5 Complexities: Seasonality, Mixtures, and Degradates

The occurrence of pesticides in streams and ground water, which was characterized in relation to land use and the geographic patterns in pesticide use in Chapter 4, is further complicated by three additional factors: strong seasonal patterns, the prevalence of mixtures of pesticides, and the frequent occurrence of degradates. Seasonal patterns occur year after year in most streams and dictate the timing of the highest pesticide concentrations; mixtures of multiple pesticide compounds are found more often than individual pesticides; and pesticide degradates may occur more frequently and at higher concentrations than their parent compounds, particularly in ground water. These complexities need to be understood and considered when assessing the potential effects of pesticides on water quality.

Photograph © Kemer Nelson, Aequalis Aerial Photography, Tacoma, Washington.

This chapter provides an overview of national findings and selected case studies regarding seasonal patterns, mixtures, and degradates of pesticides.

Seasonal Patterns in Streams

Concentrations of pesticides in streams typically follow marked seasonal patterns year after year. These patterns generally are characterized by long periods of low or undetectable concentrations, punctuated by a few weeks or months of higher concentrations—a seasonal pulse. Such patterns are governed primarily by the timing and intensity of pesticide use in relation to hydrologic factors that affect the transport of pesticides to streams. Key hydrologic factors include the timing and amount of runoff from rainfall and irrigation, the presence or absence of surface or subsurface drainage systems, and the degree of interaction between streams and ground water. Seasonal patterns are important to characterize because they dictate the timing and duration of the highest concentrations of pesticides that may affect the suitability of water for humans, aquatic life, and wildlife.

NAWQA findings show that concentrations of pesticides in agricultural and urban streams across the Nation usually were highest during the growing season and lowest during the winter (fig. 5–1). The highest concentrations of herbicides—generally higher in agricultural streams than in urban streams—usually occurred during

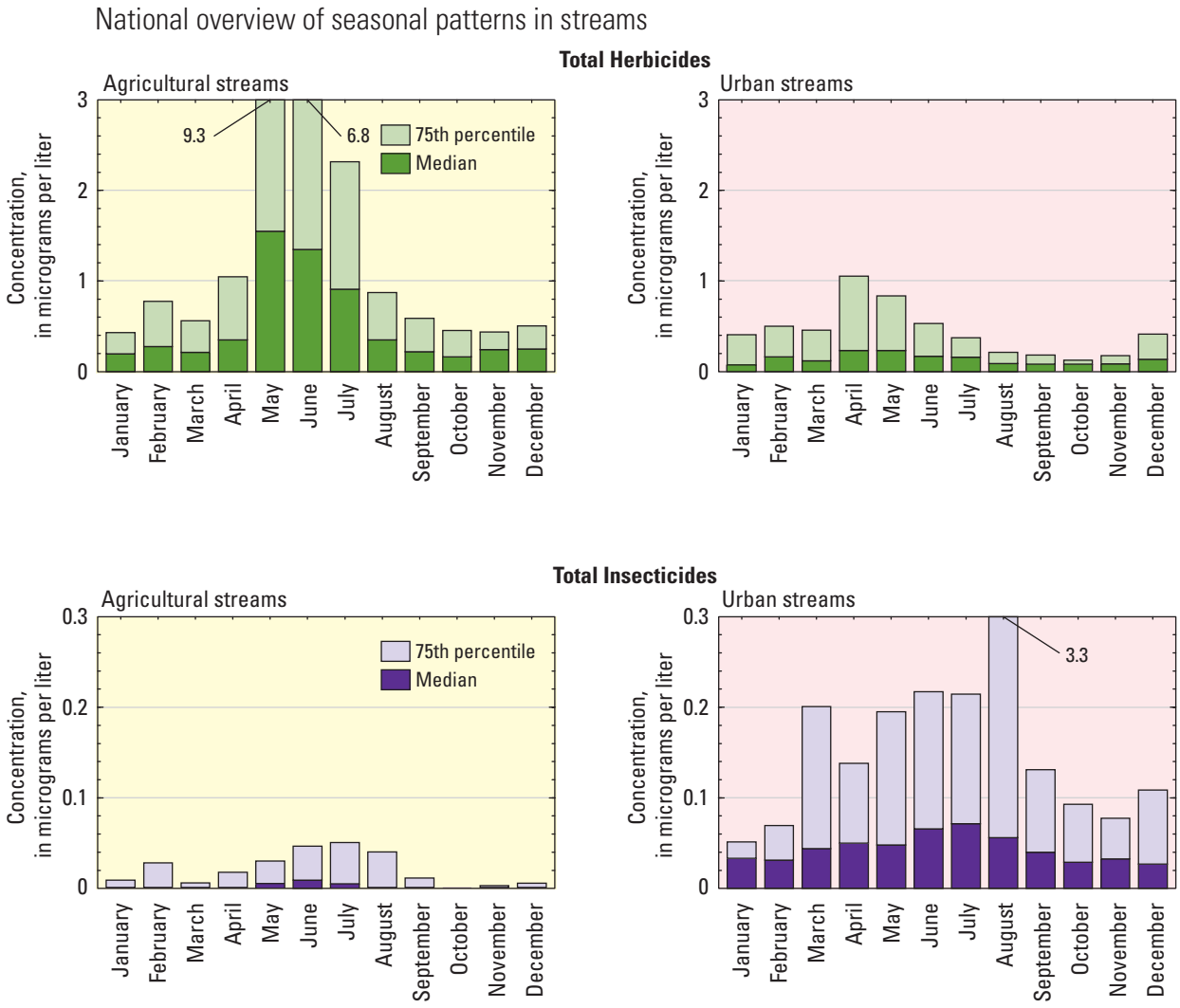

Figure 5–1. The timing and magnitude of seasonal pulses in the concentrations of herbicides and insecticides differed between agricultural and urban streams. Herbicide concentrations tended to be higher and seasonal patterns more pronounced in agricultural streams, but insecticide concentrations generally were higher in urban streams. Median and 75th percentile concentrations were determined after aggregating the total concentrations of herbicides and insecticides for all samples from agricultural streams and for all samples from urban streams.

April–July. In contrast, the highest concentrations of insecticides—generally higher in urban streams than in most agricultural streams—usually occurred at various times over a longer period, from March through September. Differences that may occur in seasonal patterns between agricultural and urban streams, even within the same geographic area, are illustrated by findings from the Mobile River Basin (fig. 5–2). Numerous additional examples of seasonal patterns have been characterized for streams in different parts of the country in individual NAWQA studies (see reports for the 51 NAWQA Study Units: *http://water.usgs.gov/nawqa/nawqasum/*).

Collecting a water sample from Cahaba Valley Creek.

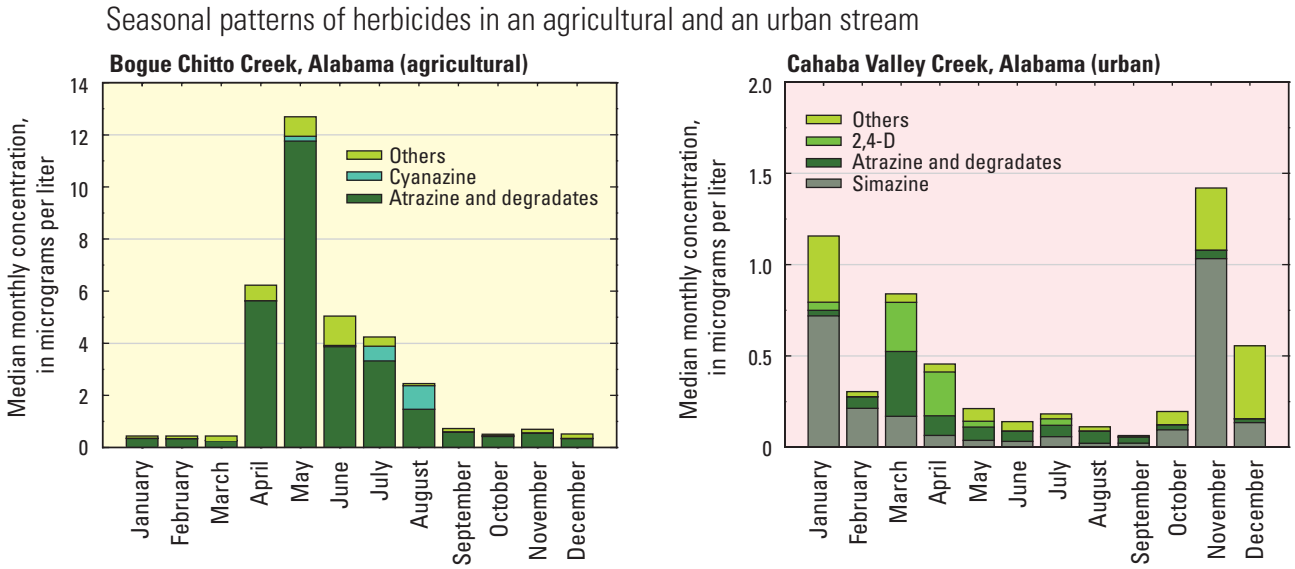

Figure 5–2. Atrazine and its degradates dominated herbicide concentrations in Bogue Chitto Creek, an agricultural stream (Mobile River Basin), with concentrations peaking in the spring following applications on corn fields and gradually declining throughout the summer and winter. In nearby Cahaba Valley Creek, an urban stream, herbicide concentrations were highest during November–April, and the dominant herbicide was simazine (Atkins and others, 2004).

Geographic Variability of Seasonal Patterns

Although the occurrence and concentrations of pesticides followed distinct seasonal patterns in most of the agricultural and urban streams sampled, the specific timing and magnitude of the observed patterns varied regionally and locally. This variability results from differences in such factors as the timing and amounts of pesticide use, climate, and the frequency and magnitude of runoff from rainstorms or irrigation. Seasonal patterns were particularly consistent within regions in which climate, land use, and crop types are relatively uniform, such as in the Corn Belt. The accompanying map and graphs (fig. 5–3) show examples that illustrate regional consistency, variability among streams, and land-use influences on seasonality using findings for atrazine, prometon, and diazinon in selected streams.

- Corn Belt Streams—Concentrations of atrazine, the dominant herbicide used in the Corn Belt during the study period, typically peaked after applications in the spring, as shown in four streams draining parts of Iowa, Indiana, Ohio, and Mississippi. Atrazine use generally is consistent from year to year, closely following annual patterns of weather and weed growth. Concentrations of prometon in these streams had weaker seasonal patterns and were lower than concentrations of atrazine, because prometon is used in smaller quantities and for a variety of nonagricultural purposes. Concentrations of diazinon were low or undetectable during most or all of the year in all Corn Belt streams except the Maumee River. The Maumee River has more urban land in its watershed compared with the other Corn Belt streams shown and was probably influenced more by nonagricultural diazinon use than the other streams.
- Urban Streams—Seasonal concentration patterns in three streams draining urban areas in Virginia, Georgia, and Nevada were more erratic than those observed in most agricultural areas. This was typical of the urban streams sampled nationwide, probably because pesticides are applied more sporadically in residential and commercial settings to control outbreaks of insects and weeds as they occur. Prometon and diazinon were generally detected at higher concentrations than atrazine in Las Vegas Wash and Accotink Creek, with the highest concentrations occurring during spring or summer. Sope Creek had higher concentrations of atrazine and lower concentrations of prometon than the other urban streams. The higher atrazine concentrations in Sope Creek may have resulted from the use of atrazine for treating turf grass in Georgia.
- Palouse River—Concentrations of prometon and atrazine were highest during winter and spring in the Palouse River in Washington, but were low overall compared with agricultural streams draining the Corn Belt. The Palouse River drains mostly nonirrigated cropland where wheat and other grains are the primary crops and pesticide use is relatively low.
- Orestimba Creek—Diazinon concentrations peaked during early winter and midsummer in Orestimba Creek, California, which drains irrigated farmlands dominated by orchards, vegetables, and alfalfa. Diazinon was used extensively in this watershed on almond orchards in January and February and on vegetable crops during the summer.

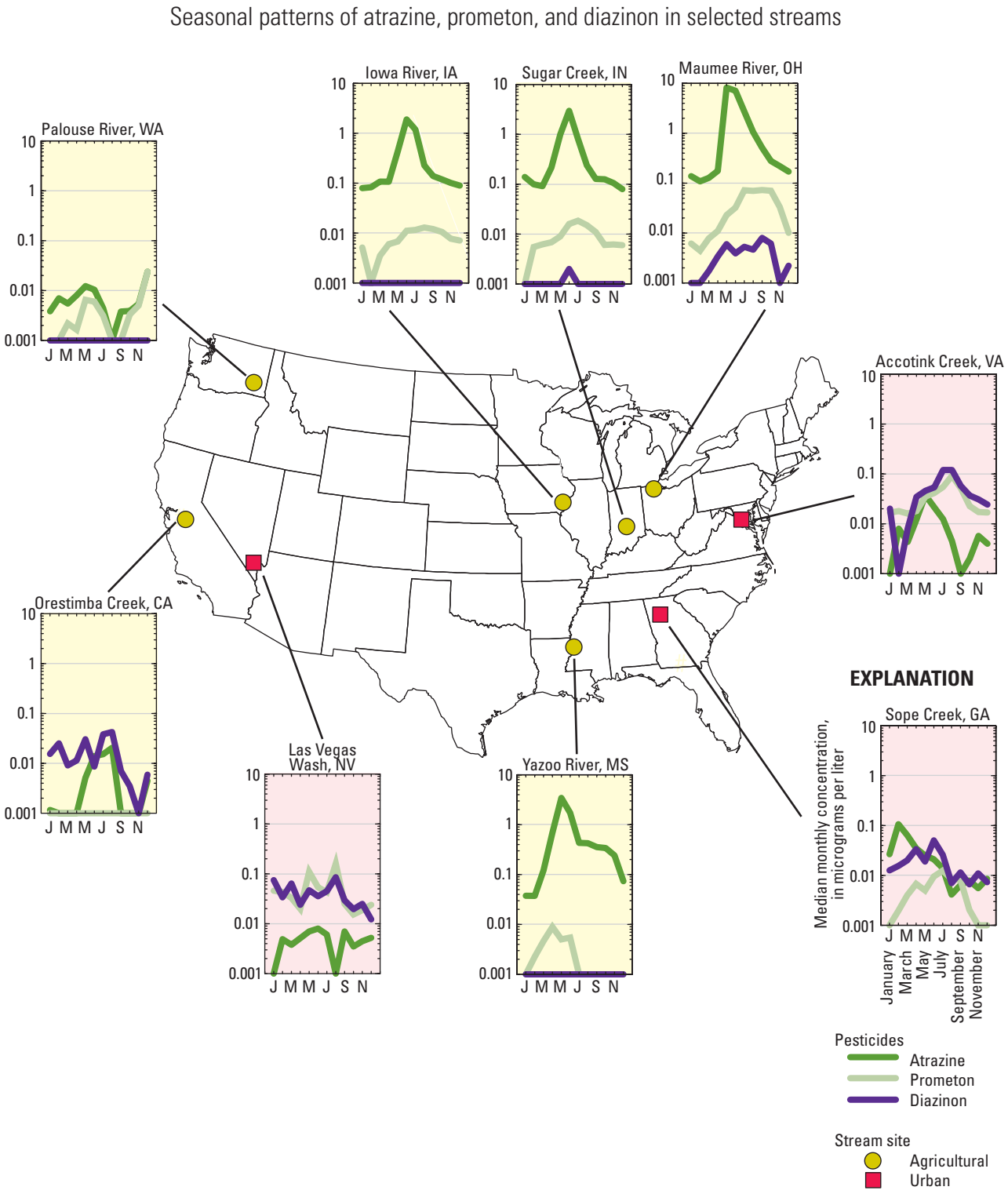

Figure 5–3. Examples of seasonal patterns in concentrations of atrazine, prometon, and diazinon in selected agricultural and urban streams illustrate (1) the regional consistency of patterns for atrazine within the Corn Belt, an area that has relatively uniform agricultural practices; (2) the variability among streams in different regions of the country; and (3) the differing influences of land use on seasonality. Median concentrations for each month were computed from at least 6 years of data for each site and nondetections are plotted at 0.001 µg/L.

Repetition of Seasonal Patterns

Seasonal patterns of pesticide concentrations in each particular stream generally repeat with varying degrees of consistency each year, as long as the pesticides are still in use. For example, atrazine concentrations in the White River followed the same pattern each year from 1992 to 2001 (fig. 5–4). Corn is planted in the region between mid-April and the end of May, and atrazine is applied each year to nearly all of the corn acreage during this time period. Runoff resulting from rainfall in May and June transports atrazine to streams, giving rise to the highest concentrations of the year during and after application. In contrast, patterns in chlorpyrifos concentrations in the White River were less regular (fig. 5–4) because the insecticide is generally applied only if and when it is needed to control outbreaks of corn root worm.

Importance of Seasonal Patterns

Seasonal patterns in pesticide concentrations are important to understand because they may affect the management of water quality for some drinking-water supplies and often define critical conditions of pesticide exposure for aquatic life in a stream. Although NAWQA did not measure pesticide concentrations at drinking-water intakes, NAWQA results for the wide range of streams sampled indicate that seasonal pulses of pesticide concentrations probably occur in some streams that are used as sources of drinking water—primarily those with substantial agricultural or urban land use in their watersheds. For drinking-water sources where seasonal patterns are evident, seasonal monitoring is important to support water-quality management decisions. For example, some drinking-water utilities that withdraw water from streams in agricultural areas employ specific management strategies to avoid use of stream water, or to increase treatment of the water, during known seasonal periods of high concentrations in source waters.

The seasonal timing of elevated pesticide concentrations in relation to the timing of changes in populations and life stages of aquatic organisms may largely determine whether pesticides have a substantial effect on aquatic life in a stream. USEPA's Office of Pesticide Programs, for example, evaluates potential acute effects of exposure on the basis of peak concentration, and potential chronic effects on the basis of the peak 21-day average for invertebrates and the peak 60-day average for fish (see Chapter 6). As indicated by figures 5–1 through 5–4, in most streams, these daily and multiday average concentrations are most likely to be approached or exceeded during relatively distinct seasonal periods for each pesticide. Knowledge of the seasonal timing of the highest concentrations for each pesticide—together with an understanding of the life stages of aquatic organisms present in each season—can be used to target and refine assessments of potential effects, and to design efficient pesticide monitoring strategies that will yield reliable estimates of the concentration statistics required for site-specific risk assessments.

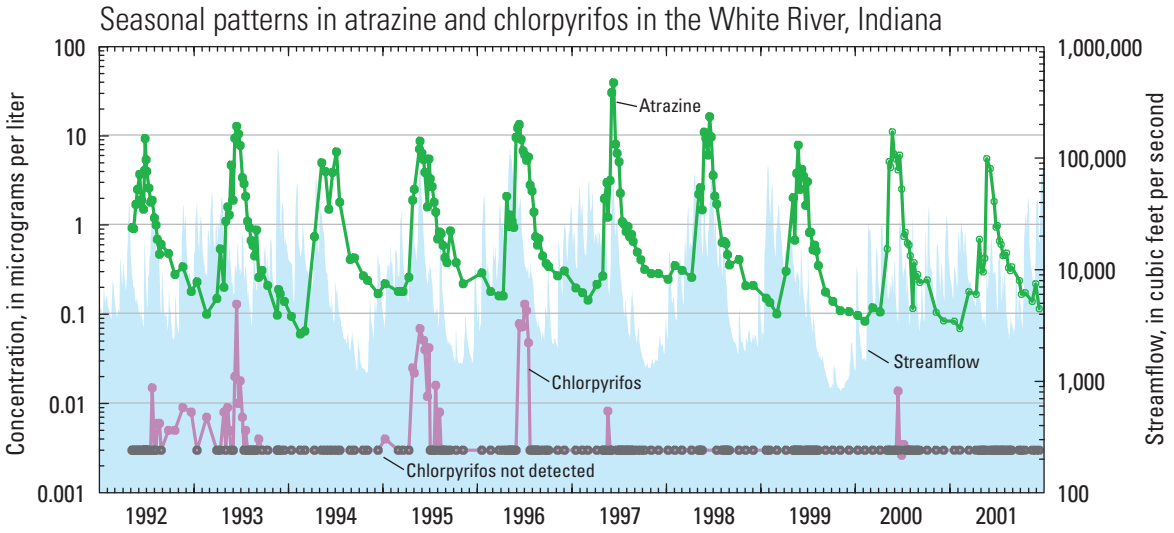

Figure 5–4. Atrazine concentrations in the White River (White River Basin) followed the same pattern each year during 1992–2001, corresponding to its use for weed control on nearly all of the corn acreage in the watershed each spring. In contrast, seasonal patterns in concentrations of chlorpyrifos and other insecticides tend to be more variable because insecticides are typically applied more sporadically than herbicides.

Mixtures of Pesticides

Assessment of the effects of pesticides on water quality is further complicated by the simultaneous occurrence of multiple pesticides and degradates as mixtures. The mixtures result from the use of different pesticides for multiple purposes within a watershed or ground-water recharge area. Pesticides generally occur more often as mixtures than as individual compounds. As a result, evaluation of the potential effects of mixtures of pesticides and other contaminants is an increasingly important component of the risk assessment methods used by USEPA, the Agency for Toxic Substances and Disease Registry (ATSDR), and other agencies (see Chapter 6).

Consistent with the results for individual compounds discussed in Chapter 4, mixtures of pesticides were detected more often in streams than in ground water (fig. 5–5) and at relatively similar frequencies in streams draining areas of agricultural, urban, and mixed land use. More than 90 percent of the time, water from streams in these developed land-use settings had detections of 2 or more pesticides or degradates; about 70 percent of the time, streams had 5 or more, and about 20 percent of the time, streams had detections of 10 or more pesticides or degradates. Mixtures also were found in streams draining undeveloped watersheds, but with far fewer compounds—about 25 percent of the time, undeveloped streams had detections of 5 or more pesticides or degradates, and no samples had more than 10.

In ground water, pesticide mixtures were detected most frequently in shallow wells in agricultural and urban areas—47 percent of wells sampled in agricultural areas and 37 percent of wells in urban areas had detections of 2 or more pesticides or degradates. Only about 9 percent of the wells sampled in these areas contained 5 or more pesticides or degradates, and less than 1 percent contained more than 10. Consistent with the slow rate of ground-water movement and the resulting greater opportunities for sorption and transformation with increasing residence time, co-occurrences of multiple pesticides and degradates were less frequent in wells that tap major aquifers—only about 20 percent of such wells had detections of 2 or more pesticides or degradates. Mixtures were least prevalent in wells sampled in undeveloped areas.

Mixtures of organochlorine pesticide compounds also were common in fish-tissue samples from most streams (fig. 5–6). About 90 percent of fish samples collected from urban streams contained 2 or more pesticide compounds and 33 percent contained 10 or more. Similarly, 75 percent of fish samples from streams draining watersheds with agricultural and mixed land use contained 2 or more pesticide compounds and 10 percent had 10 or more. As with water samples, mixtures were detected least often in fish from undeveloped streams, in which 2 or more compounds were detected in about 25 percent of the fish-tissue samples.

The potential for effects of mixtures on humans, aquatic life, and fish-eating wildlife is ultimately determined by the specific combinations of compounds that occur together, their concentrations, and when and where they occur. A unique mixture is defined in this report as a combination of 2 or more particular compounds detected in a given sample, regardless of whether other compounds were also detected in the same sample (Squillace and others, 2002). For example, a sample containing compounds A, B, and

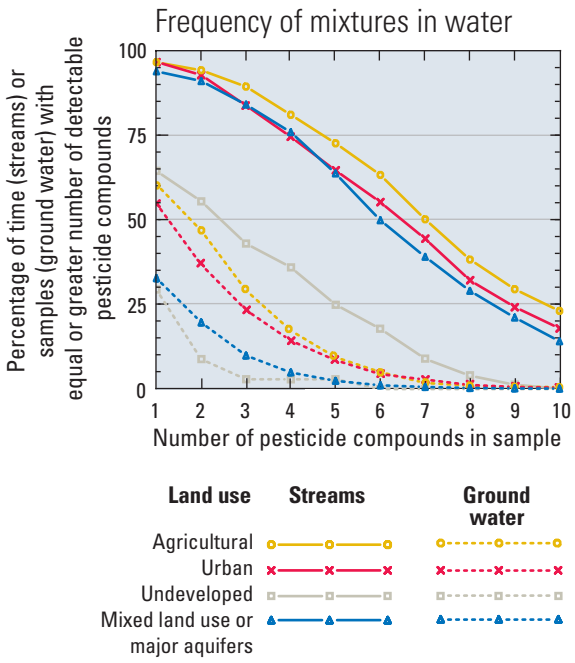

Figure 5–5. Mixtures of pesticide compounds analyzed in water were common in streams draining watersheds with agricultural, urban, and mixed land use. More than 90 percent of the time, water from streams in these land-use settings had detections of 2 or more pesticides or degradates, and almost 20 percent of the time, streams had detections of 10 or more. Mixtures were less common in ground water, but shallow wells in agricultural and urban areas had the most frequent occurrences of mixtures among all ground-water samples.

C contains four unique mixtures—AB, AC, BC, and ABC. The number of unique mixtures in one sample can be very large if many compounds are detected. A sample with 2 compounds has only one mixture, but a sample with five compounds contains 26 unique mixtures. Unique mixtures examined in this report were limited to those composed of the most commonly detected pesticide compounds—specifically, 25 compounds in water and 15 in fish tissue (figs. 4–2 and 4–4)—and were further limited to unique mixtures that occurred at least 2 percent of the time in streams or in at least 2 percent of samples for ground water and fish tissue.

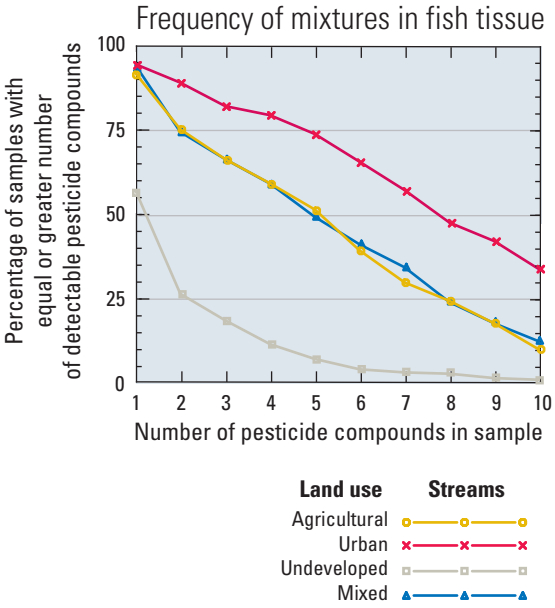

Figure 5–6. Mixtures of organochlorine pesticide compounds were detected in samples of whole fish from most streams. Fish in urban streams had the greatest numbers of organochlorine compounds detected, with about 90 percent of fish samples containing 2 or more compounds and 33 percent containing 10 or more. Streams in areas of agricultural and mixed land use had about 75 percent of fish-tissue samples with 2 or more compounds and 10 percent with 10 or more.

Unique Mixtures in Water

Streams have more unique mixtures than ground water (fig. 5–7), which is consistent with the more frequent detection of pesticides and their degradates in stream water compared with ground water. Analysis of all detections indicates that more than 6,000 unique mixtures of five pesticides were detected in agricultural streams, compared with only one unique mixture of five pesticides detected in shallow ground water within agricultural areas.

The number of unique mixtures varied with land use. For example, the greatest number of unique mixtures occurred in agricultural streams, probably because of the wide variety of agricultural settings represented, each involving the use of different combinations of pesticides (note the logarithmic scale in fig. 5–7). In ground water, however, the greatest number of unique mixtures occurred in shallow wells within urban areas, resulting primarily from the detection of urban herbicides that were not used or detected as frequently in agricultural settings. Major aquifers had the fewest mixtures, consistent with the lower frequencies of detection for individual compounds in these deeper ground waters.

The number of unique mixtures that can be detected is strongly influenced by the detection level for individual pesticides. In ground water, where pesticide concentrations usually are low, only 1 unique mixture of 2 compounds (atrazine and deethylatrazine in agricultural areas) was identified when the analysis was restricted to detected concentrations greater than 0.1 µg/L. In streams, however, many unique mixtures were detected—even when evaluating only detections greater than 0.1 µg/L (fig. 5–7). At the 0.1 µg/L detection level, greater distinctions were evident between land-use settings. For example, about 50 unique 5-compound mixtures were detected in agricultural streams when only individual pesticides at concentrations greater than 0.1 µg/L are considered (compared with more than 6,000 when including all detections at any concentration). In urban streams, only 6 unique 5-compound mixtures were detected above the 0.1 µg/L level.

The most frequent contributors to mixtures, not surprisingly, are the individual pesticides that were detected most often (fig. 5–8). These include the herbicides atrazine (and its degradate deethylatrazine), metolachlor, simazine, and prometon, each of which was present in more than 30 percent of all mixtures found in agricultural and urban areas, and in both streams and ground water. Also present in more than 30 percent of the mixtures were cyanazine, alachlor, metribuzin, and trifluralin in agricultural streams, and dacthal and the insecticides diazinon, chlorpyrifos, carbaryl, and malathion in urban streams. The most notable difference between urban and agricultural streams was the more common occurrence of insecticides in mixtures found in urban streams—consistent with the generally more frequent occurrence of insecticides in urban

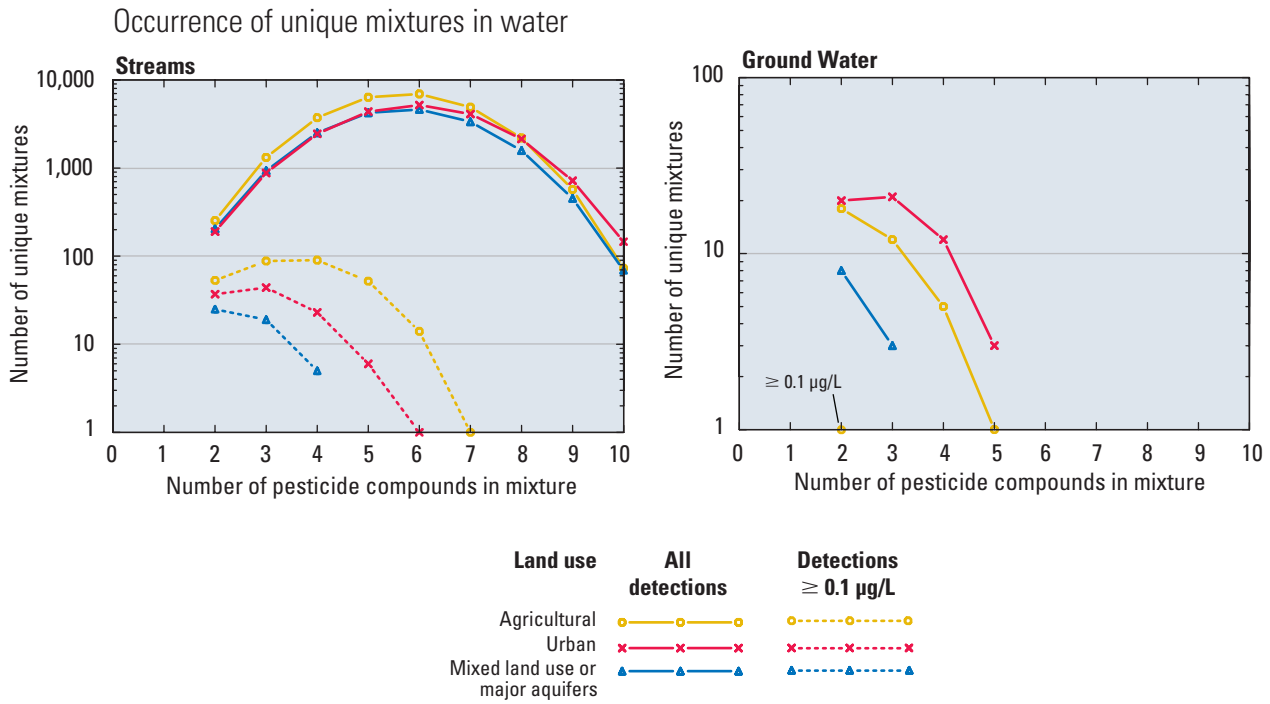

Figure 5–7. The number of unique mixtures detected in water was much greater in streams than in ground water. Considering all detections, more than 6,000 unique 5-compound mixtures were found in samples from agricultural streams, whereas only 1 unique 5-compound mixture was detected in shallow ground water beneath agricultural areas. Considering only pesticides detected at concentrations greater than or equal to 0.1 µg/L, the number of unique mixtures was far less. These graphs include only those unique mixtures that were composed of the 25 most prevalent pesticides and were detected in at least 2 percent of the samples.

streams. A notable difference in ground water between urban and agricultural areas was the occurrence of tebuthiuron, which was present in about 35 percent of the mixtures detected in wells in urban areas, but in less than 2 percent of the mixtures in wells in agricultural areas.

The unique mixtures detected most frequently in streams and ground water are summarized in table 5–1. This assessment is limited to the pesticides measured by NAWQA and by the sensitivity of the analytical method for each pesticide. For example, the analysis under-represents the contributions of 2,4-D, bentazon, bromacil, carbaryl, diuron, and norflurazon to mixtures, relative to the other pesticides, because these compounds were only detectable at higher concentrations. Most notably, 2,4-D was one of the most prevalent components of mixtures in both agricultural and urban streams at concentrations of 0.1 µg/L or greater. This implies that 2,4-D is also likely to be one of the most important contributors to mixtures at lower concentrations as well, but the low concentrations could not be measured.

Combinations of agricultural and urban land uses, such as those on Oahu, Hawaii, result in use of many different pesticides, leading to complex mixtures of pesticide compounds in streams and ground water (Landsat satellite image from the Pacific Disaster Center).

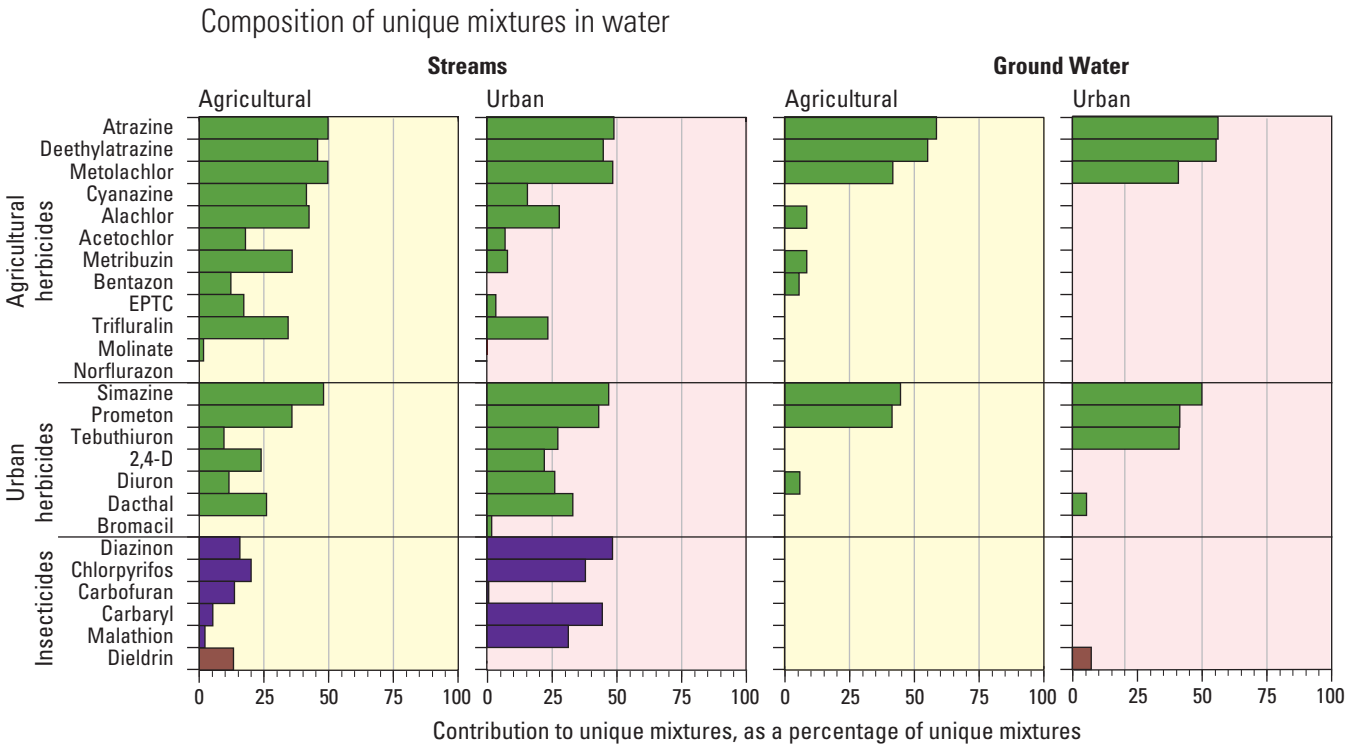

Figure 5–8. The most common components of mixtures, not surprisingly, were the pesticides and degradates that were detected most often. The most frequent contributors to unique mixtures were the herbicides atrazine (and deethylatrazine), metolachlor, simazine, and prometon—all of which were detected in more than 30 percent of all unique mixtures found in agricultural and urban areas and in streams and ground water. The most notable differences between agricultural and urban areas were (1) the greater contribution of insecticides to the mixtures detected in urban streams, and (2) the greater contribution of tebuthiuron to the mixtures found in shallow ground water in urban areas. This analysis is based on detections at any concentration, but includes only those unique mixtures that were composed of the 25 most prevalent pesticides and were detected in at least 2 percent of samples.

Table 5–1. The most common unique mixtures of pesticides and degradates found in stream water and ground water illustrate the diversity and complexity of mixtures that occur in agricultural and urban areas. The mixtures detected most frequently for each number of compounds are shown for each land use, with all detections included, regardless of concentration. These most common unique mixtures serve as examples, rather than as a comprehensive compilation of all the most important mixtures, because other mixtures occurred almost as frequently.

Mixture	Frequency of detection (percentage of time for streams, or samples for ground water)			
	Streams		Ground water	
	Urban	Agricultural	Urban	Agricultural
2-compound mixtures				
Atrazine Prometon	79	50	15	10
Prometon Simazine	75	41	10	7
Atrazine Simazine	74	64	17	18
Atrazine Metolachlor	55	77	8	15
Atrazine Deethylatrazine	53	77	26	39
Deethylatrazine Simazine	49	57	15	17
Deethylatrazine Metolachlor	42	69	7	14
3-compound mixtures				
Atrazine Prometon Simazine	68	41	9	7
Atrazine Diazinon Prometon	60	10	1	0
Atrazine Diazinon Simazine	59	16	1	0
Diazinon Prometon Simazine	59	9	1	0
Atrazine Deethylatrazine Prometon	50	48	12	9
Atrazine Deethylatrazine Simazine	48	57	15	16
Atrazine Metolachlor Simazine	48	57	6	7
Atrazine Deethylatrazine Metolachlor	41	69	7	14
4-compound mixtures				
Atrazine Diazinon Prometon Simazine	53	9	1	0
Atrazine Deethylatrazine Prometon Simazine	46	39	8	7
Atrazine Metolachlor Prometon Simazine	43	38	4	4
Atrazine Deethylatrazine Metolachlor Prometon	39	45	5	6
Atrazine Deethylatrazine Metolachlor Simazine	37	52	5	7
Alachlor Atrazine Deethylatrazine Metolachlor	14	42	0	2
5-compound mixtures				
Atrazine Carbaryl Diazinon Prometon Simazine	36	2	0	0
Atrazine Deethylatrazine Diazinon Prometon Simazine	35	8	1	0
Atrazine Deethylatrazine Metolachlor Prometon Simazine	35	37	4	4
Atrazine Diazinon Metolachlor Prometon Simazine	35	8	0	0
Atrazine Deethylatrazine Prometon Simazine Tebuthiuron	28	16	2	1
Atrazine Deethylatrazine Metolachlor Simazine Tebuthiuron	22	19	2	1
Alachlor Atrazine Deethylatrazine Metolachlor Prometon	13	33	0	1
Alachlor Atrazine Deethylatrazine Metolachlor Simazine	13	33	0	1
Alachlor Atrazine Deethylatrazine Prometon Simazine	12	26	0	1
Atrazine Cyanazine Deethylatrazine Metolachlor Simazine	5	33	1	1

Unique Mixtures in Fish Tissue

The numbers of unique mixtures of organochlorine pesticide compounds found in fish tissue are summarized in figure 5–9. Each individual parent compound, degradate, and by-product included in figure 4–4 was counted separately. Urban streams had more unique mixtures of these compounds in fish than streams draining areas with agricultural or mixed land use. For example, about 1,400 unique 5-compound mixtures were found in fish from urban streams, whereas streams in areas with agricultural or mixed land use had fewer than 800 unique 5-compound mixtures.

The relative contributions of most organochlorine compounds to mixtures in fish were about the same for urban and agricultural streams (fig. 5–10). This reflects the fact that most of these compounds originated with a small number of pesticide products that were applied many years ago in both land-use settings. The most frequent contributors were compounds derived from formulations of DDT and DDD (especially the *p,p′* isomers), dieldrin (resulting from use of either aldrin or dieldrin), chlordane, and heptachlor epoxide (resulting from use of heptachlor)(table 5–2). The most notable difference between agricultural and urban streams was the greater importance in urban streams of hexachlorobenzene (an industrial compound, as well as a fungicide) and both *o,p′*- and *p,p′*-DDT. The greater prevalence of DDT isomers in mixtures in urban streams, relative to agricultural streams, is consistent with the finding that the parent compounds (*o,p′*- and *p,p′*-DDT) made up a higher proportion of total DDT residues in fish from urban streams (16 percent) than in fish from streams with agricultural, undeveloped, or mixed-land-use watersheds (2–3 percent). These results indicate either that DDT was applied more recently in urban watersheds, or that there has been more recent transport of DDT-contaminated soils to the streams in urban areas than to streams in most agricultural watersheds. (DDT breaks down more rapidly in the absence of dissolved oxygen and is, in general, less persistent in aquatic sediment than in soil.)

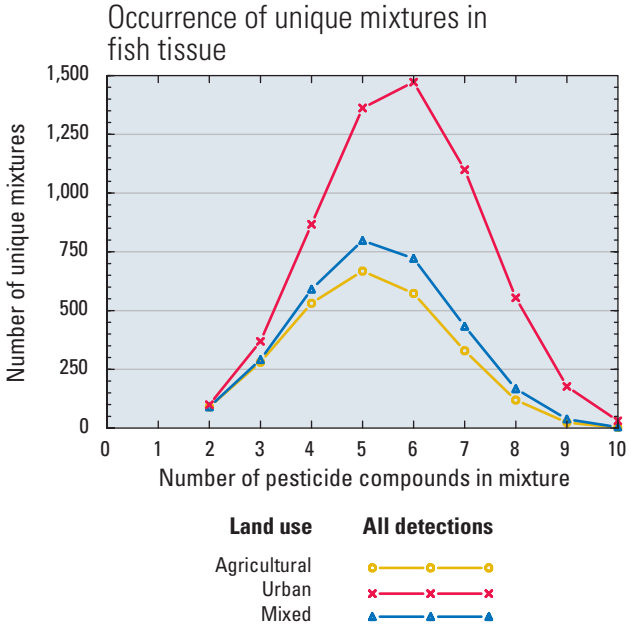

Figure 5–9. The numbers of unique mixtures of organochlorine pesticide compounds found in whole-fish tissue samples were greater in urban streams than in streams with agricultural or mixed-land-use watersheds. For example, about 1,400 unique 5-compound mixtures were found in fish from urban streams, whereas fewer than 800 unique 5-compound mixtures were detected in fish from agricultural and mixed-land-use streams. This analysis includes all detections, but only those unique mixtures that were composed of the 15 organochlorine pesticide compounds included in figure 4–4 and that were detected in at least 2 percent of samples.

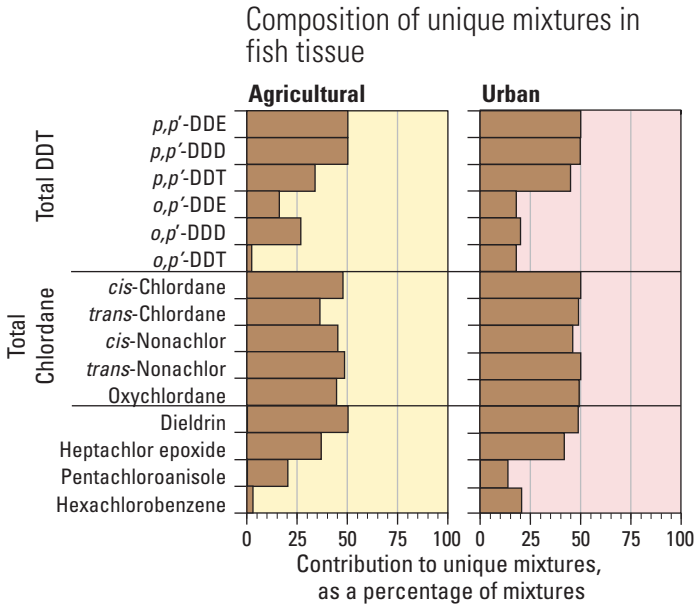

Figure 5–10. For the most part, compounds that contributed to unique mixtures found in fish tissue were similar for agricultural and urban streams, and 10 of the 15 compounds included in the analysis contributed to more than 30 percent of the mixtures in both land-use settings.

Table 5–2. The most common unique mixtures of organochlorine pesticide compounds found in fish tissue were dominated by compounds derived from commercial formulations of DDT, DDD, and chlordane, as well as dieldrin. The mixtures detected most frequently for each number of compounds are shown for each land use. These most common mixtures serve as examples, rather than having unique importance, because many other mixtures occur almost as frequently.

Mixture	Frequency of detection (percentage of samples) Fish tissue	
	Urban streams	Agricultural streams
2-compound mixtures		
p,p′-DDE *trans*-Nonachlor	72	49
cis-Chlordane *p,p′*-DDE	72	37
cis-Chlordane *trans*-Nonachlor	72	35
p,p′-DDD *p,p′*-DDE	64	59
Dieldrin *p,p′*-DDE	53	59
3-compound mixtures		
cis-Chlordane *p,p′*-DDE *trans*-Nonachlor	68	35
cis-Chlordane *p,p′*-DDD *p,p′*-DDE	60	28
cis-Chlordane *p,p′*-DDD *trans*-Nonachlor	57	27
p,p′-DDD *p,p′*-DDE *trans*-Nonachlor	57	37
Dieldrin *p,p′*-DDE *trans*-Nonachlor	53	42
Dieldrin *p,p′*-DDD *p,p′*-DDE	40	47
4-compound mixtures		
cis-Chlordane *p,p′*-DDD *p,p′*-DDE *trans*-Nonachlor	56	27
cis-Chlordane *p,p′*-DDE *trans*-Chlordane *trans*-Nonachlor	51	25
cis-Chlordane *p,p′*-DDE *p,p′*-DDT *trans*-Nonachlor	51	9
cis-Chlordane Dieldrin *p,p′*-DDE *trans*-Nonachlor	50	33
cis-Chlordane Dieldrin *p,p′*-DDD *p,p′*-DDE	40	27
Dieldrin *p,p′*-DDD *p,p′*-DDE *trans*-Nonachlor	40	34
5-compound mixtures		
cis-Chlordane *p,p′*-DDD *p,p′*-DDE *trans*-Chlordane *trans*-Nonachlor	46	19
cis-Chlordane *p,p′*-DDD *p,p′*-DDE *p,p′*-DDT *trans*-Nonachlor	44	9
cis-Chlordane Dieldrin *p,p′*-DDE *trans*-Chlordane *trans*-Nonachlor	43	24
cis-Chlordane Dieldrin *p,p′*-DDD *p,p′*-DDE *trans*-Nonachlor	40	26
cis-Chlordane *cis*-Nonachlor Dieldrin *p,p′*-DDE *trans*-Nonachlor	39	23

Importance of Mixtures

The frequent detection of pesticide mixtures in NAWQA samples from streams and ground water indicates that aquatic life, fish-eating wildlife, and potentially humans, are exposed primarily to mixtures of pesticides, rather than to individual compounds. As examined in Chapter 6, determining the potential effects of mixtures is an increasingly important aspect of risk-assessment procedures for pesticides. These procedures generally rely on indirect estimates of mixture toxicity—made from the toxicities of individual pesticides that occur—primarily because toxicity data are seldom available for specific unique mixtures that occur in the environment. The large number of unique mixtures present in streams, and to a lesser extent in ground water, make it impractical to assess the potential effects of all that are encountered (Lydy and others, 2004). NAWQA results provide an assessment of the unique mixtures that were detected most frequently—such as those summarized in tables 5–1 and 5–2—and make it possible to prioritize specific mixtures for further investigation. In developing a strategy for investigation, however, it must be kept in mind that findings about mixtures, like those regarding individual pesticides, are limited to the pesticides measured, and are influenced by the analytical methods used in this study. Thus, NAWQA data yield a minimum assessment of the occurrence of mixtures because of the limited number of pesticides and degradates that were analyzed.

NAWQA data on mixtures are beginning to be used to prioritize toxicological investigations. For example, the ATSDR is in the process of evaluating the toxicity of the mixture of atrazine, deethylatrazine, diazinon, nitrate, and simazine (ATSDR, 2004a) because of the frequency of its occurrence in public-supply and domestic wells that were sampled by NAWQA (Squillace and others, 2002). The importance to aquatic life, wildlife, and humans of mixtures that occur in streams and ground water is difficult to determine, and will require multiple approaches over an extended period of time.

Pesticide Degradates

Once released into the environment, pesticides are transformed over time by a variety of chemical, photochemical, and biologically mediated reactions into other compounds, which are referred to in this report as degradates. With time, degradates may become as prevalent as parent pesticides—or more so—depending on their rate of formation and their relative persistence. For example, deethylatrazine, which is a degradate of atrazine and other triazine herbicides, was one of the few degradates included in routine NAWQA analyses, one of the most frequently detected pesticide compounds in water (fig. 4–2), and one of the most frequent contributors to pesticide mixtures (fig. 5–8). In addition, degradates and by-products of organochlorine pesticides were among the most commonly detected pesticide compounds in fish (fig. 4–4). This and other evidence from many studies in a wide range of settings indicate that a diverse range of pesticide compounds routinely occur along with mixtures of parent pesticides (Boxall and others, 2004).

Degradates, like their parent compounds, have the potential to adversely affect water quality, depending on their toxicity. Degradates may be either more or less toxic than their parent pesticides, although most have toxicities to aquatic life that are similar to, or lower than, those of their parent compounds (Sinclair and Boxall, 2003; see accompanying sidebar, p. 81). For some pesticides that have not been registered or reregistered by USEPA during the last several years, the toxicities of degradates have not been evaluated, but current registration requirements include assessment of the toxicities of major degradates, as described in the accompanying sidebar on USEPA risk assessments (p. 86).

The rates of pesticide transformation and degradate formation vary widely among pesticides and under different environmental conditions, as discussed in Chapter 2. Each transformation reaction requires specific physical, chemical, and biological conditions. For example, most oxidation reactions require the presence of dissolved oxygen, whereas reduction reactions require its absence. Photochemical reactions require the presence of sunlight that has sufficient energy to break specific chemical bonds. Many transformations—such as the conversion of atrazine to deethylatrazine, or the formation of alachlor ethanesulfonic acid (ESA) from alachlor in soil—will not occur without the assistance of microbes or other organisms (Barbash, 2004). Selected transformations of atrazine are dis-

Potential Risks of Pesticide Degradates to Aquatic Life

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Recent advances in analytical methodology and greater access to analytical standards have led to the detection of degradates from a wide variety of pesticides and other compounds in surface water, ground water, precipitation, air, and sediment (Boxall and others, 2004). Many of these degradates are more persistent in the environment than their parent compounds, and many are more mobile, as well.

In most cases, degradates have similar or lower toxicity to aquatic life than their parents, but some are more toxic. In a recent review of available ecotoxicity data for degradates of pesticides and other compounds, Sinclair and Boxall (2003) reported that 41 percent of degradates were less toxic than their parent compounds and 39 percent had a toxicity similar to their parents; however, 20 percent were more than 3 times more toxic than their parent compound and 9 percent were more than 10 times more toxic. In general, the greatest increases in toxicity from parent to degradate were observed for parent compounds that had a low toxicity. Similar patterns are apparent for degradates of 8 pesticides frequently detected by NAWQA (fig. 5–11), with 28 percent of the degradates being more toxic to fish than their parent compounds and 21 percent being more toxic to daphnids.

Because pesticides and their degradates are more commonly detected in environmental media as mixtures than as isolated compounds, assessments of their potential biological effects should account for the combined effects of multiple substances. As discussed in further detail in Chapter 6 of this report, the influence of a given compound A on the toxicity of a second compound B may be antagonistic (overall toxicity less than that of A and B combined), additive (overall toxicity is roughly equal to that of A and B combined) or synergistic (overall toxicity exceeds the added effects of the two compounds). The "mixture risk quotient" can be used to assess the combined risk of multiple compounds (parent compounds and/or degradates) simultaneously, based on the assumption that the toxic effects of different compounds are additive. This approach was recently applied by Fenner and others (2002) to assess the potential toxicities of predicted concentrations of nonylphenol ethoxylate (NPEO, a widely used nonionic surfactant) and its degradates to aquatic biota in Switzerland.

Although a variety of methods have been used to estimate mixture risk quotients, Fenner and others (2002) computed this parameter by summing the ratios of the concentrations predicted in Swiss rivers to the no-effect levels (for acute health effects in aquatic organisms) predicted for individual compounds in hypothetical mixtures of NPEO and its degradates. Risk quotients for NPEO alone and for each of the individual NPEO degradates were all below 1 for water and sediment, indicating relatively low risk to aquatic ecosystems with respect to acute (but not necessarily chronic) effects. The risk quotient calculated for the mixture of NPEO plus all of its transformation products, however, was 2.2, indicating a high risk of acute health effects for aquatic organisms if the toxicities are additive. This and other studies indicate that, in some instances, degradates from pesticides and other anthropogenic compounds may be of concern in the environment. An improved understanding is therefore needed of the environmental distributions, patterns of co-occurrence, and toxicities of these compounds in the hydrologic system—both in isolation and in mixtures.

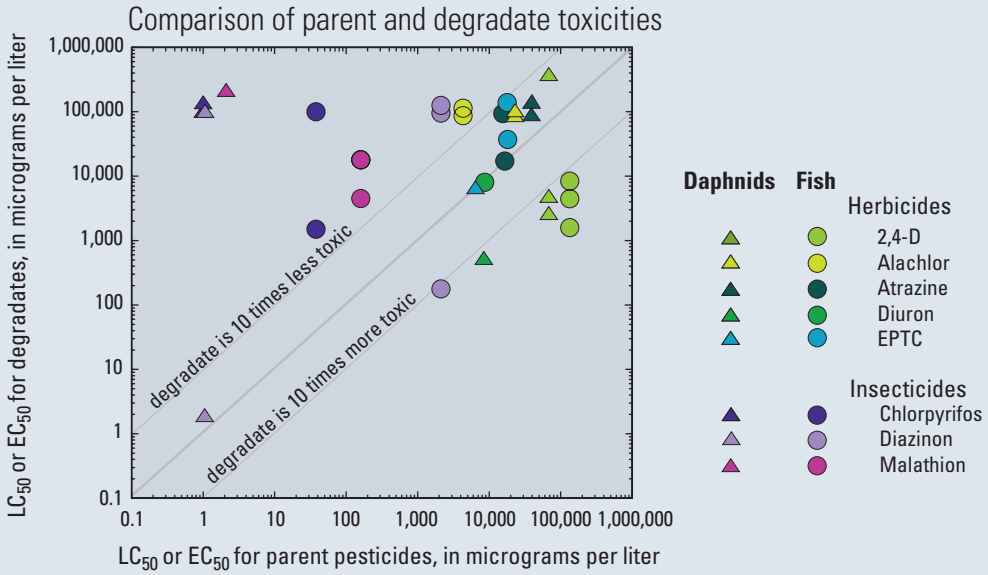

Figure 5–11. Comparison of acute toxicity values (LC_{50} or EC_{50}; see glossary) for parent compounds and degradates for 8 pesticides frequently detected by NAWQA in water samples from streams shows that 28 percent were more toxic to fish and 21 percent of the degradates were more toxic to daphnids than the parent pesticides. Multiples of the same symbol are different degradates of the same parent pesticide.

played in figure 5–12, to show three of the multiple pathways that these reactions may involve, and to provide a sense of the complexity involved with tracking the formation, transport and fate of degradates for all of the pesticides in use. This example also illustrates the varying effects of different reactions on toxicity, discussed earlier. The first two reactions produce degradates with mammalian toxicities similar to that of the parent compound (atrazine). By contrast, the third reaction generates a compound (hydroxyatrazine) with substantially lower mammalian toxicity, owing to the removal of chlorine (Jordan and others, 1970; Rodriguez and Harkin, 1997).

As noted earlier, degradates are often more prevalent than their parent pesticides in streams and ground water, particularly when conditions favor transformation to degradates that are chemically persistent. In parts of some hydrologic systems, the concentrations of degradates may exceed those of the parent pesticides throughout much of the year. In surface waters, degradates often predominate when much of the streamflow is either from ground water, or from surface runoff occurring long enough after pesticide applications for the parent pesticide to have substantially transformed. For example, the summed concentrations of atrazine, cyanazine, acetochlor, alachlor, and metolachlor in the Iowa River in the Eastern Iowa Basins changed rapidly in response to the timing of their applications, but the summed concentrations of their degradates were higher and relatively constant throughout most of the year (fig. 5–13). Similarly, in the Mermentau River in the Acadian–Pontchartrain Drainages, the concentration of the insecticide fipronil reached its maximum value immediately following the spring application season, and then declined, to be exceeded by concentrations of fipronil degradates from June to February. This cycle repeated itself with the springtime applications the following year (fig. 5–14). Information on the concentrations and fluxes of degradates—especially in relation to those of their parent

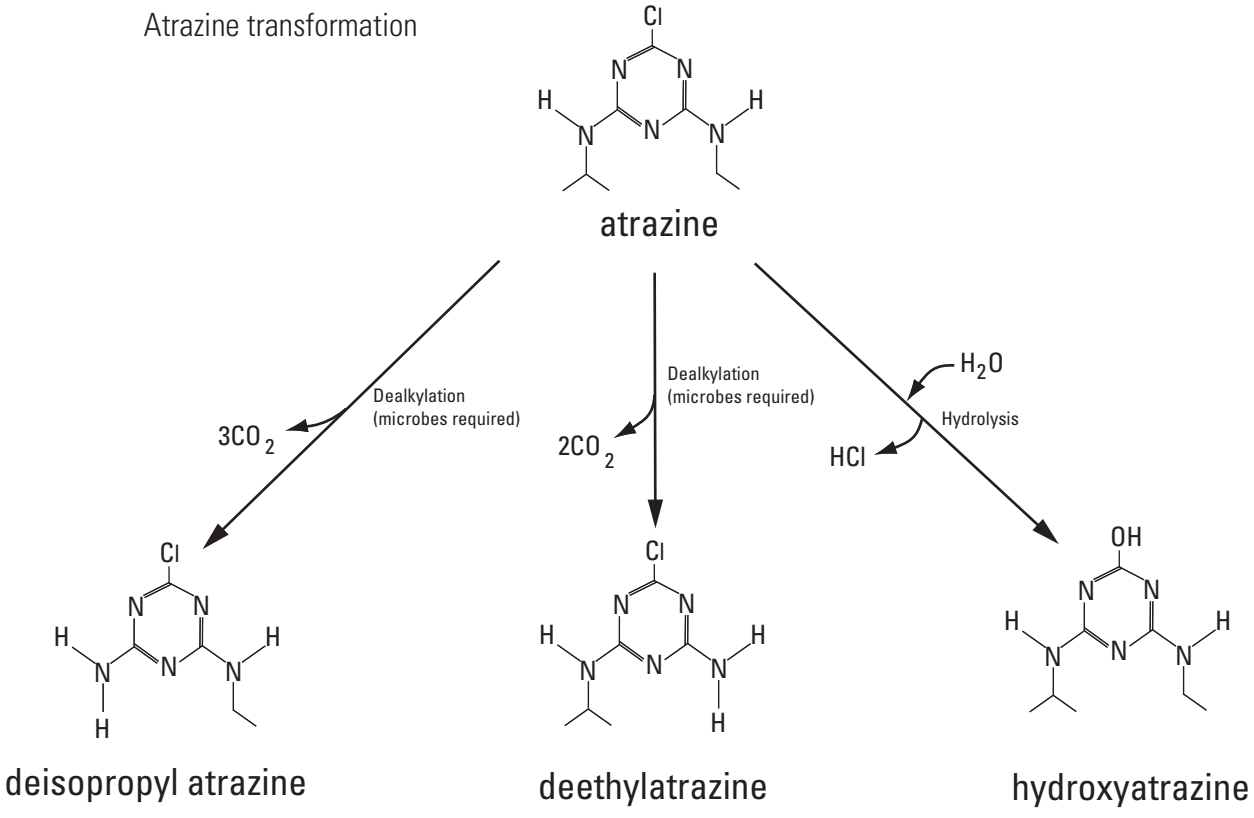

Figure 5–12. Atrazine transforms to three primary degradates (although there are others as well), one of which—deethylatrazine—was routinely measured by NAWQA. Two of these transformation reactions require microbes, resulting in the formation of deethylatrazine and deisopropyl atrazine. The third is hydrolysis, an abiotic reaction with water that produces the degradate hydroxyatrazine.

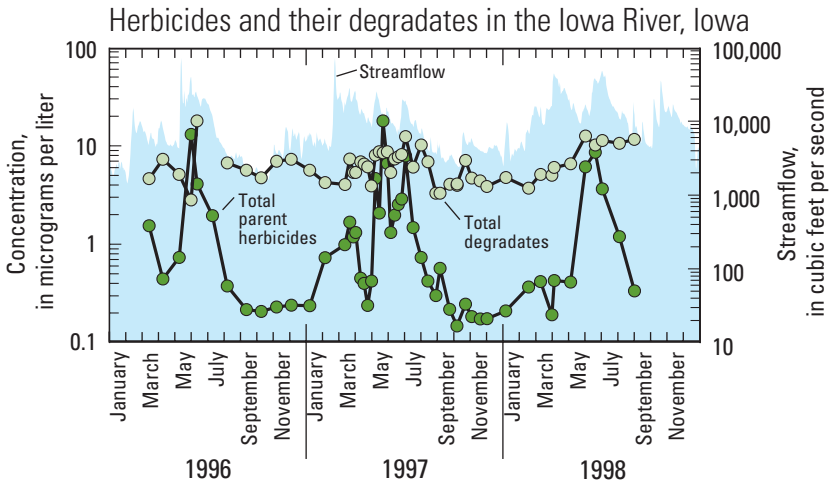

Figure 5–13. The summed concentrations of the parent herbicides atrazine, cyanazine, acetochlor, alachlor, and metolachlor in the Iowa River (Eastern Iowa Basins) rose and fell in response to spring applications, whereas the summed concentrations of their degradates remained relatively steady and at higher levels throughout most of the year (Schnoebelen and others, 2003).

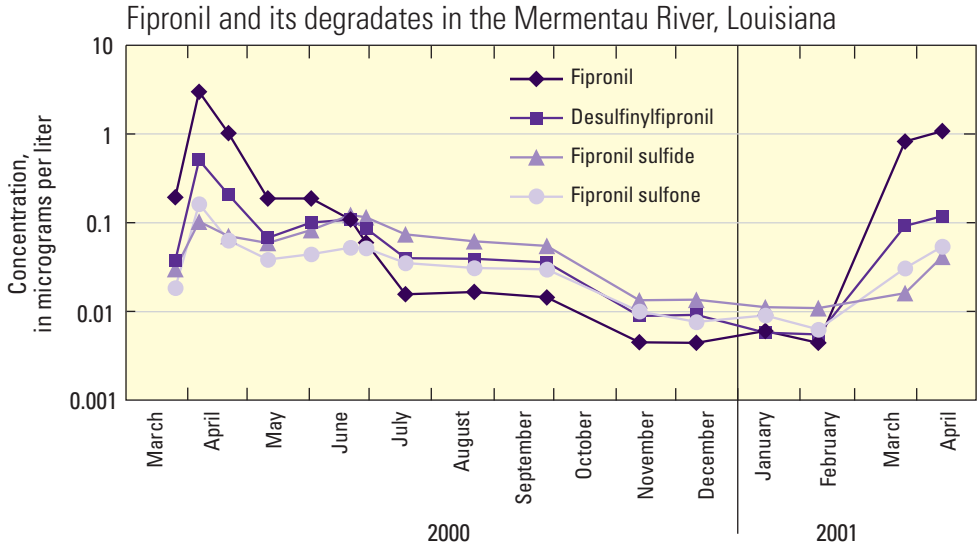

Figure 5–14. Concentrations of the insecticide fipronil and its degradates in the Mermentau River (Acadian–Pontchartrain Drainages) peaked in March or April, following applications. Although fipronil dominated the total concentration of fipronil compounds during the high-use period, concentrations of its degradates were greater during the rest of the year (Demcheck and others, 2004).

pesticides—contributes to our understanding of the environmental fate of pesticides as they move and transform within the hydrologic system.

In ground water, degradates were often detected more frequently, or at higher concentrations, than their parent pesticides. For example, in ground water of the Upper Illinois River Basin, degradates of acetochlor, alachlor, metolachlor, and atrazine accounted for substantially more detections than the parent compounds (fig. 5–15). Two of the principal factors likely to be responsible for this general observation are that (1) ground water recharges through soil where microbial populations—and thus transformation rates—are relatively high, and (2) residence times in ground water are usually long prior to sample collection, allowing more time for transformations to occur than is usually the case for surface waters.

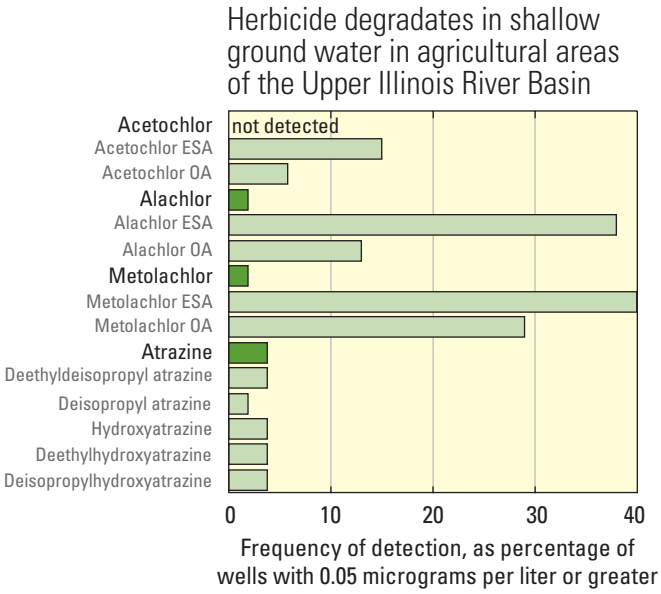

Figure 5–15. In ground water of the Upper Illinois River Basin, degradates (light bars) were generally detected more frequently than parent compounds (dark bars) for the acetanilide herbicides (acetochlor, alachlor, and metolachlor), but at comparable frequencies for atrazine (Groschen and others, 2004).

Deethylatrazine-to-Atrazine Ratios

As pesticides are transported through the hydrologic system, transformations occur continuously and at various rates, resulting in changes in the proportional relations between parent pesticides and their degradates with time and space. In general, the extent of transformation increases with increasing residence time in the hydrologic system. As a result, degradate-to-parent compound concentration ratios—such as the deethylatrazine-to-atrazine ratio (Adams and Thurman, 1991)—have been used as indicators of residence time in the environment. Because the transformation of atrazine to deethylatrazine requires microbial assistance (fig. 5–12)—and microbial populations are generally much higher in the soil than at greater depths beneath the land surface or in surface waters—the deethylatrazine-to-atrazine ratio provides an indication of the amount of time that atrazine has been in contact with soil. In streams, the deethylatrazine-to-atrazine ratio increased with the time elapsed between atrazine applications and sampling—from the lowest values during atrazine applications in the spring, to higher values in autumn, and to the highest values in winter, just before applications (fig. 5–16). Figure 5–17 shows how the ratio changed over time during the year in the White River. Because the analytical recovery (the proportion of the actual total concentration that could be measured) for deethylatrazine was lower than for atrazine, the ratios reported here underestimate the true value, but the focus of this analysis is on the relative magnitudes of the ratios among different media, settings, and times of year, rather than their absolute values.

Deethylatrazine-to-atrazine ratios were generally higher in ground water than in streams throughout the year, reflecting the longer periods of time spent in contact with soil for the atrazine detected in the ground-water system, relative to streams (fig. 5–16). The proportions of deethylatrazine in water collected from major aquifers—which generally represents ground water that is deeper and older than water collected from shallow wells—were typically higher than those measured in the shallow ground water sampled within agricultural areas.

Importance of Pesticide Degradates

NAWQA results are consistent with findings from other studies that found that pesticide degradates occur frequently in streams and ground water (Battaglin and others, 2001; Scribner and others, 2003; Kolpin and others, 1998; Kolpin and others, 2004). Assessment of the occurrence, distribution, and toxicities of pesticide degradates in the hydrologic system is important because of the potential effects of these compounds on human health and the environment (Sinclair and Boxall, 2003), as well as their value for understanding the ultimate fate of pesticides in the hydrologic system (Barbash, 2004). Pesticide degradates should continue to be considered and accounted for in assessments of pesticide exposure and in evaluating the potential effects of pesticides. Improved assessment of pesticide degradates will require expanded coverage of degradates in water-quality monitoring, continued research on pesticide transformations and transport, and continued attention to these compounds in toxicity studies, including as components of pesticide mixtures (see Chapter 6).

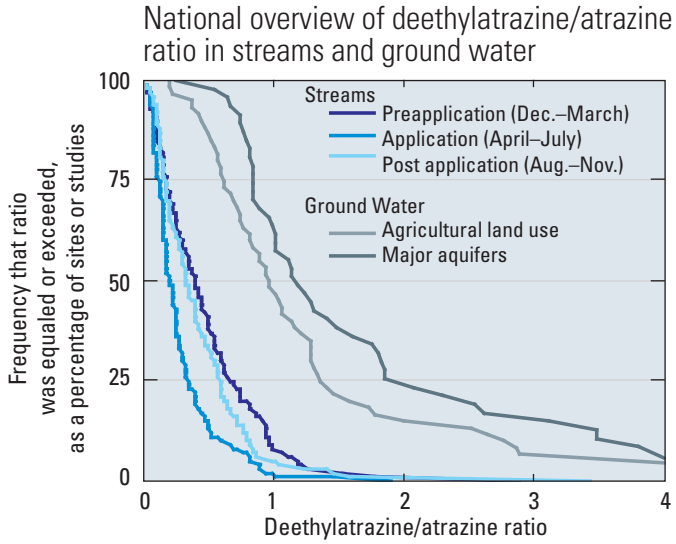

Figure 5–16. The ratios of deethylatrazine to atrazine concentrations—which increase with the transformation of atrazine to deethylatrazine—increased with increasing residence time in the hydrologic system. (Ratios were computed from µg/L concentrations for all NAWQA stream and ground-water samples in which both compounds were detected.)

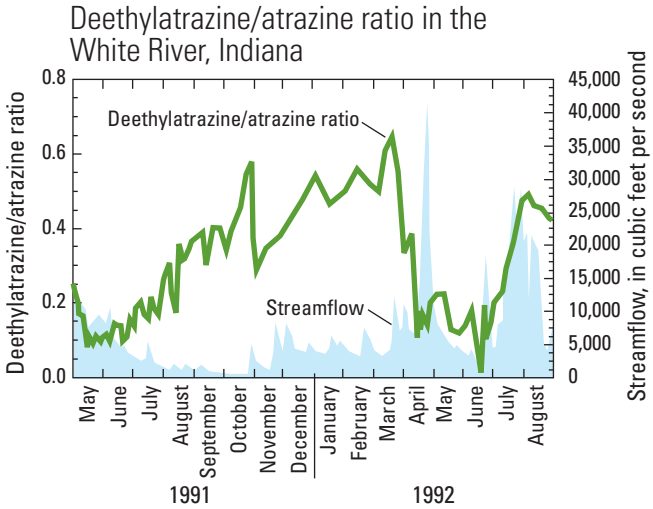

Figure 5–17. The ratios of deethylatrazine to atrazine concentrations in the White River (White River Basin) were lowest in the spring, following widespread atrazine applications. The ratio generally increased through the summer and winter as atrazine transformed to deethylatrazine and ground water made up an increasing proportion of streamflow. (Ratios were computed from µg/L concentrations; modified from Carter and others, 1995.)

White River, Indiana.

Pesticide Degradates in USEPA Risk Assessments and Regulations

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

When USEPA characterizes the risks of a pesticide to humans and the environment to meet the requirements of FIFRA, the agency evaluates both the parent pesticide and its degradates. Before a pesticide is registered, USEPA reviews and evaluates available studies on the pesticide's properties and effects, including its degradates (USEPA, 2005a). The types of data needed vary depending on how and where the pesticide is used (USEPA, 2004a).

Available studies may provide information on the degradation rates, mobility parameters, and toxicity for potentially important degradates. If adequate data are not available for specific degradates, USEPA's risk assessments for drinking-water exposure under FIFRA assume that degradates are highly persistent and mobile. If different toxicities are expected between degradates and the parent pesticide, concentrations are estimated separately. If the same toxicity is expected, concentrations of the parent and degradates are added together. These risk estimates are often conservative (protective) because it is frequently assumed that the degradate and parent have equal toxicities and that they are mobile and persistent. If data are available for a specific degradate, however, then those data are used. In some cases, degradates are known to be more toxic than the parent compound. In situations where degradates occur in substantial amounts or are of toxicological concern, risk assessments include a quantitative or qualitative analysis of the potential implications of an organism's exposure to these degradates, in addition to the parent pesticide.

USEPA environmental fate scientists work with human health and ecotoxicology scientists to identify the degradates of toxicological concern. The formation of degradates is monitored as part of fate studies required for pesticide registration. Methods are used that have detection limits sufficiently low to allow for detailed tracking of the production of degradates. Degradates formed at greater than 10 percent of radioactively labeled parent pesticide are considered major degradates and must be identified (USEPA, 1982). The 10-percent criterion is a general guideline, such that degradates approaching concentrations of 10 percent of the parent are usually identified as well. In addition, degradates of known toxicological or ecotoxicological concern must be quantified and identified even when present at lower levels.

When environmental monitoring data are available for pesticide degradates, the data are characterized and summarized in USEPA's assessments for FIFRA. In evaluating monitoring data, scientists evaluate the analytical methods used, pesticide-use information, and the design of the monitoring studies. Monitoring data on the occurrence of degradates are included in the FIFRA risk assessment, but the assessment of risk also depends on a variety of additional factors, including the mode of toxicity of the degradate—information that is needed to determine if concentrations of the parent pesticide and degradates can reasonably be aggregated to assess risk.

Clean Water Act (CWA)

Ambient water-quality criteria, developed by USEPA under section 304(a) of the CWA, focus on individual chemicals. If a degradate is toxicologically important, a separate criterion may be developed for the degradate. Human health ambient water-quality criteria exist for DDT, DDE, and DDD; endrin and endrin aldehyde; heptachlor and heptachlor epoxide; and endosulfan and endosulfan sulfate. Whole-effluent toxicity tests, described in Chapter 6 in relation to assessing potential effects of pesticide mixtures on aquatic life, also provide an approach for assessing degradate toxicity.

Safe Drinking Water Act (SDWA)

Maximum Contaminant Levels (MCLs) are legally enforceable drinking-water standards developed by USEPA under the SDWA. Although drinking-water standards have typically been developed only for the pesticide parent, the SDWA does not preclude USEPA from developing standards for pesticide degradates. Several unregulated pesticide degradates are listed on USEPA's drinking-water Contaminant Candidate List (CCL) and its Unregulated Contaminant Monitoring Regulation (UCMR) (USEPA, 2005b,c). Once sufficient information and data are available on health risks, occurrence, analytical methods, and treatment technologies, USEPA will determine whether any of the listed pesticide degradates are candidates for future drinking-water standards.

USEPA also develops drinking-water Health Advisories for chemical substances, including some pesticides and pesticide degradates. Health Advisories, which are not legally enforceable, provide technical guidance for Federal, State, Tribal and local officials in the event of an emergency spill or contamination situation. USEPA periodically updates Health Advisories when new information becomes available (USEPA, 2005d).