8 Long-Term Trends

Long-term trends and changes in pesticide concentrations in streams and ground water are controlled largely by shifts in pesticide use, but the rates and geographic distributions of changes are also influenced by the chemical and physical properties of the pesticides and characteristics of the hydrologic settings. The first decade of NAWQA assessments focused primarily on establishing baseline conditions for comparison with future measurements as part of a long-term approach to tracking trends. Many trends, particularly those on a national scale, cannot yet be evaluated because not enough time has elapsed. Trends and changes are already evident, however, for some pesticides in selected localities and regions.

Photograph used with permission from Larry Mayer

This chapter provides selected examples of trends and illustrates the range of different factors that govern trends for various pesticides in fish tissue, bed sediment, stream water, and ground water.

Organochlorine Pesticide Compounds in Fish

One of the most striking trends evident from historical data and more recent NAWQA findings is a national reduction in concentrations of organochlorine insecticides in fish tissue, as illustrated by concentrations of total DDT, total chlordane, and dieldrin measured by NAWQA and the U.S. Fish and Wildlife Service. NAWQA data from 1992 to 2001 for whole fish in streams draining watersheds with mixed land use were combined with 1969–1986 data from the U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP), which sampled mainly large streams in watersheds with mixed land use.

The median and 90th-percentile concentrations of total DDT in whole fish declined markedly from 1969 to about the mid-1970s, with less dramatic declines through the 1990s (fig. 8–1). Concentrations of total chlordane in fish, for which consistent data were not available until 1978, declined similarly during the 1980s and appeared to level off during the 1990s. For dieldrin, the median and particularly the 90th percentile concentrations varied substantially during the early 1970s, but concentrations during the late 1970s were lower than in 1969, and then continued to decline slowly through the early 1990s. Variability in trends in organochlorine pesticides during the 1990s, which is evident in figure 8–1, probably represents differences among groups of NAWQA sites rather than actual trends.

The observed trends reflect the regulatory history of these three insecticides in the United States. Agricultural uses of all three were cancelled during the early 1970s, whereas use of aldrin, dieldrin, and chlordane was permitted for termite control through the late 1980s. The declines shown in figure 8–1 are consistent with an exponential rate of decline in which concentrations decrease by half within a constant interval of time (half-life), following the elimination of use. Nationally, the half-lives in whole fish, as estimated either from the NCBP data alone or from the combined NCBP and NAWQA data, are about 7 years for total DDT, 11–13 years for total chlordane, and about 30 years for dieldrin. The declines in concentrations of total DDT, total chlordane, and dieldrin in whole-fish tissue over the past three decades reflect past regulatory actions to discontinue their use, yet also illustrate that changes can take a long time to occur for pesticides with long half-lives.

Data Used to Evaluate Trends in Organochlorine Concentrations in Fish Tissue

Although few sites were sampled by both the NCBP and the NAWQA Programs, the sites used in this comparison had similar land uses, and the fish-sampling and compositing strategies of the two programs were comparable. Of the 117 NCBP sites, most were sampled every 1–3 years during 1969–1986 (Schmitt and Bunck, 1995). Each of the 228 NAWQA sites was sampled only once during 1992–2001, and sites generally were sampled in three groups corresponding to the rotational investigations of NAWQA Study Units (see Chapter 3). NAWQA sites plotted as 1992 in figure 8–1 actually were sampled during the period 1992–1994 (with most sampled during the first year), sites plotted as 1995 were sampled during 1995–1997, and sites plotted as 1998 were sampled during 1998–2001. Because NAWQA sampled three groups of sites in three different time periods, the variability in NAWQA results includes differences among sites as well as differences over time.

There were also some differences in analytical methods between NAWQA and NCBP. The NCBP measured only concentrations of *p,p′* isomers of DDT, DDD, and DDE in whole fish. For consistency, therefore, NAWQA data for the *o,p′* isomers of DDT, DDD, and DDE were not included when computing total DDT for evaluating trends in whole fish (fig. 8–1). On average, the *p,p′* isomers of DDT, DDD, and DDE made up 99 percent of total DDT (the sum of *o,p′* and *p,p′* isomers DDT, DDD, and DDE) in whole fish.

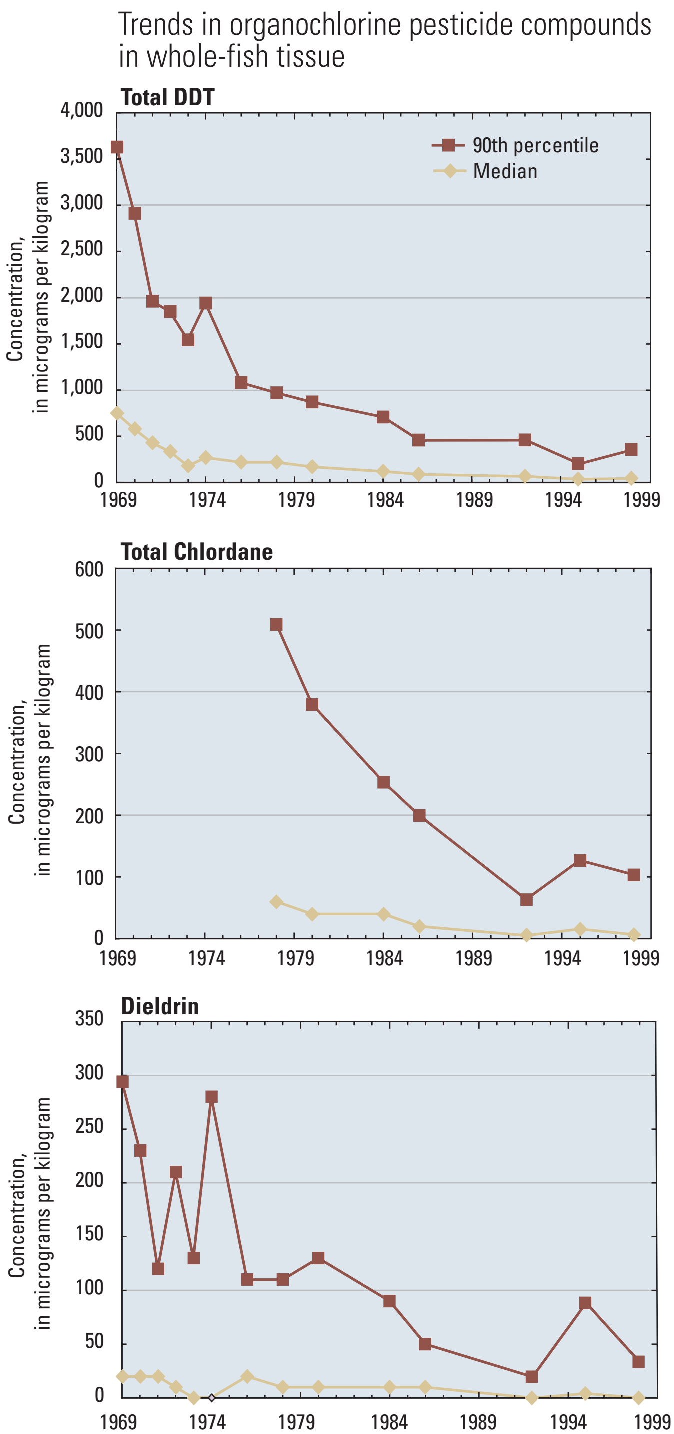

Figure 8–1. Concentrations of total DDT, total chlordane, and dieldrin in whole fish collected from streams draining watersheds with mixed land use throughout the United States have declined over the last 20 to 30 years. The declines followed discontinuation of their uses during the 1970s (agricultural uses of all three) and 1980s (use of aldrin, dieldrin, and chlordane for termite control). Despite the national decline in concentrations, these persistent compounds still are frequently detected in fish. (Data from 1969 to 1986 are from the U.S. Fish and Wildlife Service, Schmitt and Bunck, 1995; and data shown from 1992 to 1998 are from NAWQA. All concentrations are for wet weight of fish tissue.)

Trends in Total DDT and Chlordane in Lake Sediments

Peter C. Van Metre, U.S. Geological Survey

In addition to the studies of organochlorine pesticides in fish and bed sediment from streams, NAWQA also assessed long-term trends in the concentrations of these compounds through the analysis of sediment cores from lakes and reservoirs, which “record” a history of contaminant concentrations. As soils in a watershed erode, they are deposited as sediment in layers on the bottom of downstream lakes and reservoirs, along with organic particles from aquatic plants and animals. Age-dated sediment cores that penetrate these layered deposits can be used to track trends in total DDT and total chlordane, as well as other sediment-associated contaminants that are relatively stable over time.

Sediment cores from 41 lakes and reservoirs in 16 States—collectively referred to as lakes for the purposes of this report—were analyzed by Van Metre and Mahler (2005). The study included 31 lakes in urban settings, 7 lakes in undeveloped settings, and 3 additional lakes in watersheds dominated by agriculture. Urban lakes were selected to represent watersheds with primarily residential and commercial land uses; only a few of the sites are known to be influenced by significant point-source discharges. The statistical significance of trends (assessed at the 90-percent confidence level) was determined using the Kendall’s tau test for trends in concentrations with depth in the core (which is directly related to sediment age). Trends were also evaluated by comparing mean decadal concentrations for 1965–1975 with those for the period from 1990 to approximately 2000 (the top of the core).

Concentrations of total DDT (defined by Van Metre and Mahler (2005) as the sum of the concentrations of *p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD) declined significantly since about 1970 in all three of the agricultural lakes, 58 percent of the urban lakes, and 43 percent of the lakes in undeveloped watersheds (fig. 8–2). No lake had a significant upward trend in total DDT. Decadal mean concentrations declined in most lakes from 1965–1975 to 1990–2000, including the lakes without statistically significant trends within the core samples. Overall, the mean total DDT concentration during 1990–2000 was lower than the

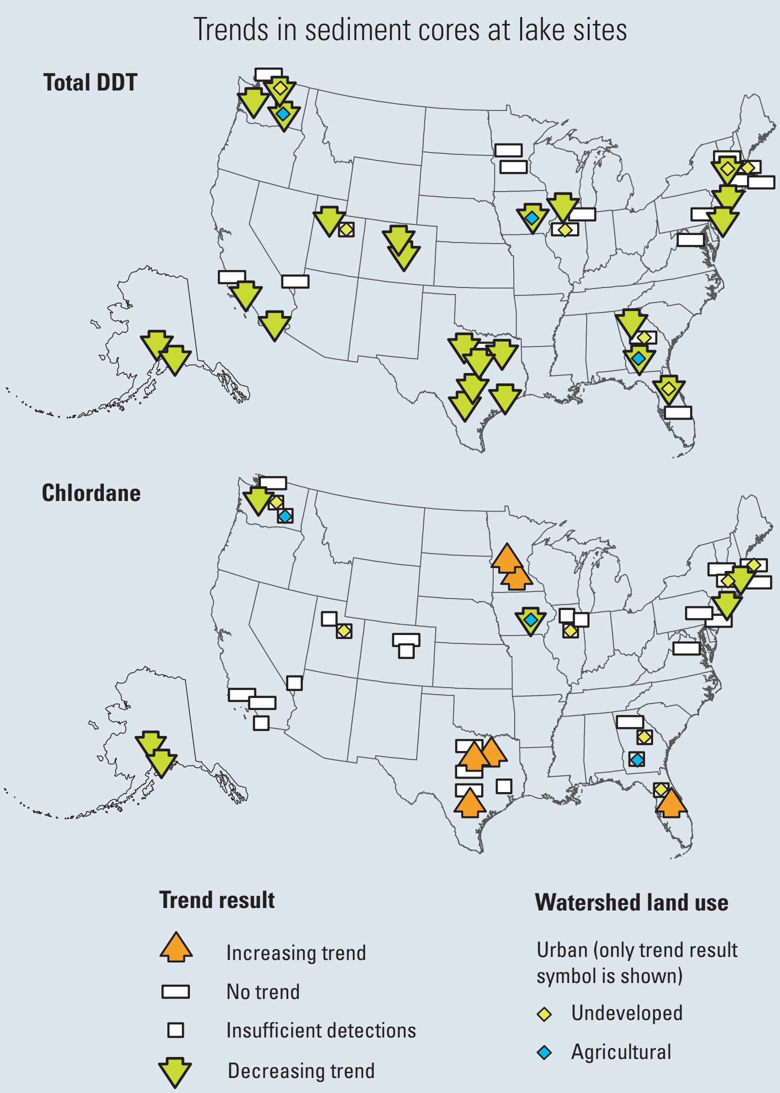

Figure 8–2. Concentrations of total DDT declined in most sediment cores collected from 41 lakes in 16 States, most of which were located in urban areas. The sediment cores were analyzed to track historical changes from about 1970 through 2000. The downward trends are consistent with historical changes in DDT use. Upward and downward trends in the concentrations of chlordane, however, were more evenly distributed, reflecting its continued use to control termites until at least 1990.

Analyses of sediment cores from lakes were used to reconstruct historical trends in DDT, chlordane, and other contaminants.

Trends in DDT in an agricultural and an urban lake

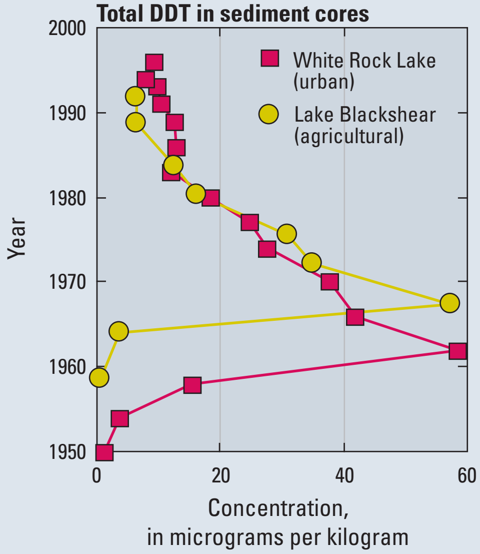

Figure 8–3. Decreases in the concentrations of DDT typically followed an exponential curve after uses began to decline during the 1960s and were cancelled in the early 1970s, as shown in sediment cores collected from White Rock Lake, Texas, and Lake Blackshear, Georgia. The rate of change indicates that an additional 50-percent reduction in concentrations of total DDT is likely to occur by approximately 2015.

mean 1965–1975 concentration in 90 percent of the lakes (37 out of 41). The median change in total DDT concentration was a decrease of 68 percent.

These results are consistent with the historical use and regulatory history of DDT, as well as with trends in total DDT concentrations in whole fish (fig. 8–1). As was observed in fish tissue, the decreases in DDT and other persistent hydrophobic contaminants typically followed an exponential curve after use was discontinued (Van Metre and others, 1998), with a steep initial drop followed by a gradual slowing of the change (fig. 8–3). The resulting half-lives for total DDT concentrations in lake sediment range between about 10 and 15 years (Van Metre and others, 1998; Van Metre and Mahler, 2005). Applied in this way, the half-life does not represent a single specific process (for example, chemical degradation), but is a simple measure of the rate of change in lake sediment concentrations over time as a result of a combination of reduced input, chemical transformations, and dilution. The rate of change observed for total DDT provides an indication of what might be expected in the future—an additional 50-percent reduction from present concentrations of these compounds during the next 10 to 15 years.

Trends in total (technical) chlordane (estimated by Van Metre and Mahler [2005] from the concentrations of *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor) in the sediment cores were more variable than those for total DDT, with upward and downward trends split evenly, and most showing either no significant trend or insufficient data (fig. 8–2). Sixteen percent of urban lakes showed significant downward trends, 19 percent showed upward trends, 42 percent showed no trend, and 22 percent could not be tested for trends because of insufficient detections. Lakes in undeveloped watersheds either showed no trend (29 percent), or could not be tested for trends because of insufficient detections (71 percent). Only one of the three agricultural lakes could be tested for a trend and it was significantly downward.

As with total DDT, these results for total chlordane are generally consistent with its historical use and regulation. Chlordane use in agriculture, which was primarily for corn, was discontinued in 1978; however, chlordane use for termite control exceeded its use in agriculture (Andrilenas, 1974; Esworthy, 1987) and continued until 1988 or later (USEPA, 2004g). In addition, use of existing chlordane stocks by homeowners was permitted after 1988 and was common in a 1990 survey (Whitmore and others, 1992). Therefore, it is not surprising that most urban lakes did not show significant downward trends from 1970 to 2000. This result for urban lakes, however, contrasts with the clear decline in total chlordane in fish from watersheds with mixed land uses (fig. 8–1). The difference may be caused by the contrasts in land use—the fish data from large watersheds with mixed land use may be influenced more by agricultural lands, where chlordane use stopped in 1978. Another possible explanation for the apparent upward trends in some of the urban lake cores is that chemical degradation of one or more of the chlordane-derived compounds could be occurring in some of the deeper core samples, thus making it appear that concentrations have increased over time (Van Metre and Mahler, 2005).

The cancellation of DDT and chlordane uses has generally resulted in decreased contaminant levels in samples of sediment and fish tissue from lakes. However, the continuing high levels of chlordane in urban areas, the slow rate of decreasing trends for DDT, and the continuing concern for human exposure from consumption of fish and shellfish (USEPA, 2004h, 2005g) indicate that these organochlorine pesticides will remain a concern for many years to come.

Herbicides in Agricultural Streams of the Corn Belt

Concentrations of modern, relatively short-lived pesticides in stream water generally respond rapidly to changes in use. Concentrations of the most heavily used herbicides in streams in the Corn Belt showed both increases and decreases on a regional scale from 1992 to 2001, correlating with changes in use during the same period (see sidebar on p. 133). For example, concentrations of atrazine, alachlor, acetochlor, cyanazine, and metolachlor in the White River—a large stream in Indiana that drains an extensive agricultural area dominated by corn and soybeans—followed regional trends in use (fig. 8–4). Acetochlor concentrations in the White River rapidly increased following its introduction in 1994, whereas alachlor concentrations decreased to less than one-tenth of its 1994 concentrations by 2001, as acetochlor replaced part of alachlor use (note the logarithmic scale in figs. 8–4 and 8–5). Among these five herbicides, the concentrations of atrazine changed the least through the decade, consistent with its relatively stable use during this time. Cyanazine concentrations declined most dramatically, following the reductions in its use, which began in the mid-1990s. The consistency of these trends in the region is illustrated by cyanazine results from 1996 to 2001 for streams in five different States within the Corn Belt (fig. 8–5).

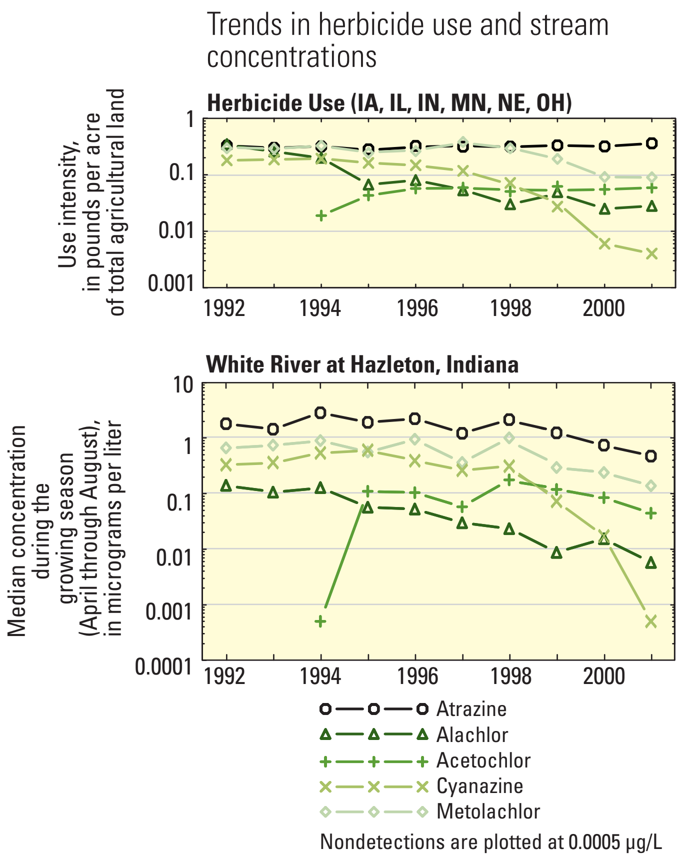

Figure 8–4. Concentrations of herbicides measured in the White River (White River Basin) during 1992–2001 show the correlation between stream concentrations and the regional trends in use intensity in Corn Belt States. The most dramatic examples are the increase in acetochlor concentrations after its introduction in 1994 and the decreases in alachlor and cyanazine that followed reductions in their use. (Pesticide use data are from the National Agricultural Chemical Use Database, accessed January 25, 2006 at *http://www.pestmanagement.info/nass/app_usage.cfm*.)

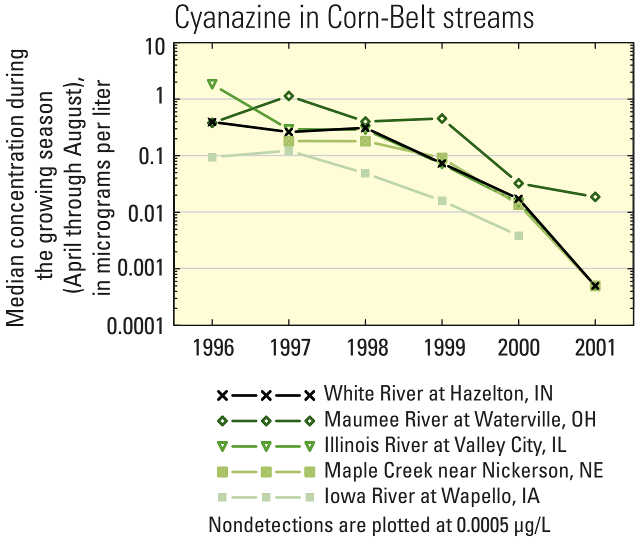

Figure 8–5. The consistency of declines in cyanazine concentrations in streams throughout the Corn Belt is illustrated by results for streams in five different States during 1996–2001. Similar consistency was evident for other major herbicides as well.

Trends in Use of Herbicides in the Corn Belt

From 1992 to 2001, there were major changes in the primary herbicides used for corn and soybean production in the Corn Belt States of Iowa, Illinois, Indiana, Minnesota, Nebraska, and Ohio (see fig. 8–4), even though the total treated crop acreage remained fairly constant. Changes in these herbicides, which combine to account for more than 40 percent of all national herbicide use, exemplify the shifts in use patterns that are typical of pesticides in response to changes in factors such as regulations, monitoring results, effectiveness, and cost.

Throughout the 1990s, atrazine was the herbicide used most widely on corn, and the area treated each year varied little. In the early 1990s, atrazine use decreased slightly because of reduced application rates resulting from regulatory agreements between USEPA and the atrazine manufacturer. This decline, however, was soon offset by increased use of atrazine in tank mixes with other herbicides, and total use remained near the 1990 level in major corn-producing States.

Metolachlor and alachlor were the second and third most heavily used herbicides in 1990, but their use declined substantially by 2001 because of the introduction of new herbicides. In 1994, acetochlor was conditionally registered for use on corn, with the goal of reducing the use of alachlor and other corn herbicides by one-third. By 1997, acetochlor had virtually replaced alachlor use and was rapidly becoming one of the most widely used herbicides (note the logarithmic scale in fig. 8–4). Also in 1997, S-metolachlor was conditionally registered for use. S-metolachlor is the more effective form of two different isomers of metolachlor (both the R- and S-metolachlor isomers were present in metolachlor products). The introduction of S-metolachlor, which has a 30-percent lower application rate, contributed to the decrease in total metolachlor use during the late 1990s. An additional development that probably contributed to the decline in the use of metolachlor and other herbicides was the introduction of bioengineered crops that were genetically modified to be resistant to specific herbicides, such as glyphosate.

The most dramatic decline in herbicide use during the 1990s was for cyanazine. Because of frequent detection of cyanazine in surface and ground water, cyanazine manufacturers began to phase out this product beginning in 1994. This phase-out, which was completed in 2000, shifted cyanazine from the fourth most heavily used herbicide in 1992, to only minor use by 2001.

Recent NAWQA Data Show that Diazinon Concentrations in Some Northeast Streams have Declined Following Recent Reductions in Use

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Scott W. Ator, U.S. Geological Survey
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Until about 2001, diazinon was one of the most widely used insecticides in the United States for residential lawn and garden pest control (accounting for almost 70 percent of the 11 million lb of diazinon used for all purposes each year), for residential indoor uses (up to 5 percent of total use), and for agricultural pest control (almost 30 percent of total use). In December 2000, USEPA and diazinon registrants agreed to phase out the sale of diazinon for residential uses (both outdoor and indoor), as well as for many agricultural uses. As part of the agreement, indoor uses of diazinon were terminated and all outdoor nonagricultural uses (principally on residential lawns and gardens) were phased out during 2002–2004. Manufacturing of diazinon for application to gardens, lawns, and other turf stopped in June 2003, and sales and distribution to retailers ended in August 2003. Retail sales ended on December 31, 2004, after which a buy-back program helped to remove from the market the remaining diazinon products. USEPA and the registrants also agreed to reduce the uses of diazinon on agricultural crops by about one-third. By 2005, these combined actions eliminated most of the use of diazinon, compared with use in 2000.

Analysis of data from seven NAWQA stream sites in the Northeast—five classified as urban streams and two as mixed land use—using Seasonal Kendall tests at the 95-percent confidence level (Schertz and others, 1991), indicate predominantly downward trends in concentrations of diazinon since the reductions in diazinon use began in 2000 (fig. 8–6). Specifically, concentrations of diazinon decreased by 20 to 41 percent since 1998 at the five sites with statistically significant changes. Concentrations at the two sites with no statistically significant change showed decreases of 13 and 22 percent for the same period. Diazinon concentrations observed in one of the five urban streams (Accotink Creek, VA) provide an illustration of how concentrations have recently declined in some streams—in this case by about 39 percent from 1998 to 2004 (fig. 8–7).

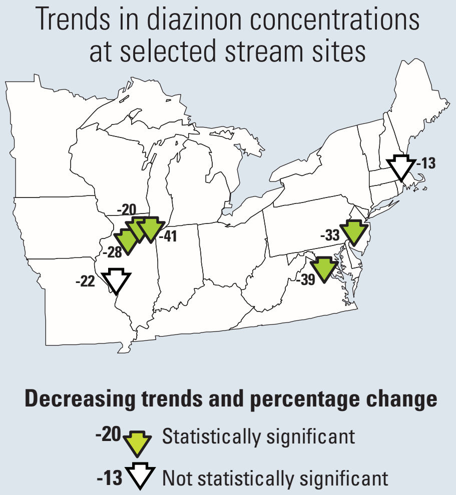

Figure 8–6. Diazinon concentrations decreased significantly from 1998 to 2004 in 5 of 7 urban and mixed-land-use streams in the northeastern United States. Trends were evaluated using the Seasonal Kendall test at the 95-percent confidence level.

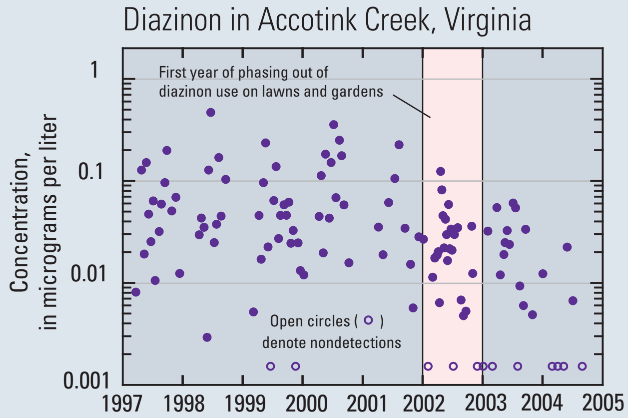

Figure 8–7. From 1997 to 2001, the levels and ranges of diazinon concentrations in Accotink Creek (Potomac River Basin) were relatively similar from year to year, but from 2002 to 2004, diazinon concentrations generally decreased. These decreases correspond to the national reduction in total sales and use of diazinon through this period, although no specific use data were available for the Accotink Creek watershed.

Ground Water

Pesticide concentrations in ground water, compared with streams, respond more slowly to changes in pesticide use or land-management practices, often lagging by years or decades, depending on the nature of the flow system and the depth and location of wells sampled. During the long periods of time that it takes for water to move through most ground-water flow systems, the types and amounts of pesticides applied at the land surface often change. This makes it difficult to link the concentrations of pesticides detected in specific wells with the locations where the pesticides were used. Evaluation of trends in ground water is also made more difficult by the complex flow paths along which ground water moves, and the resulting uncertainty about where sampled water originally entered the ground-water flow system.

For these reasons—as well as a general shortage of suitable data—trends in pesticide levels in ground water have not been extensively characterized. As noted by Barbash and Resek (1996), few previous studies have used consistent sampling and analytical methods over long enough periods, or developed a sufficient understanding of the flow system and age of sampled ground water, to reliably evaluate long-term trends in ground-water quality. Although NAWQA ground-water studies use consistent sampling and analytical methods, NAWQA monitoring has not yet covered a long enough period of time in most locations to assess trends. Despite these challenges, examples of ground-water trend assessments from USGS studies, conducted in cooperation with other agencies in Iowa and Florida, illustrate the types of trends that may occur over different time scales and demonstrate some of the approaches to trend assessment.

Herbicides in Iowa Ground Water

Results from the Iowa Ground Water Monitoring Program, a joint study by the Iowa Geological Survey, USEPA, and USGS, show that herbicide concentrations have increased in Iowa ground water with increasing herbicide use since the 1950s (Kolpin and others, 2004). Low levels of tritium (less than 0.8 tritium units [TU]) were used as an indicator of water recharged before 1953, which was prior to the onset of substantial herbicide use. All but 1 of 42 samples with detectable concentrations of herbicides or degradates were samples of water that had recharged after 1953 (fig. 8–8), whereas more than 80 percent of the samples with undetectable herbicides or degradates had recharged prior to 1953. The detection of herbicides in one sample with low tritium probably resulted from the mixing of younger and older waters in samples collected from a municipal supply well. The results from this study demonstrate the value of information on ground-water recharge dates and residence times for the analysis of data for trend assessment. Use of estimated recharge dates provided the most reliable means available for determining that most samples without detections were ground water that had recharged before the beginning of major herbicide use. In addition, because the correlations between estimated recharge date and the occurrence of pesticide

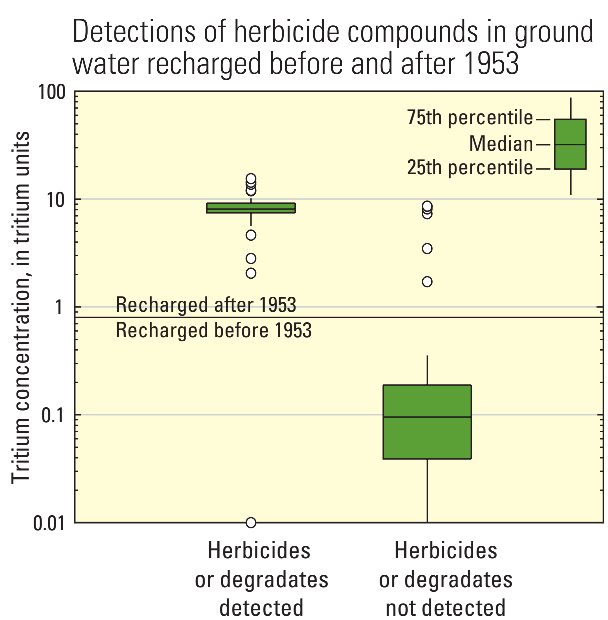

Figure 8–8. The Iowa Ground-Water Monitoring Program showed that herbicides or their degradates were detected in 41 of 42 municipal supply wells in Iowa that tap ground water recharged after 1953 (as indicated by tritium concentrations greater than 0.8 tritium units). Conversely, more than 80 percent of the samples in which herbicide compounds were not detected were samples of ground water recharged prior to 1953, before significant use of herbicides began. (Modified from Kolpin and others, 2004.)

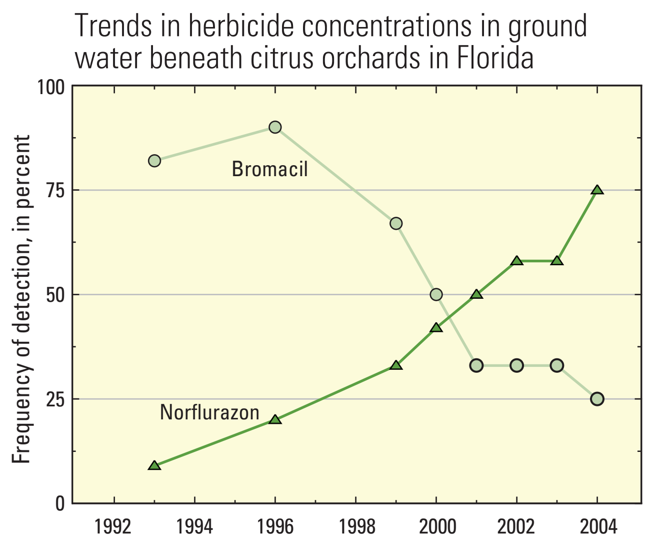

Figure 8–9. In central Florida, applications of bromacil in citrus orchards were discontinued in 1994, yet it was still detected at or above 2 µg/L in 25 percent of the sampled wells 10 years later. The frequency of detecting norflurazon, which began to replace bromacil on citrus in 1994, did not exceed that of bromacil for about 6 years. (Modified from Choquette and others, 2005.)

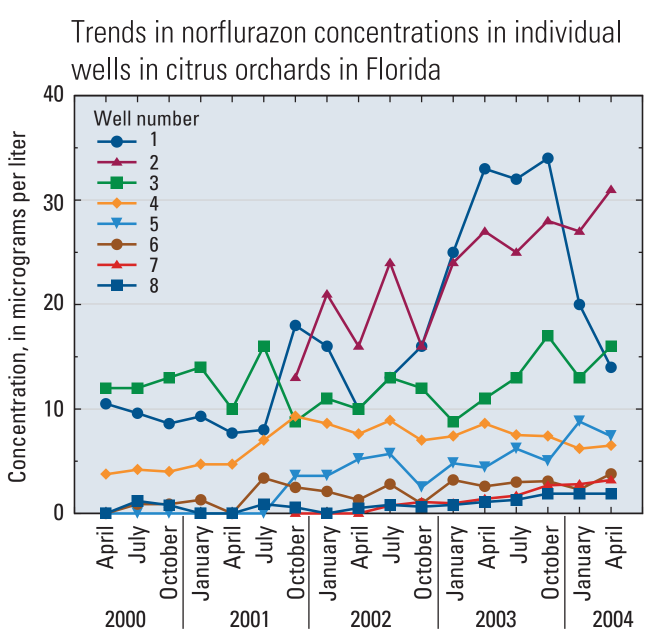

Figure 8–10. Although concentrations of norflurazon increased from 2000 to 2004, there was substantial seasonal and annual variability. Variability among wells was associated with depth to water, depth of the well screen below the water table, the length of the well screen, and the thickness of the aquifer zone sampled. (Modified from Choquette and others, 2005.)

compounds in ground water were more evident when degradates were considered, the study by Kolpin and others (2004) demonstrates the value of incorporating data on degradate occurrence for detecting trends.

Herbicides in Florida Ground Water

A study by the USGS, Florida Department of Agriculture and Consumer Services, and the Southwest Florida Water Management District was undertaken to monitor and assess the quality of shallow ground water in central Florida (Choquette and Sepúlveda, 2000). This region is dominated by citrus production and is characterized by well-drained sandy soils that are conducive to relatively rapid movement of water and pesticides to and within the ground-water flow system (Choquette and others, 2003).

The study found that bromacil, a widely used herbicide, declined but continued to be detected in 25 percent or more of the sampled wells for up to 10 years after its use in the region's citrus orchards was prohibited in 1994 (fig. 8–9). The decline in bromacil detections coincided with an increase in detections of norflurazon, which began to replace bromacil in 1994. The frequency of norflurazon detections, however, did not exceed that of bromacil until the year 2000, about 6 years after the use of bromacil was discontinued (Choquette and others, 2005).

Although figure 8–9 indicates that the overall frequency of norflurazon detection in ground water increased from 1993 to 2004 within the area studied by Choquette and others (2005), concentrations of norflurazon showed considerable seasonal and annual variability in the individual wells sampled, as well as variability among different wells (fig. 8–10). These variations were associated with differences among the wells in the age of the ground water, the depth to water, the depths of the sampled zone below the water table, and the thickness of the aquifer zone sampled. The highest and most variable concentrations (wells 1–3) occurred where depths to the water table were relatively shallow and in wells that sampled water closest to the water table. The lower and less variable concentrations occurred in the deeper wells (wells 4–8) with long screened intervals. These observations are consistent with results from previous studies, indicating that the temporal variability in pesticide concentrations generally tends to diminish with increasing well depth (Barbash and Resek, 1996).