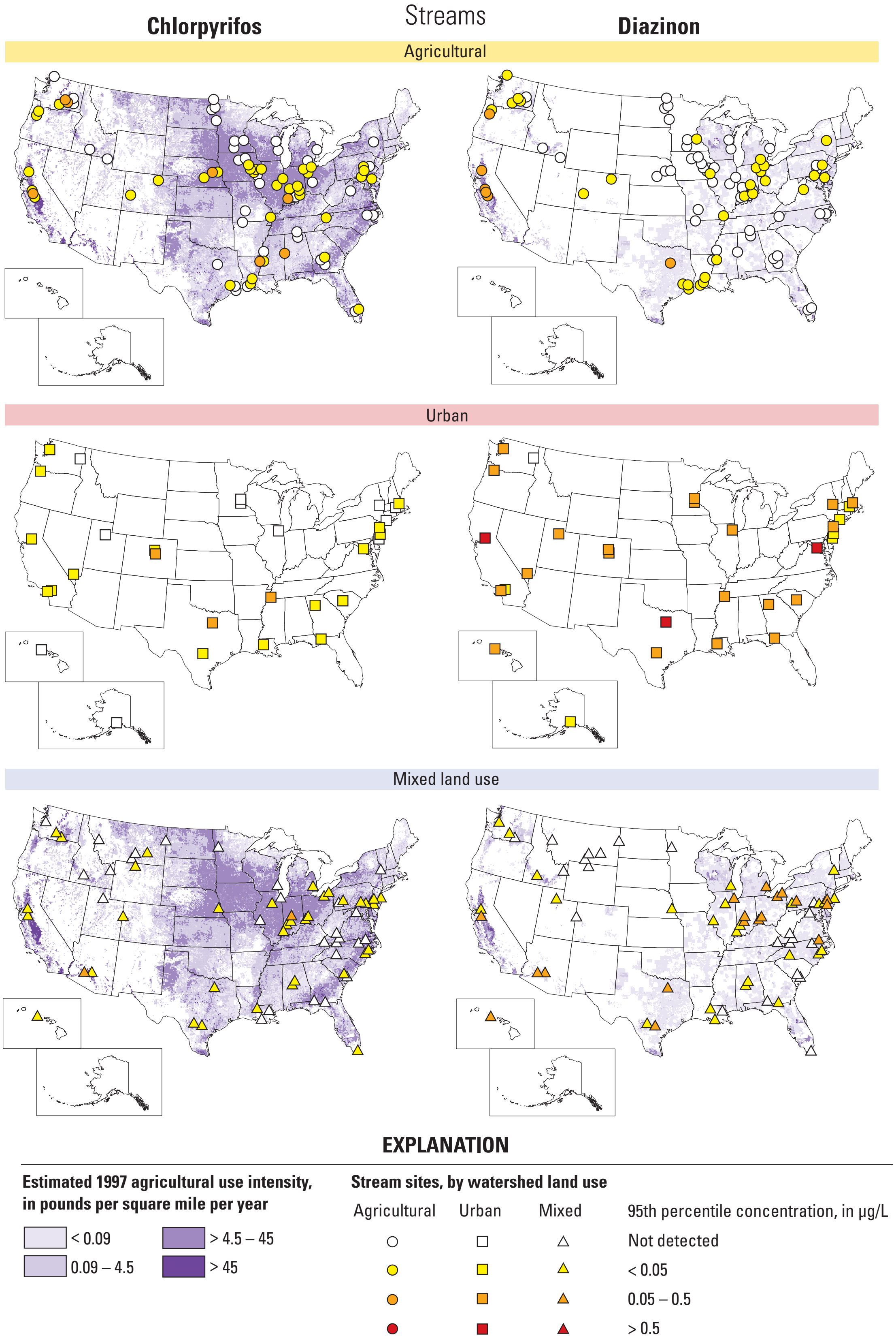

Figure 4–14. Concentrations of diazinon, and to a lesser degree chlorpyrifos, in most urban streams were greater than concentrations in most agricultural streams. Concentrations of diazinon in urban streams were generally similar to those found in agricultural areas with the greatest intensities of agricultural use. The highest concentrations of diazinon in agricultural streams were found in the West where it was used on fruits, nuts, and vegetables. The highest concentrations of chlorpyrifos in agricultural streams were detected in corn-growing areas of the central United States; the lower Mississippi River Basin, where both corn and cotton are grown; and in streams draining orchard areas in the West. Agricultural use for 1997 was estimated as described in the "Methods" sidebar on p. 53.

DDT and Dieldrin in Bed Sediment—

The geographic distributions of these historically used insecticides follow their past agricultural use and indicate that use in urban areas probably was substantial.

Although the parent pesticides were not used in the United States for about 5–20 years prior to the beginning of the study period, compounds in the DDT group and dieldrin were frequently detected in bed sediment. In 1966, the combined agricultural use of DDT and DDD was about 30 million lb (fig. 4–5), with 66 percent used on cotton, 9 percent on tobacco, 8 percent on peanuts, and 17 percent on orchards, soybeans, vegetables, potatoes, and other crops. The combined agricultural use of dieldrin and aldrin (aldrin rapidly transforms to dieldrin in the environment) was about 15 million lb in 1966, with 92 percent used on corn and 6 percent on orchards, vegetables, tobacco, and cotton. Agricultural uses of these insecticides decreased after the mid-1960s, and were discontinued by the mid-1970s. In addition to their agricultural use, aldrin and dieldrin were also widely used for termite control, most intensively in urban areas. Use of these compounds as termiticides continued until the late 1980s. Although quantitative data are not available, DDT also was used extensively in nonagricultural applications to control insects deemed to be a risk to public health (such as mosquitoes), as well as in forestry (U.S. Department of Health and Human Services, 2005; Larson and others, 1997). Compounds in the DDT group and dieldrin are all highly persistent—most with field-dissipation half-lives greater than 1,000 days (Nowell and others, 1999)—and all have a high affinity for soil organic matter (Appendix 2).

Concentrations of total DDT and dieldrin in bed-sediment samples from agricultural streams correspond reasonably well to both the total amounts and the distributions of their historical agricultural use (figs. 4–15 and 4–16). Reflecting the higher use of their parent pesticides, compounds in the DDT group were detected in bed sediment at 49 percent of agricultural stream sites, compared with 17 percent for dieldrin. The highest total DDT concentrations occurred in high-use areas of the Southeast—where cotton, tobacco, and peanuts were grown—and in a number of other high-use areas where orchard crops, potatoes, vegetables, or specialty crops were grown. Dieldrin was found at the highest overall concentrations in the Corn Belt, where use of aldrin on corn was most intensive.

Although there are few historical data on the urban use of organochlorine insecticides, the NAWQA bed-sediment results indicate that it probably was substantial. Compounds in the DDT group and dieldrin were found at higher frequencies and generally higher concentrations in urban streams than in agricultural streams, with the exception of DDT in some streams draining agricultural watersheds that had high DDT use in the past. Compounds in the DDT group were detected in 72 percent of samples from urban streams, compared with 42 percent for dieldrin.

For most streams with mixed land use in their watersheds, the concentrations of total DDT and dieldrin were generally similar to those in agricultural streams, but lower than those in urban streams. Streams in undeveloped watersheds had the lowest concentrations of these compounds.

In addition to agricultural uses, DDT also was applied to wetlands and marshes to control mosquitoes (photograph courtesy of the Tennessee Valley Authority Historic Collection, 1938).

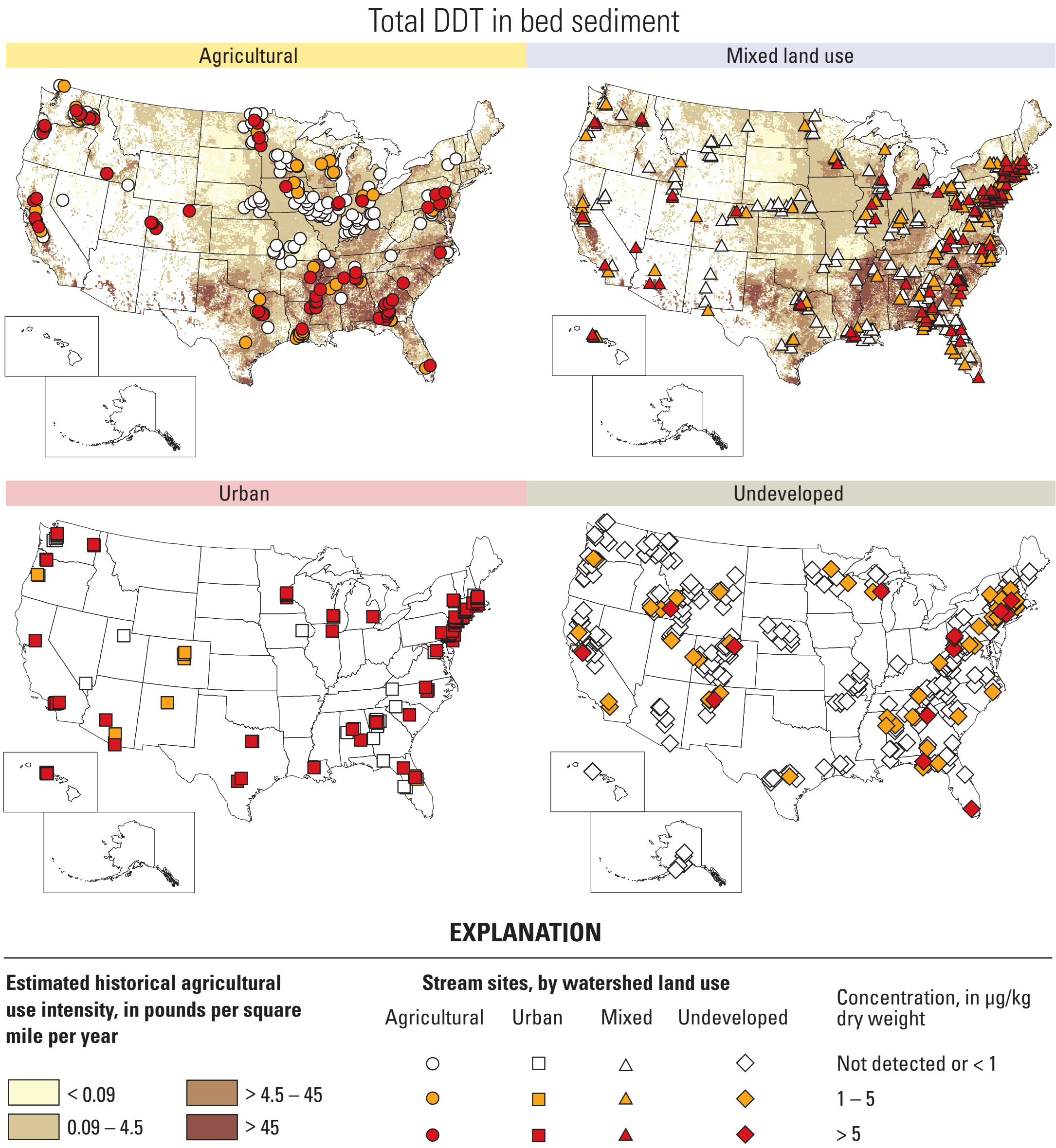

Figure 4–15. Total DDT concentrations in bed sediment were generally higher in urban streams than in agricultural and mixed-land-use streams, with the exception of a few streams draining watersheds in areas that had high agricultural use of DDT plus DDD in the past. The distribution of concentrations of total DDT found in bed sediment of agricultural streams corresponded reasonably well to both the total amount and the distribution of historical agricultural use of DDT plus DDD. Total DDT concentrations were highest in high-use areas of the Southeast where cotton, tobacco, and peanuts were grown, and in a number of other high-use areas where orchard crops, potatoes, vegetables, or specialty crops were grown. Historical use for the late 1960s was estimated as described in the “Methods” sidebar on p. 53.

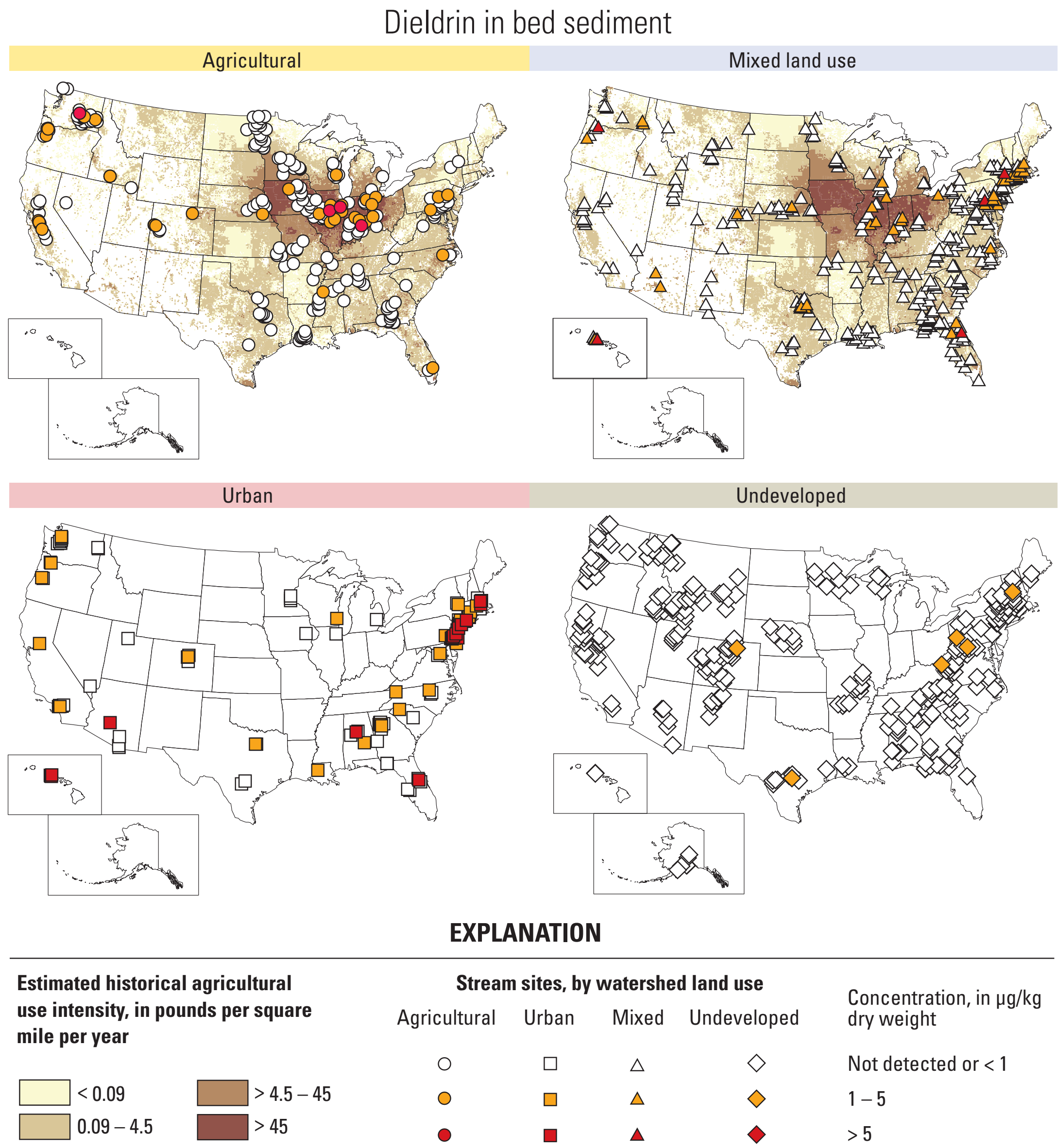

Figure 4–16. Dieldrin in bed sediment generally occurred at higher frequencies and higher concentrations in urban streams than in most agricultural streams. Concentrations of dieldrin found in bed sediment of agricultural streams corresponded reasonably well to the distribution of historical agricultural use of aldrin plus dieldrin. In agricultural streams, dieldrin was detected most frequently and at the highest overall concentrations in the Corn Belt, where past use of aldrin on corn was most intensive. Historical use for the late 1960s was estimated as described in the "Methods" sidebar on p. 53.