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Methods and Sources of Data Used to Develop Selected Water-Quality Indicators for Streams and Ground Water for *EPA's 2007 Report on the Environment: Science Report*

By Nancy T. Baker, John T. Wilson, and Michael J. Moran

National Water-Quality Assessment Program

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (*http://www.usgs.gov/*). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (*http://water.usgs.gov/nawqa*). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991–2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (*http://water.usgs.gov/nawqa/studyu.html*).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality and establish links between *sources* of contaminants, the *transport* of those contaminants through the hydrologic system, and the potential *effects* of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Conversion Factors and Abbreviations

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ton per year (ton/yr)	0.9072	metric ton per year

AMLE	adjusted maximum likelihood estimate
LOADEST	load estimation software
LT-MDL	long-term method detection level
µg/L	micrograms per liter
mg/L	milligrams per liter
NASQAN	National Stream Water Quality Accounting Network (USGS)
NAWQA	National Water Quality Assessment Program (USGS)
NLCD	National Land Cover Data
NWIS	National Water Information System (USGS)
NWQL	National Water Quality Laboratory (USGS)
ROE	2007 Report on the Environment: Science Report (USEPA)
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Methods and Sources of Data Used to Develop Selected Water-Quality Indicators for Streams and Ground Water for *EPA's 2007 Report on the Environment: Science Report*

Nancy T. Baker, John T. Wilson, and Michael J. Moran

Abstract

The U.S. Geological Survey (USGS) was one of numerous governmental agencies, private organizations, and the academic community that provided data and interpretations for the U.S. Environmental Protection Agency's (USEPA) *2007 Report on the Environment: Science Report*. This report documents the sources of data and methods used to develop selected water-quality indicators for the 2007 edition of the report compiled by USEPA. Stream and ground-water-quality data collected nationally in a consistent manner as part of the USGS's National Water-Quality Assessment Program (NAWQA) were provided for several water-quality indicators, including *Nitrogen and Phosphorus in Streams in Agricultural Watersheds; Pesticides in Streams in Agricultural Watersheds; and Nitrate and Pesticides in Shallow Ground Water in Agricultural Watersheds.* In addition, the USGS provided nitrate (nitrate plus nitrite) and phosphorus riverine load estimates calculated from water-quality and streamflow data collected as part of its National Stream Water Quality Accounting Network (NASQAN) and its Federal–State Cooperative Program for the *Nitrogen and Phosphorus Discharge from Large Rivers* indicator.

Introduction

In 2001, the U.S. Environmental Protection Agency (USEPA) compiled a compendium of indicators of national environmental conditions and trends over time of the Nation's air, water, and land resources, and associated trends in human health and ecological systems. The USEPA initially presented this information in its *Draft Report on the Environment Technical Document* (U.S. Environmental Protection Agency, 2003). Since then, USEPA has revised, updated, and refined the report in response to scientific developments, as well as feedback from its Scientific Advisory Board and stakeholders. *EPA's 2007 Report on the Environment: Science Report* (hereafter referred to as the ROE) presents the results of this work (U.S. Environmental Protection Agency, 2007). The ROE presents a compilation of indicators from currently available data that help to answer the questions that USEPA believes are of critical importance to its mission and to the national interest.

The U.S. Geological Survey (USGS) was one of numerous governmental agencies, private organizations, and members of the academic community that provided data and interpretations for the ROE. The purpose of this report is to document the data and interpretations provided by the USGS in support of the ROE. Stream and ground-water-quality data collected nationally in a consistent manner as part of the National Water-Quality Assessment Program (NAWQA), which collected data throughout the United States in 51 major hydrologic systems (referred to as study units), were provided for several water-quality indicators including; *Nitrogen and Phosphorus in Streams in Agricultural Watersheds; Pesticides in Streams in Agricultural Watersheds; and Nitrate and Pesticides in Shallow Ground Water in Agricultural Watersheds* (*table 1*). In addition, the USGS provided estimates of nitrate (nitrate plus nitrite) and phosphorus riverine loads calculated from water-quality and streamflow data collected as part of its National Stream Water Quality Accounting Network (NASQAN) and its Federal–State Cooperative Program for the *Nitrogen and Phosphorus Discharge from Large Rivers* indicator. USGS streamflow and water-quality data can be accessed through the National Water Information System (NWIS) web interface at *http://waterdata.usgs.gov/usa/nwis/nwis*. The sources, type of data including class type and class bins, and period of record for data provided by USGS for each indicator are given in *table 1* (at the back of the report).

The information provided in this report is similar to information provided in Wilson and others (2008) documenting data the USGS provided to the H. John Heinz III Center for Science, Economics and the Environment (hereafter referred to as the Heinz Center) for the 2002 and 2007 editions of their report entitled *The State of the Nation's Ecosystems* (Heinz Center, 2002 and 2007). The data sets and associated documentation provided by the USGS to both the USEPA and Heinz Center were derived from the same sources. In most cases, the data provided to the USEPA is a subset of the data provided to the Heinz Center; therefore, the documentation of data provided to the Heinz Center is more extensive than that in this report and should be used as a supplement to the documentation provided here. Specific references to the more extensive documentation (Wilson and others, 2008) are given in the appropriate sections of this report.

Water-quality indicators for *Nitrogen and Phosphorus in Streams in Agricultural Watersheds* report nitrogen and phosphorus concentrations in stream-water samples collected from agricultural watersheds from 1992–2001 by the USGS NAWQA Program and are intended to document the ranges of concentrations of these constituents in stream water (*table 1*). The *Nitrogen and Phosphorus Discharge from Large Rivers* indicator is intended to show the annual load of nitrogen and total phosphorus to coastal waters by major rivers (*table 1*). The *Pesticides in Streams in Agricultural Watersheds* indicator is intended to measure the frequency at which selected pesticides are found in agricultural watersheds and the frequency at which aquatic-life and human-health benchmarks were exceeded from 1992–2001 (*table 1*). A complete description of how benchmarks were determined for the pesticide data used for the indicators described in this report is provided in Wilson and others (2008). The *Nitrate and Pesticides in Shallow Ground Water in Agricultural Watersheds* indicator reports nitrate concentrations (for a range of concentrations) and the frequency of detection for selected pesticides in shallow wells in agricultural areas from 1992–2003 (*table 1*).

Land-Use Classification of Stream- and Ground-Water Sampling Sites

With the exception of the *Nitrogen and Phosphorus Discharge from Large Rivers* indicator, the data provided by the USGS for the ROE water-quality indicators focuses on nutrients and pesticides in agricultural watersheds. In order for USGS to provide analyses specific to agricultural watersheds, the data were aggregated by land-use category. This section documents the methods by which NAWQA classifies land use for stream-water and ground-water sampling sites.

NAWQA stream-water sampling sites were classified by the predominant land-use category within each stream's contributing watershed, which allows potential land-use influences on water quality to be determined and characterized. The stream contributing area includes the land area within a watershed from which all runoff will flow to the point of interest. The contributing area generally equals the watershed area in the eastern U.S., but can be substantially smaller than the watershed area in the arid West. This approach does not take into account all factors that affect water quality at the site (such as point sources), but instead aims to characterize the land use associated with the streamflow (water) at the site. An initial determination of land use within each watershed was made using an enhanced version of the USGS 1992 National Land Cover Data (NLCD), which classifies land use for each 30-by-30 meter area of land in the conterminous United States. The original version of the NLCD is described by Vogelmann and others (2001) and the enhanced version is described by Nakagaki and Wolock (2005). The NLCD was not available for Alaska and Hawaii, so sites in Alaska and Hawaii were classified on the basis of information from the local NAWQA study units. For some sites, the land-use classification was adjusted if the area of one or more land uses made a disproportionately large or small contribution (relative to its percentage of land area in the watershed) to streamflow at the site because of water management practices or natural variations in precipitation and runoff. This is especially common in the arid west, where water resources are heavily managed. These adjustments were based on local knowledge of the sampling site. Land-use classification and percentages of land use for watersheds used in the ROE analysis are given in *appendix 1*.

The major land-use categories that were used to characterize NAWQA stream sampling sites are agricultural, urban, and undeveloped. Table 2 lists the criteria used by NAWQA to classify each stream sampling site by its predominant land-use category. Land classified as agricultural includes cropland (row crops, grains, orchards, vineyards) and pasture. Most streams that are classified as agricultural also have small amounts of other land uses in their watersheds.

Table 2. Watershed land-use criteria used to define land-use classification of stream-water sampling sites (modified from Gilliom and others, 2006).

[>, greater than; ≤ less than or equal to]

NAWQA land-use classification	Watershed land-use criteria
Agricultural	> 50 percent agricultural land and ≤ 5 percent urban land
Urban	> 25 percent urban land and ≤ 25 percent agricultural land
Undeveloped	< 5 percent urban land and ≤ 25 percent agricultural land
Mixed	All other combinations of urban, agricultural, and undeveloped land

Land use for NAWQA ground-water sampling sites is classified by the predominant land use within a 500-meter radius of the well from which the sample is collected. NAWQA wells are classified by land-use study (Gilliom and others, 1995) and the samples for the *Nitrate and Pesticides in Shallow Ground Water in Agricultural Watersheds* indicator were collected from wells that are part of the *Agricultural Land Use* studies done across the Nation by the NAWQA Program. To the extent practicable, sampling sites were selected randomly within the agricultural land-use class so as to be representative of that land use throughout the area. Land use in the vicinity of each well was characterized according to procedures described in Gilliom and Thelin (1997).

Report on the Environment Indicators for Fresh Surface Waters

The ROE indicators for *Fresh Surface Waters* show trends in the extent and condition of fresh surface waters. The USGS provided information on nutrients and pesticides in agricultural watersheds, and nutrient loads in four major U.S. rivers. Information on nutrients is reported as flow-weighted concentrations of nitrate, total nitrogen, orthophosphate, and total phosphorus. Information on pesticides is reported as frequency of occurrence of pesticides, and frequency of exceedances of aquatic-life and human-health benchmarks. Information on nutrient loading is reported as estimated mean-annual nitrate and total phosphorus loads discharged from the Mississippi, Susquehanna, St. Lawrence, and Columbia Rivers.

Nitrogen and Phosphorus in Streams in Agricultural Watersheds

The nutrient indicators for agricultural watersheds provided in this report are nitrate, total nitrogen, orthophosphate, and total phosphorus. The USGS National Water Quality Laboratory (NWQL) reports nitrate as the sum of nitrate plus nitrite (NWQL parameter code p00631) (Fishman, 1993). Nitrate is the primary form of nitrogen dissolved in stream water and is reported in units of milligrams per liter (mg/L) of nitrogen. Total nitrogen comprises nitrate, organic nitrogen, nitrite, and ammonia compounds (NWQL parameter code p62845) and is reported in units of milligrams per liter of nitrogen (Fishman, 1993). Orthophosphate (NWQL parameter code p00671) is the most biologically active form of phosphorus, can cause water-quality problems, and is reported in units of milligrams per liter of phosphorus (Fishman, 1993). Total phosphorus comprises orthophosphate, organic phosphorus and mineral phosphorus compounds (NWQL parameter code p00666) and is reported in milligrams per liter of phosphorus (Fishman, 1993).

The indicators report the percentage of NAWQA stream sites with flow-weighted mean annual concentration in one of five class bins for nitrogen (fig. 1) and one of four class bins for phosphorus (fig. 2). Because nitrogen and phosphorus concentrations in streams usually vary with flow, a flow-weighted mean was calculated to represent the “typical” concentrations in the stream. The data used for these indicators were obtained from the 2005 NAWQA nutrient national synthesis report (Mueller and Spahr, 2005) and are available from the web site: *http://pubs.usgs.gov/ds/2005/152/*.

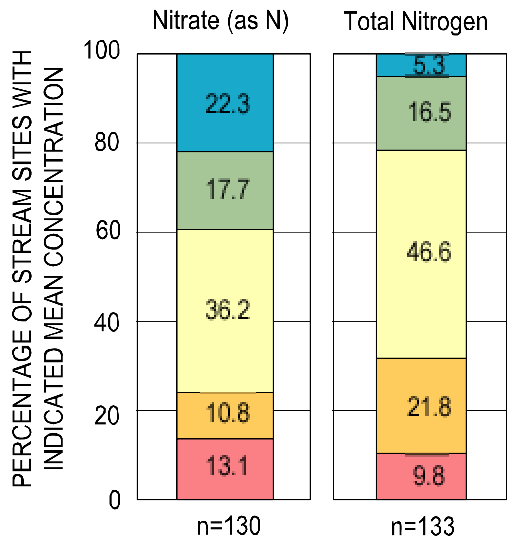
Stream sites in the NAWQA data set were assigned a land-use classification based on the criteria listed in table 2. Those sites that were assigned a land use of *Agricultural* were used to calculate the nitrogen and phosphorus concentrations in streams. The nitrate indicator was calculated using data from 130 stream sites and the total nitrogen indicator was calculated using data from 133 sites (fig. 1). The indicator reports the percentage of NAWQA stream sites with flow-weighted mean concentrations of nitrate or total nitrogen in one of five class bins (less than 1 mg/L, 1 to less than 2 mg/L, 2 to less than 6 mg/L, 6 to less than 10 mg/L, and 10 mg/L or more) (*appendix 2*). Nitrate and total nitrogen concentrations were censored at 0.05 mg/L and 0.2 mg/L, respectively. Reported concentrations that were less than the censoring level were set at the censoring level and were counted in the class bin *less than 1 mg/L*. Background concentrations (amount that occurs naturally) of nitrate vary by location but are generally lower than 0.6 mg/L (Mueller and Helsel, 1996). The orthophosphate indicator was calculated using 132 stream sites and the total phosphorus indicator was calculated using data from 129 sites (fig. 2). The indicator reports the percentage of NAWQA stream sites with flow-weighted mean concentrations of orthophosphate or total phosphorus in one of four class bins (less than 0.1 mg/L, 0.1 to less than 0.3 mg/L, 0.3 to less than 0.5 mg/L, and 0.5 mg/L or more).

A.

CONSTITUENT	PERCENTAGE* OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION				
	Less than 1 mg/L	1 to < 2 mg/L	2 to < 6 mg/L	6 to < 10 mg/L	10 mg/L or more
Nitrate (as N), n = 130	22.3	17.7	36.2	10.8	13.1
Total Nitrogen, n = 133	5.3	16.5	46.6	21.8	9.8

* Due to rounding, percentage may not add to 100

B.



EXPLANATION for B and C
Flow-weighted mean concentration

- Less than 1 mg/L
- 1 to less than 2 mg/L
- 2 to less than 6 mg/L
- 6 to less than 10 mg/L
- 10 mg/L or more

C.

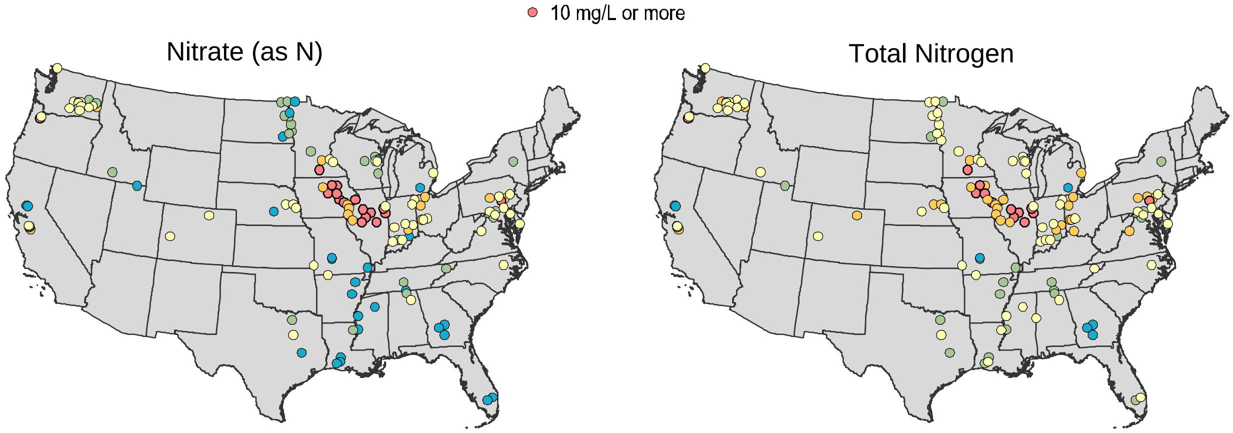


Figure 1. Flow-weighted mean concentrations of nitrate (as N) and total nitrogen in agricultural streams for 1992-2001, shown as the percentage of sites with the indicated concentration range (A) in tabular form, (B) as a graphical comparison, and (C) the spatial distribution of sites within each concentration range. [mg/L, milligrams per liter; n, number of sites; nitrate, nitrate plus nitrite]

A.

CONSTITUENT	PERCENTAGE* OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION			
	Less than 0.1 mg/L	0.1 to < 0.3 mg/L	0.3 to < 0.5 mg/L	0.5 mg/L or more
Orthophosphate (as P), n = 132	54.5	40.9	3.0	1.5
Total Phosphorus, n = 129	15.5	46.5	24.8	13.2

* Due to rounding, percentage may not add to 100

B.

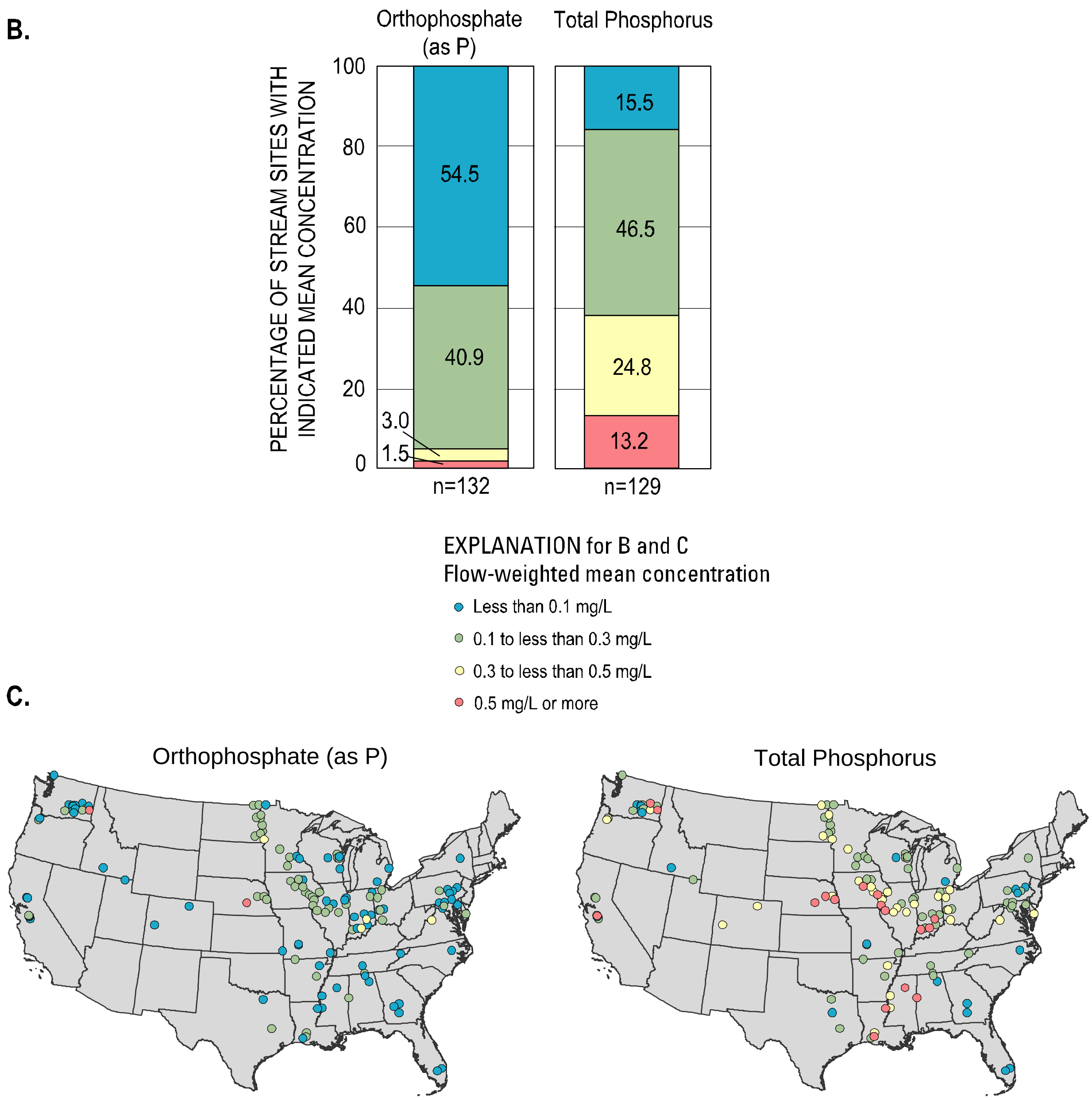


Figure 2. Flow-weighted mean concentrations of orthophosphate (as P) and total phosphorus in agricultural streams for 1992-2001, shown as the percentage of sites with the indicated concentration range (A) in tabular form, (B) as a graphical comparison, and (C) the spatial distribution of sites within each concentration range. [mg/L, milligrams per liter; n, number of sites]

Orthophosphate and total phosphorus concentrations were censored at 0.01 mg/L. Background concentrations of total phosphorus are usually less than 0.1 mg/L (Mueller and Helsel, 1996).

Flow-weighted mean annual concentrations of nitrogen and phosphorus for samples collected as part of the NAWQA Program between 1992 and 2001 were used for these indicators (*appendix 2*). Mean annual loads were estimated by relating individual sample concentrations to the corresponding stream flow for the date and time each sample was collected for each site where samples could be fit to a regression model. The flow-weighted mean concentration was calculated by dividing the total load by the total flow (Mueller and Spahr, 2005). Of the 130 sites where both nitrate and total nitrogen flow-weighted means were predicted, the regression model predicted higher nitrate concentrations than total nitrogen concentrations for eight sites. The difference between the two calculations for six sites was less than 12 percent; for two sites the predicted nitrate concentration was about 25 percent greater than the predicted total nitrogen concentration. For those two sites the model overestimated predicted nitrate concentrations (Mueller and Spahr, 2005). The results of these differences are evident in figure 1, where the percentage of stream sites with nitrate concentrations in the 10 mg/L or more class bin is 13.1 for nitrate and 9.8 for total nitrogen. Most of the flow-weighted mean concentrations for those eight sites fall within this class bin.

Nitrogen and Phosphorus Discharge from Large Rivers

The load of nitrate or total phosphorus is defined as the mass, in tons, of nitrate or total phosphorus transported to the ocean each year, and was calculated for the Mississippi, Susquehanna, St. Lawrence, and Columbia Rivers. The scope of the analysis was limited to developing estimates of the annual load of nitrate for the four rivers using historical streamflow and water-quality data collected by USGS.

The annual nitrate loads (fig. 3) estimated for these four major rivers were derived from three sources of information, and total phosphorus loads (fig. 4) were derived from two sources of information. Mississippi River nitrate loads for 1955–1967 were previously published in Goolsby and others (1999). Unpublished estimates of Mississippi River nitrate (1964–2004) and total phosphorus (1975–2004) loads were calculated by Brent T. Aulenbach (U.S. Geological Survey, written commun., 2006) (*appendix 3*). Annual nitrate and total phosphorus load estimates for Susquehanna River Basin (1971–2002), the St. Lawrence River Basin (1974–1996), and the Columbia River Basin (1975–2002) were published in Aulenbach (2006). Composite samples were used to estimate annual nitrate loads for the Mississippi River (1955–1967). Regression models were used to estimate annual nitrate (1968–2004) and total phosphorus (1975–2004) loads for the Mississippi River and for the entire period of record for the other three river basins. A compilation of annual loads estimated for these four rivers are presented in *appendix 4.*

Goolsby and others (1999) calculated nitrate loads for the Mississippi River near St. Francisville (U.S. Geological Survey water-quality station Mississippi R. near St. Francisville, LA, 07373420 and streamflow-gaging stations Mississippi River at Tarbert Landing, MS, 07295100; and Old River Outflow Channel at Knox Landing, LA, 073732865), for the period 1956–1967, from samples collected daily and composited at 10– to 30–day intervals for analysis. Nitrate flux estimates for the site were calculated from flows at Tarbert Landing plus flows diverted to the Atchafalaya River through the Old River outflow. Flux estimates for this site can be obtained from (*http://toxics.usgs.gov/hypoxia/mississippi/nutrients_80-96.html* select link *Annual Nutrient Flux and Basin Yield Estimates, 9 Major Sites, Period of Record*; Excel spreadsheet: *FluxYieldAnnual_9S.xls*).

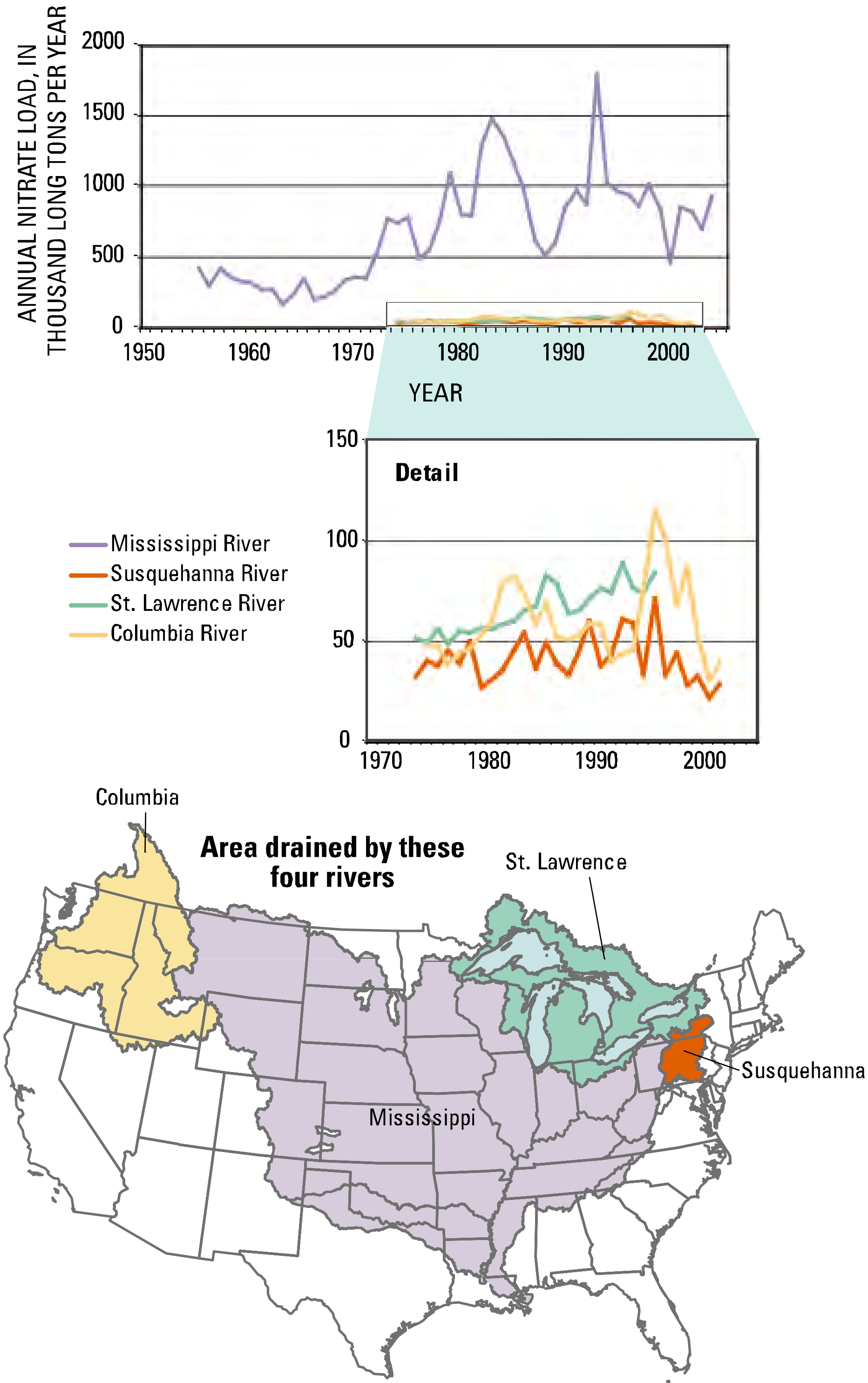


Figure 3. Annual nitrate load discharged from four major U.S. rivers, 1955-2004.

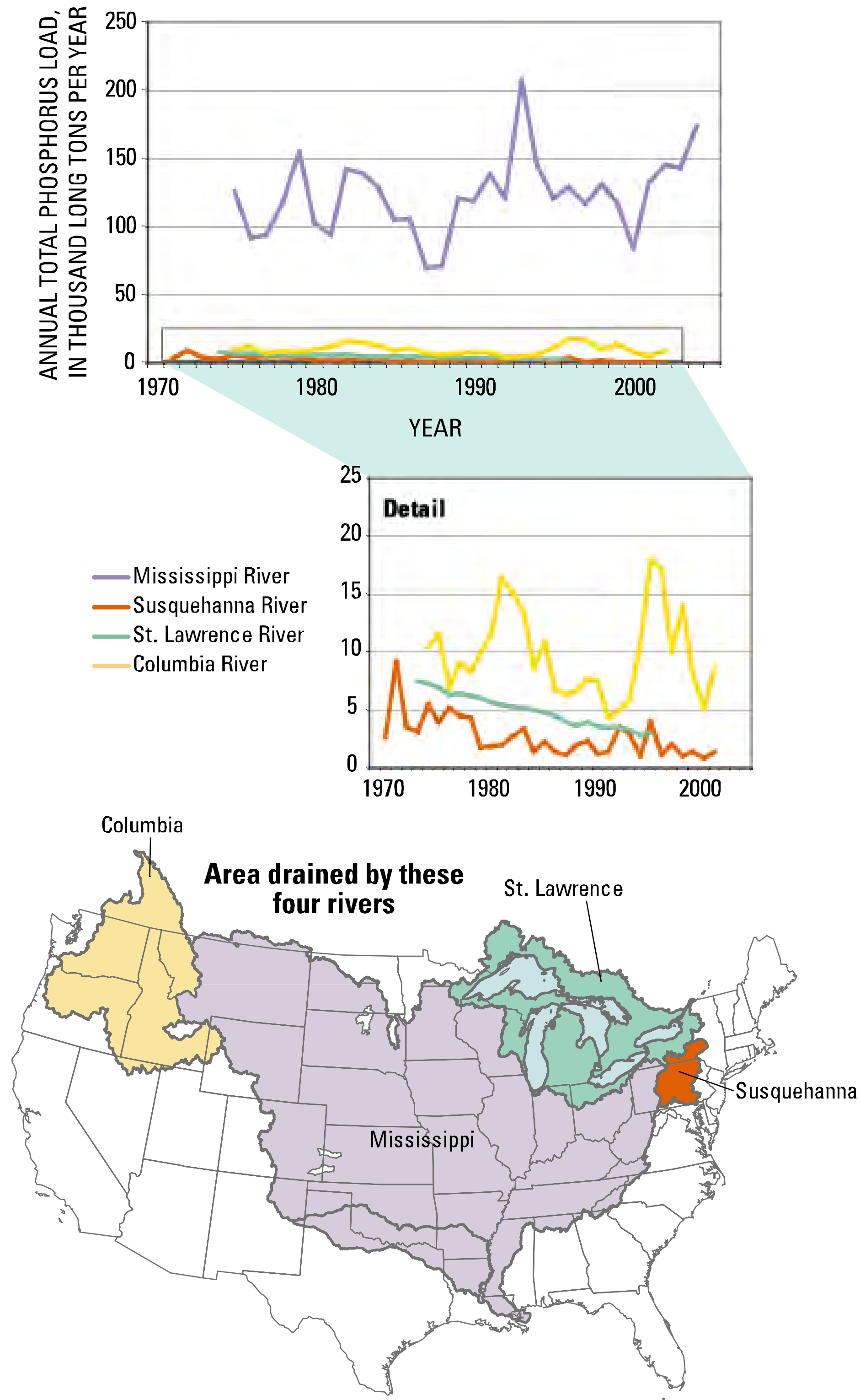


Figure 4. Annual total phosphorus load discharged from four major U.S. rivers, 1971-2004.

Aulenbach (2006) published estimated annual nitrate (1968–2004) and total phosphorus (1975–2004) loads for the Mississippi River near St. Francisville (USGS water-quality station Mississippi River near St. Francisville, La., 07373420 and streamflow-gaging station Mississippi River at Tarbert Landing, MS., 07295100). He also estimated (but did not publish) loads for the Mississippi River near St. Francisville including flows diverted through the Old River outflow at Knox Landing (USGS streamflow-gaging station Old River Outflow Channel at Knox Landing, La., 073732865). Because the 1955–1967 estimates by Goolsby and others (1999) included consideration of the Old River Outflow, the unpublished loads for the same stations were used for the remaining time period for the 2007 ROE (*appendix 3*) (Brent T. Aulenbach, U.S. Geological Survey, written commun., 2006). Nitrate loads were estimated for the time period July 1967 through June 2004 with a 10–year moving calibration window using LOADEST load estimation software and results from the adjusted maximum likelihood estimate (AMLE). Total phosphorus loads were estimated in the same manner for the time period July 1974 through June 2004. The analysis year is from July to June to correlate with the study by Goolsby and others (1999). Results are reported by calendar year. The methods used by Aulenbach are documented in *appendix 3*.

Annual nitrate and total phosphorus load estimates for the Susquehanna, Columbia, and St. Lawrence Rivers were obtained from Aulenbach (2006). For the Susquehanna and Columbia Rivers, data were available at individual stations for only part of the period of interest; therefore, loads were estimated using different station configurations at different times (Aulenbach, 2006). Annual loads were estimated using LOADEST and results from the AMLE. Methods used are documented in Aulenbach (2006).

Annual loads for the Susquehanna River for 1974 through 1978 were estimated from streamflow and water-quality data at Harrisburg, Pennsylvania (USGS station 01570500) and loads for 1979 through 2002 were estimated from streamflow and water-quality data at Conowingo, Maryland (USGS station 01578310). The reported loads (Aulenbach, 2006) for the Susquehanna River at Harrisburg, Pennsylvania were increased by 12.4 percent to account for the increase in drainage area from the Harrisburg site to the Conowingo site downstream (*appendix 4*).

Annual nitrate and total phosphorus loads for the Columbia River for 1975 through 1993 were calculated by adding the estimated annual load from the Willamette River at Portland, Oregon (USGS water-quality and streamflow-gaging station 14211720) to the estimated load from the Columbia River at Warrendale, Washington (USGS streamflow-gaging station 14128910). Loads for 1994-2002 were estimated from streamflow and water-quality data for the Columbia River at Beaver Army Terminal near Quincy, Oregon (USGS water-quality and streamflow gaging station 14246900). The reported combined loads (Aulenbach, 2006) for Warrendale and Portland were increased by 2.1 percent to account for the 2.1 percent increase in drainage area from the Warrendale plus Portland site to the Quincy site downstream (*appendix 4*).

The entire period of record (1974–1996) was available for a single station for the St. Lawrence River. Annual loads were estimated at Cornwall, Ontario near Massena, New York (USGS water-quality and streamflow-gaging station 04264331) (*appendix 4*).

Time-series plots were prepared to show the annual nitrate (fig. 3) and total phosphorus (fig. 4) load carried by the Mississippi, St. Lawrence, Columbia, and Susquehanna Rivers. Most of the year-to-year variation in the loads is due to differences in runoff, with wet years having higher loads and dry years having lower loads.

Pesticides in Streams in Agricultural Watersheds

The *Pesticides in Streams in Agricultural Watersheds* indicator is a measure of how frequently pesticides were detected in agricultural streams and how often they exceeded water-quality benchmarks. The frequency of occurrence is essentially a measure of the average number of detections per sample. The average number of detections at each site was binned into the following classes: none, 1 or 2, 3 or 4, and 5 or more detections (fig. 5). The benchmark exceedance indicators are a measure of how frequently pesticides that have been detected in water samples exceed aquatic-life benchmarks and (or) human-health benchmarks. Of the 83 pesticide compounds analyzed in NAWQA stream-water samples, aquatic-life benchmarks have been established for 62 compounds, and human-health benchmarks have been established for 73 compounds.

NAWQA stream-water samples collected from 83 agricultural watersheds were used to measure the frequency at which water-soluble pesticides were detected in water samples collected over a 12-month sampling period at each site during the 1992–2001 time period (*appendix 5*). The data used for these indicators were obtained from the 2006 NAWQA pesticide national synthesis report (Gilliom and others, 2006) available from the web site: *http://pubs.usgs.gov/circ/2005/1291/*. Selected data retrievals from the pesticide national synthesis data set were provided by Jeffrey D. Martin (U.S. Geological Survey, written commun., 2006).

The NAWQA Program collected pesticide samples for one or more years at each site using a combination of fixed-interval and extreme-flow sampling. In general, two to four samples were collected each month during seasonal periods of high pesticide use. One sample was collected each month during other periods. The 12-month period with the most samples collected and analyzed for pesticides was selected for each site to characterize the annual distribution of pesticide concentrations. Gilliom and others (2006) used a 12-month period of pesticide data to avoid biasing results to sites with multiple years of data. The number of pesticide samples collected at each of the 83 sites for the selected 12-month period ranged from 10 to 49, with a median and mean of 24. The discrete pesticide samples were used to compute time-weighted annual mean concentrations of each pesticide compound and moving-day average concentrations of selected pesticides for comparison to water-quality benchmarks. The discrete pesticide-sampling data and methods and time-weighted mean-annual concentration computations used for this analysis are described in *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/supporting_info.php* (select appendix 8, then select appendix 8A).

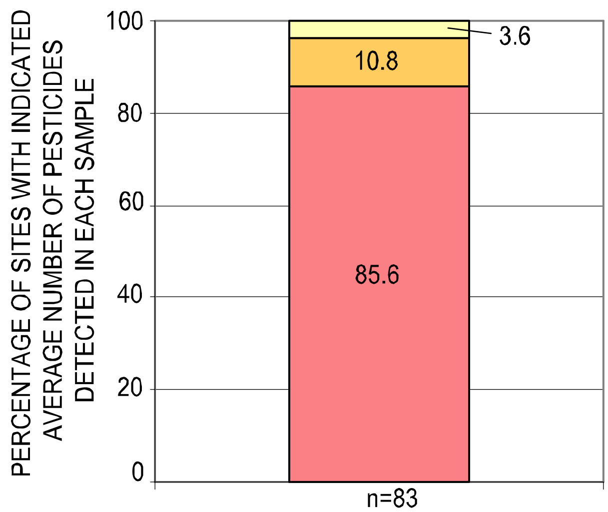
Most of the water samples were analyzed for 83 pesticide compounds from NWQL Schedules 2010 and 2060 (NWQL Schedules refer to groups of compounds measured simultaneously using the same analytical method); however, not every sample had results for every analyte (*appendix 5*, *appendix 6*). Gilliom and others (2006) list the analytical method and maximum long-term method detection level (LT-MDL) for the period 1992–2001 for each of the pesticide compounds analyzed in NAWQA samples. There are 28 different LT-MDL for the 83 pesticides analyzed in NAWQA samples, with a range of 0.001 micrograms per liter (μg/L) to 0.240 μg/L and a median of 0.011 μg/L (Childress and others, 1999).

A.

PERCENTAGE* OF SITES WITH INDICATED AVERAGE NUMBER OF PESTICIDE DETECTIONS IN EACH SAMPLE			
5 or more	3 or 4	1 or 2	None
85.6	10.8	3.6	0

* Due to rounding, percentage may not add to 100

B.



C.

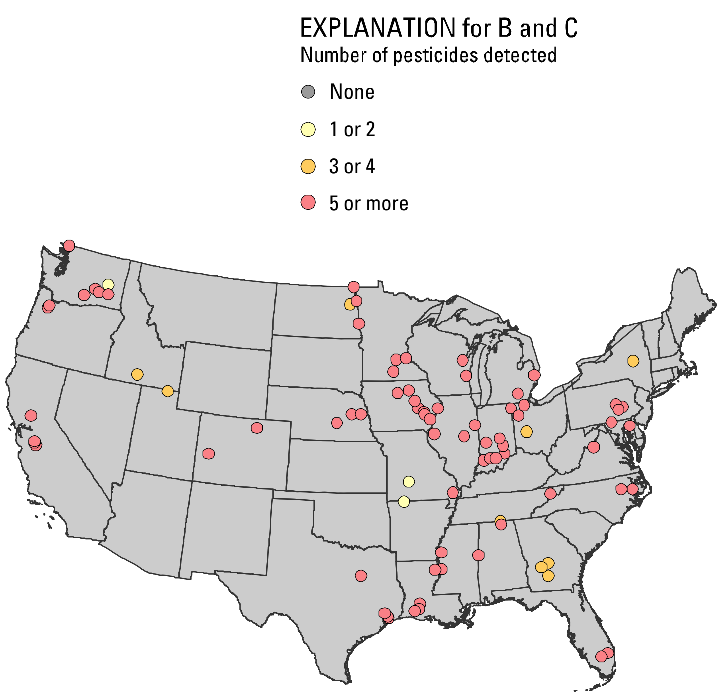


Figure 5. Pesticide occurrence in agricultural streams for 1992-2001, shown as the percentage of sites with the indicated number of detections in (A) tabular form, (B) graphical form, and (C) the spatial distribution of pesticide detections within each class bin. [n, number of sites]

Exceedances of aquatic-life and human-health benchmarks were identified when the time-weighted annual mean concentration for one or more pesticides exceeded the relevant benchmark(s) at a stream site (*appendix 7* and *appendix 8*). Twenty-one pesticide compounds did not have aquatic-life benchmarks established and 10 pesticide compounds did not have human-health benchmarks established. *Appendix 6* shows a list of analytes sampled in surface water and their associated benchmarks. A complete description of how benchmarks were determined for the pesticide data used for the indicators described in this report is provided in Wilson and others (2008).

The percentage of agricultural streams with pesticides exceeding selected numbers of aquatic-life and human-health benchmarks is shown in figure 6 and *appendix 7* and *appendix 8*. Approximately 57 percent of agricultural streams had at least one pesticide that exceeded at least one aquatic-life benchmark, and 12 percent of the sites had 4 or more pesticides that exceeded benchmarks (fig. 6, *appendix 7*). Approximately16 percent of the agricultural stream sites had one or more pesticides that exceeded a human-health benchmark and about 4 percent had 2 or 3 pesticides that exceeded a human-health benchmark (fig. 6, *appendix 8)*. The class bins initially requested by USEPA for aquatic-life and human-health benchmarks was none, 1, 2 or 3, and 4 or more exceedances. USEPA later requested classes binned for pesticides exceeding none, 1 or 2, 3 or 4, and 5 or more benchmarks (fig. 7).

Report on the Environment Indicators for Ground Water

The ROE indicators for Ground Water show trends in the extent and condition of ground water. Information on nitrate is reported in units of milligrams per liter (mg/L) as nitrogen and the frequency of exceedances of the federal drinking-water standard (10 mg/L). Information on pesticides is reported as frequency of occurrence of pesticides and the frequency of exceedances of human-health benchmarks.

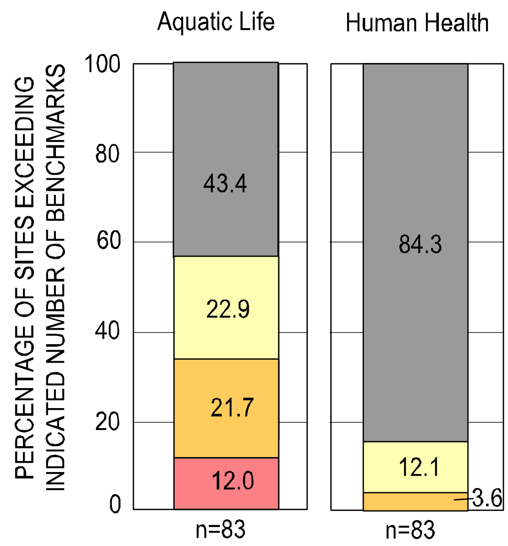
Samples of shallow ground water underlying areas of predominantly agricultural land were used to measure the concentration of nitrate, the occurrence of pesticides, and pesticide exceedances of human-health benchmarks in agricultural watersheds. All ground-water samples were collected and analyzed by the USGS according to the procedures described in Gilliom and others (1995) and Lapham and others, (1995). Sampling sites were not located in areas of known contamination but were selected to be representative of agricultural land use. Samples were collected from shallow wells screened near the top of the water table and primarily from monitoring wells and low-capacity domestic wells using sampling procedures described in (Lapham and others, 1995). Only one sample from each well was analyzed. These samples represent the first environmental sample collected from the well by the NAWQA Program. Methods for sample processing and preservation of samples can be found in Koterba and others (1995).

A.

BENCHMARK	PERCENTAGE* OF SITES EXCEEDING INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	0
Aquatic Life, n = 83	12.0	21.7	22.9	43.4
Human Health, n = 83	0.0	3.6	12.1	84.3

* Due to rounding, percentage may not add to 100

B.



EXPLANATION for B and C
Number of benchmarks exceeded

- None
- 1
- 2 or 3
- 4 or more

C.

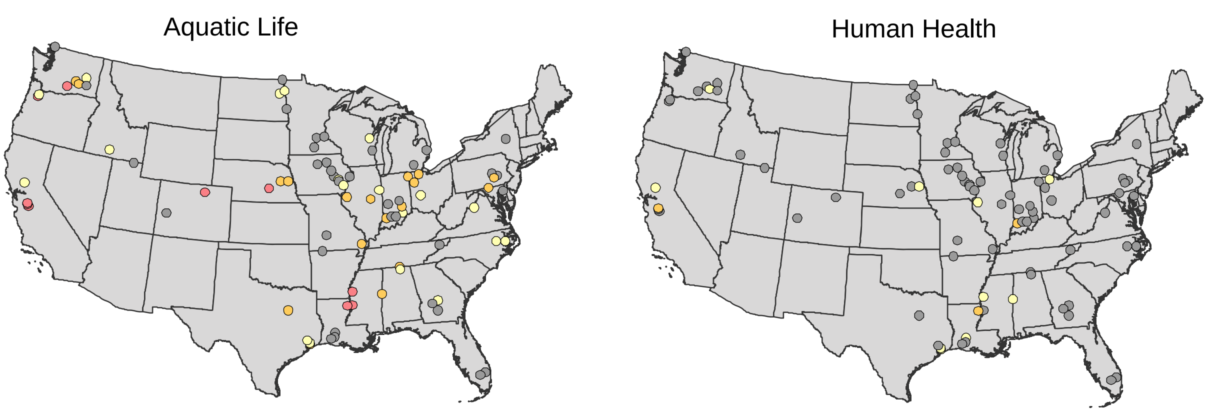


Figure 6. Pesticides in agricultural streams exceeding aquatic-life and human-health benchmarks for 1992-2001, shown as the percentage of sites exceeding the indicated number of benchmarks in (A) tabular form, (B) graphical form, and (C) the spatial distribution of sites within each exceedance class. Benchmark criteria described in Wilson and others, 2008.
[n, number of sites]

A.

BENCHMARK	PERCENTAGE* OF SITES EXCEEDING INDICATED NUMBER OF BENCHMARKS			
	5 or more	3 or 4	1 or 2	0
Aquatic Life, n = 83	7.2	12.1	37.3	43.4
Human Health, n = 83	0.0	1.2	14.5	84.3

* Due to rounding, percentage may not add to 100

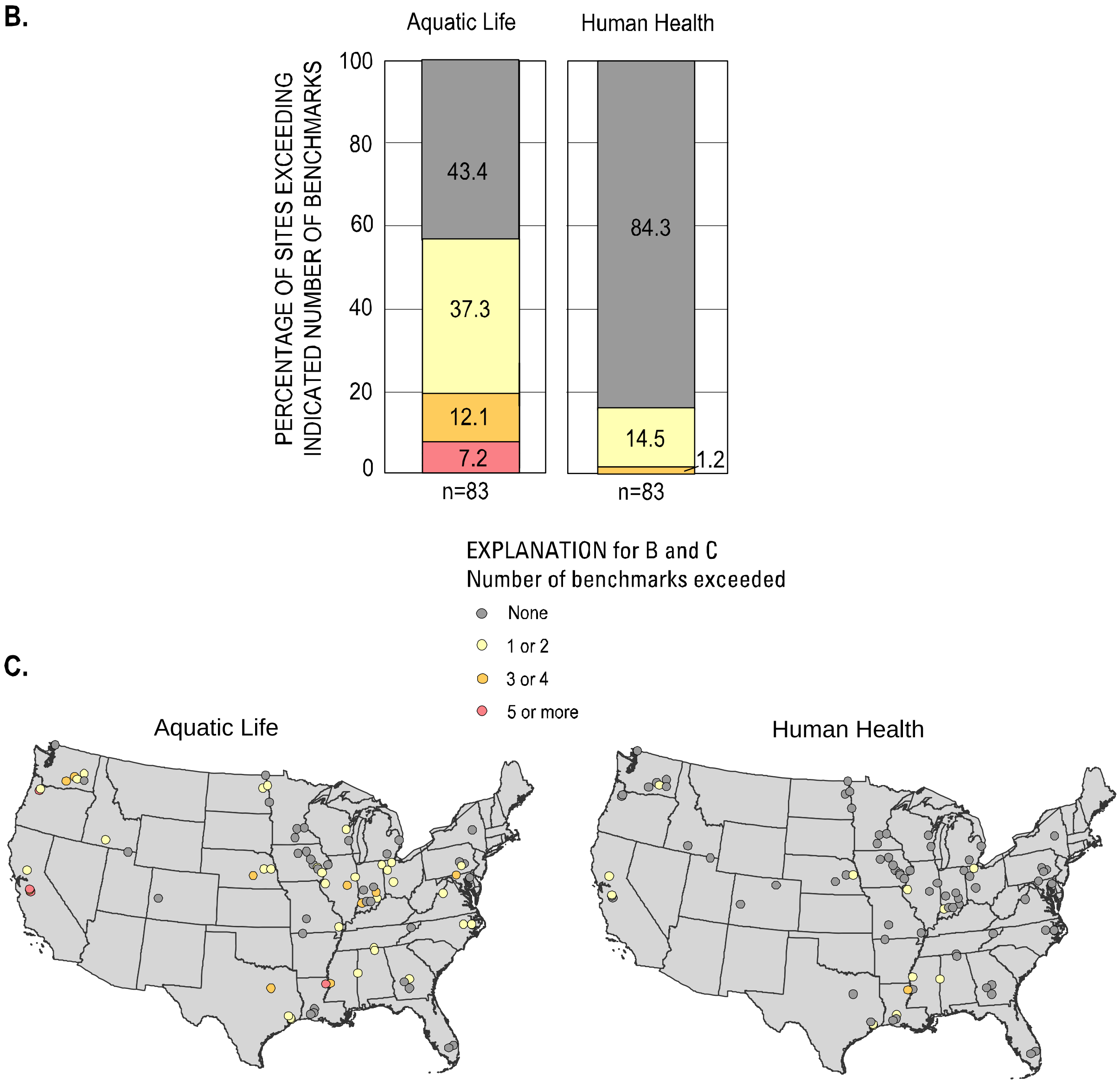


Figure 7. Pesticides in agricultural streams exceeding aquatic-life and human-health benchmarks for 1992-2001, shown as the percentage of sites exceeding the revised indicated number of benchmarks in (A) tabular form, (B) graphical form, and (C) the spatial distribution of sites within each exceedance class. The class bins were revised from: 1 to 1 or 2, 2 or 3 to 3 or 4, and 4 or more to 5 or more. Benchmark criteria described in Wilson and others, 2008. [n, number of sites]

Nitrate in Shallow Ground Water in Agricultural Watersheds

The nitrate indicator reports on the concentration of nitrate in ground water in agricultural watersheds. All of the data on nitrate in ground water were provided by Bernard T. Nolan (U.S. Geological Survey, written commun, 2006) (*appendix 9*). Specifically, the indicator reports on the percentages of wells with nitrate concentrations in one of four class bins: less than 2 mg/L, 2 to less than 6 mg/L, 6 to less than 10 mg/L, and 10 or more mg/L. Concentrations lower than the LT-MDL of 0.025 were considered non-detections and were grouped in the less than 2 mg/L class bin. Water samples were collected from 1,423 wells throughout the conterminous United States by the USGS NAWQA Program from 1992 to 2003 (fig. 8). Fishman (1993) and Patton and Truitt (1992) describe analytical methods used for determining nitrate in water.

Nitrate data were reviewed to check for obvious outliers and inconsistent results. Concentrations of nitrate were less than 2 mg/L in samples from about 42 percent of wells (fig. 8). Approximately 36 percent of wells had nitrate concentrations between 2 mg/L and 10 mg/L and about 21 percent of wells had concentrations of nitrate greater than or equal to 10 mg/L, which is the USEPA maximum contaminant level for nitrate in drinking water. A more complete description of how the data were compiled for this indicator is provided in Wilson and others (2008).

Pesticides in Shallow Ground Water in Agricultural Watersheds

The pesticide indicator reports on how frequently pesticides were found in agricultural ground water and how often concentrations exceed human-health benchmarks (figs. 9 and 10, and *appendix 10* and *appendix 11*). Water samples were collected from 1,412 wells sampled as part of the agricultural land-use studies by the USGS NAWQA Program between 1993 and 2003 (Gilliom and others, 2006). The number of pesticides detected at each site was binned into the following groups: none, 1 or 2, 3 or 4, and 5 or more. A pesticide was counted as detected if the concentration exceeded the LT-MDL for that pesticide (*appendix 6*). Exceedances of human-health benchmarks were identified when the sample concentration of one or more pesticides exceeded the relevant benchmark(s) at a site.

Concentrations of 76 commonly used pesticides and 7 pesticide degradation products were measured in ground-water samples (*appendix 6*). Zaugg and others (1995) and Werner and others (1996) describe analytical methods used for determining pesticide concentrations in ground water. A more complete description of how the data were compiled for this indicator is provided in Wilson and others (2008).

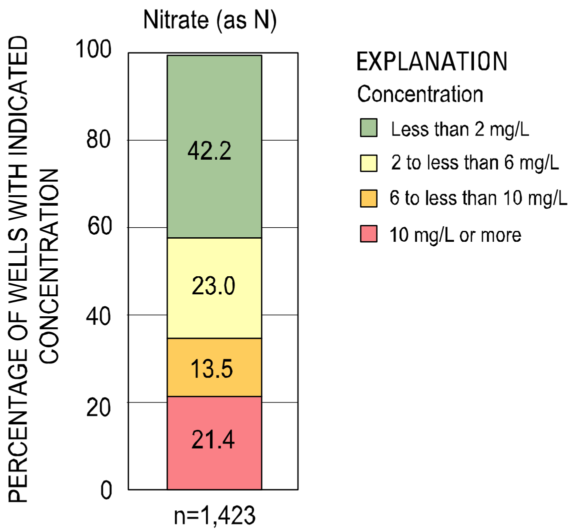
One or more pesticides were detected in about 61 percent of wells sampled in the agricultural land-use studies, and approximately 10 percent of the wells had 5 or more pesticides detected (fig. 9). Concentrations of pesticides infrequently exceeded human-health benchmarks, with approximately 1 percent of wells having a concentration of one or more pesticides that exceeded a human-health benchmark (fig. 10).

A.

CONSTITUENT	PERCENTAGE* OF WELLS WITH INDICATED CONCENTRATION			
	Less than 2 mg/L	2 to < 6 mg/L	6 to < 10 mg/L	10 mg/L or more
Nitrate (as N), n= 1,423	42.2	23.0	13.5	21.4

* Due to rounding, percentage may not add to 100

B.



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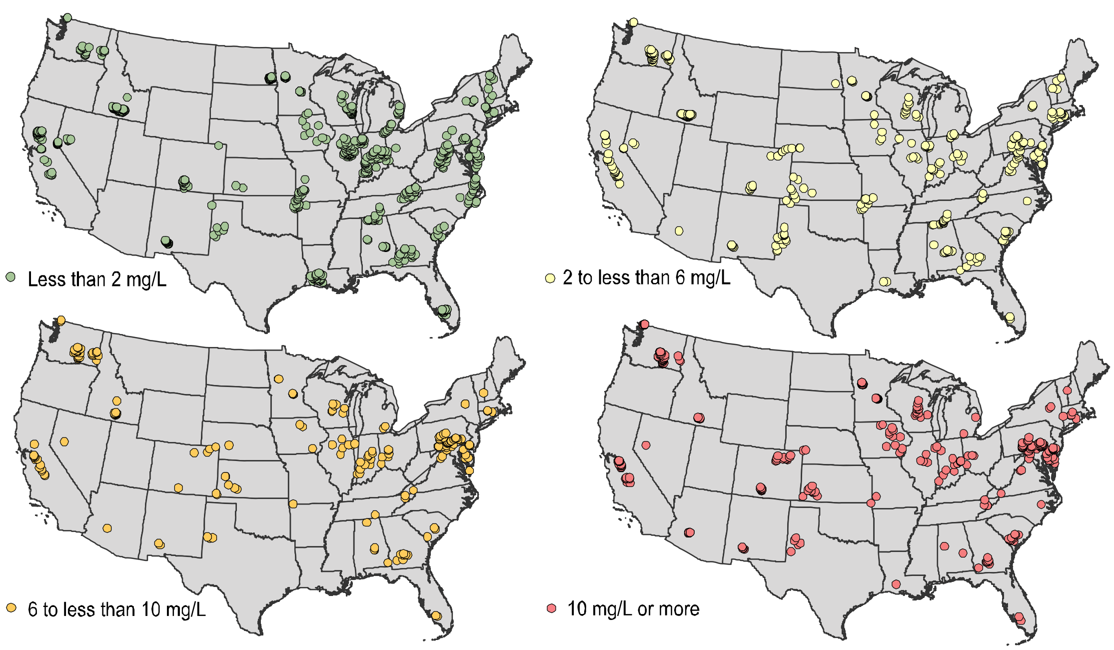


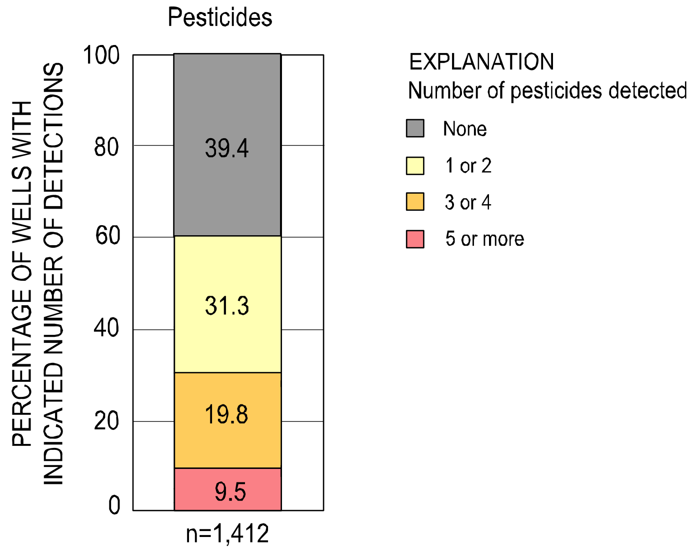
Figure 8. Nitrate (as N) concentrations in agricultural ground water for 1992-2003, shown as the percentage of sites with the indicated nitrate concentration range in (A) tabular form, (B) graphical form, and (C) the spatial distribution of sites within each concentration range. [mg/L, milligrams per liter; n, number of wells; nitrate, nitrate plus nitrite]

A.

CONSTITUENT	PERCENTAGE* OF WELLS WITH INDICATED NUMBER OF PESTICIDE DETECTIONS			
	5 or more	3 or 4	1 or 2	0
Pesticides, n = 1,412	9.5	19.8	31.3	39.4

* Due to rounding, percentage may not add to 100

B.



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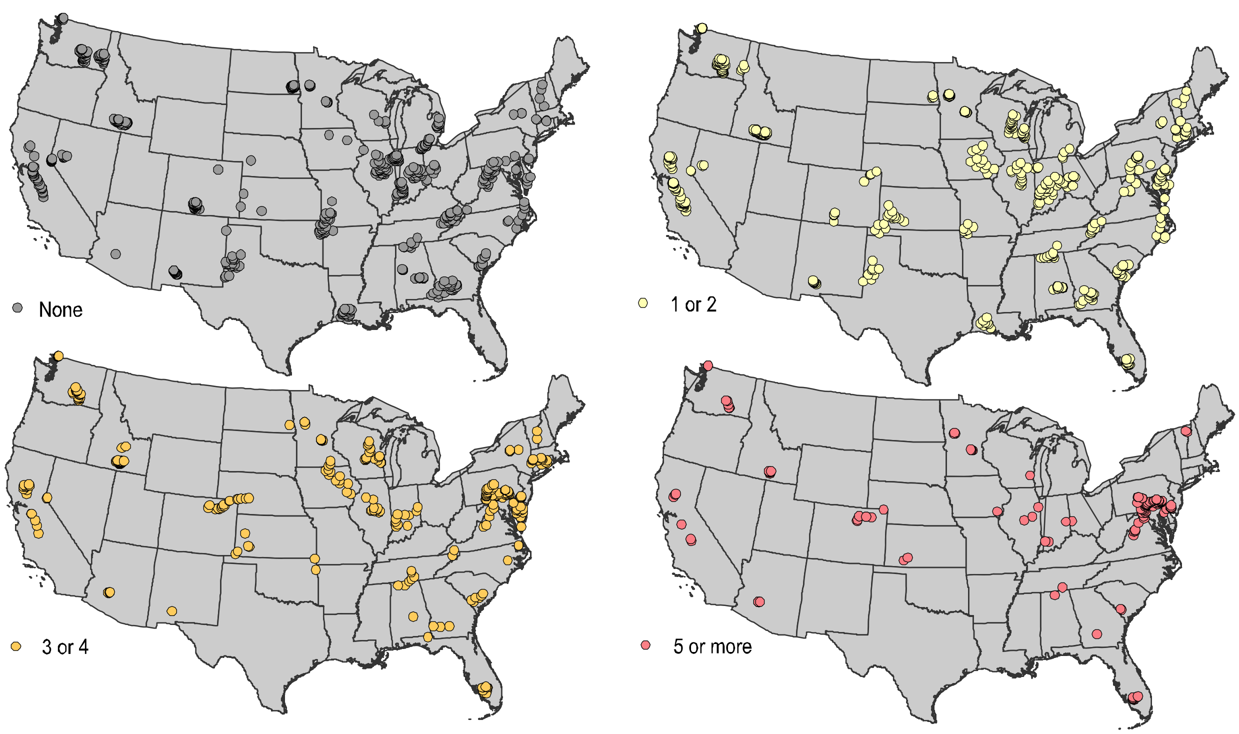


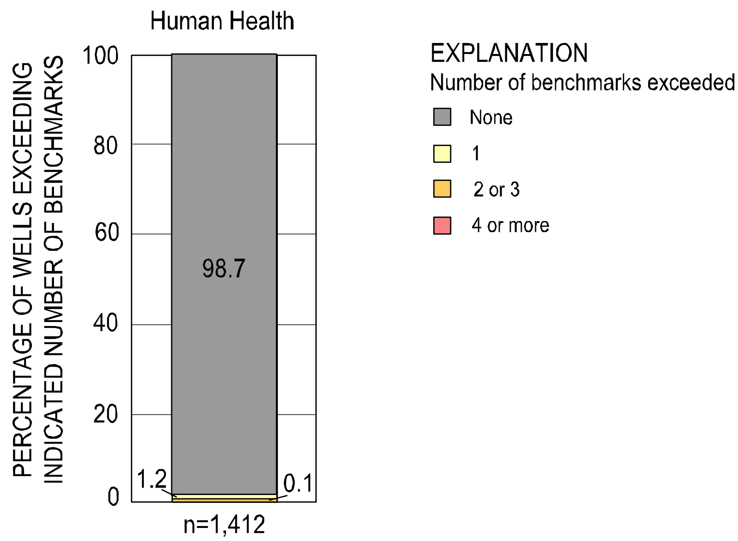
Figure 9. Pesticide occurrence in agricultural ground water for 1993-2003, shown as the percentage of wells with the indicated number of detections in (A) tabular form, (B) graphical form, and (C) the spatial distribution of pesticide detections within each class bin. [n, number of wells]

A.

CONSTITUENT	PERCENTAGE* OF WELLS EXCEEDING INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	0
Pesticides, n = 1,412	0.0	0.1	1.2	98.7

* Due to rounding, percentage may not add to 100

B.



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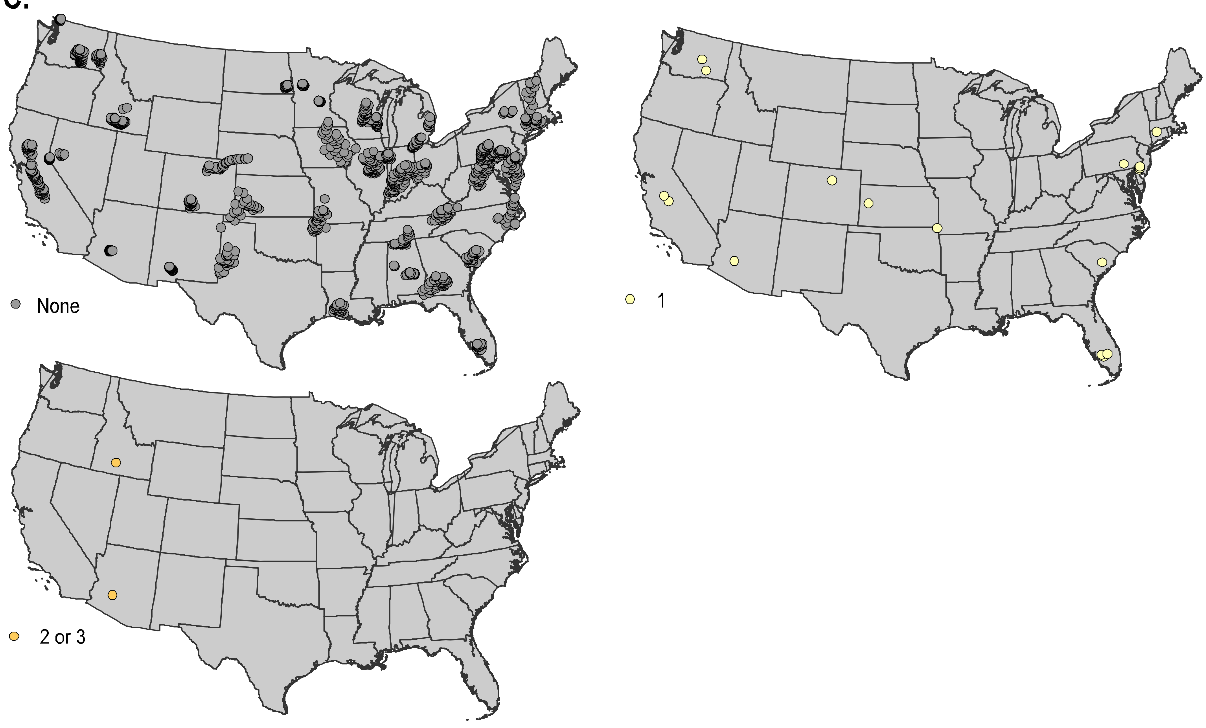

Figure 10. Pesticides in agricultural ground water exceeding human-health benchmarks for 1993-2003, shown as the percentage of sites exceeding the indicated number of benchmarks in (A) tabular form, (B) graphical form, and (C) the spatial distribution of sites within each exceedance class. Benchmark criterion described in Wilson and others (2008). [n, number of wells]

Summary

This report documents the sources of data and the methods used to develop selected water-quality indicators included in *EPA's 2007 Report on the Environment: Science Report*. Most of the water-quality data were collected between 1992 and 2003 as part of the USGS NAWQA Program, which collected data throughout the United States in 51 major hydrologic systems, referred to as study units. Other streamflow and nutrient data were collected by the USGS National Stream Water Quality Accounting Network (NASQAN) and the Federal–State Cooperative Programs.

Stream- and ground-water-quality data were provided for several indicators, including *Nitrogen and Phosphorus in Streams in Agricultural Watersheds*; *Pesticides in Streams in Agricultural Watersheds*; and *Nitrate and Pesticides in Shallow Ground Water in Agricultural Watersheds*. In addition, the USGS provided nitrate (nitrate plus nitrite) and total phosphorus riverine load estimates calculated from water-quality and streamflow data for the *Nitrogen and Phosphorus Discharge from Large Rivers* indicator.

The information provided to USEPA in this report is similar to information provided to the Heinz Center, and documents data the USGS provided for the 2007 report entitled *The State of the Nation's Ecosystems*. The data sets and associated documentation provided by the USGS for both reports were derived from the same sources, and in most cases the data provided to the USEPA is a subset of the data provided to the Heinz Center. Documentation of data provided to the Heinz Center is more extensive than is documented in this report and Wilson and others (2008) should be used to supplement the documentation provided here.

Acknowledgments

The authors are grateful for the technical reviews provided by David C. Reutter and Linda M. Debrewer, and for editorial review provided by Chester Zenone all of the USGS. Many other USGS employees provided assistance and data in the compilation of this report. Brent T. Aulenbach provided load estimates for the *Nitrogen in Major Rivers* indicator. Aulenbach also provided assistance in determining the methods used for calculating load estimates for the 2002 Heinz Center Report. Jeffrey D. Martin provided several data sets for pesticides in stream water related to work that was done by the NAWQA Pesticides National Synthesis Project and was published in Gilliom and others (2006). Members of the NAWQA Nutrients National Synthesis Project provided large amounts of data related to NAWQA stream sites. David Mueller and Neil M. Dubrovsky provided land-use classifications for all of the stream-water sampling sites with nutrient data. Bernard T. Nolan provided nutrient data for ground-water samples.

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Appendixes 1–11

1. List of NAWQA stream-water sampling sites with land-use classification used for *EPA's 2007 Report on the Environment: Science Report*
2. Water-quality data for nitrogen and phosphorus in stream-water samples from agricultural watersheds, 1992–2001
3. Annual nitrate and total phosphorus load estimates for the Mississippi River, 1968–2004
4. Annual nitrate and total phosphorus load estimates for the Mississippi, Susquehanna, St. Lawrence and Columbia Rivers
5. Water-quality data for pesticide occurrence in stream-water samples from agricultural watersheds, 1992–2001
6. List of analytes sampled in stream water and ground water with human-health and aquatic-life benchmarks
7. Pesticide exceedance of aquatic-life benchmarks in agricultural streams
8. Pesticide exceedance of human-health benchmarks in agricultural streams
9. Water-quality data for nitrate in ground-water samples from agricultural watersheds, 1992–2003
10. Water-quality data for pesticide occurrence in ground-water samples from agricultural watersheds, 1992–2003
11. Pesticide exceedance of human-health benchmarks in agricultural ground water