

National Water-Quality Assessment Program

**An Overview Comparing Results from Two Decades of
Monitoring for Pesticides in the Nation's Streams and Rivers,
1992–2001 and 2002–2011**

Scientific Investigations Report 2014–5154

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By Wesley W. Stone, Robert J. Gilliom, and Jeffrey D. Martin

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Conversion Factors and Abbreviations

SI to Inch/Pound

Multiply	By	To obtain
	Area	
square kilometer (km ²)	247.1	acre
square kilometer (km ²)	0.3861	square mile (mi ²)

Water year is the 12-month period of October 1, for any given year through September 30, of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months.

Abbreviations used in this report

ALB	Aquatic Life Benchmark
GCMS	gas chromatography/mass spectrometry
HHB	Human Health Benchmark
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
NLCD	National Land Cover Data
NLCD06	National Land Cover Data 2006
NLCDe	National Land Cover Data enhanced
NWQL	National Water Quality Laboratory
USGS	U.S. Geological Survey

An Overview Comparing Results from Two Decades of Monitoring for Pesticides in the Nation's Streams and Rivers, 1992–2001 and 2002–2011

By Wesley W. Stone, Robert J. Gilliom, and Jeffrey D. Martin

Abstract

This report provides an overview of the U.S. Geological Survey National Water-Quality Assessment program and National Stream Quality Accounting Network findings for pesticide occurrence in U.S. streams and rivers during 2002–11 and compares them to findings for the previous decade (1992–2001). In addition, pesticide stream concentrations were compared to Human Health Benchmarks (HHBs) and chronic Aquatic Life Benchmarks (ALBs). The comparisons between the decades were intended to be simple and descriptive. Trends over time are being evaluated separately in a series of studies involving rigorous trend analysis. During both decades, one or more pesticides or pesticide degradates were detected more than 90 percent of the time in streams across all types of land uses. For individual pesticides during 2002–11, atrazine (and degradate, deethylatrazine), carbaryl, fipronil (and degradates), metolachlor, prometon, and simazine were detected in streams more than 50 percent of the time. In contrast, alachlor, chlorpyrifos, cyanazine, diazinon, EPTC, Dacthal, and tebuthiuron were detected less frequently in streams during the second decade than during the first decade. During 2002–11, only one stream had an annual mean pesticide concentration that exceeded an HHB. In contrast, 17 percent of agriculture land-use streams and one mixed land-use stream had annual mean pesticide concentrations that exceeded HHBs during 1992–2001. The difference between the first and second decades in terms of percent of streams exceeding HHBs was attributed to regulatory changes. During 2002–11, nearly two-thirds of agriculture land-use streams and nearly one-half of mixed land-use streams exceeded chronic ALBs. For urban land use, 90 percent of the streams exceeded a chronic ALB. Fipronil, metolachlor, malathion, cis-permethrin, and dichlorvos exceeded chronic ALBs for more than 10 percent of the streams. For agriculture and mixed land-use streams, the overall percent of streams that exceeded a chronic ALB was very similar between the decades. For urban land-use streams, the percent of streams exceeding a chronic ALB during

2002–11 nearly doubled that seen during 1992–2001. The reason for this difference was the inclusion of fipronil monitoring during the second decade. Across all land-use streams, the percent of streams exceeding a chronic ALB for fipronil during 2002–11 was greater than all other insecticides during both decades. The percent of streams exceeding a chronic ALB for metolachlor, chlorpyrifos, diazinon, malathion, and carbaryl decreased from the first decade to the second decade. The results of the 2002–11 summary and comparison to 1992–2001 are consistent with the results from more rigorous trend analysis of pesticide stream concentrations for individual streams in various regions of the U.S.

Introduction

The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) and National Stream Quality Accounting Network (NASQAN) are monitoring programs that collect and report data for national assessments of pesticide concentrations in the Nation's streams and rivers. Gilliom and others (2006) reported findings for the first decade (1992–2001) of the NAWQA program and found that pesticides or their degradates were present in one or more water samples from every stream included in the assessment; one or more pesticides were detected more than 90 percent of the time in agricultural, urban, and mixed land-use streams; and the most frequently detected pesticides also had the greatest use.

This report builds upon the 1992–2001 assessment of pesticides in the Nation's streams (Gilliom and others, 2006) by summarizing pesticide occurrence in streams during the second decade (2002–11) of NAWQA stream monitoring, including pesticide stream concentration data from the NASQAN program, and providing descriptive comparisons between the two decades of pesticide monitoring. Gilliom and others (2006) assessed the occurrence of 83 pesticides and degradates from 186 stream sites that represented agriculture, urban, mixed, and undeveloped land uses during 1992–2001.

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Changes in the NAWQA program between the first and second decades reduced the number of monitored stream sites. The sampling design (number of samples to be collected and when they were to be collected) also changed between the decades. Specifically, the 1992–2001 sampling design was a mix of fixed-frequency sampling and high-flow sampling (to characterize times of expected higher stream pesticide concentrations); however, the 2002–11 sampling design was fixed-frequency with minimal high-flow sampling efforts. In addition, the number of pesticides and degradates that were monitored in streams sufficient for a national assessment nearly doubled during the second decade.

The changes in the NAWQA pesticide stream monitoring program from the first to second decade made it difficult to do simple, stream site to stream site comparisons between the decades and compare directly to the assessment by Gilliom and others (2006). In addition, this assessment differs from the previous assessment by Gilliom and others (2006) because (1) Human Health Benchmarks (HHBs) and chronic Aquatic Life Benchmarks (ALBs) have been updated; (2) some pesticides assessed during 1992–2001 were not sampled at enough sites to attain a reasonable national distribution during 2002–11; (3) land use ancillary data used to group sites have changed over time; (4) the stream-site selection process was revised; and (5) this assessment includes multiple years of data for sites, when available. The inclusion of multiple years of concentration data rather than a single year in the assessment, as was done by Gilliom and others (2006), was evaluated in terms of occurrence and percent of stream sites exceeding an HHB or chronic ALB for 1992–2001. The occurrence of pesticides in streams and the percent of stream sites that exceeded an HHB or chronic ALB for a single year compared to multiple years were all within 10 percent of each other for 1992–2001. Overall, the 1992–2001 results in this report are not markedly different than those reported by Gilliom and others (2006) except in cases where an ALB has been more recently established. For example, an ALB for metolachlor or *S*-metolachlor did not exist when Gilliom and others (2006) completed the initial assessment for 1992–2001; however, ALBs for *S*-metolachlor have been established and are used in this assessment. This report uses the most current HHBs and chronic ALBs for assessment of annual pesticide stream concentrations. Acute ALBs were not used in the comparisons between decades because the differences in sampling designs between them would likely bias the comparisons.

Purpose and Scope

The purpose of this report is to summarize pesticide occurrence in U.S. streams and rivers during 2002–11 in comparison to the previous decade, 1992–2001. This overview focuses on pesticide occurrence (percent of time detected) and pesticide concentrations in relation to HHBs and chronic ALBs. Although pesticide occurrence is compared between the decades for perspective, the comparisons are simple and

descriptive, and are not meant as a rigorous trend analysis. Trends are being evaluated separately in a series of studies involving quantitative site-based trend models, including Corn-Belt streams (Sullivan and others, 2009) and urban streams (Ryberg and others, 2010).

Pesticide Monitoring Design

The national design for monitoring pesticides in streams and rivers has evolved from the combination of two USGS programs, NAWQA and NASQAN. NAWQA stream monitoring during 1992–2001 focused on assessing water-quality conditions in 51 of the Nation's river basins, referred to as "Study Units," on a rotational schedule—20 Study Units during 1992–95, 16 during 1996–98, and 15 during 1998–2001 (Gilliom and others, 2006). Pesticide samples generally were collected at each stream site by using a combination of fixed-frequency and high-flow sampling (Gilliom and others, 1995). Fixed-frequency sampling means that a given number of water-quality samples were allocated to each month (more samples for months with expected higher potential for pesticide runoff and fewer samples during months of lower expected potential for pesticide runoff), and the water samples were collected at regularly spaced intervals within each month. High-flow sampling was used to allocate additional water samples to characterize high-flow events during seasonal periods of high pesticide use and potential runoff. Changes to the design of the NAWQA program during 2002–2011 included reduction in the number of long-term stream-monitoring sites, an increased emphasis on regional assessments, and supplemental high-flow sampling was limited to special regional studies.

The NASQAN program was redesigned in 1995 to estimate the mass flux of pesticides and other constituents at 41 monitoring sites in four large river systems: the Mississippi, the Rio Grande, the Columbia, and the Colorado. Similar to the NAWQA program, water samples generally were collected at each stream site by using a combination of fixed-frequency and high-flow sampling (Hooper and others, 2001). Also similar to the NAWQA program, the frequency of water-quality sampling typically changed seasonally, with more frequent samples during the peak pesticide-runoff months. The NASQAN sampling strategy was revised in 2000 (U.S. Geological Survey, 2010), with reduced monitoring in the Columbia and Colorado River Basins.

Methods

This report summarizes pesticide stream concentration data from samples collected during 2002–11 and compares the results to findings from 1992–2001. Site selection was based on the number of years with data, watershed size, and frequency of sampling within each year. For a sampling site, all years of sampling that met the minimum sampling criteria were included in the summaries. The summaries for

both decades are based on the estimated amount of time a pesticide was detectable at a stream site and the number of times HHBs and chronic ALBs were exceeded. For summary purposes, sampling sites were grouped by dominant land-use classification.

Pesticides

During any given year more than 400 different pesticides are used in agricultural settings (Stone, 2013). The large number of pesticides in use and the phasing out and introduction of new pesticides make it not possible to monitor all pesticides because of budget and method constraints. This report includes a selected subset of pesticides in use over the last two decades that were sampled at enough sites to attain a reasonable national distribution during 2002–11.

Pesticides included in this report are listed in appendix 1 (table 1–1). Martin (2009) determined that only pesticide data from a single laboratory and analytical method were sufficiently extensive in time and space for a national assessment across decades. Hence, only pesticides and pesticide data that were analyzed at the National Water-Quality Laboratory (NWQL) by a gas chromatography/mass spectrometry (GCMS) method were included in this report. The NAWQA and NASQAN programs periodically evaluate the full range of pesticides in use to prioritize monitoring to include the most important ones in relation to ecosystem and human health (Norman and others, 2012). This prioritization process also evaluates the likelihood that a pesticide will be found in surface water or sediment, based on chemical properties. During

2002–11, there were 123 pesticides and pesticide degradates with sufficient stream concentration data to include in this assessment. Gilliom and others (2006) included 83 pesticides in their assessment of 1992–2001; however, only 47 of these pesticides were sampled at enough sites during 2002–11 for a national-level comparison between the decades. The difference between the 47 pesticides assessed during the first decade and the 123 pesticides assessed during the second decade included 39 (or 51 percent) pesticide degradates; 21 (or 28 percent) insecticides; 8 (or 11 percent) fungicides; and the remaining were herbicides, nematicides, plant growth regulators, and defoliant.

Figure 1 shows an overview by one measure—amount used—of how pesticides included in this report relate to total national use and to selected pesticides or groups not included. A large portion of the difference between national total herbicide use and the proportion included in this report was the result of increased use of glyphosate that came with the rapid adoption of genetically modified crops resistant to glyphosate, beginning in the mid-1990s. Glyphosate is difficult and costly to measure, and efforts to assess glyphosate have been limited primarily to local or short-term studies. Other types of pesticides not comprehensively included in this report, such as fungicides and neonicotinoid insecticides, are not individually as prominent as glyphosate in terms of amounts applied, but may be environmentally important because of their greater toxicity. Finally, some hydrophobic pesticides, such as legacy organochlorines and pyrethroid insecticides, are important as contaminants of sediment and (or) tissues, but are not often found in filtered-water samples.

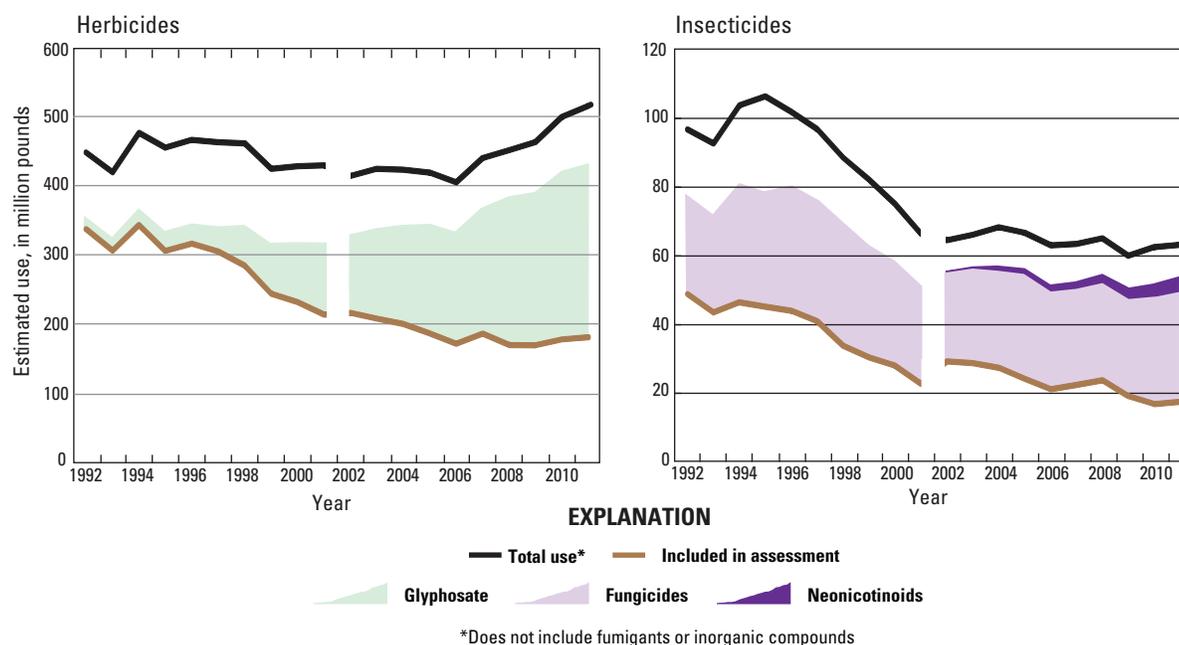


Figure 1. Estimated agricultural use of synthetic organic herbicides, insecticides, and fungicides in the conterminous U.S. during first (1992–2001) and second (2002–11) decades of stream monitoring. (GfK Kynetec, Inc., proprietary data, written commun., December 2011 and July 2013).

Stream-Site Selection

Stream-site selection was based on total number of samples each year, watershed size, and the number of samples during potentially high pesticide runoff months. A year was defined as the water year, beginning October 1 and ending September 30. Stream-site selection was based on modification of the criteria used in Stone and others (2013). The stream-site selection process began with an evaluation of the number of samples collected for the water year compared to minimums based on watershed size (table 1). Stream sites retained from the previous step were then evaluated to make sure there was at least one sample during the months of May, June, and July. These three months are typically the months of expected higher transport of pesticides to streams for the most heavily used pesticides (Stone and others, 2013). Stream sites retained to this point were then evaluated to ensure that samples were present during times when pesticides are less likely transported to streams in order to better represent their occurrence during the entire water year. Specifically, each stream site could not have a consecutive 3-month period without a sample. The stream-site selection process was done by individual pesticide because changing analysis schedules over time caused variations in sample numbers between pesticides for some years. The stream-site selection process also did not limit the selection to a single year; all years of sampling at a stream site that met the selection criteria were included in this summary. Stream sites selected for the summary are shown in figure 2 and listed in appendix 1 (table 1–2).

Table 1. Minimum samples, per water year, by watershed size.

[km², square kilometer; water year, the 12-month period of October 1, for any given year through September 30, of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months]

Watershed size (km ²)	Minimum number of samples
Less than 500	16
500 to 4,999	12
5,000 to 50,000	10
Greater than 50,000	8

Detection Frequency and Concentration Statistics

Time-weighted detection frequencies account for the more frequent sample collection during some months than in other months and provide an estimate of the percentage of time (throughout the water year) that a pesticide was detected. The weights were calculated as the amount of time extending from one-half the time interval between an observation and the preceding observation and one-half the time interval extending from the observation to the subsequent observation, divided by the total time in one year. Sample weights for a pesticide at

a stream site sum to one for each year; therefore, the sum of the weights for samples with detections represent the percentage of time that pesticide was detected for that stream site and year. When there were multiple water years for a stream site and pesticide, the median percentage of time detected across the years was used for that stream site and pesticide. Both the mean and median were evaluated for sites and pesticides with multiple water years of data, and there was not a large difference between the two statistics for the sites and pesticides used in this summary.

Annual concentration statistics were calculated for each stream site and pesticide for comparison to HHBs (Toccalino and others, 2014) and chronic ALBs (U.S. Environmental Protection Agency Office of Pesticide Program, http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm, accessed July 2013). Specifically, the annual mean concentration for comparison to HHBs, the annual maximum 21-day moving-average concentration for comparison to the chronic invertebrate ALBs, and the annual maximum 60-day moving-average concentration for comparison to chronic fish and chronic aquatic community (atrazine) ALBs were calculated for this comparison.

Annual mean pesticide concentrations were calculated following the methods described in Larson and others (2004). Specifically, each observed concentration was weighted according to the amount of time it was used to represent the pesticide concentration in the stream. The weights were calculated as the amount of time extending from one-half the time interval between an observation and the preceding observation and one-half the time interval extending from the observation to the subsequent observation, divided by the total time in 1 year. Censored observations complicate the calculation of annual mean concentrations. As described in Larson and others (2004), if less than 10 percent of the weighted data for a site, pesticide, and year combination were censored, censored observations were replaced by one-half the censoring threshold reported by the laboratory. If more than 10 percent of the weighted data were censored, and there were at least 20 annual observations with at least 10 uncensored observations and at least 33 percent of the sample weights were represented by uncensored observations, then the log-regression method (Gilliom and Helsel, 1986; Helsel and Gilliom, 1986) was used to approximate the annual mean concentration. Otherwise, the annual mean concentration was considered to be censored at the censoring threshold reported by the laboratory. For stream sites and pesticides with multiple years of data, if an HHB was exceeded for a pesticide in any year during the first or second decade then the HHB was considered exceeded for that stream site and pesticide in the respective decade.

Annual maximum moving-average pesticide concentrations were calculated following the methods described in Stone and others (2008). Hourly pesticide concentrations were estimated for each stream site through linear interpolation of actual observations. Censored observations were assigned a value of zero for the process of linear interpolation. The hourly concentration estimates were averaged to obtain an

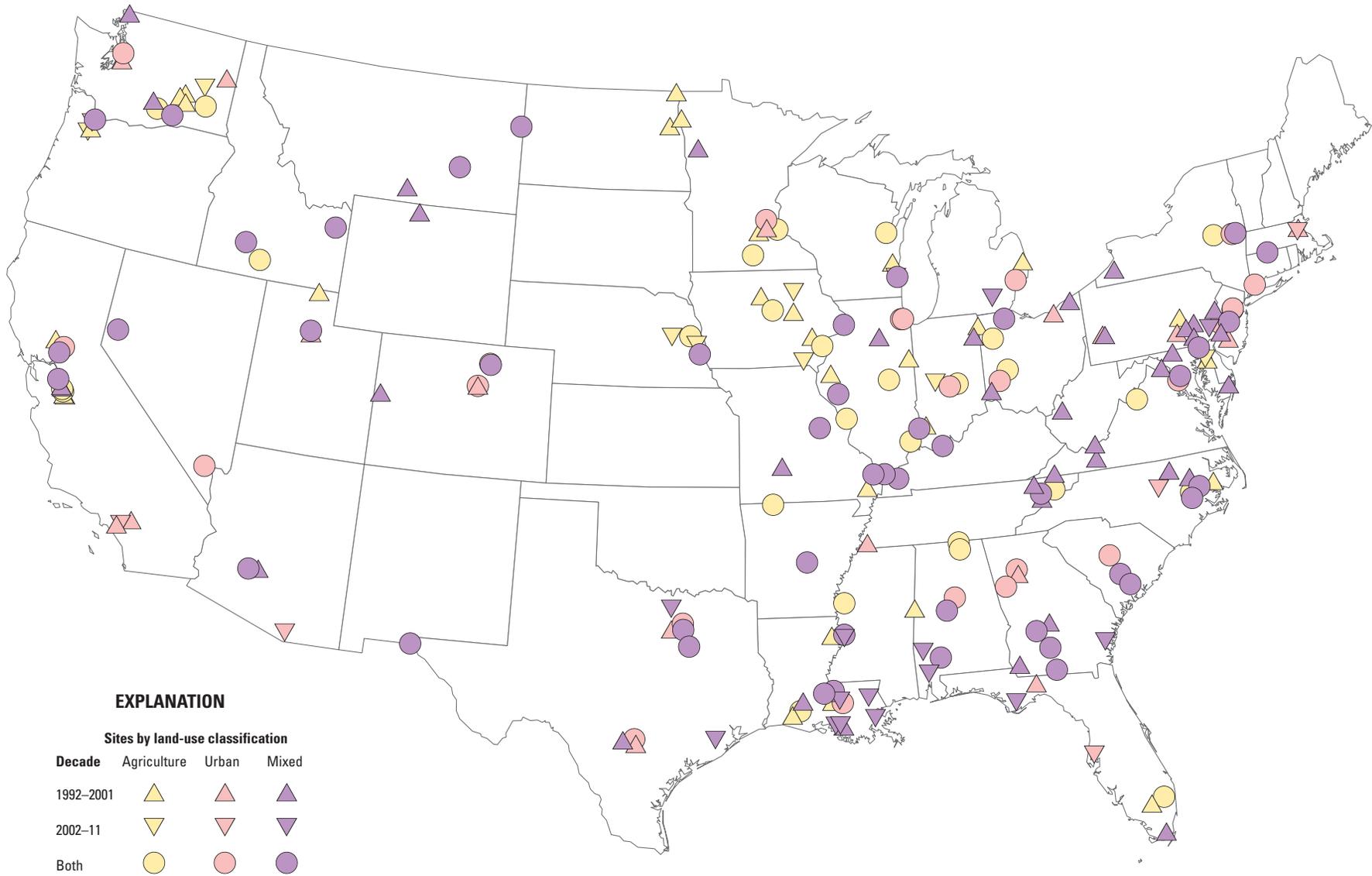


Figure 2. The national monitoring network for pesticides in streams and rivers included 182 sites during 1992–2001 and 125 sites during 2002–11, with 96 of the sites common to both decades.

estimated daily concentration. The hourly estimates facilitated computations for days with multiple samples but were not used for other purposes. Moving-average concentrations for the selected durations (21 and 60 days) were computed for each day. The annual maximum moving-average pesticide concentrations for each duration were then determined for each stream site/year combination meeting the selection criteria. In most cases, insufficient observations were available for stream sites to calculate moving-average concentrations (21- or 60-day durations) for the beginning of the selected year used in the summary. For example, if the selected year for a stream site was 1993, and there were no observations available prior to that year. To address this issue and estimate moving-average concentrations for the beginning of the selected year, the actual observations for the selected year for that stream site and pesticide were used as surrogate observations for the prior year. For stream sites and pesticides with multiple years of data, if a chronic ALB was exceeded for a pesticide in any year during the first or second decade then the chronic ALB was considered exceeded for that stream site and pesticide in the respective decade.

For discussion and illustration purposes, the percentage of time pesticides were detected in streams and percent of streams exceeding an HHB or chronic ALB were grouped by land-use classification, which is discussed in the subsequent section. The percentage of time a pesticide was detected in a stream for a land-use classification was normalized by the number of stream sites within that land-use classification to avoid one stream site having more influence than another in the summary.

Land-Use Classifications

The summaries and comparisons in this report group streams into three land-use classifications: agriculture, urban, and mixed. The land-use classifications and watershed land-use criteria are similar to those used in Gilliom and others (2006), with two modifications. First, the 2006 National Land Cover Data (NLCD06) was used to classify streams based on land use instead of the 1992 enhanced NLCD (NLCDe). Second, the amount of urban land use allowable in a watershed for the agriculture stream classification was increased from 5 to 10 percent because of the differences in methodology between NLCDe and NLCD06. In addition, Gilliom and others (2006) included streams with a land-use classification of undeveloped; however, this summary does not include streams with this land-use classification. The land-use classifications and watershed land-use criteria are shown in table 2. For some streams (fewer than 5 percent), the area within the watershed that contributed the majority of water to the stream was not reflective of the land use for the total watershed area. Differences between the total watershed area and the area contributing the majority of water to a stream can be caused by natural landscape variations and water-management practices. In these cases, the land-use classification for the stream was changed to reflect the land use for the area contributing the majority of water to the stream. The land-use classifications for each stream are shown in figure 2 and listed in appendix 1 (table 1–2). The number of stream sites by land-use classification is shown in table 3.

Table 2. Land-use classifications and watershed land-use criteria.

Land-use classification	Watershed land-use criteria
Agriculture	Greater than 50 percent agricultural land and less than or equal to 10 percent urban land
Urban	Greater than 25 percent urban land and less than or equal to 25 percent agricultural land
Undeveloped	Less than or equal to 5 percent urban land and less than or equal to 25 percent agriculture land
Mixed	All other combinations of agriculture, urban, and undeveloped land use

Table 3. Number of stream sites by land-use classification.

Land-use classification	Number of stream sites 1992–2001	Number of stream sites 2002–11	Number of common stream sites
Agriculture	59	36	28
Mixed	83	59	45
Urban	40	30	23
Total	182	125	96

Pesticide Occurrence

One or more pesticides or pesticide degradates were detectable more than 90 percent of the time in streams across all land uses during 2001–11 (table 4). As mentioned previously, the data from this second decade included analysis of nearly twice as many pesticides and pesticide degradates than the first decade; however, the overall percent of time they

Table 4. Percent of time one or more pesticides or pesticide degradates were detected in streams, by land-use classification.

Land-use classification	Percent of time detected for 1992–2001	Percent of time detected for 2002–11
Agriculture	98	95
Mixed	96	96
Urban	98	99

were detected in streams was nearly the same for both decades (table 4). Variations in percent of time pesticides and pesticide degradates were detected in streams was more evident for individual compounds.

Figure 3 shows the percent of time individual compounds were detected in streams. For illustration purposes, only the top 20 most frequently detected pesticides and degradates by land-use classification and decade are shown. The top 20 most frequently detected are a composite of the top 10 most frequently detected from each land use/decade combination. Across all land-use classifications, the herbicides atrazine, deethylatrazine (atrazine degradate), metolachlor, and simazine were detected more than 50 percent of the time in streams during 2002–11 (fig. 3). The herbicide prometon was detected more than 50 percent of the time in mixed and urban land-use classification streams during 2002–11. The insecticides fipronil, fipronil sulfide (degradate), and carbaryl, were detected more than 50 percent of the time in urban land-use classification streams during 2002–11.

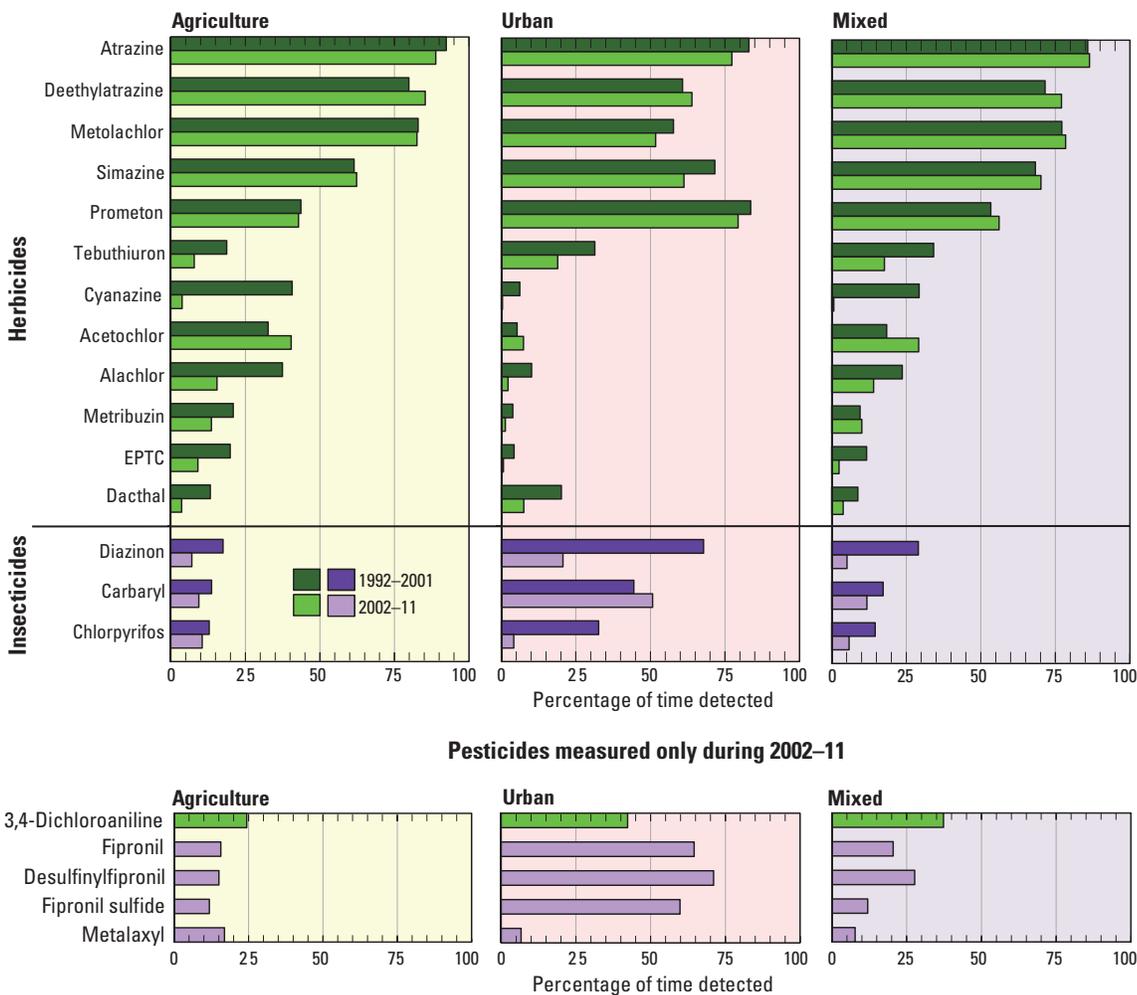


Figure 3. Percentage of time during a year that the most frequently detected pesticides were detected in streams and rivers in relation to land-use classification.

The herbicides alachlor, cyanazine, EPTC, Dacthal, and tebuthiuron were detected less frequently in streams (more than 10 percent change) during the second decade than during the first decade. Sullivan and others (2009) found generally decreasing stream concentration trends for alachlor, cyanazine, and EPTC at individual stream sites within the Corn Belt. The decrease in the amount of time these pesticides were detected in streams between decades may reflect use changes from pesticide-registration cancellations and increased use of other herbicides. For example, cyanazine registration was voluntarily cancelled in the mid-1990s, which was followed by a rapid decline in cyanazine use. Alachlor use steadily declined after the introduction of acetochlor in the mid-1990s, which was an expected result following the registration of acetochlor (de Guzman and others, 2005). In addition, the introduction of genetically modified crops that are resistant to the herbicide, glyphosate, has seen rapid adoption over the course of the last two decades with a corresponding decrease in other herbicides over the same time period (fig. 1).

The organophosphate insecticides chlorpyrifos and diazinon were detected less frequently in streams (more than 10 percent change) during the second decade than during the first decade (fig. 3). Sullivan and others (2009) and Ryberg and others (2010) found generally decreasing stream concentration trends for these two pesticides at individual stream sites in agricultural and urban land-use areas, respectively. The change in detection frequency between the two decades for these pesticides reflects registration changes and changes in pesticide-use patterns. Various uses of chlorpyrifos and diazinon, primarily residential, began being voluntarily cancelled during the late-1990s, and these regulatory changes continued into the early-2000s. In addition, fipronil was first registered for use in the United States in 1996 (Jackson and others, 2009) and was suggested as an alternative to organophosphate insecticides for residential and commercial turf applications during the early-2000s (U.S. Environmental Protection Agency, 2001).

Fipronil was detected in streams across all land-use classifications from 17 to 63 percent of the time during 2002–11 (fig. 3); however, fipronil was not included in the NAWQA and NASQAN efforts during 1992–2001 because it was not registered for use until 1996. Ryberg and others (2010) found a preponderance of increasing fipronil stream concentration trends for urban land-use streams from 2000 to 2008.

An important consideration when comparing detection frequencies over time is the possible impacts of analysis instrument changes. The assumption is that improvements in laboratory instrumentation could result in increased detection sensitivity over time. Alternatively, changes in instrumentation over time could possibly result in decreased sensitivity over time. Ryberg and others (2010) evaluated detections of trace concentrations in duplicate quality-control water samples collected from 1994 to 2005. They found that for most of the pesticides evaluated, improvements to instrumentation did not result in changes to detection sensitivities through time. However, instrumentation improvements did increase the

detection sensitivity for tebuthiuron and carbaryl (Ryberg and others, 2010). As discussed previously, the amount of time tebuthiuron was detected in streams decreased from the first to the second decade (fig. 3); therefore, improvements to instrumentation was not a factor for this pesticide. For carbaryl, the differences in detection frequency between the first and second decades were less than 10 percent in all land-use classifications.

Concentrations And Benchmark Comparisons

Annual mean pesticide concentrations in streams were compared to HHBs to provide perspective; however, these comparisons are not appropriate for assessing compliance with drinking-water regulations, which are applied to treated water. The pesticide stream concentrations used in this report represent untreated water from sites that are not located at drinking-water intakes.

During 2002–11, one agriculture land-use stream had an annual mean pesticide concentration that exceeded an HHB (atrazine), and no urban or mixed land-use streams had annual mean pesticide concentrations that exceeded HHBs. In contrast, 17 percent of the agriculture land-use streams and 5 percent of mixed land-use streams exceeded HHBs during 1992–2001. During the previous decade, alpha-HCH (lindane), atrazine, cyanazine, molinate, dieldrin, and propargite annual mean concentrations exceeded HHBs in 10 agriculture and 4 mixed land-use streams. The differences in the percent of streams exceeding an HHB between the first and second decade are related to regulatory and use changes. Throughout the last three decades, various lindane uses were voluntarily cancelled by registrants; the last remaining uses were cancelled in 2006. Sullivan and others (2009) found downward trends in atrazine concentrations measured in agriculture streams of the Corn Belt. As mentioned previously, cyanazine registration was voluntarily cancelled in the mid-1990s, and cyanazine use sharply declined from the first to the second decade. During the early-2000s, molinate registration was voluntarily cancelled, and use sharply declined during 2002–11. Dieldrin registration was voluntarily cancelled during the late-1980s, and certain uses of propargite were voluntarily cancelled during the mid-1990s.

Pesticide concentrations in streams were compared to chronic ALBs. Acute ALBs were not used because the sampling frequencies do not adequately represent the highest concentrations that may be present in a stream during the year (Crawford, 2004). In addition, differences in sampling designs between the two decades limit comparisons between the decades based on the highest concentrations measured in streams. Specifically, sampling during the first decade included samples targeting high-flow events during the season when pesticides were expected to be transported to streams,

while sampling during the second decade maintained a fixed-frequency sampling design. Therefore, comparison of the highest pesticide stream concentrations between the two decades would be biased.

During 2002–11, nearly two-thirds of agriculture land-use classification streams and nearly one-half of mixed land-use classification streams exceeded a chronic ALB (table 5). For urban land-use classification streams, 90 percent exceeded a chronic ALB. The insecticide fipronil exceeded chronic ALBs for more than 20 percent of the streams across all land-use classifications (fig. 4). The herbicide metolachlor (chronic ALB for *S*-metolachlor) exceeded chronic ALBs for more than 10 percent of agriculture and mixed land-use streams. Similarly, the insecticide malathion exceeded chronic ALBs for more than 10 percent of agriculture and urban land-use streams. The insecticides cis-permethrin (chronic ALB for permethrin) and dichlorvos exceeded chronic ALBs for more than 10 percent of mixed and urban land-use streams, respectively.

Overall, the percent of streams with pesticides that exceeded a chronic ALB was very similar between the

two decades for the agriculture and mixed land-use groups (table 5). In terms of pesticides that were evaluated during both decades, the percent of urban land-use streams that exceeded a chronic ALB during the second decade was about the same as that for the first decade. However the inclusion of fipronil and dichlorvos during the second decade nearly doubled the percent of urban land-use streams that exceeded a chronic ALB during the second decade in comparison to the first decade (table 5; fig. 4).

During 2002–11, there were 21 pesticides that exceeded chronic ALBs compared to 16 that exceeded chronic ALBs during 1992–2001. Figure 4 shows a subset of the pesticides that had annual concentration statistics that exceeded a chronic ALB (pesticides and degradates that exceeded a chronic ALB for more than 5 percent of the stream sites, by pesticide and land-use classification). The second decade had a lower percent of streams exceeding a chronic ALB for the herbicide metolachlor than the first decade for all land-use classifications. For the agriculture land-use streams, this difference was greater than 10 percent. During the last part of the first decade

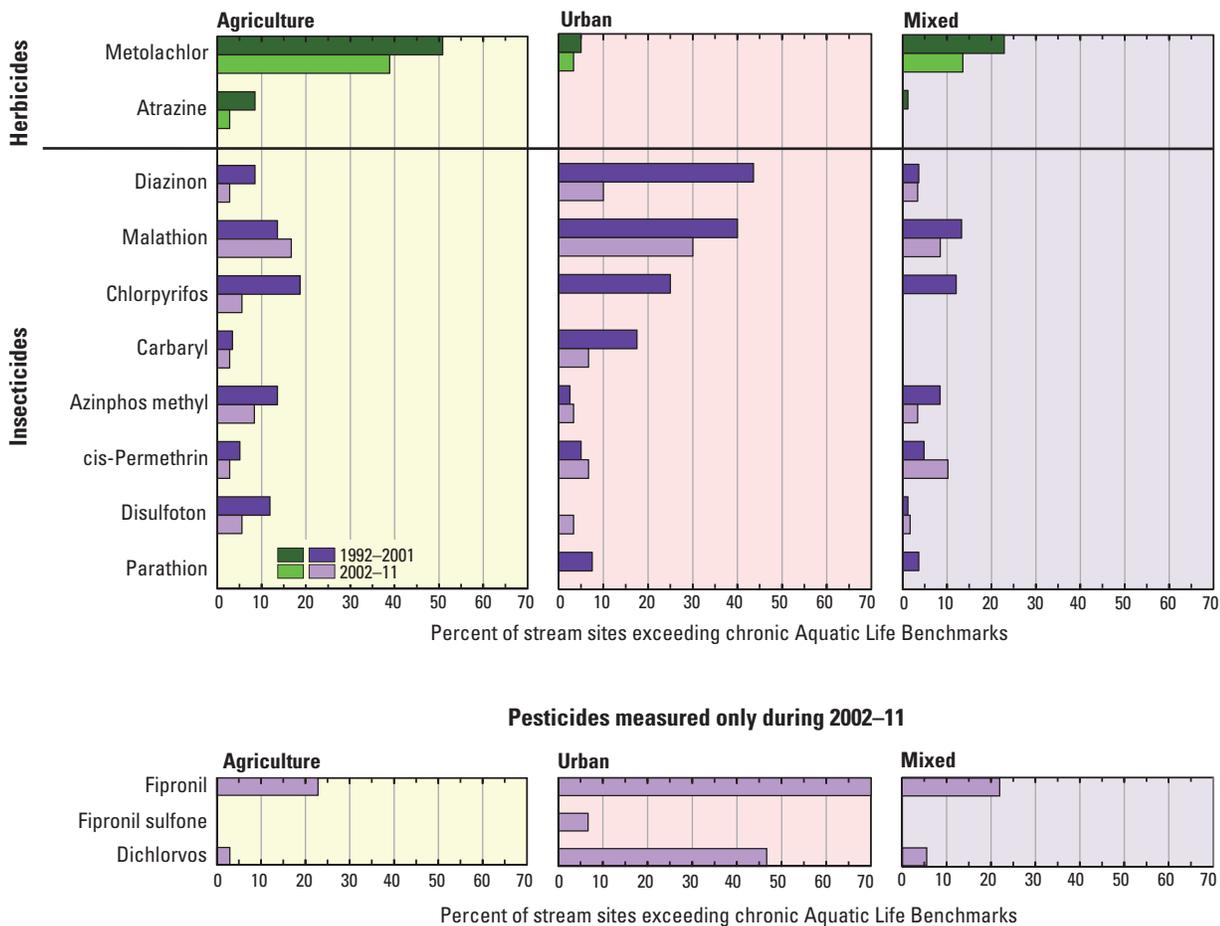


Figure 4. Pesticides that exceeded chronic Aquatic Life Benchmarks at more than 5 percent of stream sites and percent of streams by land-use classification.

Table 5. Percent of streams with one or more pesticide concentration statistics that exceeded a chronic Aquatic Life Benchmark (ALB), by land-use classification.

Land-use classification	Percent of streams exceeding ALB 1992–2001	Percent of streams exceeding ALB 2002–11
Agriculture	69	61
Mixed	45	46
Urban	53	90

replaced by the resolved isomer *S*-metolachlor, which reduces the amount of pesticide required for the same agronomic effect (Hartzler, 2000). Although metolachlor was detected in streams for nearly the same amount of time for both decades (fig. 3), the decreased use (in terms of mass applied) because of the introduction of *S*-metolachlor likely contributed to the decrease in the percent of streams that exceeded a chronic ALB during 2002–11 when compared to 1992–2001.

For streams in the urban land-use classification group, the organophosphate insecticides chlorpyrifos, diazinon, and malathion, and the carbamate insecticide carbaryl all had decreases (greater than 10 percent) in the percent of streams exceeding a chronic ALB from the first decade to the second decade (fig. 4). This is consistent with the decreasing stream concentration trends found by Ryberg and others (2010) for chlorpyrifos and diazinon in individual urban land-use streams. These pesticides also were detected less frequently in streams during 1992–2001 compared to 2002–11 (fig. 3). In contrast, the percent of streams, across all land-use classifications, exceeding a chronic ALB for fipronil during the second decade was greater than all other insecticides during both decades. As discussed previously, fipronil registration and use began toward the end of the first decade and was a suggested alternative for organophosphate insecticides during the second decade.

Summary

This report provides an overview of U.S. Geological Survey National Water-Quality Assessment (NAWQA) and National Stream Quality Accounting Network (NASQAN) findings for pesticide occurrence (percent of time pesticides were detected) in U.S. streams during 2002–11 and compares them to findings during 1992–2001. In addition, pesticide stream concentrations are compared to Human Health Benchmark (HHBs) and chronic Aquatic Life Benchmark (ALBs) and differences between the decades discussed.

Direct and simple, one to one comparisons of pesticides in stream water between the two decades are not possible because of changes in stream sampling sites, sampling designs, and pesticides monitored within the programs over the last two decades. The comparisons in this report are from a site selection and land-use classification based on 2002–11

information that is applied to evaluate results for the 1992–2001 sites. In addition, the most current chronic ALBs are used in comparison to annual concentration statistics.

During 2002–11, atrazine, deethylatrazine (atrazine degradate), carbaryl, fipronil, fipronil sulfide (fipronil degradate), metolachlor, prometon, and simazine were detected more than 50 percent of the time in streams. One or more pesticides or pesticide degradates were detected more than 90 percent of the time in streams across all land uses during both decades. The overall amount of time pesticides were detected in streams was nearly the same between the first and second decades. However, there were differences between the two decades when comparing individual pesticides. The herbicides alachlor, cyanazine, EPTC, Dacthal, and tebuthiuron were detected less frequently in streams during 2002–11 than during 1992–2001. Regulatory changes and the increased use of acetochlor and glyphosate between the first decade and the second decade may be contributing to the decrease in the amount of time these pesticides were detected in streams. The organophosphate insecticides diazinon and chlorpyrifos were detected less frequently during 2002–11 than during 1992–2001. Product registration changes as well as the registration of the insecticide fipronil during the last part of the first decade may be contributing to the decrease in the amount of time these pesticides were detected in streams.

When stream concentration statistics were compared to HHBs, only one agriculture land-use stream had an annual mean pesticide concentration that exceeded an HHB (atrazine) during 2002–11. In contrast, during 1992–2001, about 17 percent of the agriculture land-use streams and one mixed land-use stream exceeded HHBs. The HHB exceedance difference between the first and second decades was the result of regulatory changes; specifically, cancellation of pesticide registration and subsequent decreased use.

During 2002–11, most agriculture and urban land-use classification streams and nearly one-half of mixed land-use classification streams had pesticide concentration statistics that exceeded a chronic ALB. The overall percent of streams that exceeded a chronic ALB was very similar between the two decades for agricultural and mixed land-use classification streams. However, for urban land-use classification streams the percent of streams exceeding a chronic ALB during 2002–11 nearly doubled that seen during 1992–2001. The inclusion of fipronil and dichlorvos monitoring during 2002–11 was the reason for this difference.

The summaries and comparisons between the two decades in this report were intended to be simple and descriptive overviews and not substitutes for more quantitative trend analysis that account for streamflow and other factors. Pesticide stream concentration trends at individual stream sites have been evaluated with more rigorous analysis methods for regions of the U.S. and selected time periods during these decades (Sullivan and others, 2009; Ryberg and others, 2010). Pesticide stream concentration trends using NAWQA and NASQAN results will continue to be evaluated in a series of studies involving quantitative site-based trend models.

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Appendix 1.

Table 1-1. Pesticide compounds used in the 1992–2001 and 2002–11 summaries.....14

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade
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Table 1–1. Pesticide compounds used in the 1992–2001 and 2002–11 summaries.

[CASRN, Chemical Abstracts Service Registry Number®;—, not applicable]

Pesticide compound (synonym)	Type of pesticide compound (parent pesticide, if degradate)	CASRN ¹	Parameter code	1992– 2001	2002–11
Acetochlor	Herbicide	34256-82-1	49260	Yes	Yes
Alachlor	Herbicide	15972-60-8	46342	Yes	Yes
2,6-Diethylaniline	Degradate (Alachlor)	579-66-8	82660	Yes	Yes
2-Chloro-2,6-diethylacetanilide	Degradate (Alachlor)	6967-29-9	61618		Yes
alpha-Endosulfan	Insecticide	959-98-8	34362		Yes
Endosulfan ether	Degradate (alpha-Endosulfan)	3369-52-6	61642		Yes
Endosulfan sulfate	Degradate (alpha-Endosulfan, beta-Endosulfan)	1031-07-8	61590		Yes
Atrazine	Herbicide	1912-24-9	39632	Yes	Yes
Deethylatrazine	Degradate (Atrazine)	6190-65-4	04040	Yes	Yes
Azinphos-methyl (Guthion)	Insecticide	86-50-0	82686	Yes	Yes
Azinphos-methyl-oxon	Degradate (Azinphos-methyl)	961-22-8	61635		Yes
Benfluralin	Herbicide	1861-40-1	82673	Yes	Yes
2-Amino-N-isopropylbenzamide	Degradate (Bentazon)	30391-89-0	61617		Yes
beta-Endosulfan	Insecticide	33213-65-9	34357		Yes
Bifenthrin	Insecticide	82657-04-3	61580		Yes
Butylate	Herbicide	2008-41-5	04028	Yes	Yes
Carbaryl	Insecticide	63-25-2	82680	Yes	Yes
1-Naphthol	Degradate (Carbaryl, Napromide)	90-15-3	49295		Yes
Carbofuran	Insecticide	1563-66-2	82674	Yes	Yes
2,5-Dichloroaniline	Degradate (Chloramben)	95-82-9	61614		Yes
Chlorpyrifos	Insecticide	2921-88-2	38933	Yes	Yes
Chlorpyrifos_oxon	Degradate (Chlorpyrifos)	5598-15-2	61636		Yes
cis-Permethrin	Insecticide	61949-76-6	82687	Yes	Yes
cis-Propiconazole	Fungicide	112721-87-6	79846		Yes
Cyanazine	Herbicide	21725-46-2	04041	Yes	Yes
Cycloate	Herbicide	1134-23-2	04031		Yes
Cyfluthrin	Insecticide	68359-37-5	61585		Yes
cis-Methyl-3-(2,2-dichlorovinyl)- 2,2-dimethyl-(1-cyclopropane)- carboxylate	Degradate (Cyfluthrin)	59897-93-7	79842		Yes
trans-Methyl-3-(2,2-dichlorovinyl)- 2,2-dimethyl-(1-cyclopropane)- carboxylate	Degradate (Cyfluthrin)	59897-94-8	79843		Yes
Cypermethrin	Insecticide	52315-07-8	61586		Yes
Dacthal (DCPA)	Herbicide	1861-32-1	82682	Yes	Yes
Diazinon	Insecticide	333-41-5	39572	Yes	Yes
Diazoxon	Degradate (Diazinon)	962-58-3	61638		Yes
Dichlorvos	Insecticide/Fumigant/Degradate (Naled)	62-73-7	38775		Yes
Dicrotophos	Insecticide	141-66-2	38454		Yes

Table 1–1. Pesticide compounds used in the 1992–2001 and 2002–11 summaries.—Continued

[CASRN, Chemical Abstracts Service Registry Number®;—, not applicable]

Pesticide compound (synonym)	Type of pesticide compound (parent pesticide, if degradate)	CASRN ¹	Parameter code	1992– 2001	2002–11
Dieldrin	Insecticide	60-57-1	39381	Yes	Yes
Dimethoate	Insecticide	60-51-5	82662		Yes
Disulfoton	Insecticide	298-04-4	82677	Yes	Yes
Disulfoton_sulfone	Degradate (Disulfoton)	2497-06-5	61640		Yes
Disulfoton_sulfoxide	Degradate (Disulfoton)	2497-07-6	61641		Yes
E-Dimethomorph	Fungicide	—	79844		Yes
3,4-Dichloroaniline	Degradate (Diuron)	95-76-1	61625		Yes
EPTC	Herbicide	759-94-4	82668	Yes	Yes
Ethalfuralin	Herbicide	55283-68-6	82663	Yes	Yes
Ethion	Insecticide	563-12-2	82346		Yes
Ethion_monoxon	Degradate (Ethion)	17356-42-2	61644		Yes
Ethoprophos (Ethoprop)	Insecticide	13194-48-4	82672	Yes	Yes
O-Ethyl-O-methyl-S-propylphospho- rothioate	Degradate (Ethoprophos)	76960-87-7	61660		Yes
Fenamiphos	Nematocide	22224-92-6	61591		Yes
Fenamiphos_sulfone	Degradate (Fenamiphos)	31972-44-8	61645		Yes
Fenamiphos_sulfoxide	Degradate (Fenamiphos)	31972-43-7	61646		Yes
Fenthion	Insecticide	55-38-9	38801		Yes
Fenthion_sulfoxide	Degradate (Fenthion)	3761-41-9	61647		Yes
Fipronil	Insecticide	120068-37-3	62166		Yes
Desulfinylfipronil	Degradate (Fipronil)	—	62170		Yes
Desulfinylfipronil_amide	Degradate (Fipronil)	—	62169		Yes
Fipronil_sulfide	Degradate (Fipronil)	120067-83-6	62167		Yes
Fipronil_sulfone	Degradate (Fipronil)	120068-36-2	62168		Yes
Flumetralin	Plant_Growth_Regulator	62924-70-3	61592		Yes
3-(Trifluoromethyl)aniline	Degradate (Fluometuron)	98-16-8	61630		Yes
Fonofos	Insecticide	944-22-9	04095	Yes	Yes
gamma-HCH (Lindane)	Insecticide	58-89-9	39341	Yes	Yes
alpha-HCH	Degradate (gamma-HCH)	319-84-6	34253	Yes	Yes
Hexazinone	Herbicide	51235-04-2	04025		Yes
Iprodione	Fungicide	36734-19-7	61593		Yes
3,5-Dichloroaniline	Degradate (Iprodione)	626-43-7	61627		Yes
Isofenphos	Insecticide	25311-71-1	61594		Yes
lambda-Cyhalothrin	Insecticide	91465-08-6	61595		Yes
Linuron	Herbicide	330-55-2	82666	Yes	Yes
Malathion	Insecticide	121-75-5	39532	Yes	Yes
Malaoxon	Degradate (Malathion)	1634-78-2	61652		Yes
Metalaxyl	Fungicide	57837-19-1	61596		Yes
4-Chloro-2-methylphenol	Degradate (MCPA)	1570-64-5	61633		Yes
Methidathion	Insecticide	950-37-8	61598		Yes

Table 1–1. Pesticide compounds used in the 1992–2001 and 2002–11 summaries.—Continued

[CASRN, Chemical Abstracts Service Registry Number®;—, not applicable]

Pesticide compound (synonym)	Type of pesticide compound (parent pesticide, if degradate)	CASRN ¹	Parameter code	1992– 2001	2002–11
Metolachlor	Herbicide	51218-45-2	39415	Yes	Yes
2-Ethyl-6-methylaniline	Degradate (Metolachlor)	24549-06-2	61620		Yes
Metribuzin	Herbicide	21087-64-9	82630	Yes	Yes
Molinate	Herbicide	2212-67-1	82671	Yes	Yes
Myclobutanil	Fungicide	88671-89-0	61599		Yes
Napropamide	Herbicide	15299-99-7	82684	Yes	Yes
1,4-Napthaquinone	Degradate (Napromide)	130-15-4	61611		Yes
Oxyfluorfen	Herbicide	42874-03-3	61600		Yes
p,p'-DDE	Degradate (DDT)	72-55-9	34653	Yes	Yes
4,4'-Dichlorobenzophenone	Degradate (DDT, Dicofol)	90-98-2	61631		Yes
Paraoxon-ethyl	Insecticide/Degradate (Parathion)	311-45-5	61663		Yes
Parathion (Ethyl parathion)	Insecticide	56-38-2	39542	Yes	Yes
Parathion-methyl (Methyl parathion)	Insecticide	298-00-0	82667	Yes	Yes
Paraoxon-methyl	Degradate (Methyl parathion)	950-35-6	61664		Yes
Pebulate	Herbicide	1114-71-2	82669	Yes	Yes
Pendimethalin	Herbicide	40487-42-1	82683	Yes	Yes
Phorate	Insecticide	298-02-2	82664	Yes	Yes
Phorate_oxon	Degradate (Phorate)	2600-69-3	61666		Yes
Phosmet	Insecticide	732-11-6	61601		Yes
Phosmet_oxon	Degradate (Phosmet)	3735-33-9	61668		Yes
Profenofos	Insecticide	41198-08-7	61603		Yes
Prometon	Herbicide	1610-18-0	04037	Yes	Yes
Prometryn	Herbicide	7287-19-6	04036		Yes
Propachlor	Herbicide	1918-16-7	04024	Yes	Yes
Propanil	Herbicide	709-98-8	82679	Yes	Yes
Propargite	Acaricide	2312-35-8	82685	Yes	Yes
2-(4-tert-butylphenoxy)-cyclohexanol	Degradate (Propargite)	1942-71-8	61637		Yes
Propetamphos	Insecticide	31218-83-4	61604		Yes
Propyzamide (Pronamide)	Herbicide	23950-58-5	82676	Yes	Yes
Simazine	Herbicide	122-34-9	04035	Yes	Yes
Sulfotepp	Insecticide	3689-24-5	61605		Yes
Sulprofos	Insecticide	35400-43-2	38716		Yes
Tebuconazole	Fungicide	107534-96-3	62852		Yes
Tebupirimfos	Insecticide	96182-53-5	61602		Yes
Tebupirimfos_oxon	Degradate (Tebupirimfos)	—	61669		Yes
Tebuthiuron	Herbicide	34014-18-1	82670	Yes	Yes
Tefluthrin	Insecticide	79538-32-2	61606		Yes
Temephos	Insecticide	3383-96-8	61607		Yes
Terbacil	Herbicide	5902-51-2	82665	Yes	Yes

Table 1–1. Pesticide compounds used in the 1992–2001 and 2002–11 summaries.—Continued

[CASRN, Chemical Abstracts Service Registry Number®;—, not applicable]

Pesticide compound (synonym)	Type of pesticide compound (parent pesticide, if degradate)	CASRN¹	Parameter code	1992– 2001	2002–11
Terbufos	Insecticide	13071-79-9	82675	Yes	Yes
Terbufos_sulfone_oxygen_analog	Degradate (Terbufos)	56070-15-6	61674		Yes
Terbuthylazine	Herbicide	5915-41-3	04022		Yes
Thiobencarb	Herbicide	28249-77-6	82681	Yes	Yes
4-Chlorobenzylmethyl_sulfone	Degradate (Thiobencarb)	98-57-7	61634		Yes
trans-Propiconazole	Fungicide	120523-07-1	79847		Yes
Triallate	Herbicide	2303-17-5	82678	Yes	Yes
Tribuphos	Defoliant	78-48-8	61610		Yes
Trifluralin	Herbicide	1582-09-8	82661	Yes	Yes
Z-Dimethomorph	Fungicide	—	79845		Yes

¹This report contains CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client ServicesSM.

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Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.

[km², square kilometer; Cr, Creek; Ri, River; Irr Dist; Irrigation District; No., number; MA, Massachusetts; CT, Connecticut; NY, New York; NJ, New Jersey; PA, Pennsylvania; MD, Maryland; VA, Virginia; WV, West Virginia; DC, District of Columbia; NC, North Carolina; SC, South Carolina; GA, Georgia; FL, Florida; AL, Alabama; OH, Ohio; IN, Indiana; TN, Tennessee; KY, Kentucky; IL, Illinois; WI, Wisconsin; MI, Michigan; MN, Minnesota; ND, North Dakota; IA, Iowa; MT, Montana; WY, Wyoming; CO, Colorado; NE, Nebraska; MO, Missouri; AR, Arkansas; MS, Mississippi; LA, Louisiana; TX, Texas; AZ, Arizona; VT, Vermont; NV, Nevada; CA, California; WA, Washington; ID, Idaho; OR, Oregon]

Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992–2001	2002–11
01102500	Aberjona River at Winchester, MA	60	Urban	2	
01104615	Charles River near Watertown, MA	695	Urban		2
01184000	Connecticut River at Thompsonville, CT	25,000	Mixed	4	3
01209710	Norwalk River at Winnipauk, CT	85	Urban	5	3
01349150	Canajoharie Creek near Canajoharie, NY	155	Agriculture	5	3
01356190	Lisha Kill northwest of Niskayuna, NY	40	Urban	1	3
01357500	Mohawk River at Cohoes, NY	9,110	Mixed	8	2
01403300	Raritan River at Bound Brook, NJ	2,070	Urban	3	6
01403900	Bound Brook at Middlesex, NJ	126	Urban	2	2
01410784	Great Egg Harbor River near Sicklerville, NJ	39	Urban	2	
01454700	Lehigh River at Easton, PA	3,520	Mixed	1	
01463500	Delaware River at Trenton, NJ	17,600	Mixed	2	2
01464907	Little Neshaminy Creek near Warminster, PA	72	Urban	2	1
01470779	Tulpehocken Creek near Bernville, PA	179	Mixed	2	
01472157	French Creek near Phoenixville, PA	152	Mixed		1
01474500	Schuylkill River at Philadelphia, PA	4,900	Mixed	2	
01485000	Pocomoke River at Willards, MD	138	Mixed	1	
01493112	Chesterville Branch near Crumpton, MD	17	Agriculture	1	
01493500	Morgan Creek near Kennedyville, MD	33	Agriculture		3
01555400	East Mahantango Creek at Klingerstown, PA	116	Agriculture	2	
01571490	Cedar Run at Eberlys Mill, PA	33	Urban	3	
01573095	Bachman Run at Annville, PA	20	Mixed	1	
01576540	Mill Creek near Lyndon, PA	141	Mixed	2	
01578310	Susquehanna River at Conowingo, MD	70,100	Mixed	2	6
01621050	Muddy Creek at Mount Clinton, VA	37	Agriculture	2	3
01636500	Shenandoah River at Millville, WV	7,880	Mixed	1	
01639000	Monocacy River at Bridgeport, MD	449	Mixed	1	
01646580	Potomac River at Washington, DC	30,000	Mixed	4	7
01654000	Accotink Creek near Annandale, VA	61	Urban	2	4
02082731	Devils Cradle Creek near Alert, NC	35	Mixed	1	
02083500	Tar River at Tarboro, NC	5,750	Mixed	1	
02083833	Pete Mitchell Swamp near Penny Hill, NC	45	Agriculture	1	
02084160	Chicod Cr near Simpson, NC	109	Mixed	1	1
02084558	Albemarle Canal near Swindell, NC	191	Agriculture	1	
02087580	Swift Creek near Apex, NC	54	Urban		5
02089500	Neuse River at Kinston, NC	7,020	Mixed	4	7

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.—Continued

[km², square kilometer; Cr, Creek; Ri, River; Irr Dist; Irrigation District; No., number; MA, Massachusetts; CT, Connecticut; NY, New York; NJ, New Jersey; PA, Pennsylvania; MD, Maryland; VA, Virginia; WV, West Virginia; DC, District of Columbia; NC, North Carolina; SC, South Carolina; GA, Georgia; FL, Florida; AL, Alabama; OH, Ohio; IN, Indiana; TN, Tennessee; KY, Kentucky; IL, Illinois; WI, Wisconsin; MI, Michigan; MN, Minnesota; ND, North Dakota; IA, Iowa; MT, Montana; WY, Wyoming; CO, Colorado; NE, Nebraska; MO, Missouri; AR, Arkansas; MS, Mississippi; LA, Louisiana; TX, Texas; AZ, Arizona; VT, Vermont; NV, Nevada; CA, California; WA, Washington; ID, Idaho; OR, Oregon]

Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992– 2001	2002–11
02091500	Contentnea Creek at Hookerton, NC	1,910	Agriculture	3	3
02169570	Gills Creek at Columbia, SC	154	Urban	1	2
02174250	Cow Castle Creek near Bowman, SC	62	Mixed	2	2
02175000	Edisto River near Givhans, SC	7,080	Mixed	4	3
02215100	Tusawhatchee Creek near Hawkinsville, GA	420	Mixed	1	
02226160	Altamaha River near Everett City, GA	36,100	Mixed		4
02281200	Hillsboro Canal near Shawano, FL	806	Agriculture	3	1
02289034	U.S. Sugar Outflow Canal near Clewiston, FL	73	Agriculture	1	
02306774	Rocky Creek near Citrus Park, FL	46	Urban		2
02317797	Little River near Tifton, GA	335	Mixed	1	1
02318500	Withlacoochee River near Quitman, GA	3,860	Mixed	3	3
02326838	Lafayette Creek near Tallahassee, FL	25	Urban	2	
02335870	Sope Creek near Marietta, GA	80	Urban	2	4
02336300	Peachtree Creek at Atlanta, GA	222	Urban	1	
02338000	Chattahoochee River near Whitesburg, GA	6,250	Urban	3	7
02350080	Lime Creek near Cobb, GA	162	Mixed	2	4
02356980	Aycocks Creek near Boykin, GA	271	Mixed	1	
02359170	Apalachicola River near Sumatra, FL	49,800	Mixed		1
02424000	Cahaba River at Centreville, AL	2660	Mixed	2	1
02429500	Alabama River at Claiborne, AL	56,900	Mixed	1	3
02444490	Bogue Chitto near Memphis, AL	136	Agriculture	1	
02469762	Tombigbee River near Coffeetown, AL	47,800	Mixed		1
02470500	Mobile River at Mt. Vernon, AL	111,400	Mixed		4
03049625	Allegheny River at New Kensington, PA	29,700	Mixed	1	
03049646	Deer Creek near Dorseyville, PA	70	Urban	1	
03167000	Reed Creek at Grahams Forge, VA	669	Mixed	1	
03176500	New River at Glen Lyn, VA	9,780	Mixed	1	
03201300	Kanawha River at Winfield, WV	30,600	Mixed	1	
03267900	Mad River near Eagle City, OH	802	Agriculture	3	3
03274000	Great Miami River at Hamilton, OH	9,400	Mixed	2	
03303280	Ohio River at Cannelton Dam at Cannelton, IN	251,200	Mixed	6	10
03353637	Little Buck Creek near Indianapolis, IN	45	Urban	3	2
03357330	Big Walnut Creek near Roachdale, IN	339	Agriculture		2
03360895	Kessinger Ditch near Monroe City, IN	146	Agriculture	1	
03374100	White River at Hazleton, IN	29,300	Mixed	10	7
03378500	Wabash River at New Harmony, IN	75,700	Agriculture	5	10

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.—Continued

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Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992– 2001	2002–11
03455000	French Broad River near Newport, TN	4,800	Mixed	1	
03466208	Big Limestone Creek near Limestone, TN	205	Agriculture	2	1
03467609	Nolichucky River near Lowland, TN	4,370	Mixed	2	1
03526000	Copper Creek near Gate City, VA	277	Mixed	1	
03528000	Clinch River above Tazewell, TN	3,820	Mixed	1	
03575100	Flint River near Brownsboro, AL	969	Agriculture	3	2
03609750	Tennessee River at Highway 60 near Paducah, KY	104,500	Mixed	5	4
03612500	Ohio River at Dam 53 near Grand Chain, IL	526,000	Mixed	6	10
04072050	Duck Creek near Howard, WI	247	Agriculture	3	3
04087000	Milwaukee River at Milwaukee, WI	1,810	Mixed	3	2
04159492	Black River near Jeddo, MI	1,200	Agriculture	1	
04161820	Clinton River at Sterling Heights, MI	803	Urban	1	2
04175600	River Raisin near Manchester, MI	331	Mixed		1
04178000	St. Joseph River near Newville, IN	1,600	Agriculture	2	
04183000	Maumee River at New Haven, IN	5,040	Mixed	1	
04186500	Auglaize River near Fort Jennings, OH	858	Agriculture	1	2
04193500	Maumee River at Waterville, OH	16,400	Mixed	5	3
04208504	Cuyahoga River at Cleveland, OH	2,040	Urban	1	
04211820	Grand Ri at Harpersfield, OH	1,430	Mixed	1	
04213500	Cattaraugus Creek at Gowanda, NY	1,130	Mixed	1	
05062500	Wild Rice River at Twin Valley, MN	2,410	Mixed	1	
05082625	Turtle River near Arvilla, ND	658	Agriculture	1	
05085900	Snake River above Alvarado, MN	566	Agriculture	1	
05102490	Red River of the North at Pembina, ND	92,100	Agriculture	5	
05288705	Shingle Creek at Minneapolis, MN	73	Urban	1	3
05320270	Little Cobb River near Beauford, MN	336	Agriculture	1	2
05330000	Minnesota River near Jordan, MN	42,000	Agriculture	2	
05330902	Nine Mile Creek at Bloomington, MN	116	Urban	1	
05331580	Mississippi River at Hastings, MN	96,000	Agriculture	5	3
05420500	Mississippi River at Clinton, IA	221,700	Mixed	6	10
05420680	Wapsipinicon River near Tripoli, IA	897	Agriculture		1
05449500	Iowa River near Rowan, IA	1,080	Agriculture	2	
05451210	South Fork Iowa River near New Providence, IA	581	Agriculture	2	5
05455570	English River at Riverside, IA	1,620	Agriculture	1	
05464220	Wolf Creek near Dysart, IA	775	Agriculture	2	
05465500	Iowa River at Wapello, IA	32,400	Agriculture	5	3

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.—Continued

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Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992– 2001	2002–11
05490500	Des Moines River at Keosauqua, IA	36,400	Agriculture		2
05525500	Sugar Creek at Milford, IL	1,160	Agriculture	2	
05531500	Salt Creek at Western Springs, IL	291	Urban	1	2
05532500	Des Plaines River at Riverside, IL	1,630	Urban	1	1
05553500	Illinois River at Ottawa, IL	28,300	Mixed	3	
05572000	Sangamon River at Monticello, IL	1,430	Agriculture	2	2
05584500	La Moine River at Colmar, IL	1,700	Agriculture	2	
05586100	Illinois River at Valley City, IL	69,200	Mixed	5	6
05587455	Mississippi River Below Grafton, IL	443,700	Agriculture	5	7
06208500	Clarks Fork Yellowstone River near Edgar, MT	5,240	Mixed	1	
06279500	Bighorn River at Kane, WY	40,800	Mixed	1	
06295000	Yellowstone River at Forsyth, MT	102,000	Mixed	3	3
06329500	Yellowstone River near Sidney, MT	177,000	Mixed	5	4
06713500	Cherry Creek at Denver, CO	1,060	Urban	2	5
06714000	South Platte River at Denver, CO	10,000	Urban	4	
06753990	Lonetree Creek near Greeley, CO	1,480	Agriculture	2	1
06754000	South Platte River near Kersey, CO	25,000	Mixed	5	3
06795500	Shell Creek near Columbus, NE	762	Agriculture		1
06800000	Maple Creek near Nickerson, NE	955	Agriculture	5	5
06800500	Elkhorn River at Waterloo, NE	18,000	Agriculture		4
06805500	Platte River at Louisville, NE	221,000	Mixed	7	8
06923150	Dousinbury Creek near Wall Street, MO	106	Mixed	1	
06934500	Missouri River at Hermann, MO	1,353,000	Mixed	6	8
07022000	Mississippi River at Thebes, IL	1,847,000	Mixed	6	8
07031692	Fletcher Creek at Memphis, TN	79	Urban	1	
07043500	Little River Ditch No 1 near Morehouse, MO	1,140	Agriculture	2	
07053250	Yocum Creek near Oak Grove, AR	134	Agriculture	1	1
07263620	Arkansas River at David D Terry Lock and Dam below Little Rock, AR	401,000	Mixed	6	9
07288650	Bogue Phalia near Leland, MS	1,300	Agriculture	3	3
07288955	Yazoo River near Long Lake, MS	34,800	Mixed	6	10
07369500	Tensas River at Tendal, LA	721	Agriculture	4	
07373420	Mississippi River near St. Francisville, LA	2,915,000	Mixed	6	10
07374000	Mississippi River at Baton Rouge, LA	2,926,000	Mixed		7
07374525	Mississippi River at Belle Chasse, LA	2,727,000	Mixed		5
07375050	Tchefuncte River near Covington, LA	366	Mixed		1
07379960	Dawson Creek at Baton Rouge, LA	39	Urban	2	1

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.—Continued

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Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992– 2001	2002–11
07381440	Bayou Grosse Tete at Rosedale, LA	305	Agriculture	1	
07381495	Atchafalaya River at Melville, LA	241,700	Mixed	6	10
07381590	Wax Lake Outlet at Calumet, LA	5,600	Mixed		5
07381600	Lower Atchafalaya River at Morgan City, LA	245,100	Mixed		5
08010000	Bayou Des Cannes near Eunice, LA	369	Mixed	1	
08012150	Mermentau River at Mermentau, LA	3,580	Agriculture	2	2
08012470	Bayou Lacassine near Hayes, LA	767	Agriculture	3	
08049240	Rush Creek at Arlington, TX	74	Urban	1	
08051500	Clear Creek near Sanger, TX	763	Mixed		1
08057200	White Rock Creek at Dallas, TX	173	Urban	2	5
08057410	Trinity River below Dallas, TX	16,200	Mixed	5	7
08064100	Chambers Creek near Rice, TX	2,140	Mixed	1	2
08116650	Brazos River near Rosharon, TX	117,400	Mixed		2
08178800	Salado Creek at San Antonio, TX	506	Urban	1	2
08180640	Medina River at La Coste, TX	2,100	Mixed	1	
08181800	San Antonio River near Elmendorf, TX	4,530	Urban	2	
08364000	Rio Grande at El Paso, TX	77,600	Mixed	5	9
09153290	Reed Wash near Mack, CO	36	Mixed	1	
09481740	Santa Cruz River at Tubac, AZ	3,120	Urban		1
09514000	Buckeye Canal near Avondale, AZ	117,000	Mixed	2	
09517000	Hassayampa River near Arlington, AZ	3,970	Mixed	1	1
10102200	Cub River near Richmond, UT	577	Agriculture	2	
10168000	Little Cottonwood Creek at Salt Lake City, UT	117	Urban	2	
10171000	Jordan River at Salt Lake City, UT	9,100	Mixed	3	1
10350500	Truckee River at Clark, NV	4,310	Mixed	4	2
11060400	Warm Creek near San Bernardino, CA	31	Urban	2	
11074000	Santa Ana River below Prado Dam, CA	3,730	Urban		5
11075610	Santa Ana River near Anaheim, CA	3,870	Urban	2	
11261100	Salt Slough near Stevinson, CA	1,270	Agriculture	2	
11262900	Mud Slough near Gustine, CA	1,270	Agriculture	1	
11273500	Merced River near Newman, CA	3,620	Agriculture	6	3
11274538	Orestimba Creek near Crows Landing, CA	28	Agriculture	5	3
11274560	Turlock Irr Dist Lateral No. 5 near Patterson, CA	218	Mixed	1	
11274570	San Joaquin River near Patterson, CA	9,800	Mixed	1	
11303500	San Joaquin River near Vernalis, CA	19,200	Mixed	8	7
11390890	Colusa Basin Drain near Knights Landing, CA	4,260	Agriculture	1	

Table 1-2. Stream sites used in the first decade (1992–2001) and second decade (2002–11) summaries.—Continued

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Site number	Site name	Watershed area (km ²)	Land use	Number of years	
				1992– 2001	2002–11
11447360	Arcade Creek near Del Paso Heights, CA	82	Urban	1	2
11447650	Sacramento River at Freeport, CA	61,700	Mixed	5	10
12113390	Duwamish River at Tukwila, WA	1,190	Urban	5	
12128000	Thornton Creek near Seattle, WA	29	Urban	2	3
12212100	Fishtrap Creek at Lynden, WA	99	Mixed	1	
12424500	Spokane River near Spokane, WA	13,000	Urban	1	
12464770	Crab Creek near Ritzville, WA	1,190	Agriculture		1
12471400	Lind Coulee Wasteway near Warden, WA	1,820	Agriculture	3	
12472380	Crab Creek Lateral near Othello, WA	146	Agriculture	1	
12473740	El 68 D Wasteway near Othello, WA	377	Agriculture	1	
12500420	Moxee Drain near Union Gap, WA	353	Mixed	1	
12505450	Granger Drain at Granger, WA	160	Agriculture	1	4
12510500	Yakima River at Kiona, WA	14,500	Mixed	1	3
13055000	Teton River near St Anthony, ID	2,290	Mixed	1	1
13092747	Rock Creek at Twin Falls, ID	623	Agriculture	5	2
13154500	Snake River at King Hill, ID	92,900	Mixed	5	6
13351000	Palouse River at Hooper, WA	6,380	Agriculture	8	2
14201300	Zollner Creek near Mt. Angel, OR	39	Agriculture		3
14202000	Pudding River at Aurora, OR	1,260	Agriculture	1	
14206950	Fanno Creek at Durham, OR	81	Urban		5
14211720	Willamette River at Portland, OR	28,900	Mixed	6	9
040863075	North Branch Milwaukee River near Random Lake, WI	130	Agriculture	1	
040869415	Lincoln Creek at Milwaukee, WI	26	Urban		5
073814675	Bayou Boeuf at Amelia, LA	3,170	Mixed	1	
094196783	Las Vegas Wash near Las Vegas, NV	2,650	Urban	5	5
0242354750	Cahaba Valley Creek at Pelham, AL	66	Urban	2	3
0357479650	Hester Creek near Plevna, AL	76	Agriculture	2	1
252414080333200	C-111 Canal near Homestead, FL	132	Mixed	1	
322023090544500	Mississippi River above Vicksburg, MS	2,929,500	Mixed		1
393944084120700	Holes Creek at Kettering, OH	52	Urban	2	2
394340085524601	Sugar Creek at New Palestine, IN	246	Agriculture	7	5

