Methods and Sources of Data Used to Develop Selected Water-Quality Indicators for Streams and Ground Water for the 2007 Edition of *The State of the Nation's Ecosystems* Report with Comparisons to the 2002 Edition

By John T. Wilson, Nancy T. Baker, Michael J. Moran, Charles G. Crawford, Lisa H. Nowell, Patricia L. Toccalino, and William G. Wilber

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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

Abbreviations

AMLE	adjusted maximum likelihood estimate
ft^3/s	cubic feet per second
ESB	equilibrium partitioning sediment benchmark
GIRAS	Geographic Information Retrieval and Analysis System
>	greater than
HA-L	Lifetime Health Advisory
HBSL	Health Based Screening Level
LC	laboratory code
<	less than
LOADEST	load estimation software
LRL	laboratory reporting level
LT-MDL	long-term method detection level
MAS	Major Aquifer Study
MCL	maximum contaminant level
MDL	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
NOAEL	No-observed-adverse-effects level
NWIS	National Water Information System (USGS)
NWQL	National Water Quality Laboratory (USGS)
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PEL	Probable Effect Levels
RSD	Risk-Specific Dose
SVOC	semivolatile organic compound
TEL	threshold-effect concentrations
TRG	Tissue Residue Guidelines
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

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By John T. Wilson, Nancy T. Baker, Michael J. Moran, Charles G. Crawford, Lisa H. Nowell, Patricia L. Toccalino, and William G. Wilber

Abstract

The U.S. Geological Survey (USGS) was one of numerous governmental, private, and academic entities that provided input to the report *The State of the Nation's Ecosystems* published periodically by the Heinz Center. This report describes the sources of data and methods used by the USGS to develop selected water-quality indicators for the 2007 edition of the Heinz Center report and documents modifications in the data sources and interpretations between the 2002 and 2007 editions of the Heinz Center report. Stream and ground-water quality data collected nationally as part of the USGS National Water-Quality Assessment Program were used to develop the ecosystem indicators for the Heinz Center report, including *Core National* indicators for the *Movement of Nitrogen and Chemical Contamination* and for selected ecosystems classified as *Farmlands, Forest, Grasslands and Shrublands*, *Freshwater*, and *Urban and Suburban*. In addition, the USGS provided water-quality and streamflow data collected as part of the National Stream Water Quality Accounting Network and the Federal–State Cooperative Program. The documentation provided herein serves not only as a reference for current and future editions of *The State of the Nation's Ecosystems* but also provides critical information for future assessments of changes in contaminant occurrence in streams and ground water of the United States.

Introduction

In 2002, the H. John Heinz III Center for Science, Economics and the Environment (hereafter referred to as the Heinz Center) first published the report entitled *The State of the Nation's Ecosystems*, intended as a periodic series of comprehensive reports on the extent, condition, and use of the lands, waters, and living resources of the United States (Heinz Center, 2002). The Heinz Center uses key indicators to report on the condition and use of ecosystems in the U.S. The ecosystem indicators used in the Heinz Center's report were selected through a nonpartisan collaboration among government, environmental organizations, the private sector, and the academic community. These indicators are intended to provide factual, unbiased characteristics of the Nation's ecosystems. The first edition of *The State of the Nation's Ecosystems* report (Heinz Center, 2002) was issued simultaneously in a print version and in a Web version available at *http://www.heinzctr.org/ecosystems*.

The U.S. Geological Survey (USGS) was one of numerous governmental, private, and academic entities that provided data and guidance for the Heinz Center's reports. The purpose of this USGS report is to document the data and interpretations provided by the USGS in support of the second edition (2007) of the Heinz Center's report, which is due to be published in early 2008. This USGS report also documents changes to the data sets and interpretations between the 2002 and 2007 editions of the Heinz Center's report. Stream and ground-water quality data collected nationally in a consistent manner as part of the National Water-Quality Assessment (NAWQA) Program were used to develop several ecosystem indicators, including *Core National* indicators for the *Movement of Nitrogen and Chemical Contamination and for the Farmlands, Forest, Grasslands and Shrublands, Freshwater*, and *Urban and Suburban* ecosystems (*table 1* at the back of the report). In addition, the USGS provided nitrate plus nitrite (nitrate), phosphorus, and streamflow data collected as part of the National Stream Water Quality Accounting

Network (NASQAN) and the Federal–State Cooperative Program. In this report, nitrate refers to the sum of nitrate plus nitrite as reported by the USGS laboratory (parameter code p00631). Nitrate is the primary form of nitrogen dissolved in streams and ground water, and is reported in units of milligrams per liter of nitrogen. USGS streamflow and water-quality data can be accessed through the National Water Information System (NWIS): at *http://waterdata.usgs.gov/usa/nwis/nwis*. The data sources, type and period of record used to develop each indicator are shown in *table 1*.

The *Movement of Nitrogen* indicator describes the annual load and yield of nitrogen transported by selected large rivers of the U.S. and the amount of nitrogen delivered to coastal waters by major rivers (*table 1*). The indicators of *Chemical Contamination* include pesticides, nutrients, volatile organic compounds, polychlorinated biphenyl compounds, and trace elements. The indicators are a measure of how frequently chemical contaminants are detected in streams (water, streambed sediment, and fish tissue) and ground water and how often water-quality benchmarks are exceeded.

Water-quality indicators for the *Farmlands* ecosystem include nitrate in streams and ground water, phosphorus in stream water, and pesticides in stream water and ground water (*table 1*). The nitrate and phosphorus indicators document the ranges of concentrations of these constituents in stream water and ground water. The pesticides indicator is analogous to the chemical contamination indicator, and measures the frequency of detection of selected pesticides in the *Farmlands* ecosystem and how often water-quality benchmarks are exceeded.

Other water-quality indicators for which the USGS provided data and information included nitrate in streams of the *Forest* ecosystem; nitrate in ground water of the *Grasslands and Shrublands* ecosystem; and phosphorus in large rivers for the *Freshwater* ecosystem. For the *Urban and Suburban* ecosystem, USGS provided data for nitrate and phosphorus in stream water, and chemical contamination in stream water (*table 1*). Descriptions of data and methods in this report refer to the 2007 edition of the Heinz Center's report, except where noted otherwise.

The Movement of Nitrogen

The *Movement of Nitrogen*, is a *Core National* indicator in the Heinz Center reports, and refers to both the yield and load of nitrogen from major rivers to the ocean. The yield of nitrogen from major watersheds is defined as an areally averaged value contributed from the upstream watershed area and in transport at selected sites (generally at the downstream terminus of the watershed). The load of nitrate, the primary form of nitrogen dissolved in streams and ground water, is defined as the mass, in tons, of nitrate transported to the ocean annually, and was calculated for the Mississippi, Susquehanna, St. Lawrence, and Columbia Rivers.

Delivery of Total Nitrogen to Streams and Rivers from Major Watersheds

The delivery of total nitrogen to streams (in tons per square mile) was determined by computing the total annual nitrogen load for each major river and dividing it by the land area of the corresponding watershed. Riverine loads were estimated on the basis of discharge and water-quality data collected by the USGS as part of the NASQAN Program, the NAWQA Program, and the Federal–State Cooperative Program. Some additional stream gages from which data were used, most notably those at the mouth of the Mississippi River and on the Rio Grande River, are operated by the U.S. Army Corps of Engineers or the International Boundary and Water Commission rather than the USGS.

Nitrogen load and yield estimates were based on streamflow measurements and water samples collected at 44 sites from 1996 through 2005 (Data from NWIS; (Charles G. Crawford, U.S. Geological Survey, written commun., 2007). Loads were estimated for two 5-year periods to facilitate evaluation of trends. The two selected 5-year periods were water years (the 12-month period from October 1 through September 30) 1996–2000 and 2001–05. The period used to develop similar nitrogen load estimates for the 2002 Heinz Center report correspond to water years 1996–1999 for 60 sites. Load estimates were made to allow for the maximum number of sites to be included for both of the 5-year periods. Estimation of loads at a site required a minimum of 20 water samples collected in at least 3 of the 5 years and in all seasons during both time periods. Most sites had samples collected each year of both 5-year periods. The number of water samples used to estimate loads at a stream site for each 5-year period ranged from 20 to 319, with a median of 51 samples.

Nitrogen loads were estimated using transformation-bias corrected, adjusted-maximum-likelihood-estimation methods in LOADEST, a FORTRAN-based load estimation program (Runkel and others, 2004) (*appendix 1*). This program provided a regression model relating total nitrogen load to discharge, sample day-of-year (to represent seasonal effects), and sample time (to represent diurnal trends over the period) for each site using statistical techniques suitable for data with censored observations (loads derived from concentrations less than the analytical detection limit). Models were selected by site using LOADEST model option 0, which selects a best fit model on the basis of the Akaike Information Criterion (Judge and others, 1988). The selected models were then used to estimate daily total nitrogen loads. Separate models were developed for the 1996–2000 and 2001–05 time periods. Results of the models are documented in *appendix 1*.

The mean load (in pounds per day) for each 5-year period at each site was estimated and then multiplied by the average number of days per year in each period to obtain the estimated mean load (in pounds per year). The standard error of the mean-annual load estimates was generally less than 10 percent of the mean and ranged to a maximum of 18 percent. The incremental load was then calculated as the difference between the output load that flowed from the watershed and the input loads from upstream watersheds. The incremental yield (shown in the maps in figure 1) is defined as the incremental load divided by the corresponding watershed area. The white areas of the map in figure 1 are areas for which insufficient USGS data were available to calculate loads. The total land area for each incremental yield class group (bin) for both sampling periods is shown in figure 2.

Nitrate Discharged to Coastal Waters by Major U.S. Rivers

The scope of the analysis of *Nitrate Discharged to Coastal Waters by Major U.S. Rivers* included developing estimates of the annual load of nitrate for the Mississippi, Susquehanna, St. Lawrence, and Columbia Rivers using historical streamflow and water-quality data collected by USGS. The annual nitrate loads estimated for these four major rivers were derived from three sources. Mississippi River loads for 1955–67 were previously published in Goolsby and others (1999). Unpublished estimates of Mississippi River loads for 1968–2004 were calculated (Brent T. Aulenbach, U.S. Geological Survey, written commun., 2006) (*appendix 2*). Annual load estimates for Susquehanna River Basin (1974–2002), 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 loads for the Mississippi River (1955–67). Regression models were used to estimate annual loads for the Mississippi River (1968–2004) and for the entire period of record for the other three river basins. Annual nitrate load estimates for these four rivers are presented in *appendix 3*.

Goolsby and others (1999) calculated nitrate loads for the Mississippi River near St. Francisville, LA using data from the USGS water-quality station Mississippi River near St. Francisville, LA (station 07373420); and from nearby streamflow-gaging stations Mississippi River at Tarbert Landing, MS, (station 07295100); and Old River Outflow Channel at Knox Landing, LA, (station 073732865) for the period 1955–67. The loads were estimated on the basis of analyses of water samples collected daily and composited at 10- to 30-day intervals. Nitrate flux for the St. Francisville site was estimated using the sum of streamflow at Tarbert Landing plus flows diverted from the Mississippi River 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* at the link *Annual Nutrient Flux and Basin Yield Estimates, 9 Major Sites, Period of Record*; Excel spreadsheet: *FluxYieldAnnual_9S.xls*).

For the period 1968–2004, Aulenbach (2006) published estimated annual nitrate loads for the Mississippi River near St. Francisville, LA using data from USGS water-quality station Mississippi River near St. Francisville, LA (station 07373420); and from streamflow-gaging station Mississippi River at Tarbert Landing, MS (station 07295100). He also estimated (but did not publish) loads for the Mississippi River near St. Francisville including flows diverted from the Mississippi River through the Old River outflow at Knox Landing, LA. To maintain consistency with the 1955–67 estimates, which included streamflow for the Old River Outflow (Goolsby and others, 1999), the 1968–2004 unpublished loads (Brent T. Aulenbach, U.S. Geological Survey, written commun., 2006) were used for the 2007 Heinz Center report (*appendix 2*). Nitrate loads were estimated for the period July 1967 through June 2004 with a 10-year moving calibration window using LOADEST and results from the adjusted maximum likelihood estimate (AMLE). Methods used by Aulenbach are documented in *appendix 2*.

Annual nitrate 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 by using different station configurations at different times (Aulenbach, 2006). Annual nitrate load estimates were calculated using LOADEST load estimation software and results from the AMLE. Methods used are documented in Aulenbach (2006).

Annual nitrate loads for the Susquehanna River for 1974–78 were estimated from streamflow and water-quality data at Harrisburg, PA (station 01570500); and loads for 1979–2002 were estimated from streamflow and water-quality data at Conowingo, MD (station 01578310). The reported loads (Aulenbach, 2006) for the Susquehanna River at Harrisburg, PA were increased by 12.4 percent to account for the increase in drainage area from the Harrisburg site to the Conowingo site downstream (*appendix 3*).

Annual nitrate loads for the Columbia River for 1975–93 were calculated by adding the estimated annual nitrate load from the Willamette River at Portland, OR water-quality and streamflow-gaging station (station 14211720) to the estimated load from the Columbia River at Warrendale, WA streamflow-gaging station (station 14128910). Loads for 1994–2002 were estimated from streamflow and water-quality data for the Columbia River at Beaver Army Terminal near Quincy, OR, water-quality and streamflow-gaging station (station 14246900). The reported combined loads (Aulenbach, 2006) for the Warrendale and Portland stations were increased by 2.1 percent to account for the increase in drainage area from the Warrendale plus Portland station to the Quincy station downstream (*appendix 3*).

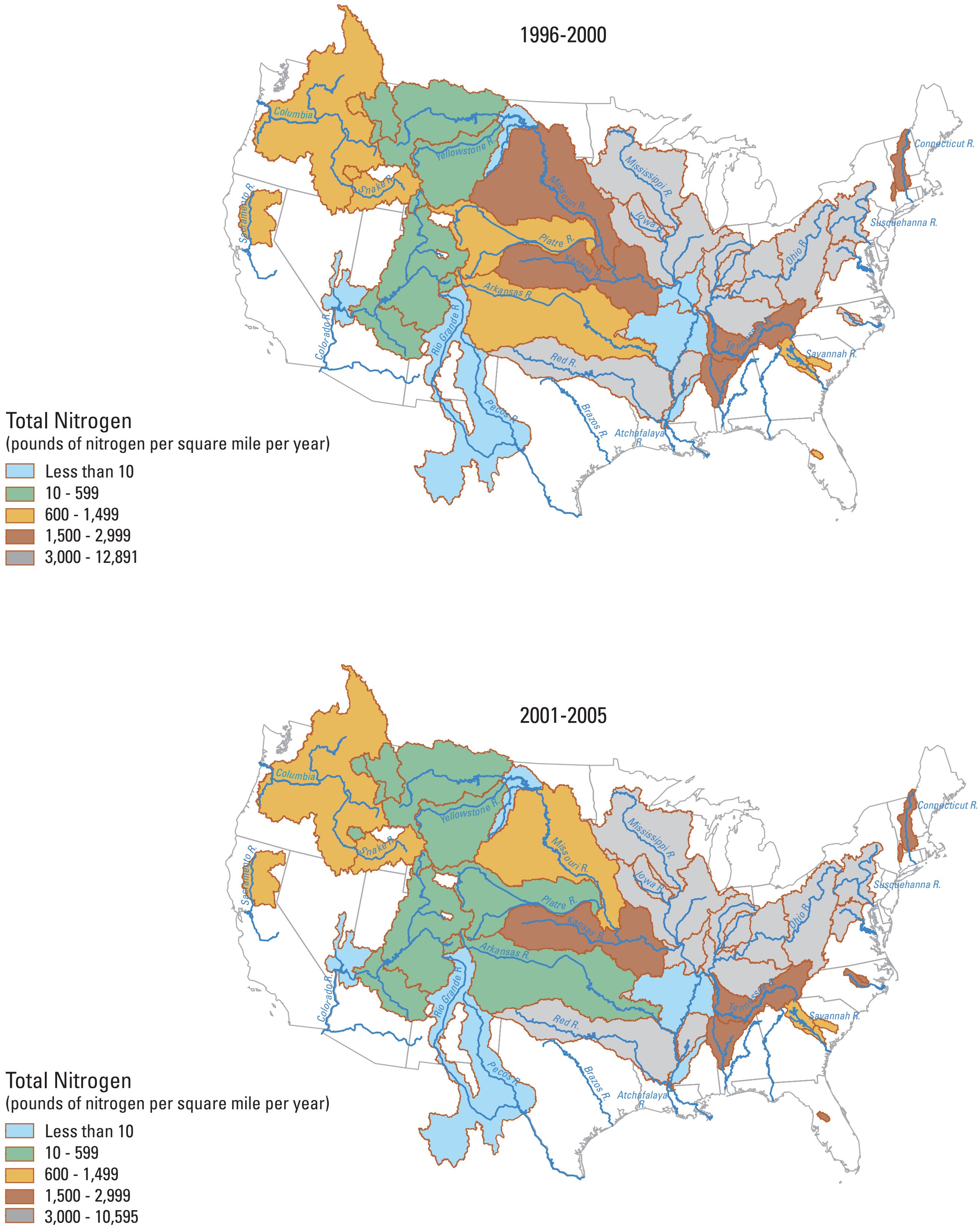

Figure 1. Delivery of total nitrogen to streams and rivers from major watersheds (1996–2000 and 2001–2005).

A

Mean Total Nitrogen Yield (pounds/square mile/year)	Total Land Area* (square miles)	
	1996-2000	2001-2005
Not Estimated	1,275,835	1,275,835
Less than 10	264,808	246,296
10 to 600	328,888	578,828
600 to 1,500	512,217	412,200
1,500 to 3,000	322,329	175,855
More than 3,000	485,120	500,184

* Conterminous U.S. only

B

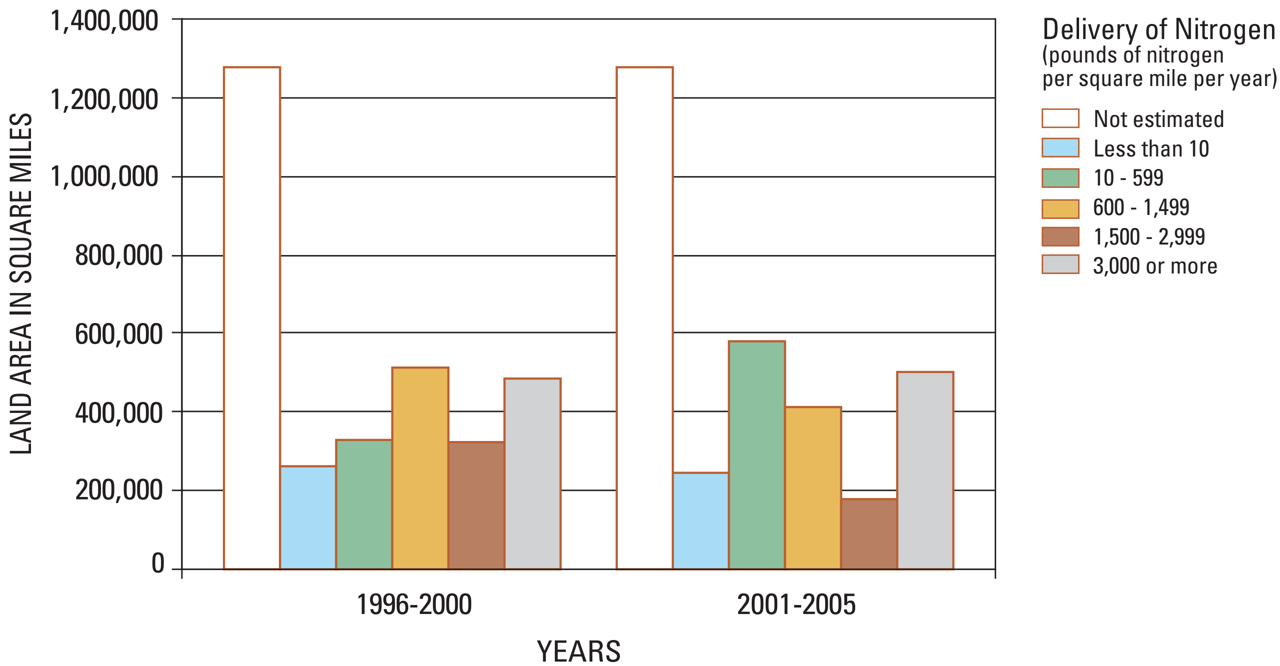

Figure 2. Total land area for each *Delivery of Nitrogen* class bin of the mean-total nitrogen yield from major watersheds (1996–2000 and 2001–2005) in (**A**) tabular and (**B**) graphical form.

Annual nitrate loads for the St. Lawrence River for 1974–96 were estimated at Cornwall, Ontario near Massena, NY water-quality and streamflow-gaging station (station 04264331) (*appendix 3*). The Heinz Center 2002 analysis included load estimates for the St. Lawrence River; however, because monitoring was discontinued after 1996, the 2007 edition of the report does not include the St. Lawrence River loads. The USGS plans to resume monitoring the St. Lawrence River as part of the NASQAN program.

Time-series plots of annual nitrate loads carried by the Mississippi, St. Lawrence, Columbia, and Susquehanna Rivers are shown in figure 3. 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.

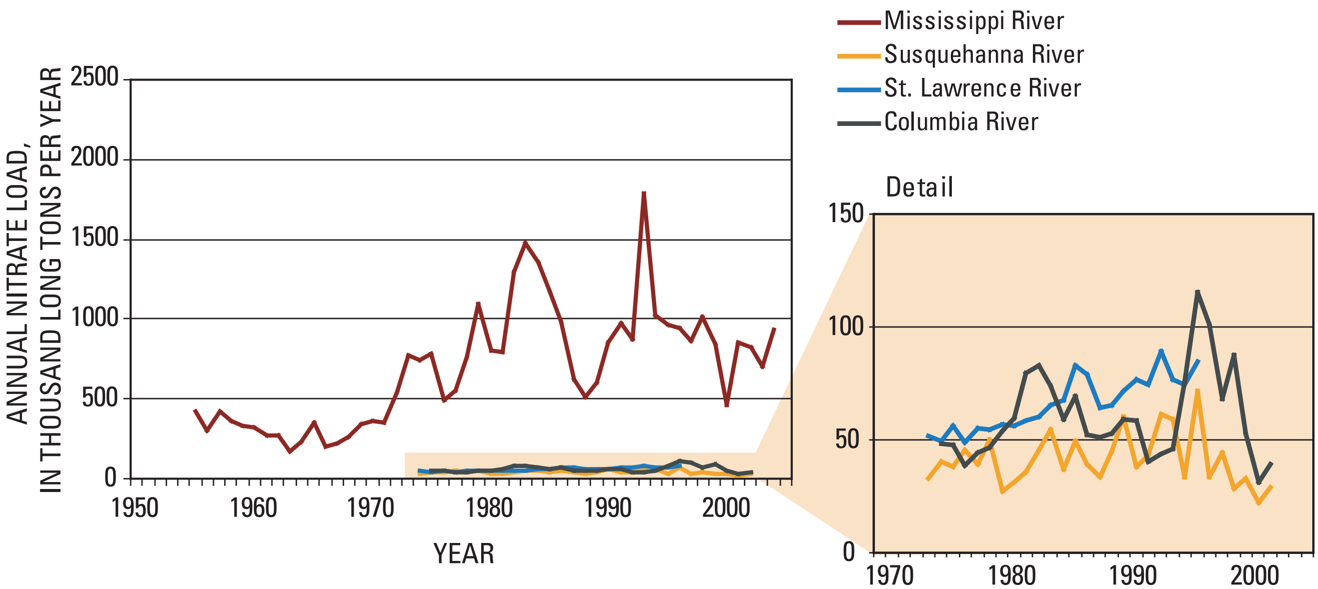

Figure 3. Annual nitrate loads discharged to coastal waters by the Mississippi, Susquehanna, St. Lawrence, and Columbia Rivers.

Classification of Stream Sites by Ecosystem

Classification of stream sites by ecosystem for the 2007 Heinz Center report included aggregating sites by Heinz Center ecosystem category based on the previously assigned NAWQA land-use classification. Land-use classification of ground-water sampling sites is described in the *Pesticides in Farmlands: Ground Water* and *Nitrate in Ground Water: Grasslands and Shrublands* sections of this report.

NAWQA land-use classification for stream sites was defined as the predominant land-use category within each stream's contributing drainage area (Lisa H. Nowell, U.S. Geological Survey written commun., 2006). The stream contributing area includes the land area within a watershed from which all runoff will flow to the point of interest. In the eastern U.S., the contributing area generally corresponds to the watershed area; but can be substantially smaller than the watershed area in the arid West. This approach does not account for all factors that may affect water quality at a site, such as upstream point sources of contamination. Generally the dominant land use within each watershed was determined using an enhanced version (Nakagaki and Wolock, 2005) of the USGS 1992 National Land Cover Data (NLCD) (Vogelmann and others, 2001), which classifies land use for each 30-by-30 meter area of land in the conterminous U.S. Land use for sites in Alaska and Hawaii, which lacked NLCD coverage, was classified using information available for local NAWQA study units. The land-use classification was adjusted for some sites where the dominant land use may not represent the conditions in the watershed. For example, if the area of one or more land uses contributes disproportionately larger or smaller streamflow (relative to its percentage of total land area in the watershed) the land-use classification was adjusted to better reflect the conditions in the watershed. Another example is interbasin transfers of water from a watershed with differing land use than the receiving watershed. Such adjustments were most common in the arid west, where water resources are heavily managed, and were based on local knowledge of the sampling site. Sites with a land-use classification based on an exception to the criteria shown in table 2 are identified as an exception in *appendix 4*.

Table 2. Criteria used to define the ecosystem classification of stream sampling sites for the 2007 Heinz Center report (modified from Gilliom and others, 2006).

[NAWQA, U.S. Geological Survey National Water-Quality Assessment Program; >, greater than; ≤ less than or equal to]

NAWQA land-use classification	Heinz Center report ecosystem classification	NAWQA land-use classification criteria
Agricultural	Farmlands	> 50 percent agricultural land and ≤ 5 percent urban land
Urban	Urban and Suburban	> 25 percent urban land and ≤ 25 percent agricultural land
Undeveloped	Forests (includes only undeveloped land where the percentage of forest land exceeds the percentage of rangeland	≤ 5 percent urban land and ≤ 25 percent agricultural land
Mixed		All other combinations of urban, agricultural, and undeveloped land

The major NAWQA land-use categories for stream sampling sites include agricultural, urban, undeveloped, and mixed. Table 2 compares the NAWQA classifications to the analogous ecosystem categories used in the Heinz Center report. NAWQA's agricultural class includes cropland (row crops, grains, orchards, vineyards) and pasture, and is analogous to the *Farmlands* ecosystem of the Heinz Center. NAWQA's urban class includes residential, commercial, and industrial areas, and is analogous to the Heinz Center's *Urban and Suburban* ecosystem. Undeveloped land includes land uses such as rangeland, forest, open water, and bare rock. Stream sites with a watershed classified as undeveloped were included in the Heinz Center's *Forest* ecosystem if the percentage of forest land was higher than the percentage of rangeland. Watersheds classified as "mixed" had combinations of agricultural, urban and undeveloped land and did not meet the criteria for the other three classes listed in table 2. Most streams classified as agricultural, urban, or undeveloped also had small amounts of other land uses in their watersheds. Sites classified as undeveloped may contain up to 25 percent agricultural land, and (or) 5 percent urban land in their watersheds, and the water quality at these sites may show some influences from developed land uses within the watershed (Gilliom and others, 2006).

NAWQA land-use classifications had previously been determined for 503 stream-water sampling sites of the NAWQA Cycle I study units (fig. 4, *appendix 4*). These sites represent the pool of sites available for the Heinz Center report analysis of Nutrients in Stream Water. Both the NAWQA land-use and Heinz Center ecosystem classifications are shown in figure 4 for the NAWQA Cycle I stream-water sampling sites and the subset of sites sampled for pesticides. The subset of 186 stream-water sampling sites represents sites with contaminant data available and that are used for the analyses *Chemical Contamination* and *Pesticides in Farmland Streams*. The sites shown in figure 4b also were used by Gilliom and others (2006) to assess pesticides in the Nation's streams.

The land-use classification for some sites differed between the 2007 and the 2002 analyses (*appendix 4*). The 2002 analysis used NAWQA land-use classifications based on a combination of the NLCD, the Geographic Information Retrieval and Analysis System (GIRAS) data set (Mitchell and others, 1977), and information from local study units.

Chemical Contamination

The *Chemical Contamination* indicator in the Heinz Center report provides a measure of how frequently chemical contaminants are detected in ecosystems (*Contaminant Occurrence*) and how often the contaminant concentrations exceed water-quality benchmarks (*Contaminants Exceeding Benchmarks). Chemical Contamination* is one of the *Core National* indicators and is also an indicator for the *Urban and Suburban* ecosystem. Media sampled by NAWQA and used to measure the *Core National* indicators include stream water, streambed sediment, freshwater-fish tissue, and ground water. Stream water was the only medium sampled to measure chemical contamination in the *Urban and Suburban* ecosystem.

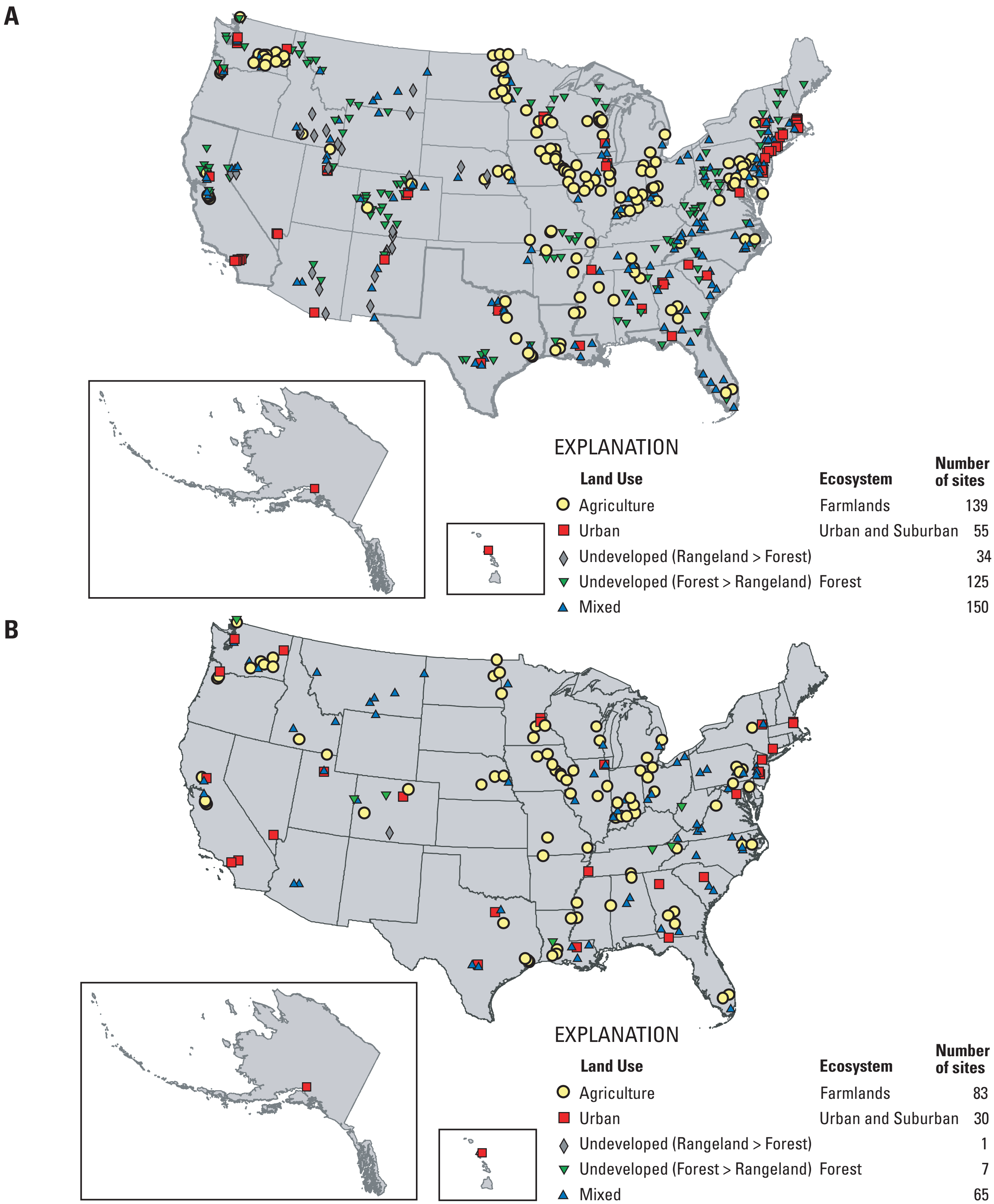

Figure 4. NAWQA land-use classification and Heinz Center report ecosystem classification for (**A**) 503 NAWQA Cycle 1 stream-water sampling sites and for (**B**) a subset of 186 stream-water sites sampled for pesticides. (NAWQA, U.S. Geological Survey National Water-Quality Assessment Program)

Contaminant Occurrence

Contaminant Occurrence indicators generally were calculated as the average number of contaminant detections per sample in each medium sampled. The average number of detections at each site was binned into the following groups: none; 1 or 2; 3 or 4; and 5 or more detections. A concentration of any contaminant was counted as a detection if the USGS National Water Quality Laboratory (NWQL) did not include a “<” remark code with the sample analysis, indicating that the concentration was greater than the laboratory reporting level (LRL). The LRL is determined by NWQL for each contaminant and is generally equal to twice the yearly determined long-term method detection level (LT-MDL). The LT-MDL is derived by determining the standard deviation of a minimum of 24 MDL spike sample measurements over an extended period of time (annually in most cases) (Childress and others, 1999). Analyte concentrations below raised reporting levels (with “<” remark code) were also treated as non-detections. For example: if the LT-MDL was 0.03 micrograms per liter (µg/L) and the reported analyte concentration for a specific sample was < 0.05 µg/L, that sampled concentration was considered to be a non-detection for that analyte. Estimated values qualified with an “E” remark code were counted as detections.

Stream Water

The occurrence of contaminants in stream water is a measure of the number of water-soluble pesticide detections in water samples collected in 51 NAWQA study units, and based on one 12-month sampling period at each site during 1992–2001. Analytical data for pesticides were available for 186 stream-water sampling sites throughout the Nation, including Alaska and Hawaii (Gilliom and others, 2006). The NAWQA Program collected samples for analysis of pesticides 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 periods of high pesticide use. One sample was collected each month during other periods. The 12-month period with the highest number of samples analyzed for pesticides was selected for each site to characterize the annual distribution of concentrations of pesticides. 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 samples collected at each of the 186 sites for the selected 12-month period ranged from 8 to 50, with a median of 22.5. The mean number of days between samples at these sites ranged from 6.6 to 36.5, with a median of 15.3 days. The discrete pesticide samples were used to compute time-weighted mean-annual 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 included on NWQL schedules 2010, 2050 and 2060 (see *http://nwql.cr.usgs.gov/usgs/catalog/index.cfm*); however, not every sample had results for every analyte (*appendix 5*, *appendix 6*). Gilliom and others (2006, p. 153) list the analytical method and maximum LT-MDL for the period 1992–2001 for each of the pesticide compounds. There were 28 different LT-MDLs for the 83 pesticides analyzed in NAWQA samples, with a range of 0.001 µg/L to 0.240 µg/L and a median of 0.011 µg/L (Childress and others, 1999).

Three types of figures illustrate the occurrence of contaminants in stream water for 1992–1998 and 1992–2001 data sets used for the 2002 and 2007 Heinz Center reports (figs. 5 and 6): (a) tables showing the percentage of sites sampled in each of the four categories of detection frequency, (b) bar graphs showing the percentages from the aforementioned table, and (c) maps showing the number of detections at each site for the 2007 data set. Figure 5 shows the occurrence of contaminants in water samples collected from the 186 stream sites sampled nationally (*Core National* indicators). *Appendix 7* includes a spreadsheet to show how the average number of contaminant detections at each site was counted. The tables and bar graphs in figures 5 and 6 also include the results from the analysis for the 2002 Heinz Center report. The *Contaminant Occurrence* indicator for the 2002 Heinz Center report included nitrate as a contaminant if concentrations of nitrate in water were equal to or greater than an estimated national “background” level (0.6 milligrams per liter (mg/L)). Nitrate was not included in the 2007 analysis of contaminant occurrence because it occurs naturally, and the background levels of nitrate differ greatly between watersheds. It was determined subsequently that a single national background level may not be appropriate for assessing chemical contamination. The use of regional or watershed-specific background levels nationally would be a more appropriate method for determining nitrate contamination. The States and U.S. Environmental Protection Agency (USEPA) are working to identify regional-scale background concentrations as part of an ongoing effort to define nutrient criteria.

Stream-water sampling sites in watersheds classified by NAWQA as urban were used to measure the contaminant occurrence in streams of the *Urban and Suburban* ecosystem in the Heinz Center report (fig. 6). A subset of 30 streams draining areas of predominantly urban and suburban land show similar rates of pesticide detections as the national set of streams (figs. 5 and 6). All 30 streams in the 1992–2001 data set had one or more pesticide detections and 73 percent of the sites had 5 or more detections.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
[2]2002 report (1992-1998); 106 sites	82.1	13.2	4.7	0
[3]2007 report (1992-2001); 186 sites	77.4	14.5	7.0	1.1

[1]Percentages may be rounded to equal 100
[2]Including nitrate detections above 0.6 mg/L
[3]Excluding nitrate detections

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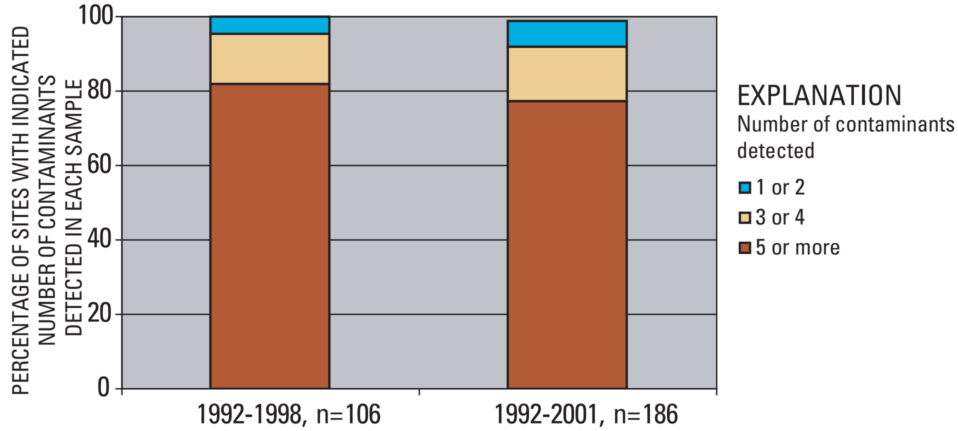

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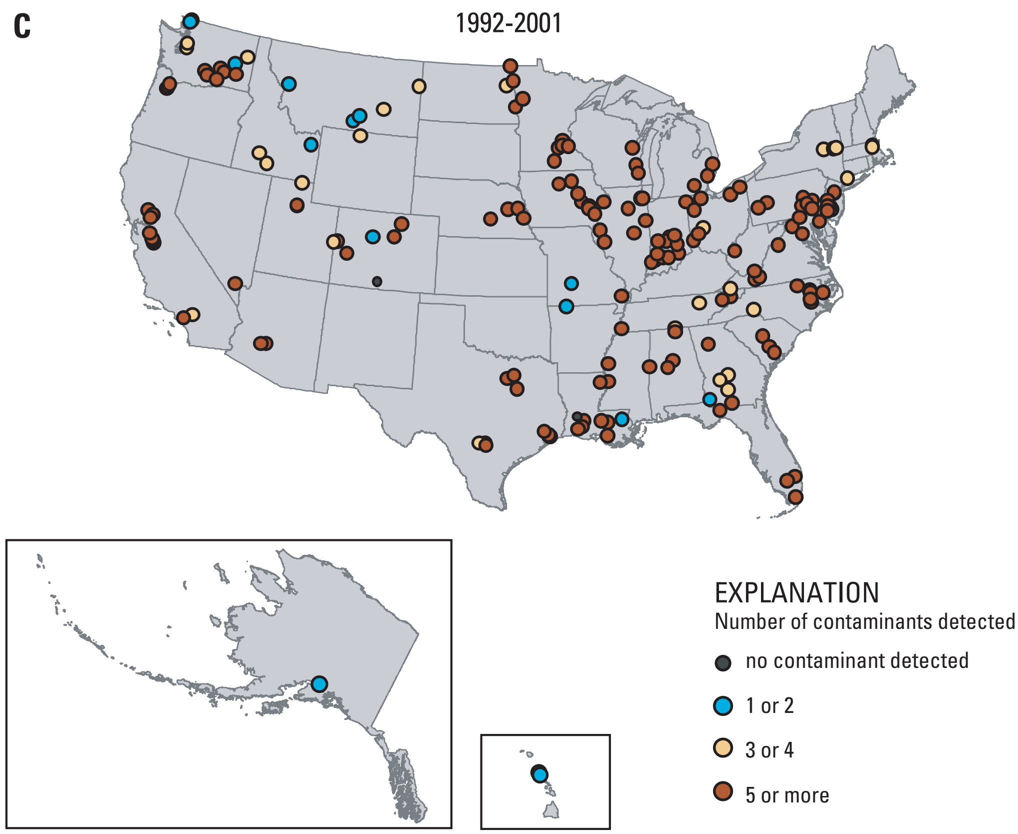


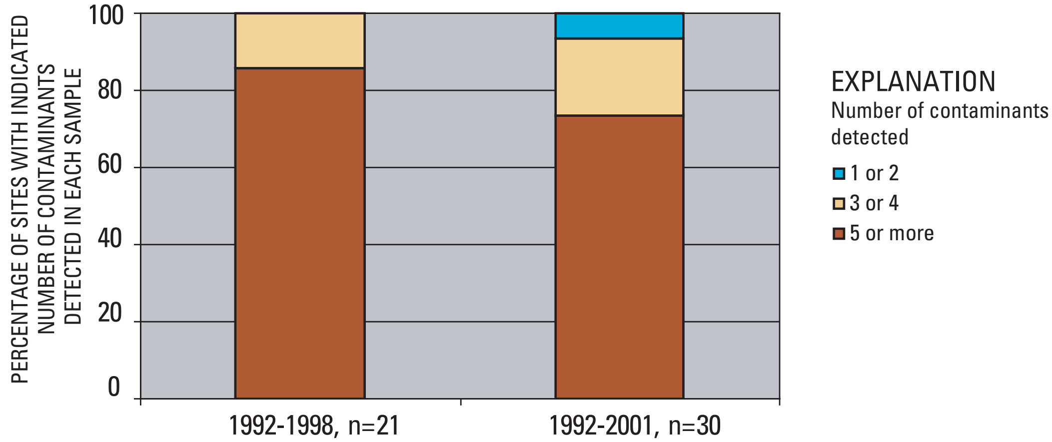
Figure 5. Contaminant occurrence in national stream water compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) a map of contaminant detections for the 2007 edition data. Targeted contaminants included pesticides and nitrate for the 2002 edition and pesticides only (excluding nitrate) for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
[2]2002 report (1992-1998); 21 sites	85.7	14.3	0	0
[3]2007 report (1992-2001); 30 sites	73.3	20.0	6.7	0

[1]Percentages may be rounded to equal 100
[2]including nitrate detections above 0.6 mg/L
[3]Excluding nitrate detections

B



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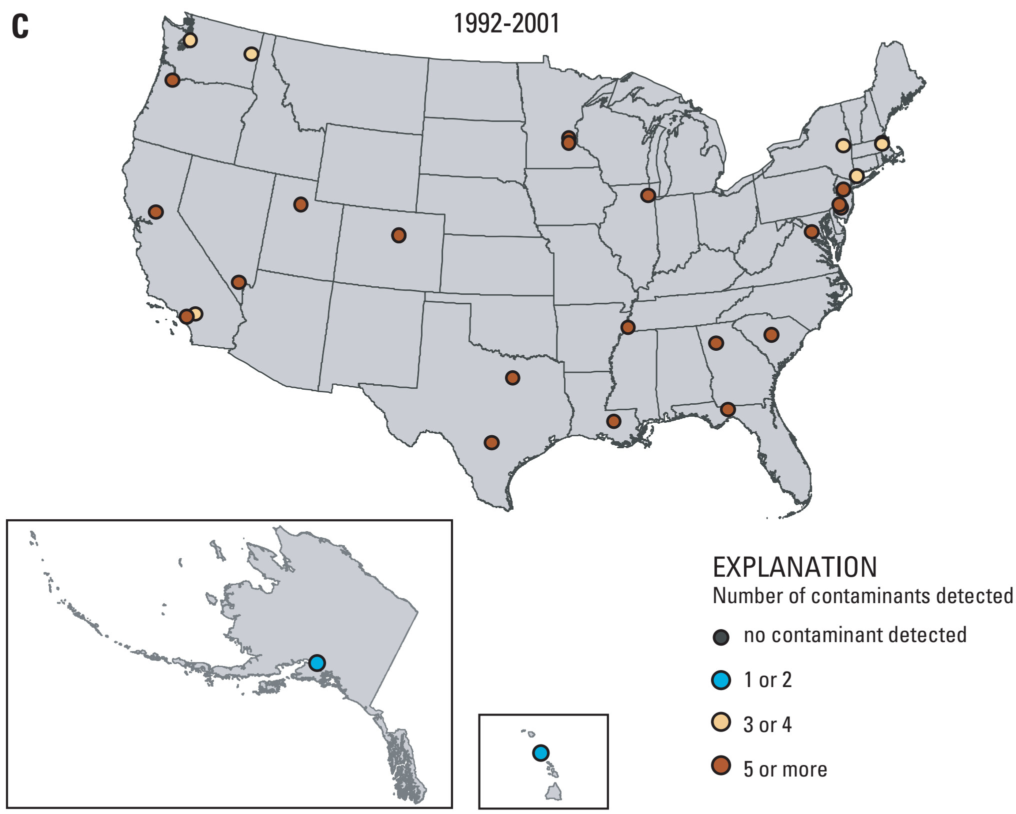

Figure 6. Contaminant occurrence in streams draining the *Urban and Suburban* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) a map of contaminant detections for the 2007 edition data. Targeted contaminants included pesticides and nitrate for the 2002 edition and pesticides only (excluding nitrate) for the 2007 edition.

Figure 7 shows how the frequency of pesticide detections in the 186 national streams changes for different censoring levels, arbitrarily chosen at 0.01, 0.1, and 0.2 µg/L. The use of a common censoring level for defining detections would help to equalize the chances of a compound being "detected", but, would underestimate the true detection level. For example, the percentage of sites with no detections increases from 1 percent when there is no censoring to 51 percent when the data are censored at 0.2 µg/L. The percentage of sites with 5 or more detections decreases from greater than 77 percent when there is no censoring to zero percent when the data are censored at 0.2 µg/L. Of the 83 pesticides analyzed in NAWQA samples, 47 percent had LT-MDLs less than or equal to 0.01 µg/L, 89 percent had LT-MDLs less than or equal to 0.1 µg/L, and 98 percent had LT-MDLs less than or equal to 0.2 µg/L. Pesticide detections were not censored in the analysis provided to the Heinz Center—the above analysis shown in figure 7 was done solely for this report.

A

CENSORING LEVEL	PERCENTAGE[1] OF SITES WITH INDICATED NUMBER OF CONTAMINANTS DETECTED (N=186)			
	5 or more	3 or 4	1 or 2	none
Not Standardized[2]	77.40	14.50	7.00	1.10
Standardized[3] at 0.01 ug/L	54.30	19.90	18.81	6.99
Standardized[3] at 0.10 ug/L	4.84	16.13	41.40	37.63
Standardized[3] at 0.20 ug/L	0.00	8.06	40.86	51.08

[1]Percentages may be rounded to equal 100
[2]Long-term method detection levels varied by analyte
[3]Standardized censoring levels arbitrarily chosen

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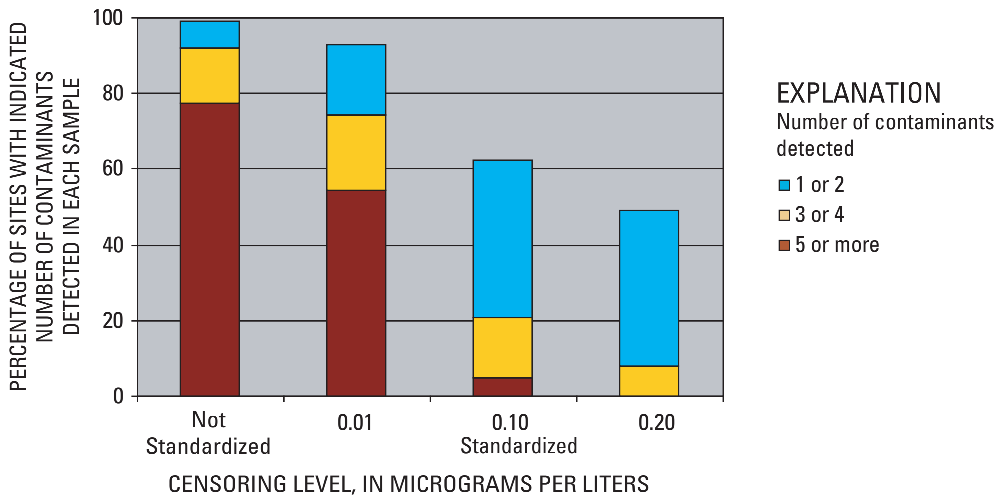

Figure 7. The effect of censoring levels on contaminant (pesticide only) occurrence in national stream water compiled for the 2007 (1992–2001) edition of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections and (**B**) a graphical comparison of pesticide detections for the various censoring levels.

Streambed Sediment

The occurrence of contaminants in streambed sediment is a measure of the number of detections of total polychlorinated biphenyls (PCBs), organochlorine pesticides and semivolatile organic compounds (SVOCs) in samples collected in 51 NAWQA study units (Data provided by Lisa H. Nowell, U.S. Geological Survey, written commun., 2006). Analytical data available for measuring chemical contamination for this indicator consist of one sample each from 957 sites across the Nation, including Alaska and Hawaii (*appendix 8*). The sediment samples were analyzed for total PCBs (NWQL Schedule 2501), organochlorine pesticides (NWQL Schedule 2501), SVOCs (NWQL Schedule 2502), and trace elements (NWQL Schedule 2420) (see *http://nwql.cr.usgs.gov/usgs/catalog/index.cfm*). Because trace elements occur naturally, and they are not considered a contaminant, the frequency of their detection is not included in the *Contaminant Occurrence* section. Trace element analysis for the 957 sites is included in the *Streambed Sediment* section of *Contaminants Exceeding Benchmarks*. A complete listing of analytes and NWQL reporting limits for streambed sediments is provided in *appendix 9*.

A total of 95 analytes were used to measure the occurrence of contaminants in streambed sediment for the 2007 edition of the Heinz Center report. The suite of analytes includes total PCBs, 31 organochlorine pesticide compounds and 63 SVOCs (*appendix 9*). Five values for phthalates from the SVOC class of contaminants were censored because of chronic contamination in laboratory blanks (table 3) (Michael P. Schroeder, U.S. Geological Survey National Water Quality Laboratory, written commun., 2006). These compounds were censored to the larger of the 95th percentile concentration in the laboratory blanks or the minimum reporting level. These censored values were used to determine both the frequency of detections (in *Chemical Contaminants*) and the frequency of benchmark exceedances (in *Contaminants Exceeding Benchmarks*).

Table 3. Semivolatile organic compounds measured in streambed sediment environmental samples, censored to the larger of the 95th percentile concentration in National Water Quality Laboratory (NWQL) blanks (C_{95} value) or the NWQL established minimum reporting level (mrl) because of chronic contamination in laboratory blanks. The C_{95} value is based on 95th percentile concentration of blank samples for the years 1995 through 2002.

[NWQL, U.S. Geological Survey National Water Quality Laboratory; C_{95}, 95th percentile concentration; µg/kg, micrograms per kilogram; mrl, minimum reporting level; V code, NWQL contamination remark code showing the C_{95} value multiplied by 10 (values between C_{95} and 10 x C_{95} may reflect a contribution from laboratory contamination); <, less than; *, value used to censor the environmental sample]

NWQL Schedule 2502 analyte	Number of blank samples	Percent frequency of blank sample contamination	C_{95} value (µg/kg)	NWQL established mrl	V code (10 x C_{95})
Phenol	113	33.6	24.7	<50*	250
Bis(2-ethylhexyl) phthalate	113	70.8	53.6*	<50	500
Butylbenzyl phthalate	113	70.8	46.5	<50*	500
Dinbutyl phthalate	113	79.6	47.9	<50*	500
Diethyl phthalate	113	38.0	18.6	<50*	200

The frequency of contaminant detections in streambed sediment samples are shown in figure 8. In the 1992–2001 data set, approximately 97 percent of the streambed sampling sites had one or more detections of a contaminant and approximately 80 percent of the sites had 5 or more detections. *Appendix 10* includes a spreadsheet to show how the average number of contaminant detections at each site was counted.

Fish Tissue

The occurrence of contaminants in fish tissue is a measure of the frequency of detection of organochlorine pesticides and total PCBs. Analytical data available for measuring chemical contamination in freshwater fish tissue consisted of composite samples collected from 700 sites across the Nation, including Alaska and Hawaii (*appendix 11*). Each fish sample was a composite of five to eight individual whole fish (all belonging to a single taxon) collected at the site on the same date. Nationally, the most commonly sampled fish taxa were common carp (29 percent) and white sucker (25 percent). A single taxon generally was sampled at each site, although multiple taxa were collected at about 10 percent of the sites. Taxa were selected from a National Target Taxa List (Crawford and Luoma, 1993), and the same taxon was sampled at as many sites as possible within each study unit (analytical approach and methods can be obtained from *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/supporting_info.php* (select appendix 8, then select appendix 8C). The analytes in this indicator include 27 organochlorine pesticides and total PCBs (NWQL Schedule 2101) (*appendix 12*). The data used for this indicator include the organochlorine pesticides data used in Gilliom and others (2006) plus corresponding total PCBs data for those samples (NAWQA Data Warehouse retrieval, Moon H. Kim, U.S. Geological Survey, written commun., 2006).

In the 1992–2001 data set, approximately 82 percent of the fish-tissue samples had one or more detections of an organochlorine pesticide or total PCBs, and approximately 43 percent of the samples had 5 or more detections of these compounds (fig. 9). No contaminants were detected in 18 percent of the samples. *Appendix 13* includes a spreadsheet to show how the average number of contaminant detections at each site was counted.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
2002 report (1992-1998); 486 sites	93.6	3.1	1.9	1.4
2007 report (1992-2001); 957 sites	80.5	7.5	8.8	3.2

[1]Percentages may be rounded to equal 100

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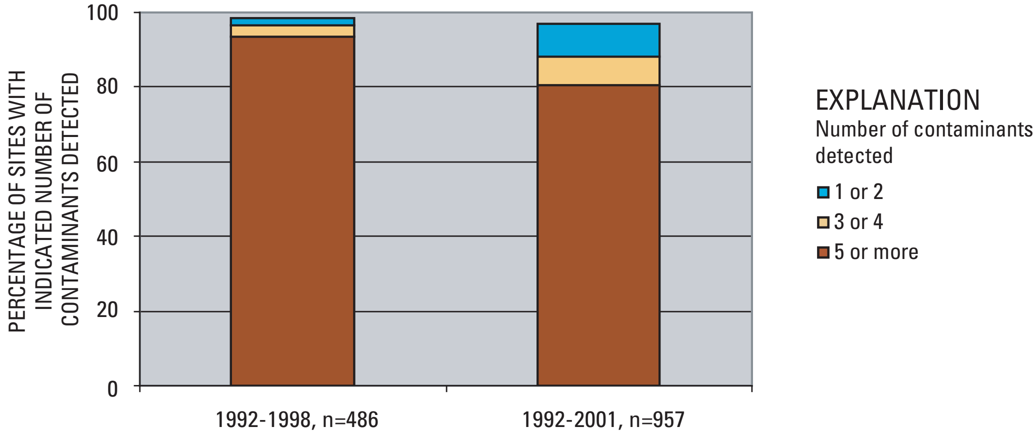

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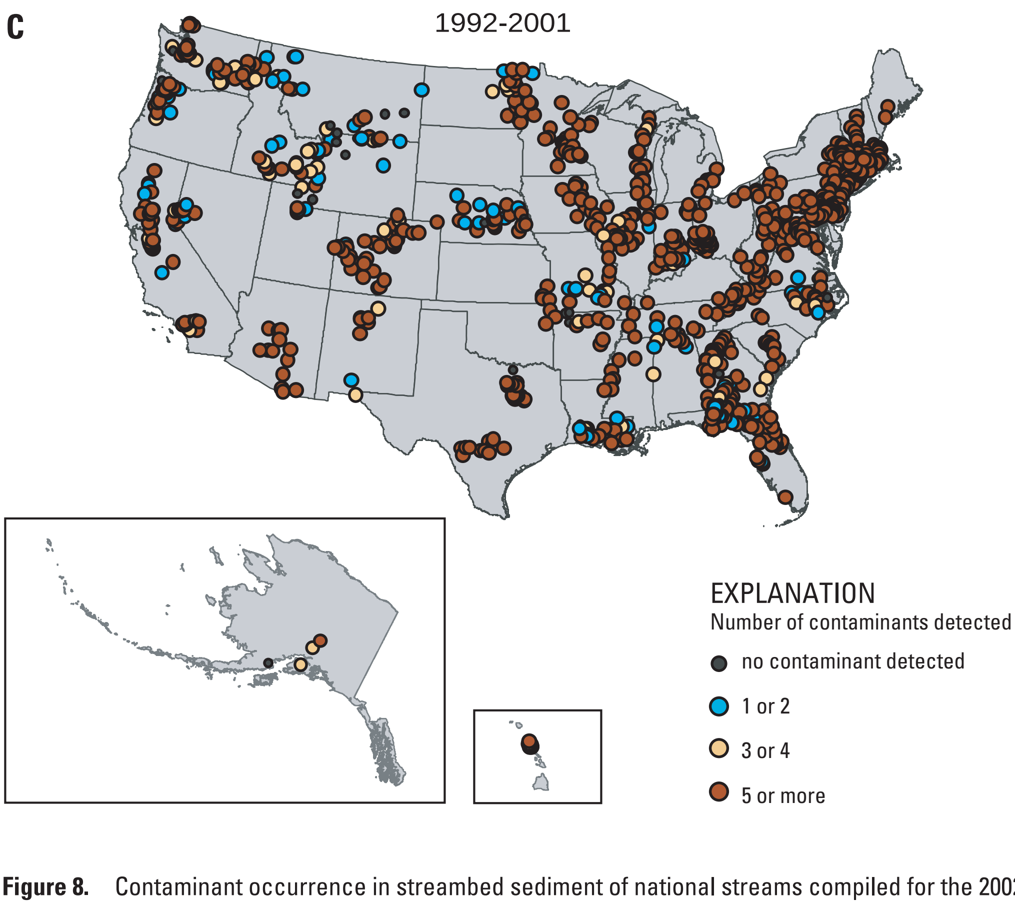

Figure 8. Contaminant occurrence in streambed sediment of national streams compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) a map of contaminant detections for the 2007 edition data. Targeted contaminants included total polychlorinated biphenyls (PCBs), organochlorine pesticides,and semivolatile organic compounds (SVOCs).

A

SAMPLING PERIOD AND NUMBER OF SAMPLES	PERCENTAGE[1] OF FISH SAMPLES WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
2002 report (1992-1998); 220 samples	53.5	11.9	28.7	5.9
2007 report (1992-2001); 700 samples	42.6	13.7	26.1	17.6

[1]Percentages may be rounded to equal 100

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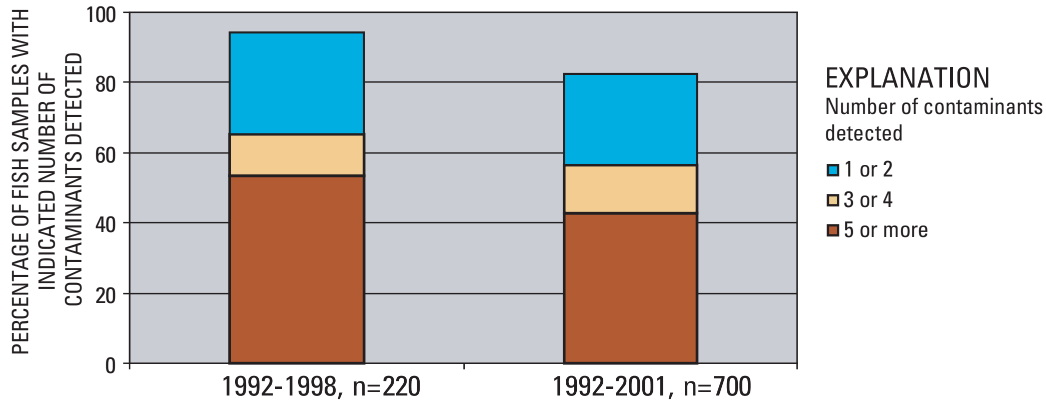

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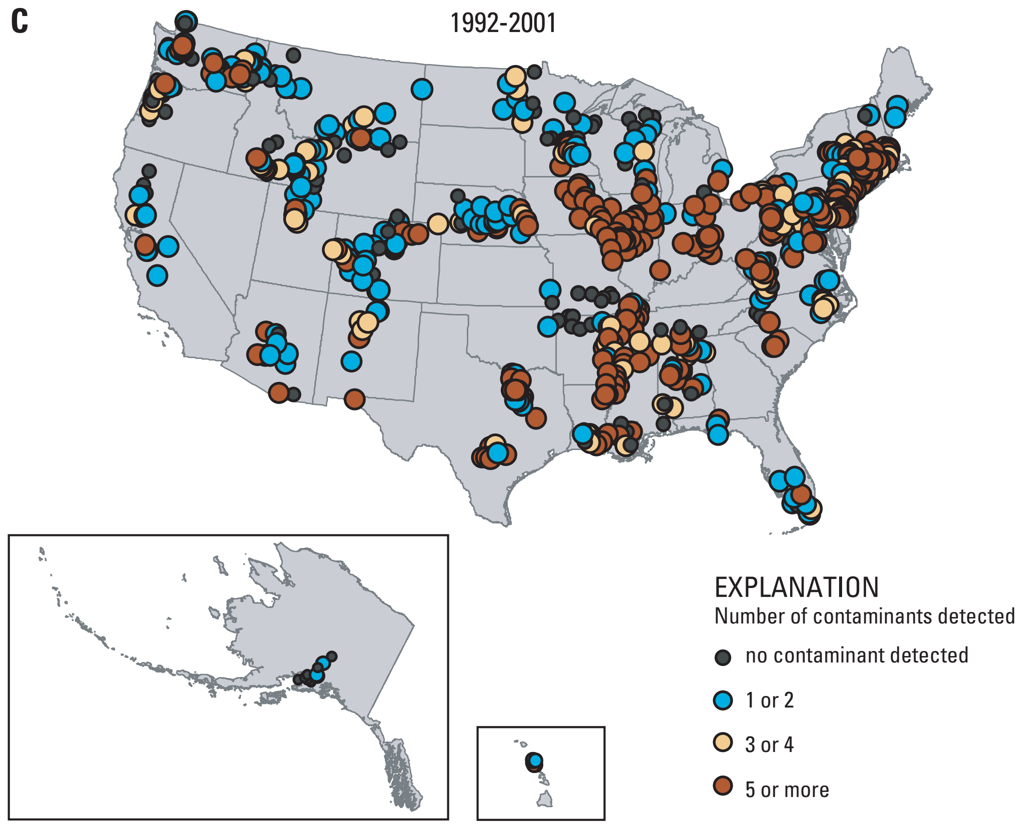

Figure 9. Contaminant occurrence in freshwater fish tissue in national streams compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) a map of contaminant detections for the 2007 edition data. Targeted contaminants included total polychlorinated biphenyls (PCBs) and organochlorine pesticides.

Ground Water

The occurrence of contaminants in ground water is a measure of how frequently nitrate, pesticides, and volatile organic compounds (VOCs) are detected in ground water. Samples collected from networks of wells in NAWQA's Major Aquifer Studies were used to measure this indicator. A major aquifer is defined as a regionally extensive aquifer or aquifer system that has the potential to be used as a source of potable water (U.S. Geological Survey, 2007). Samples were collected from existing wells that were selected randomly throughout the aquifer or hydrogeologic unit of interest. These are sites where samples were collected for analysis of pesticides (NWQL Schedules 2010, 2050 and 2060) and VOCs (NWQL Schedule 2020) in ground water.

Water samples were collected from 1993 through 2001 in 2,282 wells located throughout the Nation, including Alaska and Hawaii. Only one sample was collected from each well for this analysis. The targeted analytes included nitrate (Bernard T. Nolan, U.S. Geological Survey, written commun., 2006) (*appendix 14*), 83 pesticides (Gilliom and others, 2006), and 88 VOCs (Zogorski and others, 2006); however, all samples were not analyzed for all of these analytes. Analytical data for the 2,282 sites are listed in *appendix 15*. The analytes included for this indicator are listed in *appendix 16*.

Sampling sites were not located in areas of known contamination. Most of the ground-water samples were collected from low-capacity domestic wells using procedures that resulted in a sample from water that is used as a source of drinking water (Lapham and others, 1995). Because trace elements are naturally occurring, they are not considered a contaminant, and their frequency of detection is not included in the *Contaminant Occurrence* section. Trace element data for the 2,282 sites are included in the *Ground Water section of Contaminants Exceeding Benchmarks*.

All ground-water samples were collected and analyzed using USGS and NAWQA protocols (Gilliom and others, 1995). Methods for sample processing and preservation of ground-water samples can be found in Koterba and others (1995). Zaugg and others (1995) and Werner and others (1996) describe analytical methods used for determining pesticides in water. Rose and Schroeder (1995) and Connor and others (1998) describe analytical methods used for determining VOCs in water.

No censoring level was used to indicate the presence or absence of pesticides in ground-water samples. The analytical reporting limits used for VOCs samples collected before and after 1994 were 0.2 µg/L and 0.02 µg/L, respectively. A common censoring level of 0.2 µg/L was used to establish whether VOCs were detected in ground-water samples because the period of data collection spanned from 1993 through 2001. A censoring level of 1.0 mg/L was used as a base value for nitrate (Nolan and Hitt, 2003). Nitrate concentrations of 1.0 mg/L or higher were counted as contaminant detections in the 2007 edition of the Heinz Center report.

The national ground-water data set used in the 2007 Heinz Center report shows that approximately 61 percent of the wells had one or more detections of a contaminant, and 7 percent of the wells had 5 or more contaminant detections (fig. 10). The table and bar graph in figure 10 also include the results from the analysis that was done for the 2002 Heinz Center report. In the 2002 analysis, a concentration of 2 mg/L was used as the base level to indicate the occurrence of nitrate as a contaminant (Mueller and Helsel, 1996).

Figure 11 shows the frequency of contaminant detections in the national wells when the same censoring level (0.2 µg/L) is used for both VOCs and pesticides. The use of a common censoring level for defining detections would help to equalize the chances of a compound being detected, but would underestimate the true detection level. The use of common censoring levels results in a lower overall detection frequency but avoids the potential bias of having one or a few pesticides that can be detected at extremely low concentrations account for a disproportionately large percentage of detections. The frequency of contaminant detections shown in figure 11 includes concentrations of nitrate of at least 1.0 mg/L. The percentage of sites with no detections increases from approximately 39 percent when only the VOC values are censored (fig. 10), to approximately 49 percent when values of both VOCs and pesticides are censored at 0.2 µg/L (fig. 11). The percentage of sites with 5 or more detections decreases from approximately 7 percent when only VOCs are censored (fig. 10) to 1 percent when both VOCs and pesticides are censored at 0.2 µg/L (fig. 11). Pesticide detections in ground water were not censored in the analysis provided to the Heinz Center—the above analysis shown in figure 11 was made solely for this report to document how the frequency of detection changes when an elevated common censoring level is used.

A

SAMPLING PERIOD AND NUMBER OF WELLS	PERCENTAGE[1] OF WELLS WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
[2]2002 report (1993-1998); 917 wells	39.7	20.2	29.3	10.8
[3]2007 report (1993-2001); 2,282 wells	6.9	14.2	39.5	39.4

[1]Percentages may be rounded to equal 100
[2]Includes nitrate detections 2.0 mg/L or higher
[3]Includes nitrate detections 1.0 mg/L or higher

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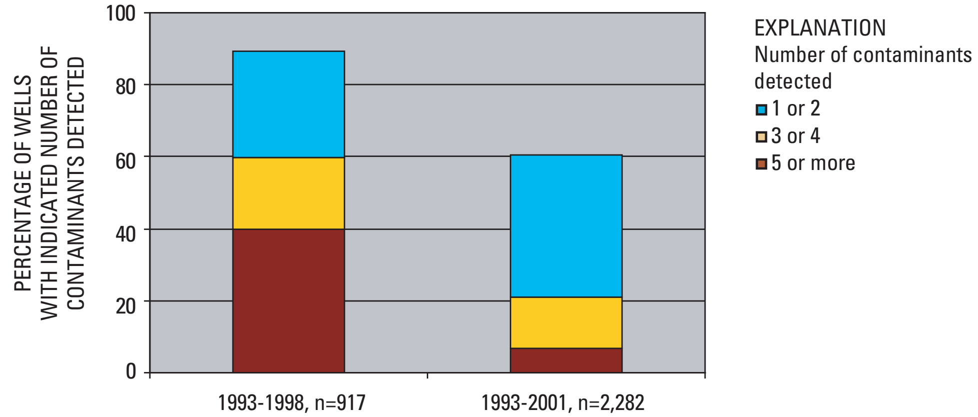

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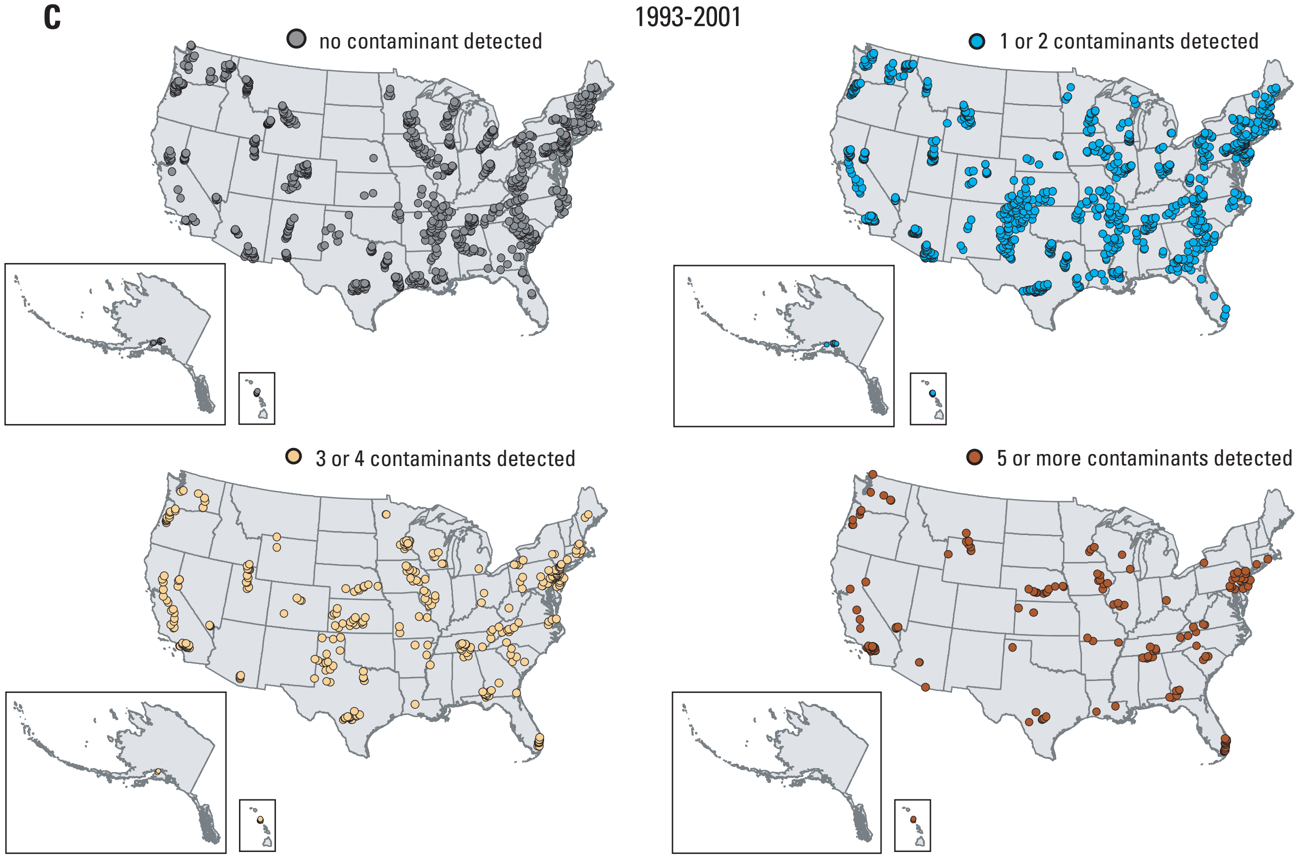

Figure 10. Contaminant occurrence in national ground water compiled for the 2002 (1993–1998) and 2007 (1993–2001) editions of the Heinz Center report, showing (**A**) the percentage of wells with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) maps of contaminant detections for the 2002 edition data. Targeted contaminants included pesticides, volatile organic compounds (VOCs), and concentrations of nitrate 2 mg/L or higher for the 2002 edition and 1 mg/L or higher for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF WELLS	PERCENTAGE[1] OF WELLS WITH INDICATED NUMBER OF CONTAMINANTS DETECTED			
	5 or more	3 or 4	1 or 2	none
[2]2007 report (1993-2001); 2,282 wells	1.0	4.6	45.2	49.2

[1]Percentages may be rounded to equal 100
[2]Concentrations of pesticides and VOCs censored at 0.2 µg/L or higher and concentrations of nitrate censored at 1 mg/L or higher.

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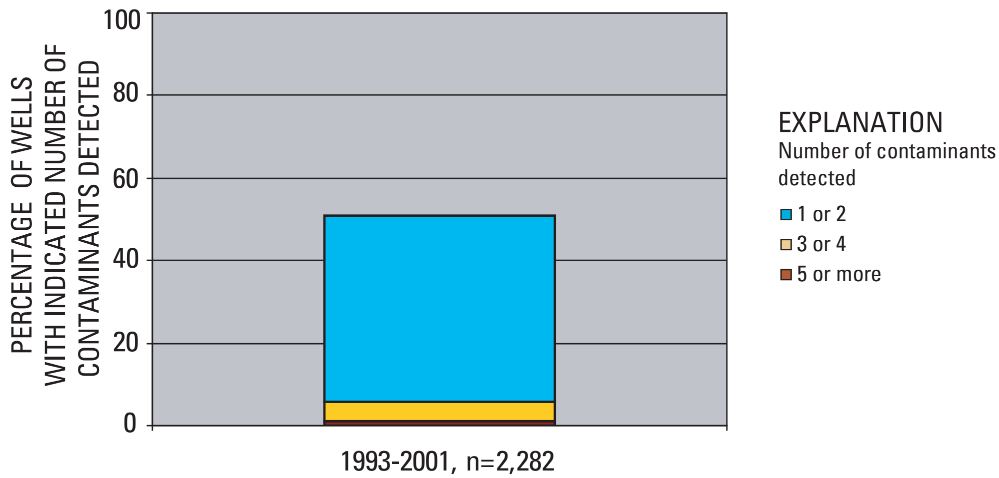

Figure 11. Contaminant occurrence in national ground water compiled for the 2007 (1993–2001) edition of the Heinz Center report using a standardized censoring level for pesticides, volatile organochlorine compounds (VOCs), and nitrate, showing (**A**) the percentage of sites with the indicated number of detections and (**B**) a graph of contaminant detections. Targeted contaminants included pesticides and VOCs censored at concentrations of 0.2 µg/L or higher and nitrate censored at concentrations of 1 mg/L or higher.

Contaminants Exceeding Benchmarks

Benchmark exceedance is defined as a measure of how frequently the concentrations at which chemical contaminants have been detected in water, sediment, or fish-tissue samples exceed human-health and (or) aquatic-life benchmarks. The same sets of sites were used to determine the frequency of contaminant occurrence and the frequency of contaminants exceeding benchmarks. Stream water and ground water were assessed in terms of human-health benchmarks for nitrate, most pesticides, VOCs (ground water), and trace elements (ground water). Stream water was assessed in terms of aquatic-life benchmarks for ammonia and most pesticides, and streambed sediment was assessed for aquatic-life benchmarks for organochlorine pesticides, total PCBs, some VOCs, and trace elements. Fish tissue was assessed for whole-fish benchmarks for protection of fish-eating wildlife for organochlorine pesticides and total PCBs. The number of constituents exceeding benchmarks at each site was grouped into the following class bins: none; 1; 2 or 3; and 4 or more.

Two types of human-health benchmarks were used for the 2007 Heinz Center report to evaluate the frequency of contaminants exceeding benchmarks in stream water and ground water: (1) USEPA Maximum Contaminant Levels (MCLs) for compounds regulated in drinking water (U.S. Environmental Protection Agency, 2006a), and (2) Health-Based Screening Levels (HBSLs) for unregulated compounds (Toccalino, 2007; Toccalino and others, 2005, 2006a, 2006b). The MCL is the maximum permissible concentration of a contaminant in water that is delivered to any user of a public water system (U.S. Environmental Protection Agency, 2006b). This is an enforceable standard issued by USEPA under the Safe Drinking Water Act and established on the basis of health effects and other factors (analytical and treatment technologies, and cost). HBSLs are estimates of benchmark concentrations of contaminants in water, which if exceeded, may be of potential concern for human health. HBSLs are non-enforceable benchmarks that were developed by the USGS in collaboration with USEPA and others using USEPA methodologies for establishing drinking-water guidelines and the most current, USEPA peer-reviewed, publicly-available human-health toxicity information. HBSLs are regularly reviewed and, as needed, revised to incorporate the most recent toxicity information and research findings (Toccalino, 2007; Toccalino and others, 2005, 2006a, 2006b). Zogorski and others (2006, p. 29) used MCLs and HBSLs in their assessment of VOCs in drinking-water supply wells. Gilliom and others (2006, p. 91) used

MCLs, 10^{-6} Cancer Risk Concentrations, and Lifetime Health Advisory values in their assessment of pesticides in streams and ground water.

For stream water, time-weighted mean-annual concentrations of regulated contaminants were compared to their MCLs and concentrations of unregulated contaminants were compared to their HBSLs, when available. Individual ground-water sample concentrations were compared to MCLs and HBSLs. For potential carcinogens, the lower values of the HBSL range were used, which corresponds to an excess estimated lifetime cancer risk of 1 in 1,000,000. MCLs and HBSLs are concentrations typically pertaining to lifetime exposure through drinking water.

In 2002, three types of USEPA standards and guidelines were used as human-health benchmarks: (1) MCLs, (2) Risk-Specific Dose (RSD), and (3) Lifetime Health Advisory (HA-L) (*appendix 6*). Values for these criteria were obtained by the USGS from USEPA drinking-water standards and health advisories (U.S. Environmental Protection Agency, 2006a). The RSD is a guideline for potential carcinogens based on drinking-water exposure over a 70-year lifetime, and is associated with a specified cancer risk. The RSDs used in the 2002 analysis were associated with a cancer risk of 1 in 100,000. The HA-L is an advisory guideline for drinking-water exposure over a 70-year lifetime, considering noncarcinogenic adverse health effects. More detail on these types of benchmarks, their derivation, and their underlying assumptions is provided in Nowell and Resek (1994). For some constituents, more than one of these three types of benchmarks was available, in which case the MCL was used if available; otherwise, the lowest of the RSD (at 1 in 100,000 cancer risk) or HA-L value was selected. The RSD and HA-L were replaced with HBSLs for the 2007 analysis, which allows for use of the most current toxicity information in the interpretation of water-quality data (Toccalino, 2007). Note that some constituents that are potential carcinogens and were compared to the RSD (1 in 100,000 cancer risk) for the 2002 Heinz Center report were compared to the lower HBSLs (1 in 1,000,000 cancer risk) for the 2007 Heinz Center report.

Stream Water

Contaminants exceeding benchmarks in stream water were assessed for the *Core National* and *Urban and Suburban* indicators. The frequency of contaminants in stream water exceeding human-health benchmarks was measured for nitrate and for 73 of the 83 pesticide compounds. The frequency of contaminants in stream water exceeding aquatic-life benchmarks was measured for ammonia and for 62 of the 83 pesticides. Ten pesticide compounds did not have human-health benchmarks and 21 pesticide compounds did not have aquatic-life benchmarks established. *Appendix 6* shows a list of analytes sampled in stream water and their associated MCL, HBSL, and aquatic-life benchmarks.

Human Health

For pesticides in stream water, exceedances of human-health benchmarks were identified when the time-weighted mean-annual concentration (*appendix 17*) for one or more pesticides exceeded the relevant benchmark(s) at a stream site. Time-weighted mean concentrations for each site and pesticide were computed using several approaches, depending on the number of non-detected values (Jeffrey D. Martin, U.S. Geological Survey, written commun., 2006). Methods and approach are given in *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/supporting_info.php* (select appendix 8, then select appendix 8A). If a large percentage of the values for samples analyzed for a given pesticide were non-detections, the calculated mean was remarked "<" to indicate that the time-weighted mean was less than the calculated value. Time-weighted concentrations of pesticides with a "<" remark code (*appendix 17*) were counted as non-exceedances because of the indeterminate nature of the calculated mean. Individual nitrate samples at stream-water sites matched the 12-month period of record for which individual pesticide samples were used (*appendix 5*). For nitrate in stream water, an exceedance of the human-health benchmark was indicated when the concentration of nitrate in any individual sample from a given stream site exceeded the nitrate MCL (10 mg/L).

A total of 19 exceedances of a pesticide human-health benchmark occurred at 15 of the 186 sites. The concentration of nitrate exceeded the MCL in one or more samples from 24 stream sites. Of these 24 sites, the number of samples in which the MCL for nitrate was exceeded ranged from 1 to 20 with an average of 5.5 exceedances. The number of nitrate samples at each site ranged from 0 to 49 with an average of 23 samples. There was one site in Iowa with no nitrate samples collected by USGS; this site was used because it was one of the 186 sites used by Gilliom and others (2006).

Figures 12 and 13 show the frequency at which contaminant concentrations in stream water exceeded a human-health benchmarks in (a) tables showing the percentage of sites with the various bins of contaminants above a benchmark, (b) bar graphs showing the percentages from the table, and (c) a map showing the number of benchmark exceedances at each site for the 1992–2001 data set used for the 2007 Heinz Center report. Of the 186 national stream sites, which represent one of the *Core National* indicators, 20 percent (37) of the sites had one or more contaminants that exceeded a benchmark and none of the sites exceeded more than 3 benchmarks (fig. 12, *appendix 17*). The table and bar graph in figure 12 also include the results from the previous analysis for the 2002 Heinz Center report, and the results when the new benchmarks (MCLs and HBSLs) from the 2007 analysis are applied to the 1992–1998 data set used for the 2002 analysis.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BMs; 106 sites	0	2.8	10.4	86.8
2002 report (1992-1998) using 2007 BMs; 106 sites	0	2.8	16.1	81.1
2007 report (1992-2001) using 2007 BMs; 186 sites	0	2.2	17.7	80.1

[1]Percentages may be rounded to equal 100

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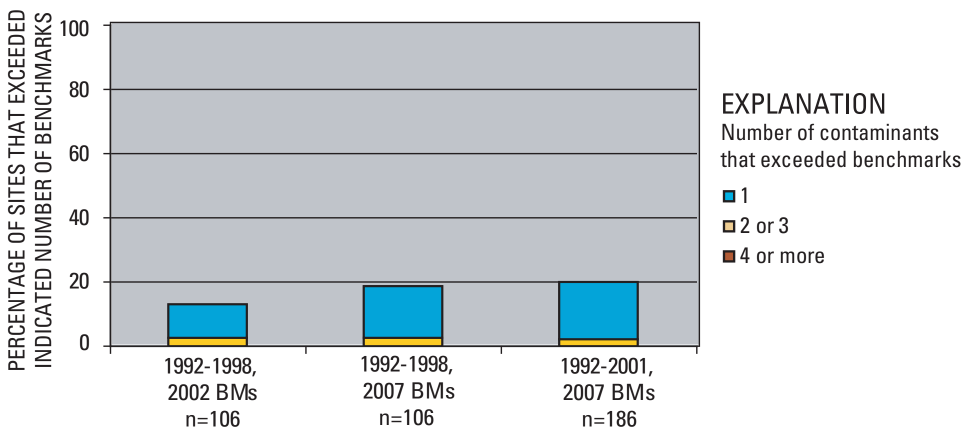

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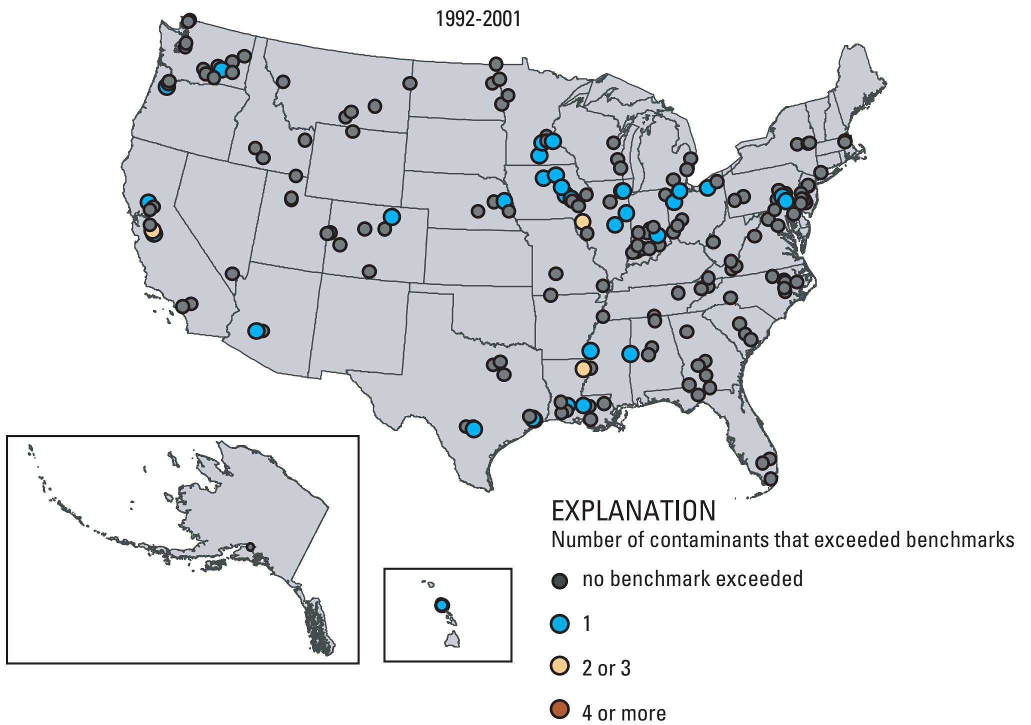

Figure 12. The number of contaminants that exceeded human-health benchmarks in national stream water compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks; (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and the 2007 data using 2007 edition benchmarks; and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BMs; 21 sites	0	0	4.8	95.2
2002 report (1992-1998) using 2007 BMs; 21 sites	0	0	4.8	95.2
2007 report (1992-2001) using 2007 BMs; 30 sites	0	0	6.7	93.3

[1]Percentages may be rounded to equal 100

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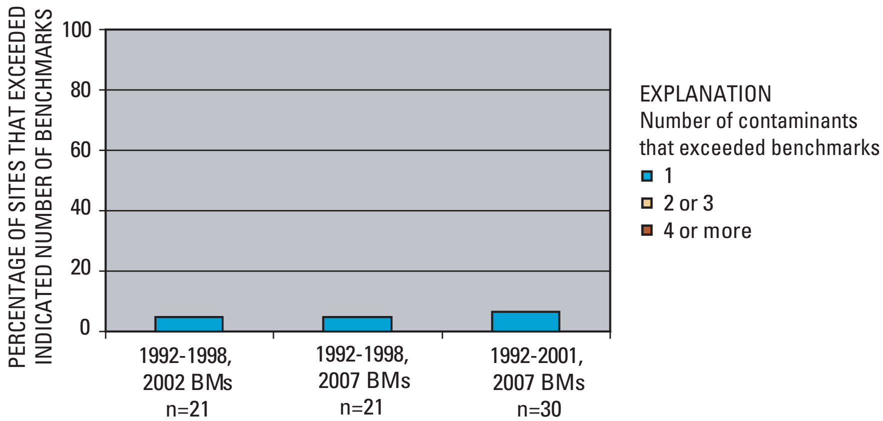

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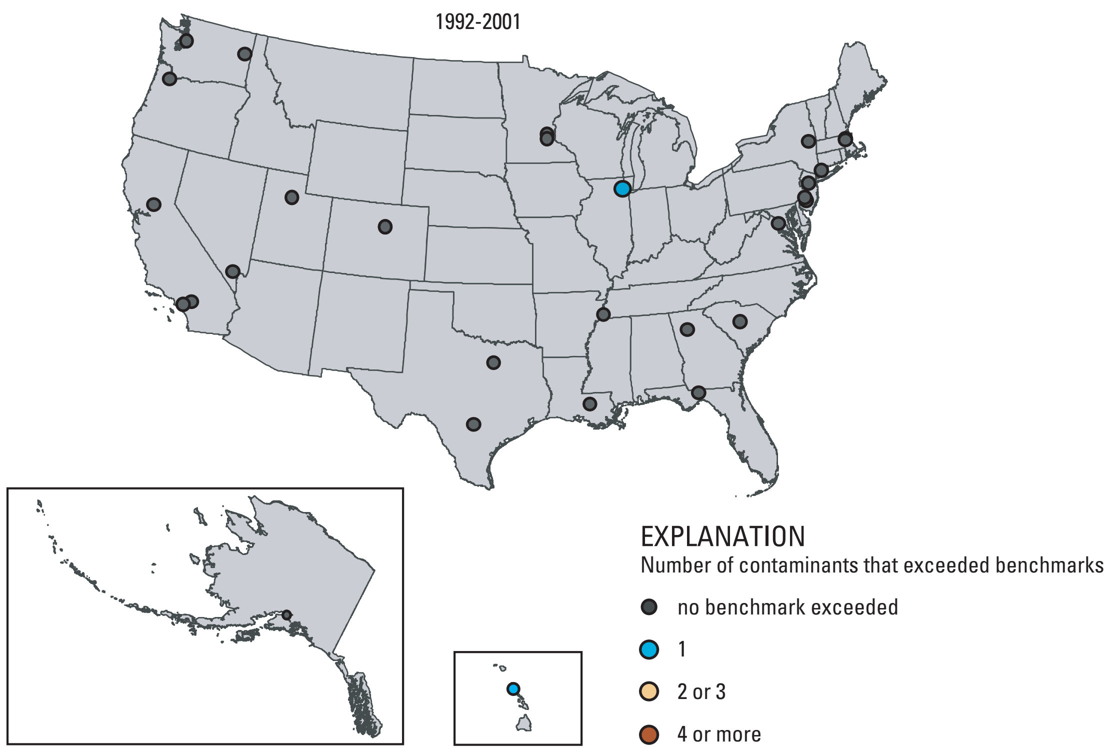

Figure 13. The number of contaminants that exceeded human-health benchmarks in streams draining the *Urban and Suburban* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks; (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and the 2007 data using 2007 edition benchmarks; and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

The subset of 30 streams from the *Urban and Suburban* ecosystem had a smaller percentage of sites with contaminant concentrations in stream water above a human-health benchmark than did the set of national streams (fig. 13). Two of the urban streams (approximately 7 percent) had one contaminant in stream water with a concentration above a benchmark, and none of the sites had more than one benchmark exceedance. Four water samples from one stream in northern Illinois exceeded the nitrate MCL, and one sample from a stream in Hawaii exceeded the HBSL for dieldrin (fig. 13c, *appendix 17*).

Aquatic Life

Exceedances of the aquatic-life criteria for ammonia were based on the ammonia concentration, temperature and pH of individual samples, using the USEPA ambient water-quality criteria (U.S. Environmental Protection Agency, 1999a). Ammonia samples at stream-water sites matched the 12-month period of record of the pesticides and nitrate samples. Instantaneous and moving time-weighted mean concentrations of a given pesticide in stream water were compared with up to 9 benchmarks for the protection of aquatic life. Each benchmark applies to a different combination of contaminant exposure duration and type of organism(s) affected. A benchmark exceedance was counted for each pesticide measurement that occurred at a concentration that exceeded one or more aquatic-life benchmarks. For example, if a single sample had a concentration of the pesticide chlorpyrifos that exceeded 4 of the aquatic-life benchmarks, it would count as one exceedance.

The 9 types of aquatic-life benchmarks for pesticides in stream water (*appendix 6*) and the environmental concentrations they are compared with are:

1. USEPA acute water-quality criterion for protection of aquatic organisms (U.S. Environmental Protection Agency, 2004)—this is compared with concentrations of pesticides in each individual sample;
2. USEPA chronic water-quality criterion for protection of aquatic organisms (U.S. Environmental Protection Agency, 2004)—this is compared with the 4-day moving average pesticide concentration;
3. Acute-fish benchmark (Gilliom and others, 2006, p. 161)—compared with concentrations of pesticides in each individual sample;
4. Chronic-fish benchmark (Gilliom and others, 2006, p. 161)—compared with the 60-day time-weighted moving average pesticide concentration;
5. Acute-invertebrate benchmark (Gilliom and others, 2006, p. 161)—compared with concentrations of pesticides in each individual sample;
6. Chronic-invertebrate benchmark (Gilliom and others, 2006, p. 161)—this is compared with the 21-day time-weighted moving average pesticide concentration;
7. Acute-nonvascular plant benchmark (Gilliom and others, 2006, p. 161)—compared with concentrations of pesticides in each individual sample;
8. Acute-vascular plant benchmark (Gilliom and others, 2006, p. 161)—compared with concentrations of pesticides in each individual sample;
9. Aquatic-community benchmark (Gilliom and others, 2006, p. 161)—compared with the 60-day moving average pesticide concentration.

Benchmarks 3–9 were developed using USEPA (Office of Pesticide Programs) procedures for ecological risk assessment and toxicity information obtained from USEPA re-registration and risk assessment documents.

Pesticide exceedances of aquatic-life benchmarks are presented in Gilliom and others, (2006, p. 97). A data set of these exceedances for the 186 NAWQA sites is available from the online documentation of Gilliom and others (2006, fig. 6-5). Calculations of acute and chronic criteria values for NAWQA samples that were analyzed for ammonia were provided by the Nutrients National Synthesis Project (Gregory M. Clark, U.S. Geological Survey, written commun., 2006). Acute and chronic criteria for ammonia were calculated using the equations and methods in USEPA (1999a). A subset of samples that were analyzed for ammonia that matched the period of record of the pesticide samples at each site was used in the analysis for the Heinz Center (*appendix 18*).

Exceedances of the chronic criterion for ammonia were estimated by using the method outlined by the USEPA (1999a, p. 85). For each sample, the criterion was determined at the pH and temperature of the sample, and the concentration of ammonia was divided by the criterion to determine a quotient. The chronic criterion was attained if the mean of the quotients was less than 1 over the duration of the averaging period (in this case, 12 months). This method is used to approximate/estimate the chronic criterion without having 30-day average values of pH, temperature, and ammonia concentrations. It was not practical to estimate 30-day average concentrations of ammonia when most sites only had monthly samples during certain periods of the year. Based on the data set of discrete samples that was analyzed for ammonia that matched the 12-month period of the pesticide samples, there were no exceedances of the acute criterion for ammonia. Also, there were no exceedances of the chronic criterion for ammonia when the 12-month period of samples was used as the averaging period; however, 18 individual samples exceeded the chronic criterion at a total of six sites. It is possible that if 30-day moving average concentrations were calculated, the chronic criterion for ammonia would be exceeded at some of the six sites.

Because there were no exceedances of the ammonia criteria, pesticide compounds accounted for all the exceedances of aquatic-life benchmarks. Of the 186 national streams, which represent one of the *Core National* indicators, approximately 54 percent (100) of the sites had one or more contaminants that exceeded a benchmark and 10 percent of the sites had four or more contaminants that exceeded benchmarks (fig. 14, *appendix 18*). The number of pesticides exceeding an aquatic-life benchmark ranged from 1 to 9; if a pesticide concentration exceeded multiple aquatic-life benchmarks (potentially 9), it was counted as one exceedance for that site. The table and bar graph in figure 14 also include the results from the 2002 Heinz Center report for comparison.

Results for the 2007 edition of the Heinz Center report indicate that the subset of 30 streams draining *Urban and Suburban* watersheds (fig. 15) had a higher frequency of contaminant concentrations exceeding an aquatic-life benchmark than did the 186 streams sampled nationally (fig. 14). Approximately 83 percent of the urban streams had one or more contaminants that exceeded an aquatic-life benchmark, and 20 percent of the sites exceeded 4 or more benchmarks.

Streambed Sediment

Contaminants exceeding benchmarks in streambed sediment were assessed for the *Core National* indicator. This indicator is a measure of how often organochlorine pesticides, total PCBs, SVOCs, and trace elements in streambed sediment exceed aquatic-life benchmarks established for the protection of benthic aquatic organisms. Aquatic-life benchmarks have been established for 41 of the 95 contaminants or groups of contaminants (such as total DDT) measured in streambed sediment (*appendix 9*). Streambed sediment benchmarks for the organochlorine pesticide compounds are consensus-based threshold-effect concentrations (TEC) (MacDonald and others, 2000). Benchmark values can be obtained from *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/supporting_info.php* (select appendix 3, then select appendix 3B). Benchmarks for SVOCs, total PCBs, and trace elements (except selenium) use either a TEC (MacDonald and others, 2000) or a USEPA equilibrium partitioning sediment benchmark (ESB) (U.S. Environmental Protection Agency, 2003a, 2003b, 2003c). The selenium benchmark used is the toxicity threshold from the National Irrigation Water Quality Program (1998) because no TEC or ESB exists. Trace element data were limited to nine “priority” trace metals for which aquatic-life benchmarks have been established. A list of available aquatic-life benchmarks for sediment is included with the list of analytes sampled in streambed sediment (*appendix 9*).

The consensus-based TEC defines the concentration below which adverse effects on sediment-dwelling organisms are not expected to occur. These benchmarks were developed by MacDonald and others (2000) by compiling multiple sediment-quality guidelines for a given contaminant (both causally and empirically based), identifying those that meet certain selection criteria, and using the geometric mean as a consensus-based guideline. This method attempts to provide a unifying synthesis of existing guidelines. In validation tests, the incidence of toxicity ranged from about 70 to 100 percent in samples with concentrations greater than the TEC, for all pesticides except endrin (40 percent). Validation tests for other constituent groups show similar results, with toxicity observed in about 60 percent of samples with concentrations above the TEC for total PCBs, and 75 to 80 percent of samples on average for polycyclic aromatic hydrocarbons (PAHs) and trace elements.

The USEPA ESBs recommend the chemical concentrations in sediment that will not adversely affect most benthic organisms. ESBs apply to nonionic organic compounds (that is, pesticides, total PCBs, and SVOCs), but not to trace elements. ESBs are causally based, not empirically based—they are based on an equilibrium partitioning model, which assumes that the toxicity of an organic contaminant in sediment is causally related to bioavailability and that bioavailability is controlled by contaminant sorption to sediment organic carbon. For ESBs the chemical is assumed to be in equilibrium with the sediment particles and sediment pore water. Each ESB is designed to predict toxicity caused by a specific contaminant and it is not expected to correctly predict toxicity when other contaminants are present in toxic amounts, such as may occur in field-collected sediments. The ESB values used are based on chronic toxicity to aquatic life. ESBs are expressed on a sediment organic carbon content basis; therefore, a contaminant concentration in sediment must be normalized by the organic carbon content of the sediment prior to comparison with an ESB. The ESBs, which have units of micrograms per gram of organic carbon, were compared to concentrations of eight SVOCs and three organochlorine pesticides, after normalizing the concentrations to organic carbon content. This comparison was done by dividing the analyte concentration (micrograms per kilogram) by the organic carbon content (grams per kilogram). This math is performed in the method scripts and spreadsheets used to count the number of contaminants at concentrations above benchmarks—the raw data have not been adjusted because this data transformation is required only for comparison to the ESB, not for counting detections. Sediment organic carbon content is from NWQL Schedule LC2320 parameter code 49271, and is included in the table of analytical data for streambed sediment (*appendix 8*).

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) 106 sites	25.4	27.4	25.5	21.7
2007 report (1992-2001) 186 sites	10.2	18.8	24.7	46.3

[1]Percentages may be rounded to equal 100

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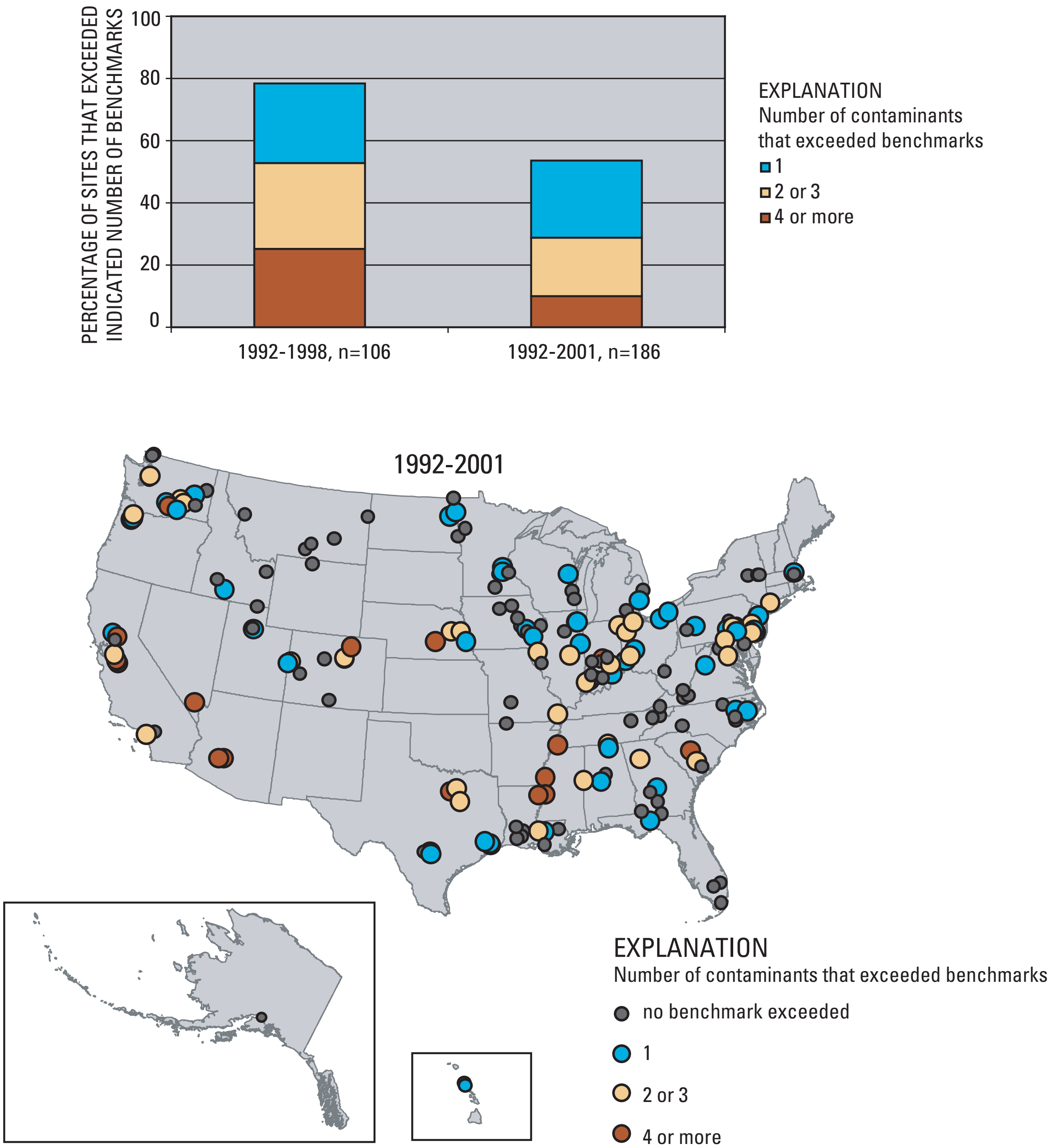

Figure 14. The number of contaminants that exceeded aquatic-life benchmarks in national stream water compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the two data sets, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) 21 sites	38.1	38.1	23.8	0
2007 report (1992-2001) 30 sites	20.0	26.7	36.7	16.6

[1]Percentages may be rounded to equal 100

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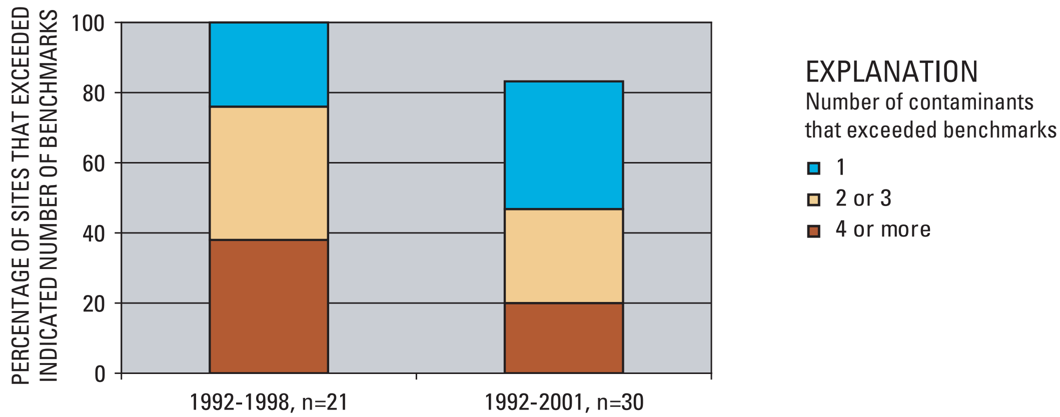

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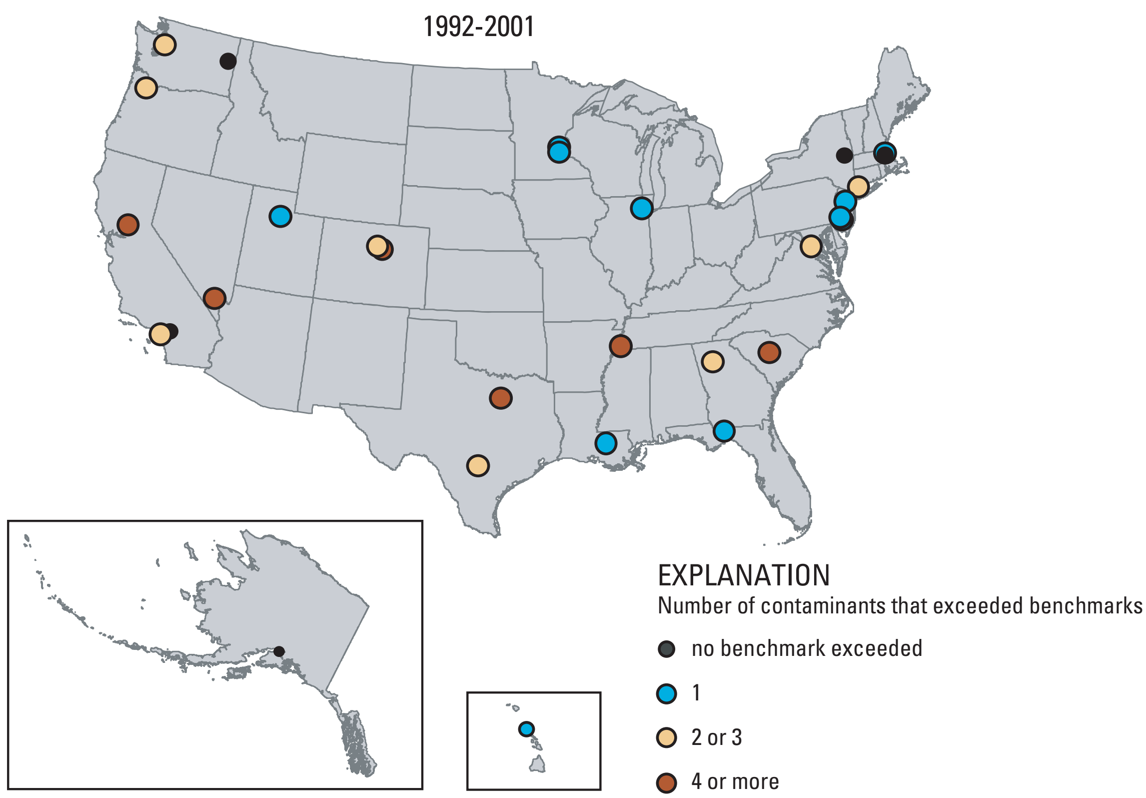

Figure 15. The number of contaminants that exceeded aquatic-life benchmarks in streams draining the *Urban and Suburban* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the two data sets, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

If both a TEC and an ESB were available for a given contaminant, preference was given to the TEC, which is designed to predict toxicity in field-collected sediment. ESBs provided benchmarks for a few additional pesticides that did not have TECs. The TECs were available for some organochlorine pesticides, total PCBs, PAHs, and trace elements; ESBs were available for some additional organochlorine pesticides and a few SVOCs other than PAHs.

In the 1992–2001 data set used for the 2007 Heinz Center report, approximately 94 percent of sites had streambed sediment containing one or more contaminant concentration above an aquatic-life benchmark, and 58 percent of sites had streambed sediment containing four or more contaminant concentrations above an aquatic-life benchmark (fig. 16, *appendix 19*). A comparison of benchmark exceedances by contaminant class shows that the nine trace elements account for 53 percent of the contaminants exceeding a benchmark (fig. 17). SVOCs (individual compounds and groups of related compounds, such as total PAH) account for 32 percent of the contaminants exceeding a benchmark, and organochlorine pesticides (individual pesticides and groups of related compounds, such as total DDT) together with total PCBs account for approximately 15 percent of the contaminants exceeding a benchmark.

Fish Tissue

Contaminants exceeding benchmarks in freshwater fish tissue were assessed for the *Core National* indicator. The frequency of contaminant detections in whole-fish-tissue samples were measured for organochlorine pesticides and total PCBs exceeding wildlife benchmarks established for the protection of fish-eating wildlife. There are two categories of benchmarks, $benchmark_{low}$ and $benchmark_{high}$, which refer to the range of benchmark values from the literature. $Benchmark_{low}$ is the lowest value in the range of wildlife benchmarks available for a given compound or related group of compounds. $Benchmark_{high}$ is the highest value in the range of wildlife benchmarks available for a given compound or group. Whole-fish benchmarks for the organochlorine pesticide compounds are show in *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/supporting_info.php* (select appendix 3, then select appendix 3B)

The analysis of contaminants exceeding benchmarks in freshwater whole-fish tissue was based on one composite sample of a single species collected on a single date at each site. Exceedances were identified when the measured concentration of a contaminant exceeded its respective benchmark. Contaminants assessed include organochlorine pesticides and total PCBs. There are wildlife benchmarks for 15 of these contaminants or groups of these contaminants analyzed in whole fish (*appendix 12*). Only two organochlorine compounds had no benchmark available; the remaining contaminants had benchmarks applicable to them either individually or in combination with other components of a group (such as total DDT or total HCH).

Contaminant concentrations were compared to both the low and high end of the range in available benchmarks for wildlife. Gilliom and others (2006) referred to the low and high end benchmark values as $benchmark_{low}$ and $benchmark_{high}$. The available benchmarks were selected from four types of wildlife guidelines:

1. New York fish-flesh criteria for protection of piscivorous (fish-eating) wildlife, noncancer value. These criteria are intended to protect target wildlife species from adverse effects other than cancer, such as mortality, reproductive impairment, and organ damage (Newell and others, 1987).

2. Canadian Tissue Residue Guidelines (TRG). The TRG is designed to protect all life stages of all wildlife during lifetime exposure to a substance present as a contaminant in aquatic food sources. TRGs are calculated from the most sensitive of the available toxicity tests (for which test endpoints may include mortality, mutagenicity, genotoxicity, reproduction, development, growth, survival of young, etc.) and applied to the Canadian wildlife species with the highest food intake/body weight ratio (Canadian Council of Ministers of the Environment, 1998). Values are from Canadian Council of Ministers of the Environment (1999a, 1999b, 2003).

3. No-observed-adverse-effects level (NOAEL) based toxicological benchmarks for fish-eating wildlife (based on Sample and others, 1996). This is the NOAEL-equivalent concentration in food derived for the most sensitive fish-eating wildlife species for which data are available. NOAEL-equivalent concentrations in food were derived for a variety of wildlife species by Sample and others (1996) for the Department of Energy, Oak Ridge National Laboratory, for use in ecological risk assessments at waste sites. Endpoints included reproductive and developmental toxicity and reduced survival; for some contaminants, data were limited and other endpoints (such as organ-specific toxic effects) were used.

4. Proposed criteria from the Contaminant Hazard Review series. These proposed tissue-based criteria for wildlife are included among recommendations for protection of natural resources in the Contaminant Hazard Review series developed by the U.S. Fish and Wildlife Service (Eisler and Jacknow, 1985; Eisler, 1990).

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BMs; 486 sites	12.3	15.4	19.8	52.5
2002 report (1992-1998) using 2007 BMs; 486 sites	60.1	25.1	9.9	4.9
2007 report (1992-2001) using 2007 BMs; 957 sites	58.4	25.2	10.6	5.8

[1]Percentages may be rounded to equal 100

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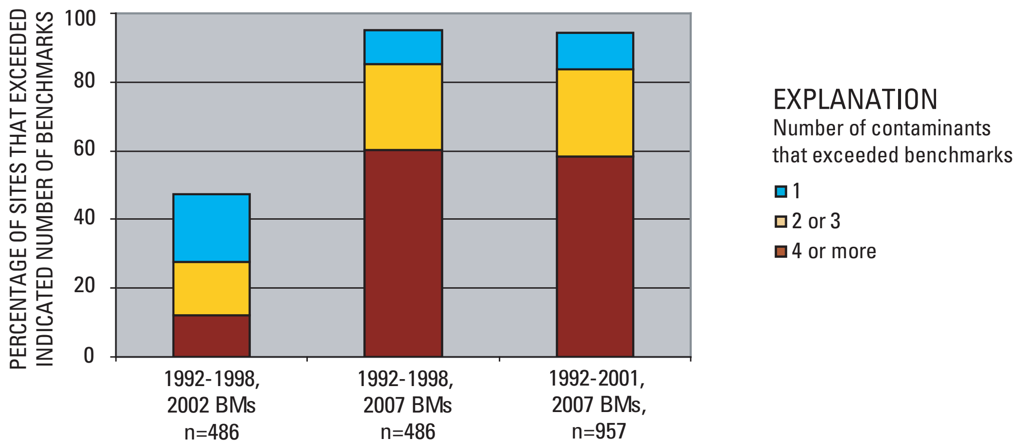

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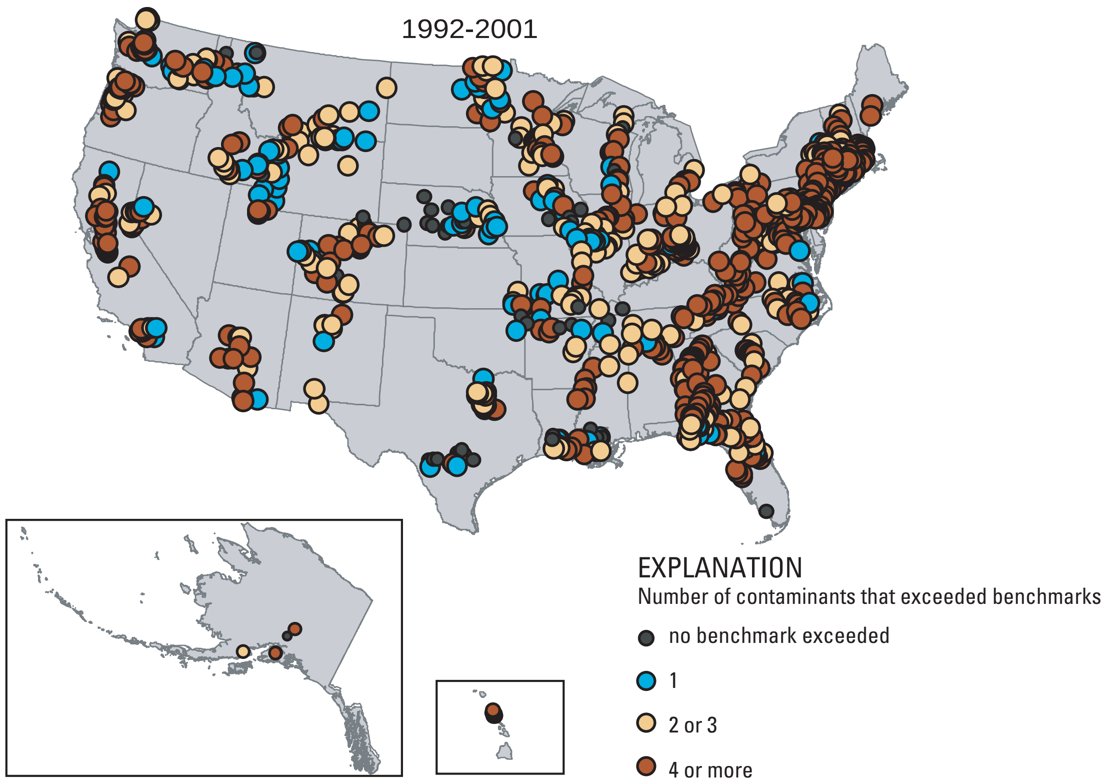

Figure 16. The number of contaminants that exceeded aquatic-life benchmarks in streambed sediments of national streams compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks; (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and the 2007 data using 2007 edition benchmarks; and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

CONTAMINANT CLASS AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
All Classes; 6,392 sites	58.4	25.2	10.6	5.8
Trace Elements; 3,398 sites	48.0	31.8	13.8	6.4
Semivolatile Organic Compounds (SVOCs); 2,066 sites	23.8	2.4	3.6	70.2
Organochlorine (OC) Pesticides; 928 sites	10.1	14.5	8.9	66.5

[1]Percentages may be rounded to equal 100

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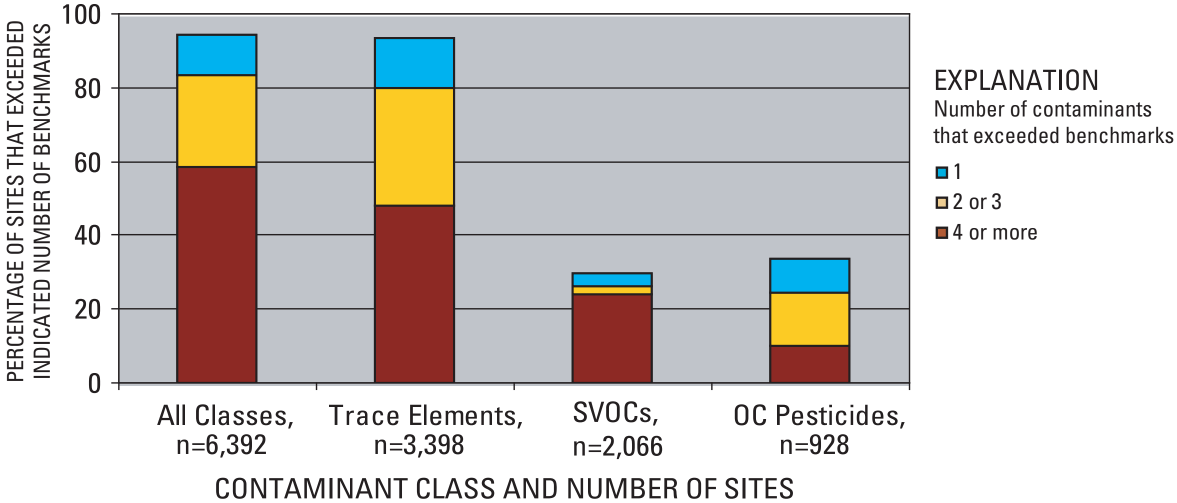

Figure 17. The number of aquatic-life benchmarks that were exceeded in streambed-sediment samples of national streams grouped by contaminant class compiled for the 2007 (1992–2001) edition of the Heinz Center report, showing (**A**) table and (**B**) graph, the percentage of sites that exceeded the indicated number of benchmarks for each contaminant class.

The data on freshwater fish tissue do not include information relative to human-health standards because such standards apply to edible fish tissue (e.g., fillets), whereas whole fish were analyzed for the data reported here and in Gilliom and others (2006). The indicator, contaminants exceeding benchmarks for fish tissue, was determined by calculating the percentage of sites sampled exceeding wildlife benchmarks (*appendix 20*). Figure 18 shows the percentage of samples exceeding the $benchmark_{low}$ values for the 700 sites included in the 1992–2001 data set used for the 2007 Heinz Center report. About 77 percent of the samples have one or more contaminant concentrations that exceed one of the 15 $benchmark_{low}$ values, and about 1 percent of the samples have 4 or more contaminant concentrations that exceed a $benchmark_{low}$ value. Results are also shown for the 1992–1998 data set (220 sites) and benchmarks from the 2002 Heinz Center report, and for the 1992–1998 data set when the 2007 $benchmark_{low}$ values are applied (figs. 18a and 18b).

Figure 19 shows the percentage of samples exceeding the $benchmark_{high}$ values for the 2007 data set of 700 sites. The frequency of exceedance of $benchmark_{high}$ values is much lower than for the $benchmark_{low}$ values because the values are higher. About 43 percent of the samples have one or more contaminants with a concentration exceeding a $benchmark_{high}$ value, and none of the samples have more than 3 contaminant concentrations that exceed a $benchmark_{high}$ value. Results are also shown for the 1992–1998 data set (220 sites) and benchmarks from the 2002 Heinz Center report, and for the 1992–1998 data set when the 2007 $benchmark_{high}$ values are applied (figs. 19a and 19b).

Ground Water

Contaminants exceeding benchmarks in ground water were assessed for the *Core National* indicator. The frequency of contaminant detections in ground-water samples was measured for pesticides (Gilliom and others, 2006), VOCs (Zogorski and others, 2006), and trace elements (JoAnn M. Gronberg, U.S. Geological Survey, written commun., 2006) (*appendix 21*) exceeding human-health benchmarks. Human-health benchmarks are available for nitrate, 73 of the 83 pesticide compounds, 55 of the 88 VOCs or groups of related VOCs, and 19 of the 24 trace metals analyzed in NAWQA water samples (*appendix 15*). A list of analytes sampled in ground water and the 148 MCLs and HBSLs available for these compounds and groups of compounds are available in *appendix 16*.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF FISH SAMPLES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BM; 220 sites	0.0	9.6	40.0	50.4
2002 report (1992-1998) using 2007 BM_{Low}; 220 sites	1.4	44.1	42.7	11.8
2007 report (1992-2001) using 2007 BM_{Low}; 700 sites	0.8	36.3	39.6	23.3

[1]Percentages may be rounded to equal 100

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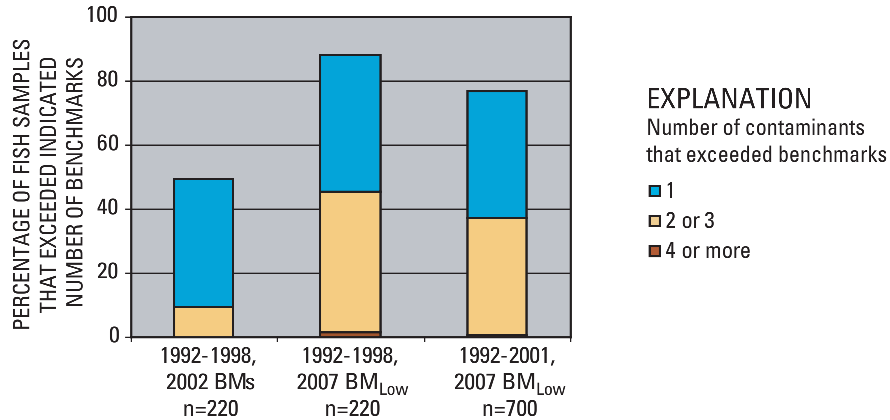

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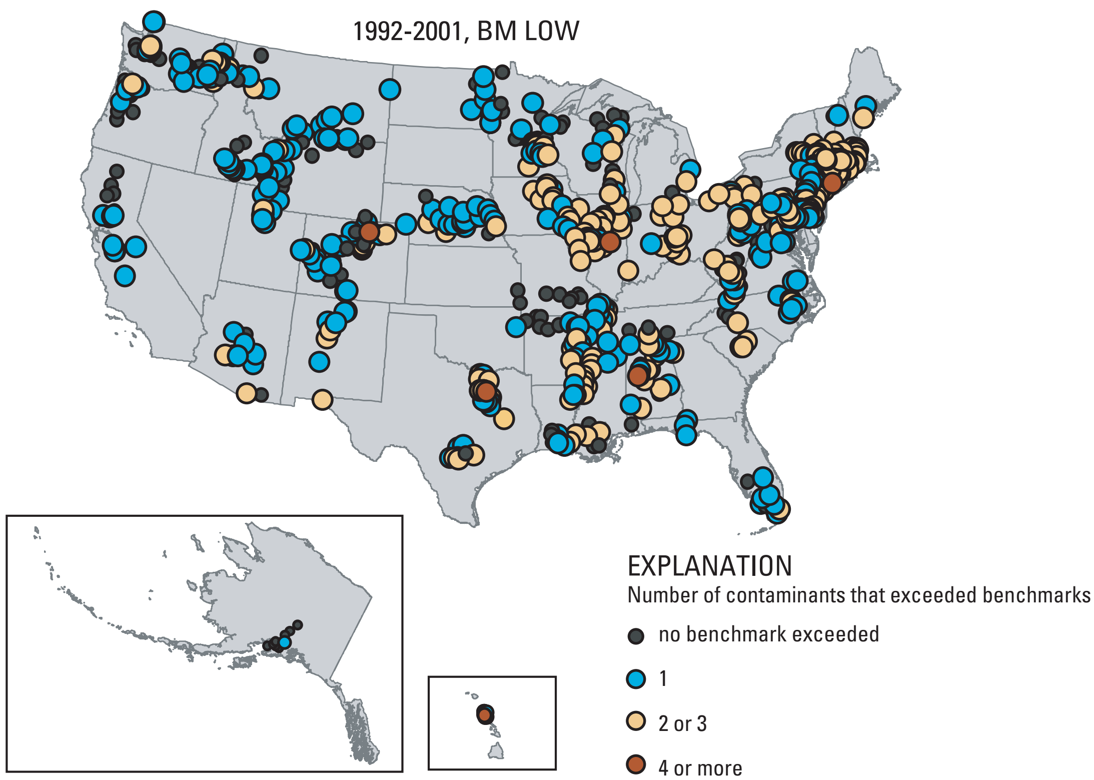

Figure 18. The number of contaminants that exceeded $benchmark_{low}$ values in fish-tissue samples in national streams compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks; (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and the 2007 data using 2007 edition benchmarks; and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF FISH SAMPLES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BM; 220 sites	0.0	9.6	40.0	50.4
2002 report (1992-1998) using 2007 BM_{High}; 220 sites	0.0	9.1	40.4	50.5
2007 report (1992-2001) using 2007 BM_{High}; 700 sites	0.0	8.6	34.1	57.3

[1]Percentages may be rounded to equal 100

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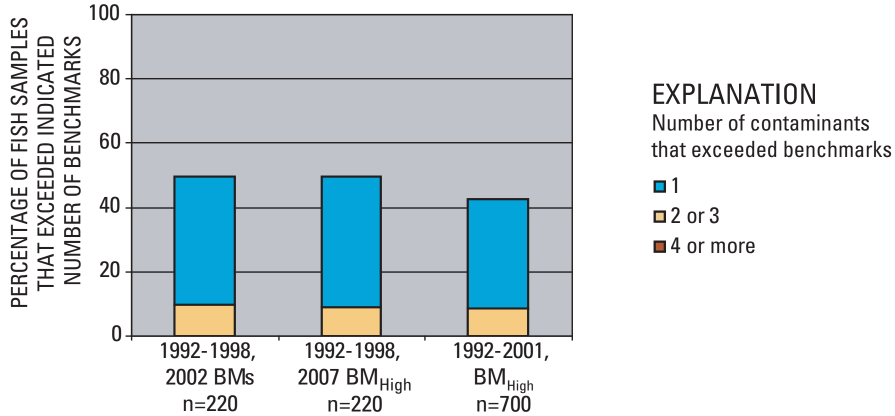

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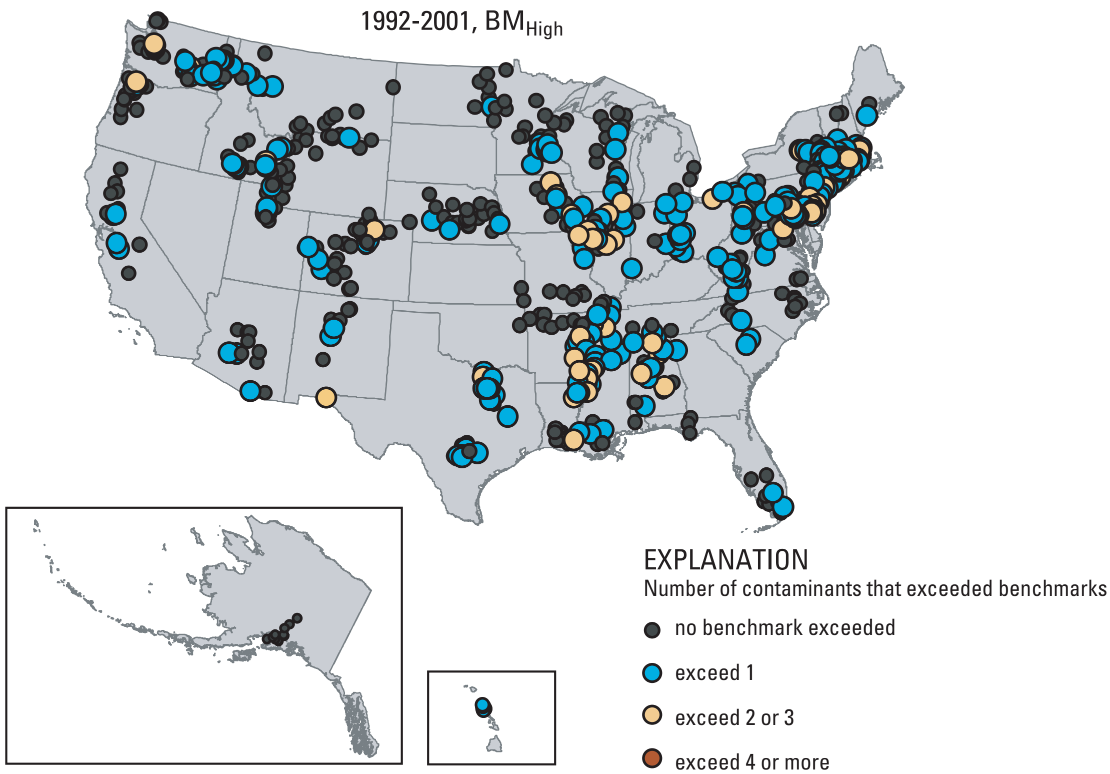


Figure 19. The number of contaminants that exceeded $benchmark_{high}$ values in fish-tissue samples in national streams compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks; (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and the 2007 data using 2007 edition benchmarks; and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

For contaminants in ground water, exceedances of human-health benchmarks were identified when the concentration of one or more compounds exceeded the relevant benchmark(s) at that site. It should be pointed out that exceedances of human-health benchmarks in this analysis are based on the concentration in a single ground-water sample, and not an annual mean concentration as was done with pesticides in stream water. No censoring was applied to any chemical data used in comparison to human-health benchmarks. Of the 2,282 wells sampled within the NAWQA Major Aquifer Studies, approximately 20 percent of the sites have one or more contaminants that exceeded a benchmark, and only six sites (0.3 percent) had 4 or more contaminants with concentrations that exceeded a benchmark (fig. 20). The table and bar graph also include the results from the analysis that was done for the 2002 Heinz Center report.

Differences between Methods Applied in the 2002 and 2007 Analyses and Effects on Results

There are several differences between the analyses of *Chemical Contamination* indicators for the 20002 and 2007 editions of the Heinz Center report (*table 1*). Because the 2002 report was compiled before all of the Cycle I NAWQA studies were completed, the period of record for data used for most indicator analyses was 1992–98. The 2007 edition includes data collected for the sites used in the 2002 edition and data from sampling sites for several additional NAWQA studies that started in 1997. The period of record for most indicator analyses for the 2007 edition was 1992–2001. The 2002 sampling sites were a subset of the sites used in the 2007 analyses. There were also differences between the 2002 and 2007 editions in the evaluation of some indicators and in the specification of certain water-quality benchmarks.

Stream Water

For the *Core National* indicator for *Chemical Contamination* in stream water, 106 sampling sites (2002 report) and 186 sampling sites (2007 report) were analyzed. For the *Urban and Suburban* ecosystem indicator, 21 sampling sites (2002 report) and 30 sampling sites (2007 report) were analyzed. In 2002, all 106 sites had one or more detections of pesticides or nitrate (nitrate concentration at or above a base level of 0.6 mg/L) and 82 percent of the sites had five or more detections. In 2007, 99 percent of national sites had one or more detections of pesticides and 77 percent had five or more detections (fig. 5). In 2002, 100 percent of the urban and suburban sites had at least three detections of pesticides and nitrate (nitrate concentration at or above a base level of 0.6 mg/L) and in 2007, 92 percent of urban and suburban sites had at least three detections of pesticides (fig. 6).

In the 2002 analysis for contaminant occurrence in stream water, nitrate was included in the calculation of the statistics for the *Core National* and *Urban and Suburban* ecosystem indicators. An occurrence of nitrate was counted if the concentration of a sample was greater than or equal to a “background” or baseline concentration of 0.6 mg/L (Mueller and others, 1995). However, nitrate was not included in the analysis of contaminant occurrence in stream water in 2007. Nitrate occurs naturally in streams, and the States and USEPA are working to identify regional-scale background concentrations as part of an ongoing effort to define nutrient criteria. This work should be completed before nitrate can be included as part of this indicator.

The number of human-health benchmarks for pesticides increased from 45 in the 2002 edition of the Heinz Center report to 73 in the 2007 edition as a result of the development of HBSLs after 2002. In addition, values of several human-health benchmarks have changed (some higher, some lower) between the 2002 and 2007 editions (*appendix 6*). In the 2002 analysis, the occurrence of unregulated carcinogens was evaluated using risk-specific dose values corresponding to a 1 in 100,000 (10^{-5}) cancer risk. In the 2007 analysis, the occurrence of unregulated carcinogens was evaluated using the low end of an HBSL range corresponding to a 1 in 1,000,000 (10^{-6}) cancer risk. The addition of several new benchmarks resulted in a slightly higher rate of exceedances in 2007 compared to 2002 (figs. 12 and 13).

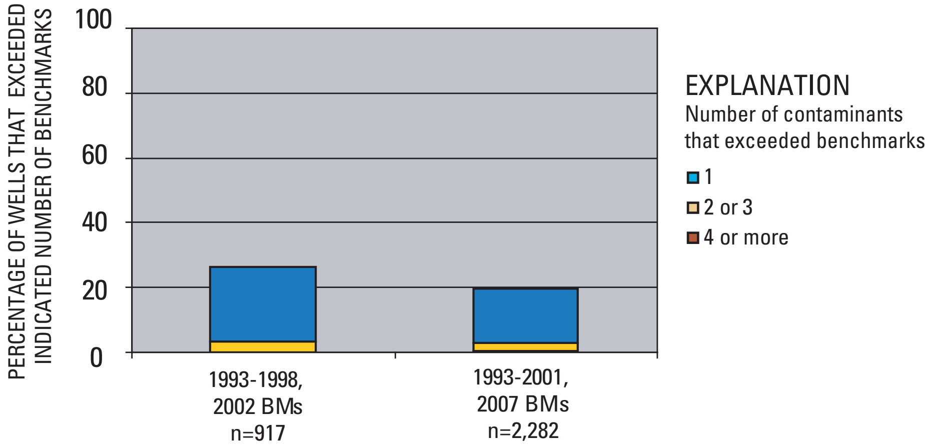
In both the 2002 and 2007 analyses, concentrations of discrete nitrate samples were used to determine exceedances of the MCL. In 2002, the full period of record for nitrate samples was used for each site, but in 2007, the period of record for nitrate samples matched the 12-month period of record used for pesticide samples. This was done to be consistent with the pesticides data already available from Gilliom and others (2006), and to not bias the results from having more exceedances of the nitrate MCL because of multiple years of data. Time-weighted mean-annual concentrations of pesticides were compared to their human-health benchmarks in both the 2002 and 2007 analyses. However, in 2002 a time-weighted mean concentration was computed for the first full year of pesticide data collection at each site. In the 2007 analysis, time-weighted mean concentrations are based on the 12-month period at each site with the most samples and analytes. Therefore, the period of record used to calculate time-weighted mean concentrations of pesticides for the 2007 analysis likely differed from the period of record used in 2002 for many sites.

A

SAMPLING PERIOD AND NUMBER OF WELLS	PERCENTAGE[1] OF WELLS THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1993-1998) 917 sites	0	3.3	23.2	73.5
2007 report (1993-2001) 2,282 sites	0.3	2.7	16.8	80.2

[1]Percentages may be rounded to equal 100

B



1993-2001

C

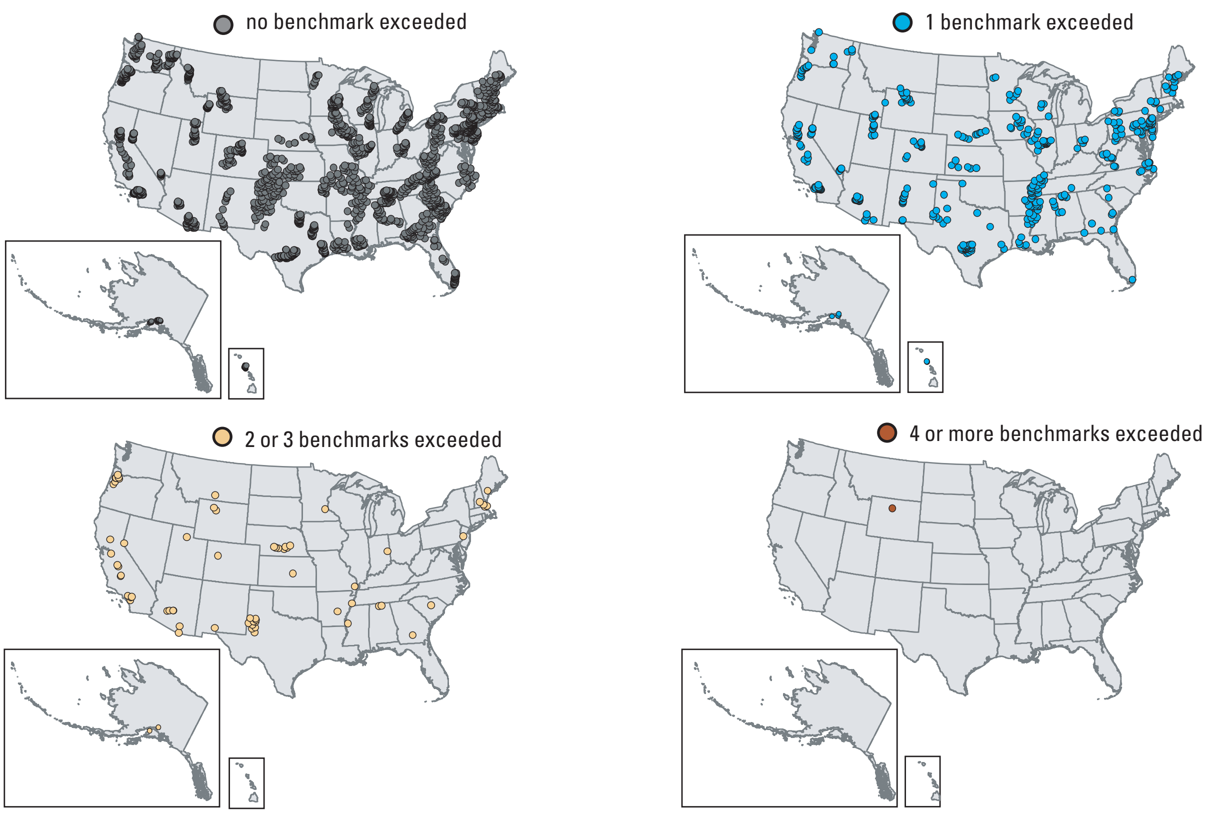


Figure 20. The number of contaminants that exceeded human-health benchmarks in national ground water compiled for the 2002 (1993–1998) and 2007 (1993–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the two data sets, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

In 2002, one of the urban stream sites had one contaminant with a concentration above a benchmark—the South Platte River at Denver, CO, exceeded the nitrate MCL. When the 2007 edition's benchmarks and methods were applied to the 2002 data set of 21 sites, the results indicated that one urban stream site had one contaminant exceeding a benchmark, but it was a different site (East Fork Double Bayou near Anahuac, TX), and the exceedance was the HBSL for the herbicide molinate. This example demonstrates how changes in the analytical methods between 2002 and 2007 resulted in minor changes to the percentage of sites exceeding benchmarks. The South Platte River site exceeded the nitrate MCL in the 2002 analysis but not in the 2007 analysis, because the 12-month period of record used in 2007 did not include the samples that had concentrations above the MCL. The East Fork Double Bayou site exceeded the HBSL for molinate in the 2007 analysis; however, because HBSLs were not used in the 2002 analysis, this site did not exceed any human-health benchmarks. The East Fork Double Bayou site was also affected by a change in land-use classification. In the 2002 analysis, this site was misclassified as urban, but in the 2007 analysis the site was classified as agricultural/farmland.

In 2002, 13 percent of the stream sites had one or more contaminants that exceeded a benchmark, based on 47 human-health benchmarks available at the time. When the new set of MCLs and HBSLs (74 benchmarks) are applied to the 2002 data set of 106 sites, the results are similar to the 2007 results for the 186 sites. This comparison indicates that the number of benchmarks, and their values, had a greater influence on the increase in human-health benchmark exceedances between the 2002 and 2007 results than the increase in the number of sites from 106 to 186.

In 2002, individual sample concentrations were used to determine exceedances of all aquatic-life benchmarks. The 2002 analysis used three types of aquatic life guidelines: (1) USEPA chronic water-quality criteria for protection of aquatic organisms; (2) Canadian water-quality guidelines for aquatic life; and (3) Great Lakes water-quality objectives for aquatic life (U.S. Environmental Protection Agency, 1999b; Canadian Council of Ministers of the Environment, 2001; International Joint Commission, 1987). For those pesticides that had more than one of these three types of benchmarks available, the priority of use is the order in which they are listed above. The 2007 analysis used different aquatic-life benchmarks (see section on Aquatic Life), as well as different environmental concentration statistics for pesticides depending on which of the 9 types of available benchmarks were used. Acute benchmarks used concentrations of discrete samples, whereas chronic benchmarks used the 4-, 21-, or 60-day moving average concentration.

In 2002, 78 percent of the stream-water sampling sites had one or more contaminants that exceeded a benchmark and 25 percent of the sites had four or more contaminants that exceeded benchmarks. There were 32 constituents with aquatic-life benchmarks available for the 2002 analysis, and there were 63 constituents with aquatic-life benchmarks available for the 2007 analysis. The aquatic-life benchmarks used for the 2007 analysis were not applied to the 2002 data set because n-moving day average concentrations were not available for the 2002 data set. One might expect an increase in the rate of exceedances between the 2002 and 2007 analyses because of the large increase in the number of constituents with benchmarks and the increase in the types of aquatic-life benchmarks available for pesticides. However, there was a higher rate of exceedances in 2002 than in the 2007 analysis (figs. 14 and 15). This was most likely caused by two factors: some of the benchmarks used in 2002 had lower values than those used in the 2007 analysis, and several of the new benchmarks use n-day moving average concentrations of pesticides instead of concentrations of discrete samples. Time-averaged concentrations of pesticides are lower than the highest concentrations of discrete samples. In the 2002 report, discrete sample concentrations for 32 pesticides were compared to only 1 aquatic-life benchmark (instead of 9). In the calculations for the 2002 Heinz Center report, 100 percent of the 21 urban streams had one or more constituents that exceeded an aquatic-life benchmark, and 38 percent of the sites had four or more constituents that exceeded benchmarks. In the 2007 analysis, 83 percent of the 30 urban streams had one or more constituents that exceeded an aquatic-life benchmark, and 20 percent of the sites had four or more constituents that exceeded benchmarks. The reduction in aquatic-life benchmark exceedances between 2002 and 2007 can be attributed to the change in methods and should not be interpreted as evidence of a trend.

Some discrepancies and errors were discovered in the 2002 methods used for the stream-water sites to count pesticide detections and the number of concentrations of pesticides greater than human-health and aquatic-life benchmarks. The methods used in 2002 counted an analyte concentration as an exceedance if it was greater than or equal to the benchmark, whereas the 2007 analysis required concentrations to exceed the benchmark. Also, a typographical error prevented detections and aquatic-life exceedances of simazine (parameter code 04035) from being counted. These discrepancies and errors were corrected for the 2007 methods used to count pesticide detections and exceedances of benchmarks. Also, the 2002 data sets used for counting pesticide detections and exceedances of human-health benchmarks did not use the same 106 sites. There were three sites used in 2002 to count detections that were not used to count exceedances, and there were three sites used to count exceedances that were not used to count detections. This discrepancy went undetected because both analyses included a total number of 106 sites. There were also three sites used for counting detections of pesticides in 2002 that had only one sample in the data set. It is uncertain why more individual samples were not in the data set for these three sites because time-weighted mean concentrations had been computed for the sites.

Streambed Sediment

There were several differences between the 2002 and 2007 analyses of contaminants in streambed sediment. First, the number of aquatic-life benchmarks available to compare with contaminant concentrations increased from 29 benchmarks in 2002 to 41 benchmarks in 2007. Second, the types of benchmarks used for the 2007 analysis were different from the benchmarks used in 2002. TECs and ESBs were used in the 2007 analysis, whereas the Canadian interim Probable Effect Levels (PEL) (Canadian Council of Ministers of the Environment, 2001) was used in the 2002 analysis (*appendix 9*). The TECs and ESBs for several compounds were lower than the corresponding PELs. Third, the number of streambed sediment sites in the 2007 analysis (957) was 97 percent larger than the number of streambed sediment sites used in the 2002 analysis (486). The large increase in sample size was due to the addition of samples collected from 1998–2001 and a mistake made in the 2002 analysis that resulted in the accidental exclusion of some sites sampled between 1992 and 1997 that should have been included. Finally, five of the SVOC compounds were censored at higher levels to account for chronic laboratory blank contamination in the 2007 analysis. There is no record of such censoring in the 2002 analysis, although blank contamination for these five compounds also occurred in the 2002 data set. Censoring these compounds had a larger effect on the number of detections (contaminant occurrence) than on the number of samples exceeding a benchmark.

Two errors were discovered in the counting methods that may have had an effect on the number of benchmark exceedances in the 2002 report. In the 2002 report, a streambed sediment analyte was counted as an exceedance if it was greater than or equal to the benchmark, whereas in the 2007 report, the analyte was counted as an exceedance only if the contaminant concentration was greater than the benchmark. Also, there was an error in the parameter codes that were summed to get the concentration of total chlordane in the 2002 report. The two methoxychlor compounds (p49346 and p49347) were included in the summation instead of trans-nonachlor (p49317) and trans-chlordane (p49321).

The frequency of contaminants above an aquatic-life benchmark in streambed sediment was higher for the 2007 analysis than for the 2002 analysis. In 2002, approximately 48 percent of sites had one or more contaminants exceeding a benchmark, and 12 percent of sites had 4 or more contaminants above a benchmark (fig. 16). In the 2007 analysis, approximately 94 percent of sites had one or more contaminant exceeding a benchmark, and 58 percent of sites had 4 or more contaminants above a benchmark (fig. 16). This large difference was due to (1) the general increase between 2002 and 2007 in the number of contaminants with benchmarks, and (2) the decrease in many of the benchmark concentrations for streambed contaminants.

Fish Tissue

There were several major differences between the 2002 and 2007 analysis of contaminants in fish tissue. First, the benchmarks for the protection of fish-eating wildlife used in the 2002 report were significantly different from the benchmarks used in the 2007 report. Second, for the 2002 analysis, benchmarks were available for only 9 compounds or groups of related compounds, whereas for the 2007 analysis, benchmarks were available for 15 compounds or groups of compounds (*appendix 12*). Third, the 2007 analysis was based on the analysis of fish-tissue samples from 700 sites and the 2002 analysis used samples from 220 sites. The 2002 analysis included samples from the 1991 and 1994 NAWQA study units, whereas the 2007 analysis added samples collected from sites in 15 additional study unit investigations started in 1997. The addition of the samples from the 1997 study units should have increased the sample count by 190. There should have been 510 samples available in 2002; however, the methods that were used to count detections and exceedances filtered the available data to include only those sites where both organochlorine pesticides data (NWQL schedule 2101) and trace metals data (NWQL schedule 2200) were measured in fish tissue. Because trace metals were not included in the analysis of chemical contamination in fish tissue, this filtering process inadvertently eliminated many tissue samples that would have been included.

The frequency of exceedance of $\text{benchmark}_{\text{low}}$ values for the 2007 data set was significantly greater than the frequency of exceedance for the data set used in the 2002 report (figs. 18a, b). The 2002 analysis did not use a range of benchmark values; it used one benchmark value from the New York fish-flesh criterion of Newell and others (1987) for nine compounds or compound groups (*appendix 12*). In 2002, 50 percent of the samples had one or more contaminants concentration that exceeded a benchmark and none of the samples had more than 3 contaminant concentrations that exceeded a benchmark. If the 2007 set of $\text{benchmark}_{\text{low}}$ values were compared to the 220 samples used in the 2002 report, the number of sites with at least one contaminant exceeding a $\text{benchmark}_{\text{low}}$ value would increase from 50 percent to 88 percent and the number of samples with 4 or more contaminants exceeding a $\text{benchmark}_{\text{low}}$ value would increase from none to slightly more than 1 percent (figs. 18a, b). If the 2007 set of $\text{benchmark}_{\text{high}}$ values were compared to the 2002 data set, the results are similar to the 2007 analysis (figs. 19a, b) because 6 $\text{benchmark}_{\text{high}}$ values used in the 2007 analysis are the same as the benchmark values used for those compounds in 2002.

Ground Water

The major differences between the 2002 and 2007 analyses for the *Chemical Contamination* indicator for ground water included: (1) a decrease in the frequency of contaminant detections between 2002 and 2007; (2) differences in the aquifer study wells used for analysis (table 4); (3) changes in censoring levels (table 4); and (4) changes in the human-health benchmarks.

Table 4. Differences between the analyses for the 2002 and 2007 Heinz Center reports for chemical contamination in national ground water.

[MAS, Major Aquifer Study; AgLUS, Agricultural Land Use Study, UrbLUS, Urban Land Use Study; mg/L, milligrams per liter; µg/L, micrograms per liter]

Data	2002 Report	2007 Report	Expected change in outcome
Nitrate	Base level of 2.0 mg/L; data from MAS, AgLUS, UrbLUS	Base level of 1.0 mg/L; data from MAS	Lower detection frequency in 2007 due to exclusion of land-use studies
VOCs	No censoring (data from low-level analytical method only); data from MAS, AgLUS, UrbLUS	Analytical data censored at 0.2 µg/L; data from MAS	Lower detection frequency in 2007 due to inclusion of early analytical data, higher censoring level, and exclusion of land-use studies
Pesticides	No censoring; data from MAS, AgLUS, UrbLUS	No censoring; data from MAS	Lower detection frequency in 2007 due to exclusion of land-use studies

The number of sites used for analysis was 917 in the 2002 report and 2,282 in the 2007 report. In the 2002 analysis, approximately 89 percent of the wells had one or more detections of a contaminant, and approximately 40 percent of the wells had 5 or more contaminant detections (fig. 10). In the 2007 analysis, approximately 61 percent of the wells had one or more detections of a contaminant, and approximately 7 percent of the wells had 5 or more contaminant detections. This decrease in the frequency of contaminant detections was caused by changes in data compilation methods.

In the 2002 analysis, data from all three types of NAWQA studies were used for the *Chemical Contamination* indicator (table 4). These include (1) Major Aquifer Studies, (2) agricultural land-use studies, and (3) urban land-use studies. Major Aquifer Studies were designed to assess the occurrence of contaminants in aquifers used for drinking-water supply while land-use studies were designed to assess the occurrence of contaminants in shallow ground water underlying areas of intensive land use. In general, data analyzed with low-level analytical methods and data from land-use studies tend to have higher detection frequencies of contaminants compared to data analyzed using a higher censoring level and from Major Aquifer Studies. In the 2007 analysis, only data from the NAWQA Major Aquifer Studies were used for two reasons: (1) samples were collected primarily from domestic wells, which generally provided a more consistent and representative sampling of the used portion of the ground-water resource, and (2) domestic wells in Major Aquifer Studies were generally sampled for many groups of contaminants leading to a greater number of samples that had analyses for multiple constituent groups (table 4).

In the 2002 analysis, data for VOCs were not censored, and only those samples analyzed with the low-level VOC analytical method were considered (table 4). In the 2007 analysis, VOCs in ground water were censored at 0.2 µg/L so that data collected prior to April 1996 (0.2 µg/L reporting level) could be included in the analysis with post April 1996 data (0.02 µg/L reporting level). The lack of a censoring level for VOCs, the use of only low-level analytical data for VOCs, and the use of data from NAWQA land-use studies led to a high detection frequency of contaminants in the 2002 analysis relative to the 2007 analysis. Many human-health benchmarks for pesticides, VOCs, and trace elements in ground water were not available at the time of the 2002 report and (or) their values have changed between 2002 and 2007 (*appendix 16*). Forty nine pesticides, 19 VOCs, and 5 trace elements had new or different human-health benchmarks in the 2007 report compared to the 2002 report. The reasons for the differences in human-health benchmarks between the reports included: (1) the addition of new pesticide analytes with MCLs or HBSLs, (2) changes in MCL values for some pesticides, and (3) the addition of HBSLs to the 2007 study.

Pesticides in Farmlands

Stream Water

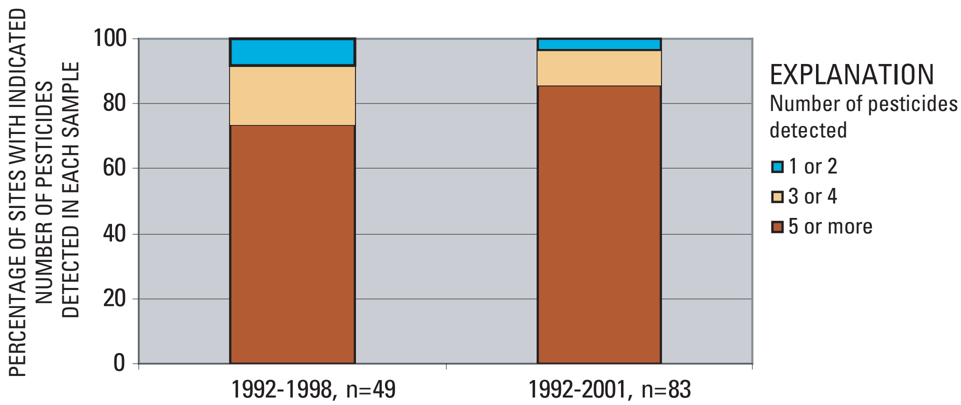
NAWQA stream-water samples collected from 83 agricultural watersheds were used to measure the occurrence of pesticides in stream water of the *Farmlands* ecosystem (*appendix 5*) (Gilliom and others, 2006 and Jeffrey D. Martin, U.S. Geological Survey, written commun., 2006). All 83 farmland streams had one or more pesticide detections and more than 85 percent of the sites had 5 or more pesticide detections (fig. 21, *appendix 7*). In 2002, pesticide samples from 49 sites were used to measure the occurrence of pesticides in farmland streams. All 49 sites had one or more pesticide detections and more than 73 percent of the sites had 5 or more detections (fig. 21).

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED NUMBER OF PESTICIDES DETECTED			
	5 or more	3 or 4	1 or 2	none
2002 report (1992-1998); 49 sites	73.5	18.4	8.1	0
2007 report (1992-2001); 83 sites	85.6	10.8	3.6	0

[1]Percentages may be rounded to equal 100

B



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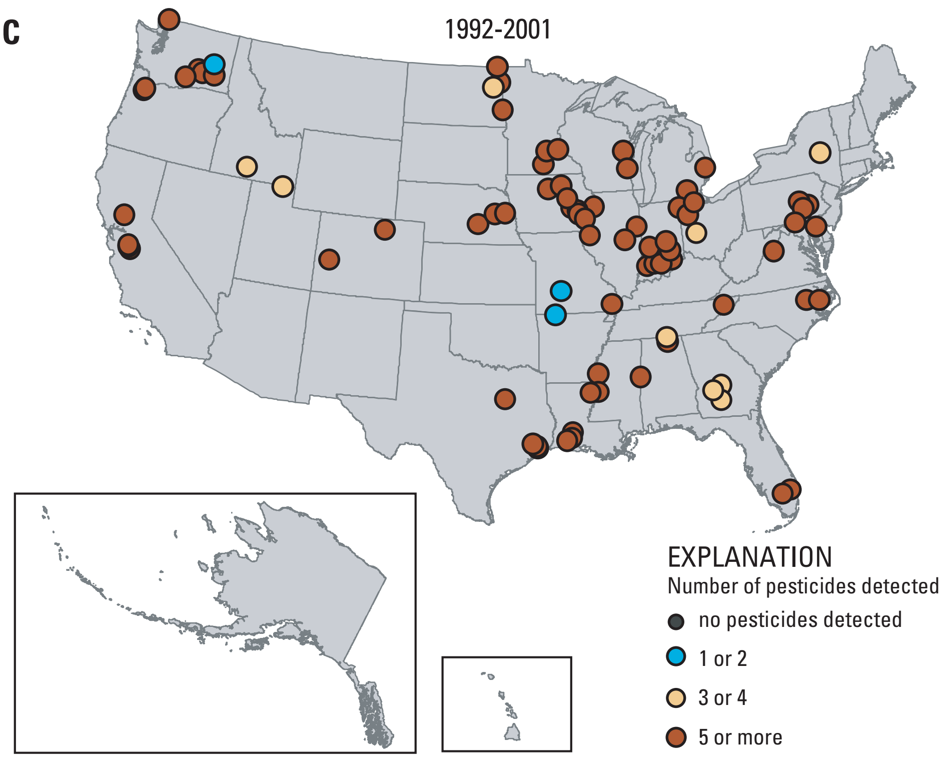


Figure 21. Pesticide occurrence in streams draining the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated number of detections, (**B**) a graphical comparison of pesticide detections for the two data sets, and (**C**) a map of pesticide detections for the 2007 edition.

The percentage of these farmland streams with pesticides exceeding selected numbers of human-health benchmarks is shown in figure 22 and *appendix 17*. Thirteen (16 percent) of the farmland streams had one or more pesticide that exceeded a human-health benchmark and about 4 percent had 2 or 3 pesticides that exceeded a human-health benchmark. In the 2002 analysis, 6 percent of the sites had one or more pesticides that exceeded one of the 45 human-health benchmarks available at the time. When the new set of MCLs and HBSLs are applied to the 2002 data set of 49 sites, the results are similar to the 2007 results for the 83 sites. About 14 percent of the sites had one or more pesticide that exceeded a human-health benchmark and about 4 percent had 2 or 3 pesticides that exceeded a human-health benchmark. The data set used in 2002 was a subset of the data set used for the 2007 analysis.

The percentage of aquatic-life benchmark exceedances for the farmland streams was similar to that for the national streams. Approximately 57 percent of the farmland streams had one or more pesticides that exceeded one or more aquatic-life benchmark, and 12 percent of the sites had 4 or more pesticides that exceeded benchmarks (fig. 23, *appendix 18*). As with the national and urban streams, there was a lower percentage of benchmark exceedances for the 2007 analysis than in 2002. In 2002, approximately 84 percent of the sites had one or more pesticides above a benchmark, and 33 percent of the sites had 4 or more pesticides that exceeded a benchmark.

Ground Water

Samples of shallow ground water underlying areas of predominantly agricultural land use were used to measure the occurrence of pesticides in the *Farmlands* ecosystem and their exceedance of human-health benchmarks (*appendix 14* and *appendix 22*). Water samples were collected from 1,412 wells sampled as part of the agricultural land-use studies by the USGS NAWQA Program between 1993–2003 (Gilliom and others, 2006).

All samples were collected and analyzed by the USGS according to the procedures described in Gilliom and others (1995). Sampling sites were not located in areas of known contamination but were selected to be representative of the dominant land use in the area. Land use in the vicinity of each well was characterized according to procedures described in Gilliom and Thelin (1997). Samples of ground water were collected from shallow wells screened near the top of the water table and where land use within a 500-meter radius of the well was primarily agricultural.

Ground-water samples were collected 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). Concentrations of 76 commonly used pesticides and 7 pesticide degradation products were determined in ground-water samples (*appendix 16*). Zaugg and others (1995) and Werner and others (1996) describe analytical methods used for determining concentration of pesticides in ground water. No censoring level was used in analyzing concentrations of pesticides in ground water.

One or more pesticides were detected in about 61 percent of wells sampled in the agricultural land-use studies in the 2007 analysis, and 5 or more pesticides detected in approximately 10 percent of the wells (fig. 24). These frequencies of detection are similar to those calculated for the 2002 analysis, which used a data set of 1,068 wells (figs. 24A and B). Concentrations of pesticides infrequently exceeded human-health benchmarks, with only a few wells (1.3 percent) having a concentration of one or more pesticides that exceeded a human-health benchmark (fig. 25). This low frequency of exceedance was similar to the results of the 2002 analysis, in which only 7 of the 1,068 wells (0.7 percent) had a pesticide concentration that exceeded one of the 45 benchmarks established at the time (fig. 25A and B).

There were several differences between the 2002 and 2007 analyses of pesticides in farmland streams and ground water. First, there was an increase in sample size. The number of streams sites sampled for the *Farmlands* ecosystem increased from 49 to 83 between 2002 and 2007, respectively. Similarly, the number of wells sampled in the *Farmlands* ecosystem increased from 1,068 to 1,412.

Many of the human-health benchmarks used to determine exceedances of standards and guidelines for pesticides changed after 2002 or were newly added as part of the 2007 study. The reasons for the differences in human-health benchmarks include: (1) addition of new pesticide MCLs and HBSLs, and (2) changes to existing MCL values.

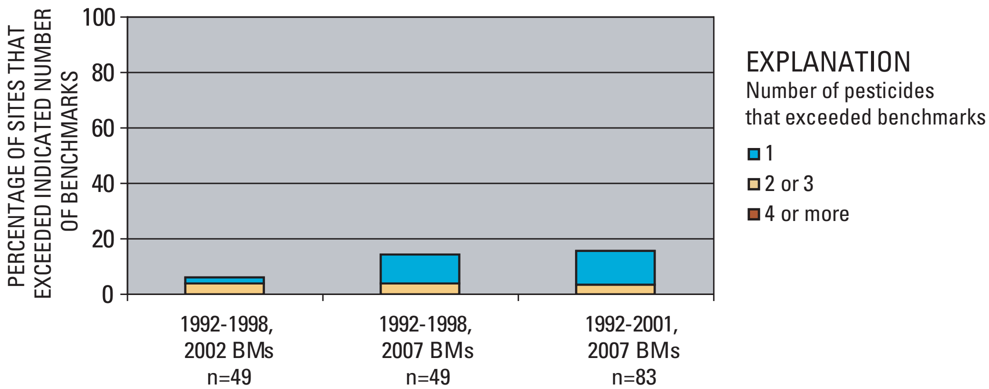
The prior section on differences from 2002 for *Chemical Contamination* in stream water covers several differences that are also valid for pesticides in farmland streams. The discussions about the change in human-health and aquatic-life benchmarks for pesticides also applies to pesticides in farmland streams, as does the error in the omission of simazine (NWQL parameter code p04035) data.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) using 2002 BMs; 49 sites	0	4.1	2.0	93.9
2002 report (1992-1998) using 2007 BMs; 49 sites	0	4.1	10.2	85.7
2007 report (1992-2001) using 2007 BMs; 83 sites	0	3.6	12.1	84.3

[1]Percentages may be rounded to equal 100

B



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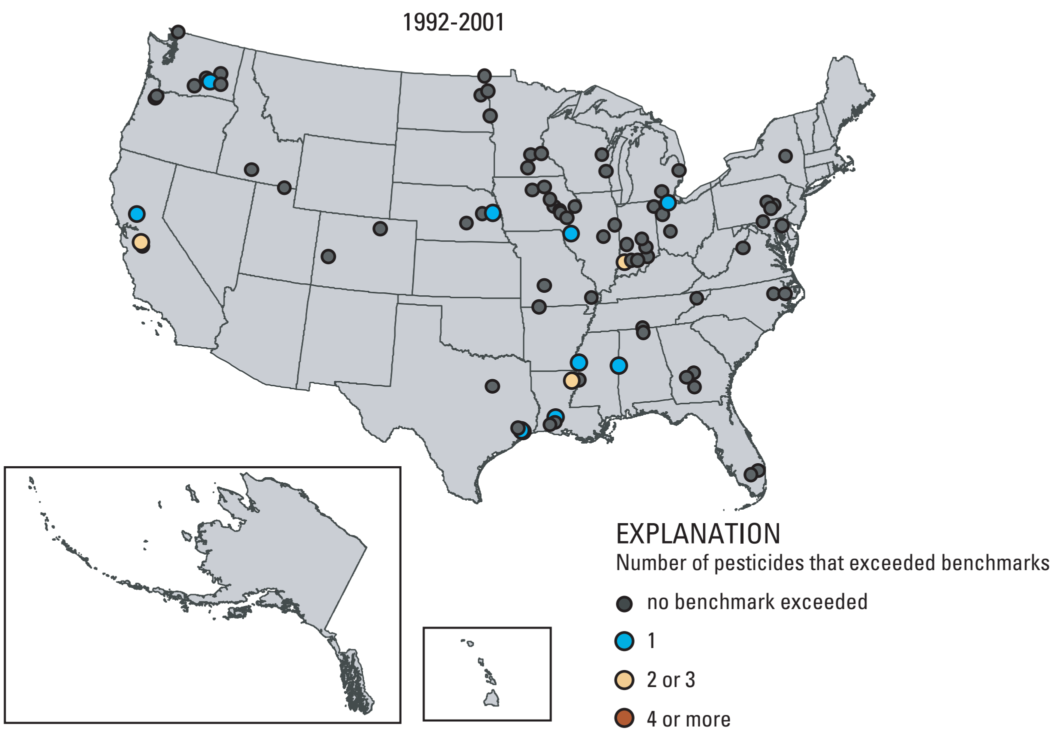


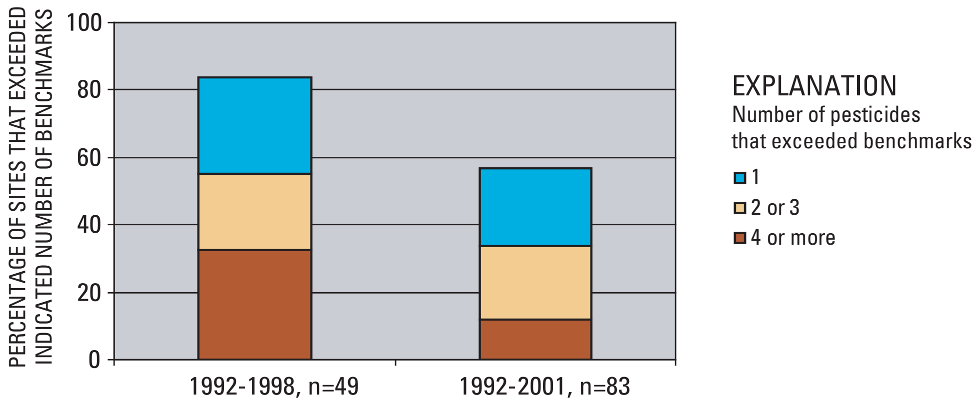
Figure 22. The number of pesticides that exceeded human-health benchmarks in streams draining the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the 2002 data using 2002 and 2007 edition benchmarks, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1992-1998) 49 sites	32.6	22.5	28.6	16.3
2007 report (1992-2001) 83 sites	12.0	21.7	22.9	43.4

[1]Percentages may be rounded to equal 100

B



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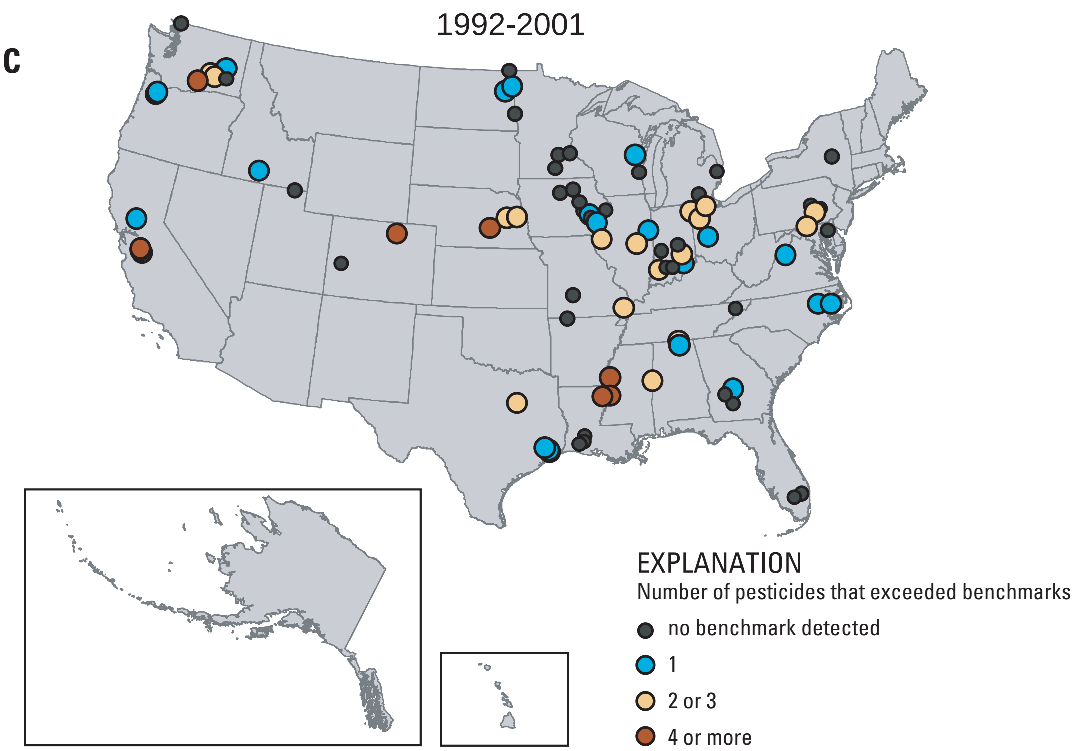


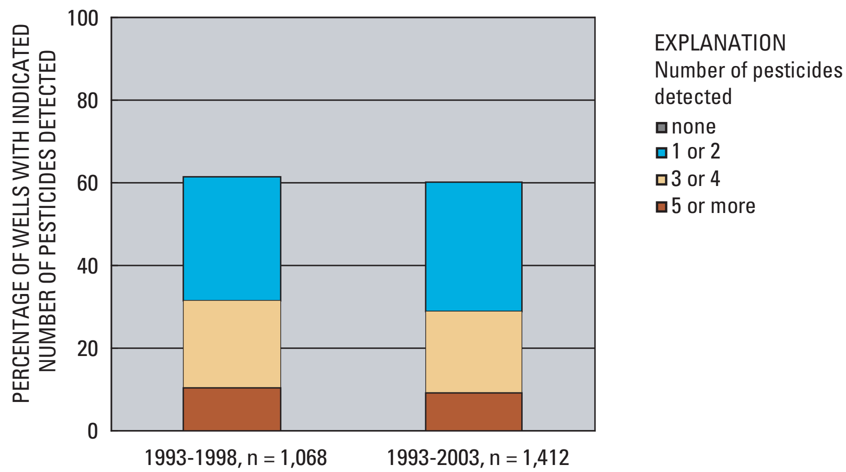
Figure 23. The number of pesticides that exceeded aquatic-life benchmarks in streams draining the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the two data sets, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF WELLS	PERCENTAGE[1] OF WELLS WITH INDICATED NUMBER OF PESTICIDES DETECTED			
	5 or more	3 or 4	1 or 2	none
2002 report (1993-1998); 1,068 wells	11.3	21.5	29.4	37.8
2007 report (1993-2003); 2,282 wells	9.5	19.8	31.3	39.4

[1]Percentages may be rounded to equal 100

B



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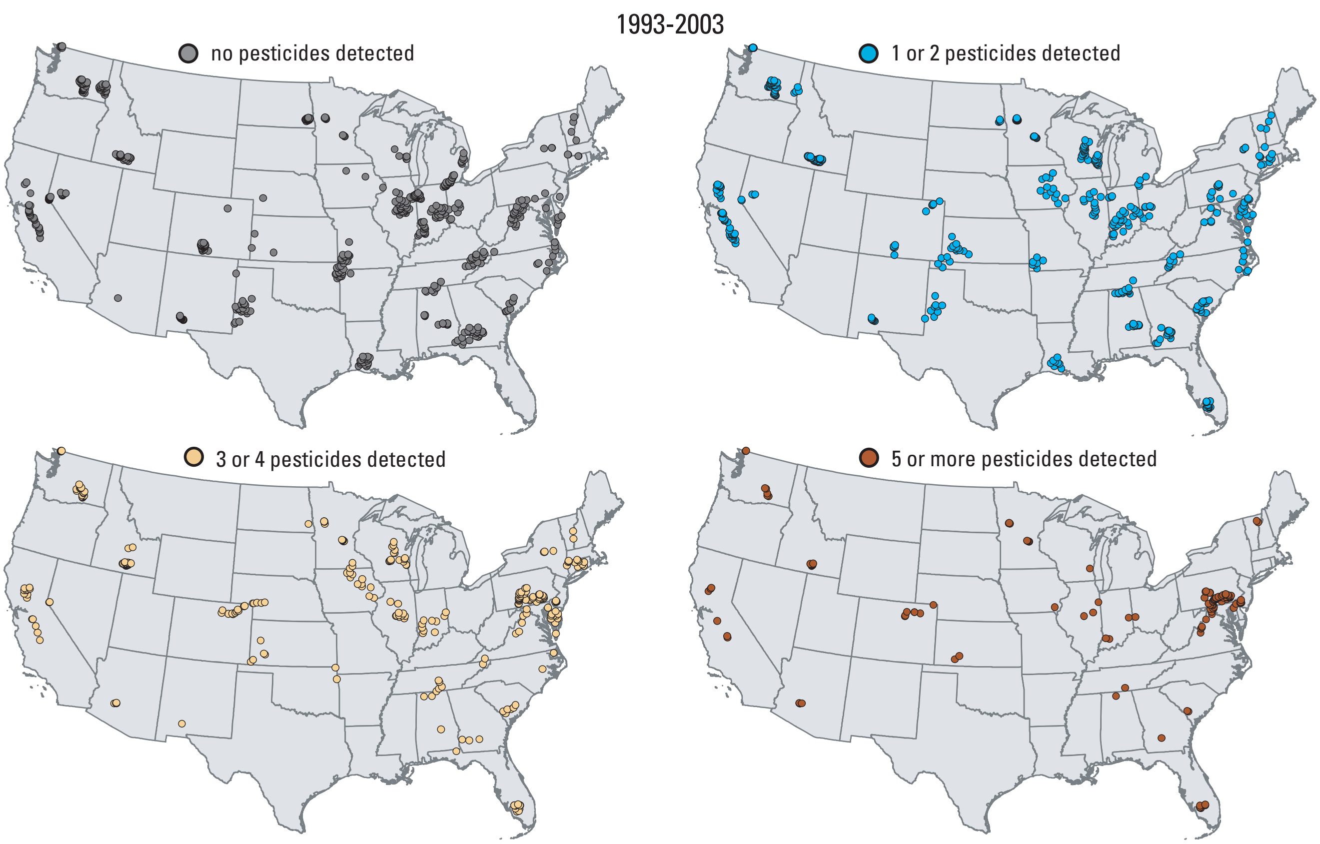


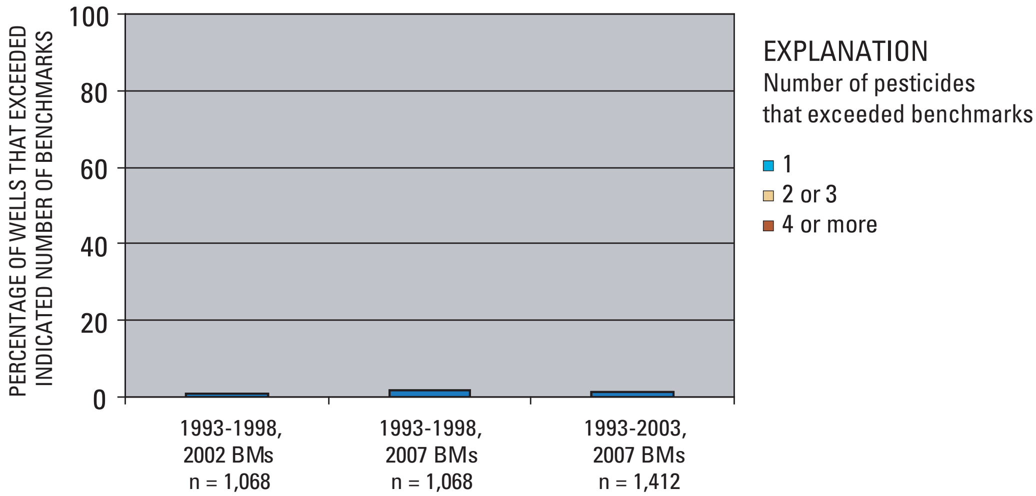
Figure 24. Pesticide occurrence in ground water from the *Farmlands* ecosystem compiled for the 2002 (1993–1998) and 2007 (1993–2003) editions of the Heinz Center report, showing (**A**) the percentage of wells with the indicated number of detections, (**B**) a graphical comparison of contaminant detections for the two data sets, and (**C**) maps of contaminant detections for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF WELLS	PERCENTAGE[1] OF WELLS THAT EXCEEDED INDICATED NUMBER OF BENCHMARKS			
	4 or more	2 or 3	1	none
2002 report (1993-1998) using 2002 BMs; 1,068 sites	0	0	0.7	99.3
2002 report (1993-1998) using 2007 BMs; 1,068 sites	0	0.1	1.5	98.4
2007 report (1993-2003) using 2007 BMs; 1,412 sites	0	0.1	1.2	98.7

[1]Percentages may be rounded to equal 100

B



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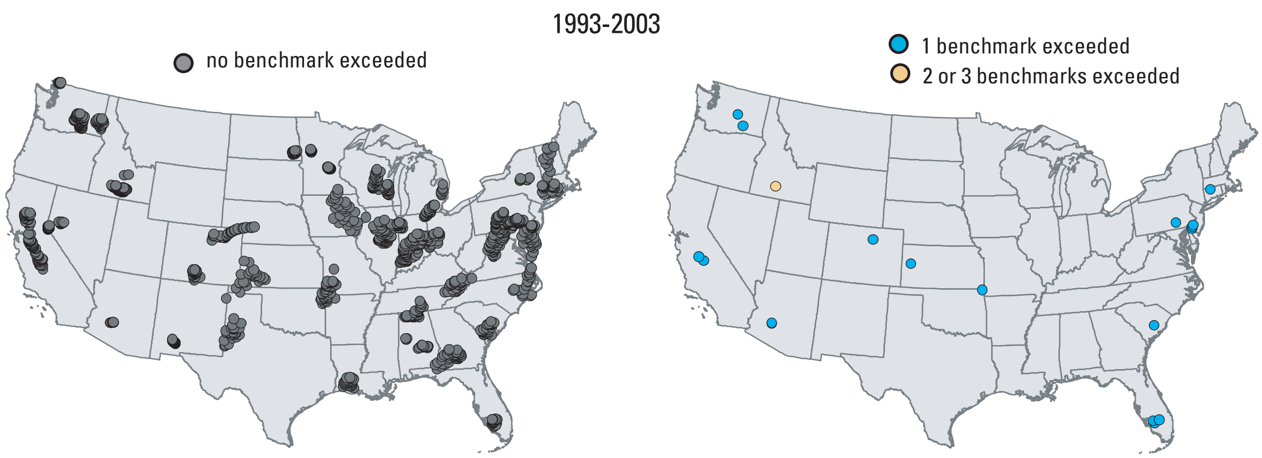


Figure 25. The number of pesticides that exceeded human-health benchmarks in ground water from the *Farmlands* ecosystem compiled for the 2002 (1993–1998) and 2007 (1993–2003) editions of the Heinz Center report, showing (**A**) the percentage of sites that exceeded the indicated number of benchmarks, (**B**) a graphical comparison of the percentage of sites that exceeded the indicated number of benchmarks for the two data sets, and (**C**) a map of the sites with the number of contaminants that exceeded benchmarks for the 2007 edition.

Nutrients in Stream Water

The nutrients in stream water indicators describe concentrations of nutrients in several ecosystems. Nutrient indicators for streams included measurements of nitrate and total phosphorus in samples from farmland streams in urban and suburban streams, and measurements of nitrate in forest stream samples. The indicators report the percentage of NAWQA stream sites with flow-weighted mean concentrations in one of four class bins. Because concentrations of nutrients in streams usually vary with flow, a flow-weighted mean was calculated to represent the "typical" concentrations in the stream. To compute flow-weighted means, mean-annual loads were estimated by relating individual sample concentrations to the corresponding streamflow 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 then calculated by dividing the total load by the total flow (Mueller and Spahr, 2005). Concentrations of nitrate and total phosphorus were censored at 0.05 mg/L and 0.01 mg/L, respectively. Reported concentrations that were less than the censoring level were set at the censoring level.

The data used for all of the nutrients in stream water indicators, except for *Phosphorus in Large Rivers*, were obtained from the 2005 NAWQA nutrient national synthesis report (Mueller and Spahr, 2005). Data used for the *Phosphorus in Large Rivers* indicator were obtained from the USGS NWIS data base.

Nitrate

The nitrate in streams indicator focused on streams in each of three ecosystems: *Farmlands*, *Forest*, and *Urban and Suburban*. Flow-weighted mean concentration of nitrate in samples collected as part of the NAWQA Program from 1992 through 2001 were used for the nitrate in streams indicators (*appendix 23*).

Data from stream sites in the NAWQA Cycle I data set that were assigned classification in the *Farmlands, Forest,* or *Urban and Suburban* ecosystems were used to calculate the nitrate in streams indicator for each ecosystem respectively. The nitrate indicator in farmland streams was calculated using data from 130 stream sites (fig. 26). The class bins for the percentage of farmland stream sites with flow-weighted mean concentrations of nitrate are: less than 2 mg/L, 2 to less than 6 mg/L, 6 to less than or equal to 10 mg/L, and more than 10 mg/L.

On the basis of evaluation of data from 105 stream sites, the results of the 2007 analysis were similar to those for the 2002 analysis. In 2002, there was a slightly higher frequency of sites with concentrations of nitrate less than 6 mg/L and a corresponding slightly lower frequency of sites with concentrations of nitrate exceeding 10 mg/L than in the 2007 analysis.

The nitrate indicator in forest streams was calculated using data from 117 stream sites. Flow-weighted mean concentrations of nitrate for forest streams were binned into four categories: less than 0.1 mg/L, 0.1 to less than 0.5 mg/L, 0.5 to less than 1 mg/L, and 1 mg/L or more. Note that these ranges in concentration of nitrate are an order of magnitude lower than those used for the *Farmlands* ecosystem. The flow-weighted mean concentrations of nitrate for 81 percent of the forested sites was less than 0.5 mg/L and only about 3 percent of the sites had mean concentrations of 1 mg/L or higher (fig. 27). In contrast, the results for this indicator in the 2002 report showed that approximately 92 percent of the sites had mean concentrations of nitrate less than 0.5 mg/L; approximately 3 percent of the sites had mean concentrations of nitrate 1 mg/L or higher. The number of forested stream sites in the 2007 data set was more than 3 times the number of sites than the 2002 data set, presumably because of a change in the land-use criteria used to characterize watersheds with a predominantly forest land use. In 2002, 36 stream sites were used to represent this indicator.

The nitrate indicator in urban and suburban streams was calculated using water-quality data from 54 stream sites (fig. 28). The four class bin categories used for concentrations of nitrate in urban and suburban streams are the same as those used for the forest streams: less than 0.1 mg/L, 0.1 to less than 0.5 mg/L, 0.5 to less than 1 mg/L, and 1 mg/L or more. About 68 percent of the sites had flow-weighted mean concentrations of nitrate greater than 0.5 mg/L, and about 39 percent of the sites had flow-weighted mean concentrations of nitrate greater than or equal to 1 mg/L (fig. 28). These results were similar to the results from the 2002 analysis, which were based on 38 stream sites (*table 1*; fig. 28A and B).

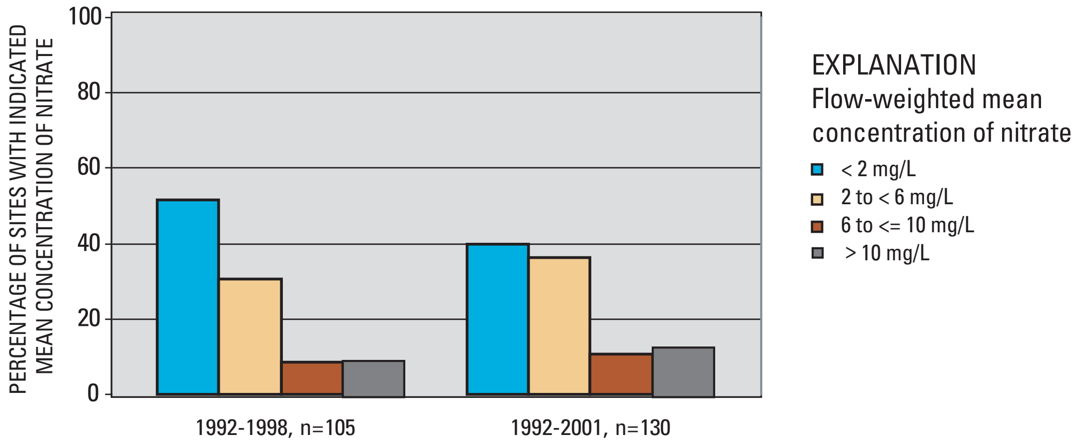
An ecosystem comparison was made to show the relative differences in concentrations of nitrate among the streams draining *Farmlands*, *Forest*, and *Urban and Suburban* ecosystems (fig. 29). Most of the sites in the *Forest* and *Urban and Suburban* ecosystems had mean concentrations of nitrate lower than 2 mg/L. In the *Farmlands* ecosystem 40 percent of the sites had mean concentrations lower than 2 mg/L and 36 percent of the sites had concentrations in the 2 mg/L to less than 6 mg/L class bin. About 22 percent of the sites in the *Urban and Suburban* ecosystem and 1 percent of sites in the *Forest* ecosystem had mean concentrations of nitrate in the 2 mg/L to less than 6 mg/L class bin. About 24 percent of sites in the *Farmlands* ecosystem had mean concentrations of nitrate equal to 6 mg/L or higher. A comparison of both the 2002 and 2007 analyses show similar results.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF NITRATE			
	< 2 mg/L	2 to < 6 mg/L	6 to <= 10 mg/L	> 10 mg/L
2002 report (1992-1998); 105 sites	51.4	30.5	8.6	9.5
2007 report (1992-2001); 130 sites	40.0	36.1	10.8	13.1

[1]Percentages may be rounded to equal 100

B



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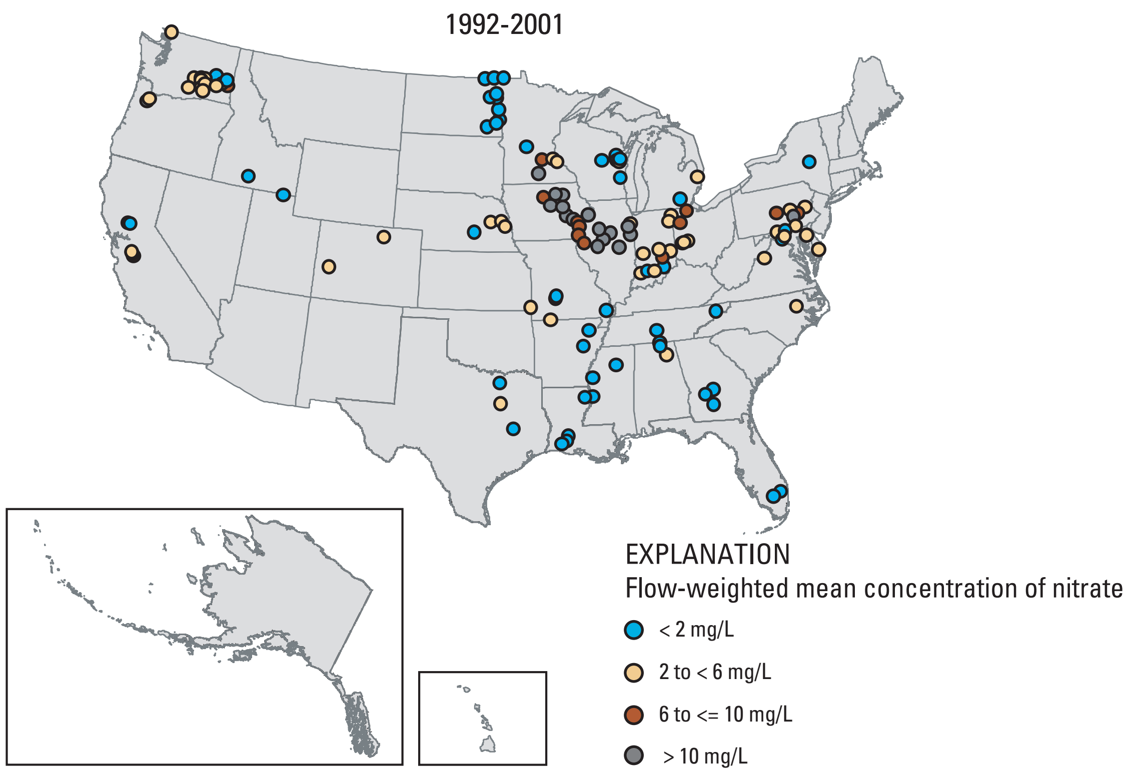


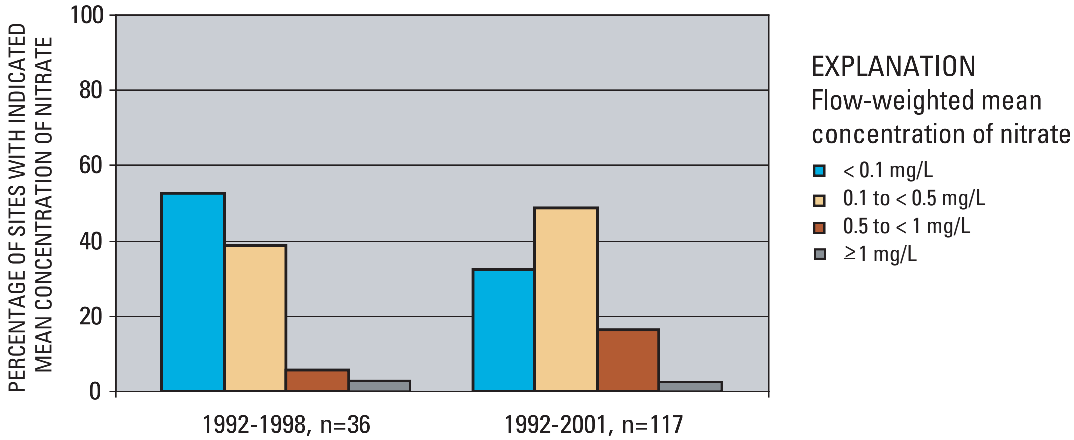
Figure 26. Flow-weighted mean concentration of nitrate in streams draining the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of nitrate, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of nitrate for the two data sets, and (**C**) a map of the sites with the indicated concentration of nitrate for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF NITRATE			
	< 0.1 mg/L	0.1 to < 0.5 mg/L	0.5 to < 1 mg/L	>= 1 mg/L
2002 report (1992-1998); 36 sites	52.8	38.9	5.5	2.8
2007 report (1992-2001); 117 sites	32.5	48.7	16.2	2.6

[1]Percentages may be rounded to equal 100

B



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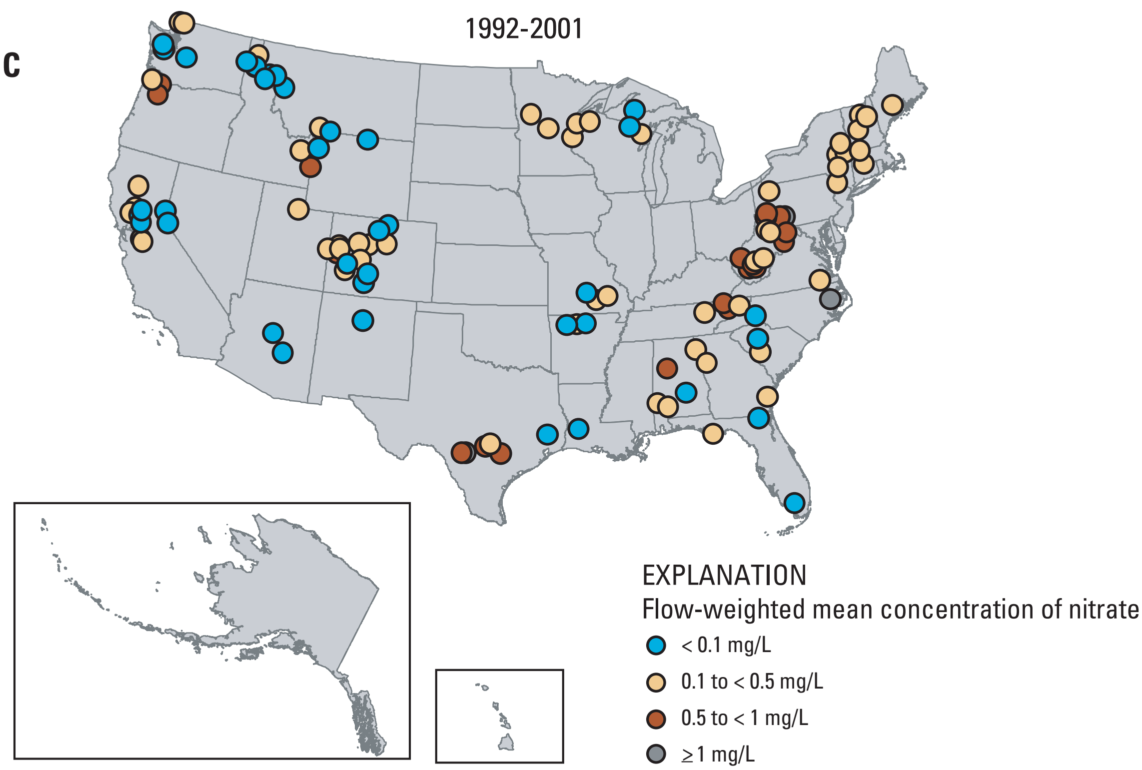


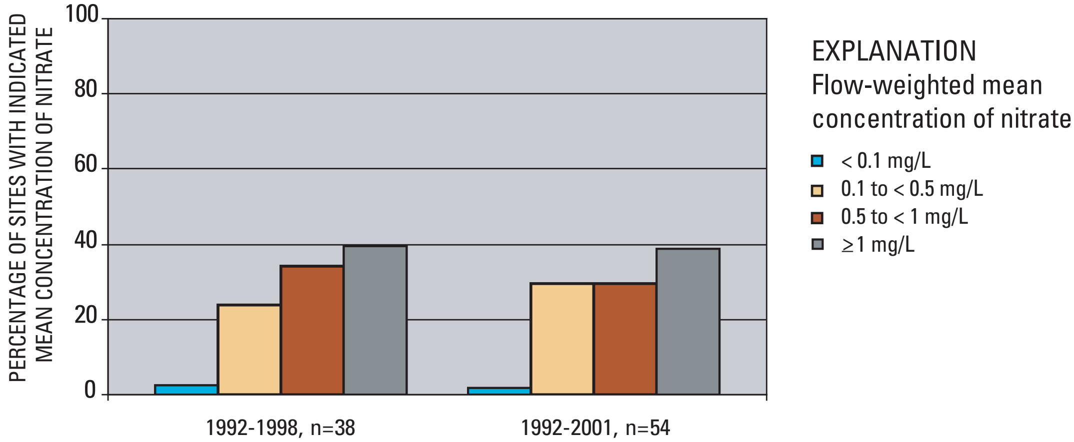
Figure 27. Flow-weighted mean concentration of nitrate in streams draining the *Forest* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of nitrate, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of nitrate for the two data sets, and (**C**) a map of the sites with the indicated concentration of nitrate for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF NITRATE			
	< 0.1 mg/L	0.1 to < 0.5 mg/L	0.5 to < 1 mg/L	>= 1 mg/L
2002 report (1992-1998); 38 sites	2.6	23.7	34.2	39.5
2007 report (1992-2001); 54 sites	1.9	29.6	29.6	38.9

[1]Percentages may be rounded to equal 100

B



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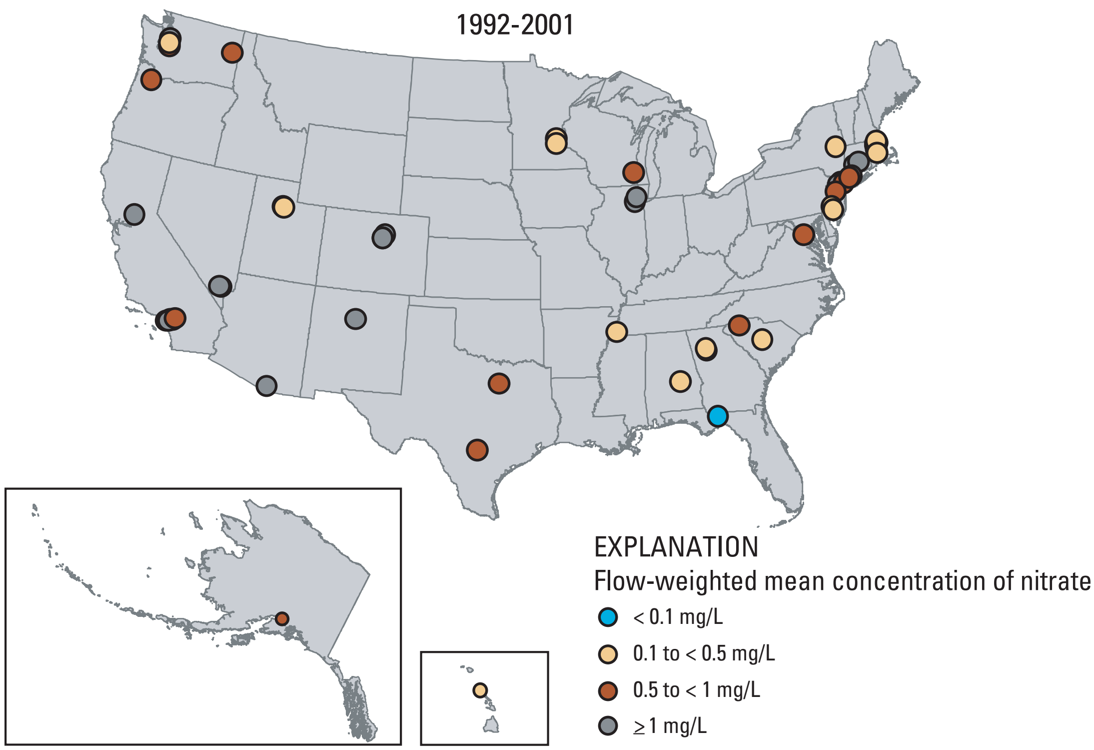


Figure 28. Flow-weighted mean concentration of nitrate in streams draining the *Urban and Suburban* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of nitrate, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of nitrate for the two data sets, and (**C**) a map of the sites with the indicated concentration of nitrate for the 2007 edition.

SAMPLING PERIOD	ECOSYSTEM	NUMBER OF SITES	PERCENTAGE OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF NITRATE			
			< 2 mg/L	2 to < 6 mg/L	6 to <= 10 mg/L	> 10 mg/L
2002 report (1992-1998)	Farmlands	105	51.4	30.5	8.6	9.5
	Forest	36	100.0	0.0	0.0	0.0
	Urban and Suburban	38	81.6	18.4	0.0	0.0
2007 report (1992-2001)	Farmlands	130	40.0	36.1	10.8	13.1
	Forest	117	99.1	0.9	0.0	0.0
	Urban and Suburban	54	77.8	22.2	0.0	0.0

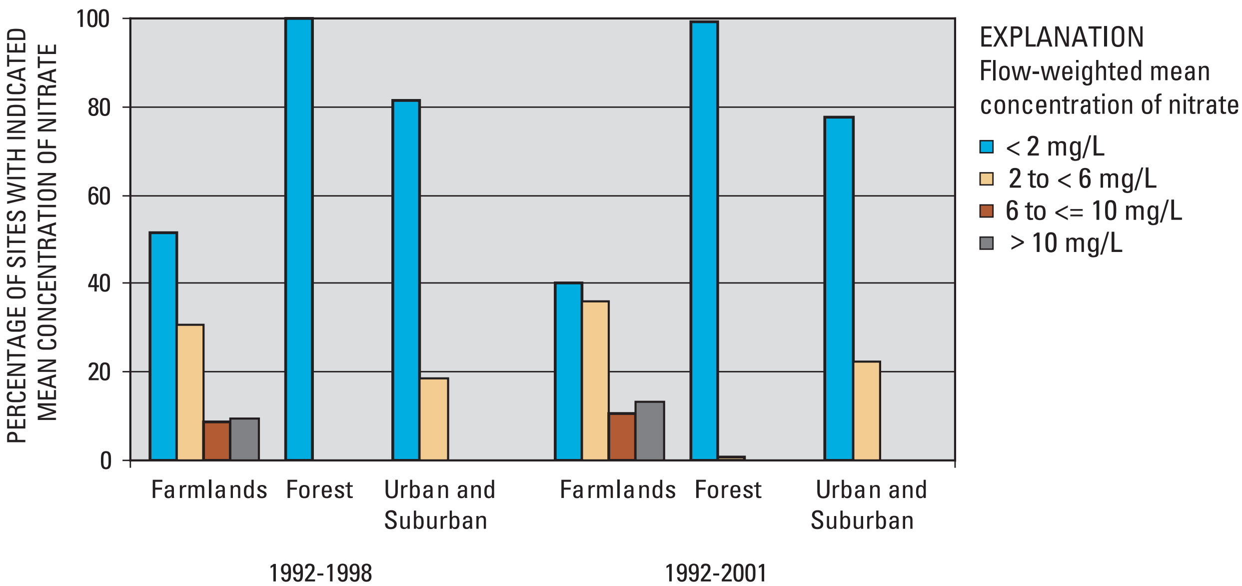


Figure 29. Comparison of mean concentration of nitrate in streams by ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report.

Phosphorus

The Heinz Center report includes two indicators for phosphorus; phosphorus in *Farmland*, and *Urban and Suburban* stream ecosystems, and *Phosphorus in Large Rivers*. Stream sites in the NAWQA Cycle I data set were used for the indicator for phosphorus in stream ecosystems, and water-quality and streamflow data for sites in the National Water Information System (NWIS) data base were used to develop the indicator for *Phosphorus in Large Rivers*.

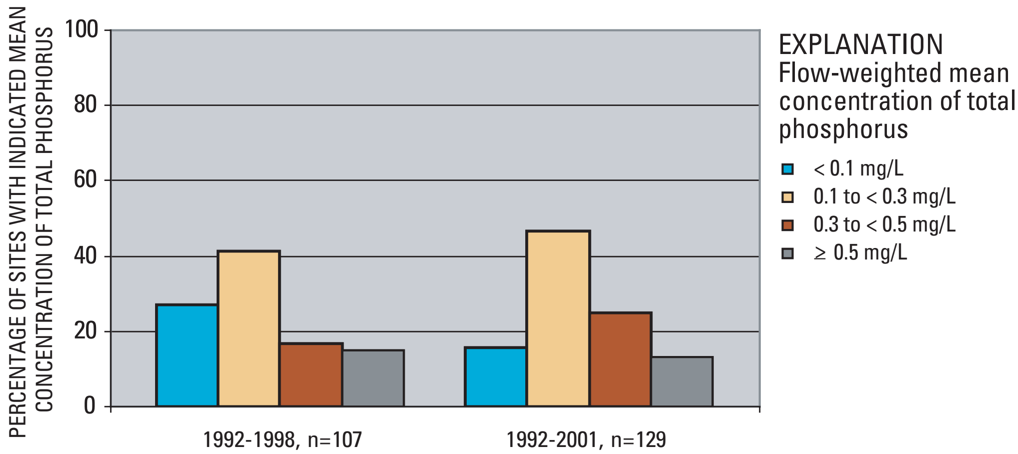
The indicator for phosphorus in streams was calculated, in the same manner as the indicator for nitrate in streams, using flow-weighted mean concentrations of total phosphorus for samples collected as part of the NAWQA Program from 1992 through 2001 (*appendix 23*) (Mueller and Spahr, 2005). The indicator reports the percentage of NAWQA stream sites with mean, flow-weighted concentrations of total phosphorus in one of four class bins: less than 0.1 mg/L, 0.1 mg/L to less than 0.3 mg/L, 0.3 mg/L to less than 0.5 mg/L, and 0.5 mg/L or more. Flow-weighted mean concentrations of total phosphorus were estimated for 129 streams draining farmland watersheds. Approximately 46 percent of the farmland streams had a flow-weighted mean concentration of total phosphorus between 0.1 and 0.3 mg/L (fig. 30). These results are similar to those calculated for the 2002 analysis, which was based on water-quality data from 107 stream sites.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF TOTAL PHOSPHORUS			
	< 0.1 mg/L	0.1 to < 0.3 mg/L	0.3 to < 0.5 mg/L	≥ 0.5 mg/L
2002 report (1992-1998); 107 sites	27.1	41.1	16.8	15.0
2007 report (1992-2001); 129 sites	15.5	46.5	24.8	13.2

[1]Percentages may be rounded to equal 100

B



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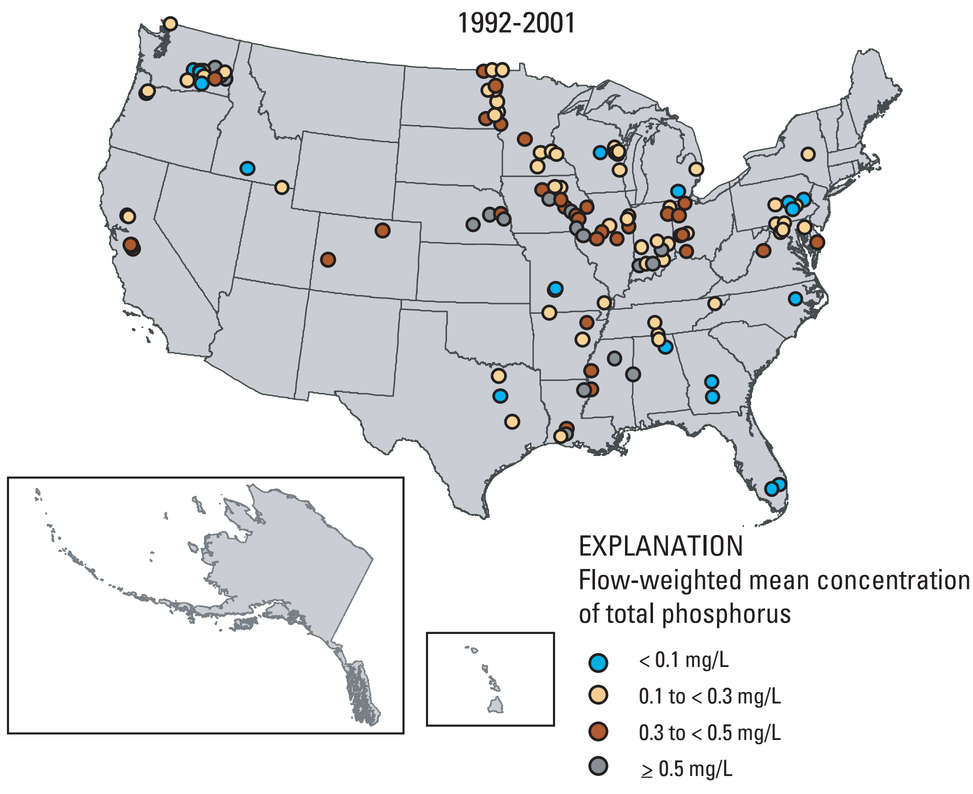


Figure 30. Flow-weighted mean concentration of total phosphorus in streams draining the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of total phosphorus, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of total phosphorus for the two data sets, and (**C**) a map of the sites with the indicated concentration of total phosphorus for the 2007 edition.

Flow-weighted mean concentrations of total phosphorus were estimated for 53 streams in the *Urban and Suburban* ecosystem. The distribution of sites within the four class bins of concentration of total phosphorus was fairly even, with a slightly higher percentage of sites in the lowest class bin of less than 0.1 mg/L (fig. 31). Compared to 2002, the 2007 analysis showed a higher percentage of sites with a mean concentration of total phosphorus greater than 0.5 mg/L.

A comparison of the mean concentrations of total phosphorus for streams draining *Farmlands, Urban and Suburban*, and *Forest* ecosystems is shown in (fig. 32). The *Forest* ecosystem was not a separate indicator in the Heinz Center report; however, it is included in the ecosystem comparison. Streams draining *Forest* ecosystems (109 sites) generally had concentrations of total phosphorus less than 0.1 mg/L, the lowest concentrations among the three ecosystems (fig. 32). A comparison of the 2002 and 2007 analyses show similar results (*table 1*; fig. 32).

Phosphorus in Large Rivers

Phosphorus in Large Rivers is an indicator of the *Freshwater* ecosystem, which includes streams and rivers, lakes and ponds, reservoirs, freshwater wetlands, ground water, and riparian areas. This ecosystem is considered separately from the other ecosystems by the Heinz Center because the indicators reflect the health of all other ecosystems.

The *Phosphorus in Large Rivers* indicator reports the time-weighted mean concentration of total phosphorus in rivers with long-term mean flows exceeding 1,000 cubic feet per second (ft^3/s). The large-river data set was restricted to rivers having long-term streamflow and water-quality data and was retrieved from the USGS NWIS data base (Charles G. Crawford, U.S. Geological Survey, written commun., 2007). To be consistent with the 2002 Heinz Center report and to facilitate evaluation of trends, time-weighted means were calculated for two, 5-year periods: water years 1996–2000 and 2001–05 (*appendix 24*). These 5-year periods start approximately at the end of the period included in the 2002 analysis (1991–96).

Data were available for 86 sites. The median number of samples per site was 49 for 1996–2000 and 56 for 2001–05 (the range was 16 to more than 100). Because of the large size of the river basins selected for this indicator, these watersheds generally have more diverse land uses than the watersheds selected for the *Farmlands*, *Forest*, and *Urban and Suburban* ecosystem indicators. Thus, these samples represent the integrating influences of many different land uses.

Only those large river sampling sites at which at least four samples per year were collected (during all seasons of the year) in at least 4 of the 5 years for each 5-year period were used for this indicator to reduce potential bias caused by uneven sampling in certain seasons and years. Although this is a small number of samples per year, Crawford (2004) has shown that for selected pesticides, four samples per year collected seasonally can provide a reasonably accurate time-weighted mean-annual concentration in large rivers. These findings should hold true for concentrations of total phosphorus in large rivers as well, because both total phosphorus and most pesticides typically have a pronounced seasonal pattern. Mean-annual concentrations of total phosphorus were reported in four class bins: below 20 µg/L, 20 to less than 50 µg/L, 50 to less than 100 µg/L, and 100 µg/L or more. The mean-annual concentrations of total phosphorus during the two 5-year periods were similar, with more than 70 percent of sites having mean concentrations above 50 µg/L (fig. 33). The period 1996–2000 had a slightly higher frequency of sites with a mean concentration less than 20 µg/L than the latter period. The period 2001–05 had a slightly higher frequency of sites with a mean concentration above 100 µg/L than did the earlier period.

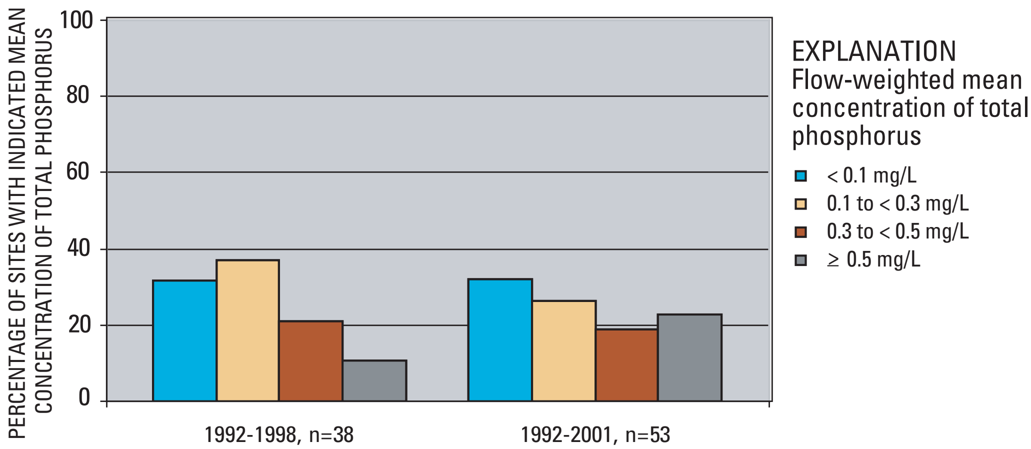
The major difference between the 2002 and 2007 analysis of total phosphorus in large rivers was the inclusion in 2007 of two different time periods of analysis. In the 2002 analysis, 140 sites were used to calculate mean-annual concentrations of total phosphorus, sampling sites were restricted to those rivers with mean-annual flows exceeding 1,000 ft^3/s, at which at least 20 measurements of flow had been made over the course of 2 years. For the 2007 analysis, sites were restricted to rivers that had at least four measurements per year collected during all seasons of the year in at least 4 of the 5 years for each time period (1996–2000 and 2001–05).

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF TOTAL PHOSPHORUS			
	< 0.1 mg/L	0.1 to < 0.3 mg/L	0.3 to < 0.5 mg/L	≥ 0.5 mg/L
2002 report (1992-1998); 38 sites	31.6	36.8	21.1	10.5
2007 report (1992-2001); 53 sites	32.1	26.4	18.9	22.6

[1]Percentages may be rounded to equal 100

B



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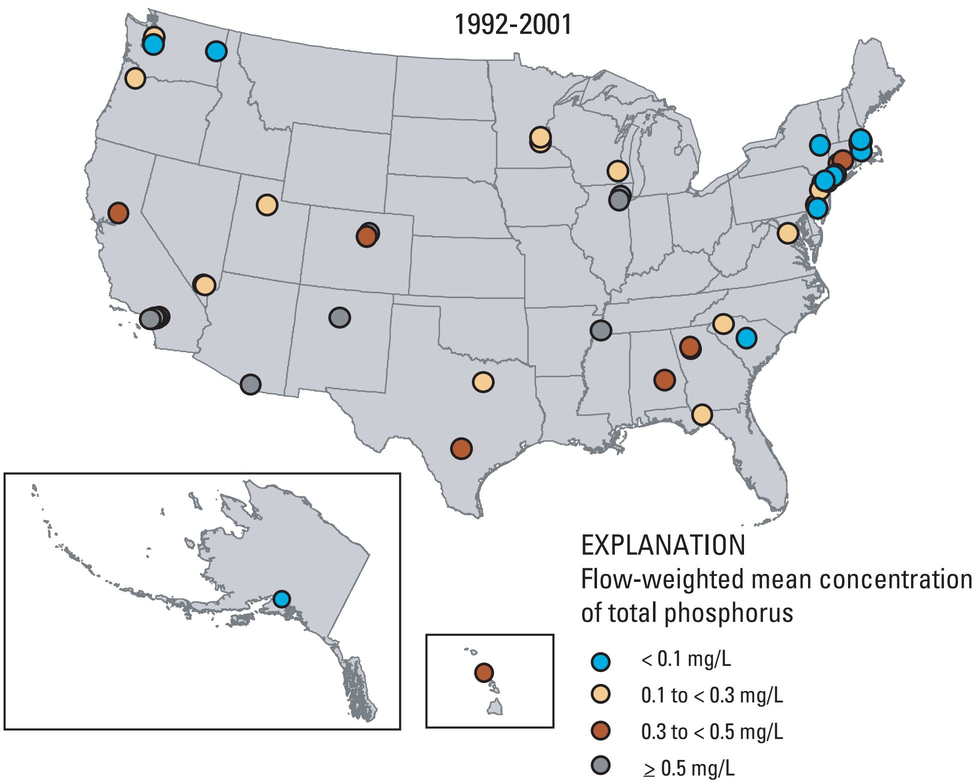


Figure 31. Flow-weighted mean concentration of total phosphorus in streams draining the *Urban and Suburban* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of total phosphorus, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of total phosphorus for the two data sets, and (**C**) a map of the sites with the indicated concentration of total phosphorus for the 2007 edition.

SAMPLING PERIOD	ECOSYSTEM	NUMBER OF SITES	PERCENTAGE OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF TOTAL PHOSPHORUS			
			< 0.1 mg/L	0.1 to < 0.3 mg/L	0.3 to < 0.5 mg/L	≥ 0.5 mg/L
2002 report (1992-1998)	Farmlands	107	27.1	41.1	16.8	15.0
	Forest	39	89.7	7.7	0.0	2.6
	Urban and Suburban	38	31.6	36.8	21.1	10.5
2007 report (1992-2001)	Farmlands	129	15.5	46.5	24.8	13.2
	Forest	109	84.4	14.7	0.9	0.0
	Urban and Suburban	53	32.1	26.4	18.9	22.6

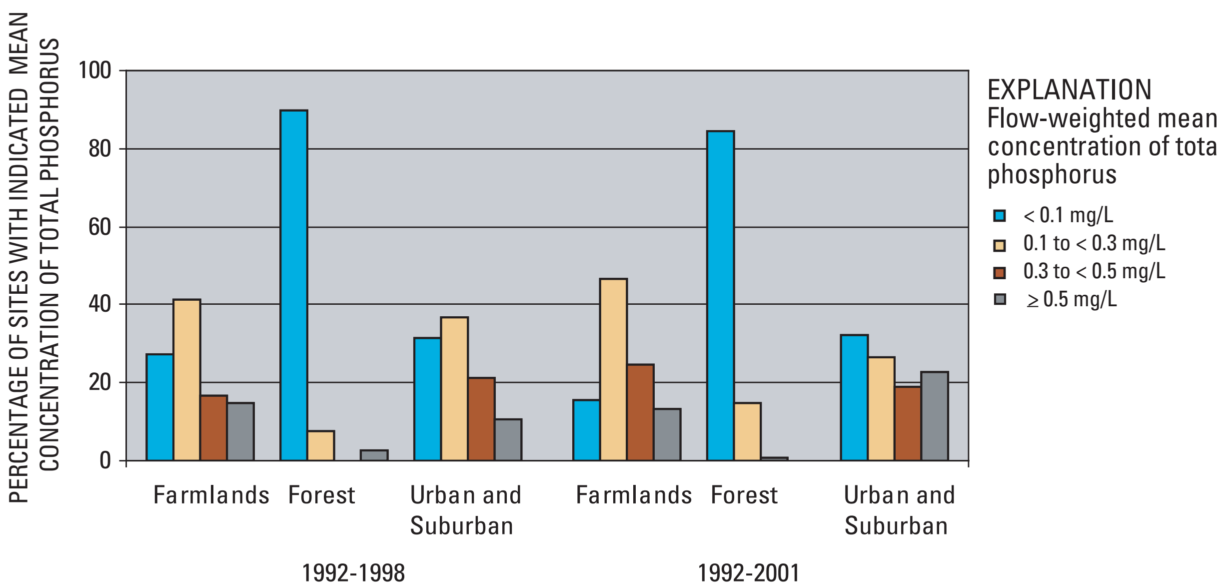


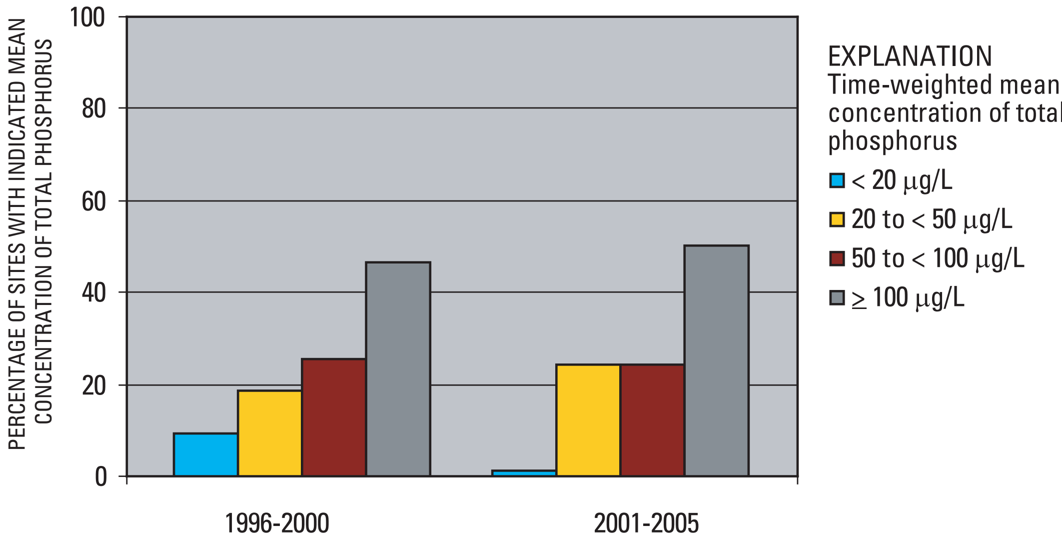
Figure 32. Comparison of mean concentration of total phosphorus in streams by ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2001) editions of the Heinz Center report.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED TIME-WEIGHTED MEAN CONCENTRATION OF TOTAL PHOSPHORUS			
	< 20 μg/L	20 to < 50 μg/L	50 to < 100 μg/L	≥ 100 μg/L
2007 report (1996-2000); 86 sites	9.3	18.6	25.6	46.5
2007 report (2001-2005); 86 sites	1.2	24.4	24.4	50.0

[1]Percentages may be rounded to equal 100

B



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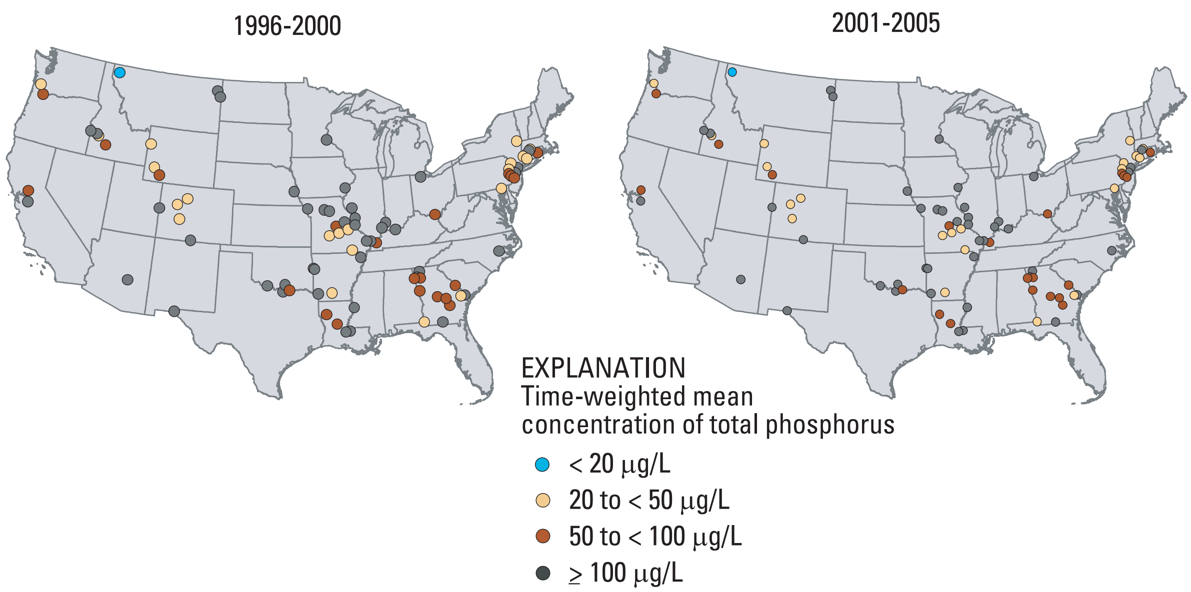


Figure 33. Time-weighted mean concentration of total phosphorus in large rivers compiled for the 2007 edition of the Heinz Center report for the 1996–2000 and 2001–2005 time periods, showing (**A**) the percentage of sites with the indicated concentration of total phosphorus, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of total phosphorus, and (**C**) a map of the sites with the indicated concentration of total phosphorus for the two data sets.

Nitrate in Ground Water

The indicators for the concentration of nitrate in ground water in the Heinz Center report included the *Farmlands* and *Grasslands and Shrublands* ecosystems. All of the data on nitrate in ground water were provided by Bernard T. Nolan (U.S. Geological Survey, written commun., 2006) (*appendix 25*). The concentration comparison by ecosystem includes the *Forest* and *Urban and Suburban* ecosystems. Specifically, the indicator reports on the percentages of wells with concentrations of nitrate in one of four class bins: less than 2 mg/L, 2 to less than 6 mg/L, 6 to less than or equal to 10 mg/L, and more than 10 mg/L.

Water samples were collected primarily from monitoring wells and low-capacity domestic wells using procedures that resulted in a sample representative of water in the aquifer (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 processing and preservation of ground-water samples can be found in Koterba and others (1995). Concentrations of nitrate were determined in ground-water samples. Fishman (1993) and Patton and Truitt (1992) describe analytical methods used for determining nitrate in water. No standardized censoring level or background concentration was used in analyzing concentrations of nitrate in ground water. Nitrate data were reviewed to check for obvious outliers and inconsistent results (*appendix 14*).

Farmlands

Water samples were collected from 1,423 wells throughout the conterminous U.S. by the NAWQA Program from 1992–2003 (*appendix 14* and *appendix 25*). All wells were selected to represent shallow ground water underlying areas of predominantly agricultural land use. All samples were collected and analyzed by the USGS according to the methods described in Gilliom and others (1995). To the extent practicable, sampling sites were selected randomly so as to be representative of the agricultural land use in the area. Land use in the vicinity of each well was characterized according to procedures described in Gilliom and Thelin (1997). Water samples were collected from shallow wells screened near the top of the water table and where land use within a 500-meter radius of the well was primarily agricultural.

Concentrations of nitrate were less than 2 mg/L in samples from about 42 percent of wells (fig. 34). Samples from approximately 38 percent of wells had concentrations of nitrate between 2 mg/L and less than or equal to 10 mg/L, and the samples from about 20 percent of wells had concentrations of nitrate more than 10 mg/L (the MCL for nitrate is 10 mg/L). These results are within a few percentage points of the results from the 2002 analysis (1992–98 data set) (fig. 34).

Grasslands and Shrublands

Water samples from 219 wells sampled from 1994–2003 by the USGS NAWQA Program were used to develop the *Nitrate in Grasslands and Shrublands Groundwater* indicator (*appendix 25*). All wells used for this indicator of nitrate in grassland ground water were sampled as part of NAWQA Major Aquifer Studies. Wells in grassland areas were defined as those meeting the following land-use criteria within a 500-meter radius buffer surrounding the well: greater than 50 percent grassland, less than or equal to 5 percent urban land use, and less than or equal to 25 percent agricultural land use. The total land area in the *Grasslands and Shrublands* ecosystem was determined by adding the land area for each of the National Land Cover Data (NLCD) land cover categories: grassland (NLCD code 71), shrubland (NLCD code 51), and bare rock (NLCD code 31) (U.S. Geological Survey, 2002).

Concentrations of nitrate less than 2 mg/L were detected in about 74 percent of wells (fig. 35). Samples from about 25 percent of wells had concentrations of nitrate between 2 and less than or equal to 10 mg/L. Only about 2 percent of wells had concentrations of nitrate greater than 10 mg/L. No indicator of nitrate in ground water beneath areas of grassland was available in the 2002 report.

Concentrations of nitrate in ground water underlying *Farmlands, Forest, Urban and Suburban*, and *Grasslands and Shrublands* ecosystems are compared in figure 36. Concentrations of nitrate less than 2 mg/L ranged from 42 percent of ground-water samples underlying *Farmlands* ecosystems to 94 percent in ground-water samples underlying *Forest* ecosystems. This is similar to the percentages indicated in the 2002 report (1992–98 data set). Concentrations of nitrate greater than or equal to 2 mg/L and less than 10 mg/L ranged from about 6 percent of ground-water samples from the *Forest* ecosystems to about 38 percent of ground-water samples underlying urban areas. Again, this is similar to the percentages indicated in the 2002 report.

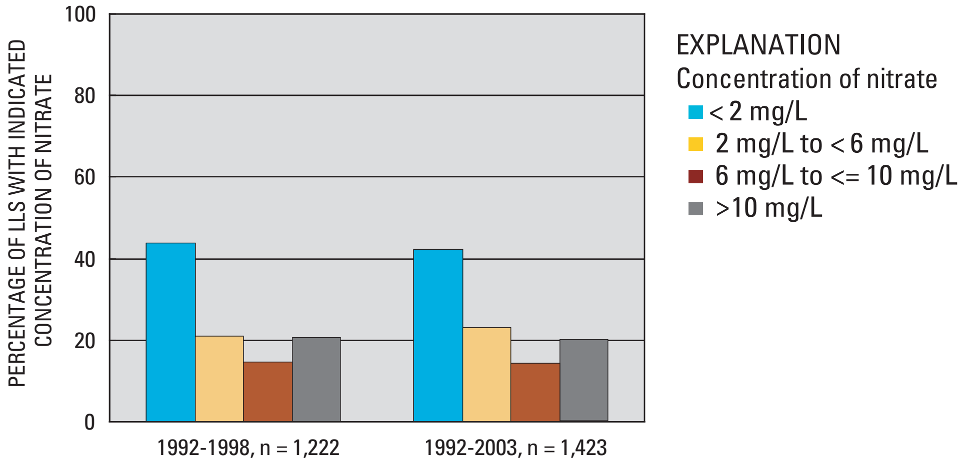
Other than differences in the number of wells sampled, there were no other major differences in the percentage of sites within each class bin between the 2002 and 2007 reports for the *Farmland*, *Forest*, and *Urban and Suburban* ecosystems. Nitrate in ground water of the *Grasslands and Shrublands* ecosystem was not evaluated in the 2002 report because of the lack of data.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED CONCENTRATION OF NITRATE			
	< 2 mg/L	2 to < 6 mg/L	6 to <= 10 mg/L	> 10 mg/L
2002 report (1992-1998); 1,222 sites	43.8	21.0	14.6	20.6
2007 report (1992-2003); 1,423 sites	42.2	23.0	14.6	20.2

[1]Percentages may be rounded to equal 100

B



C

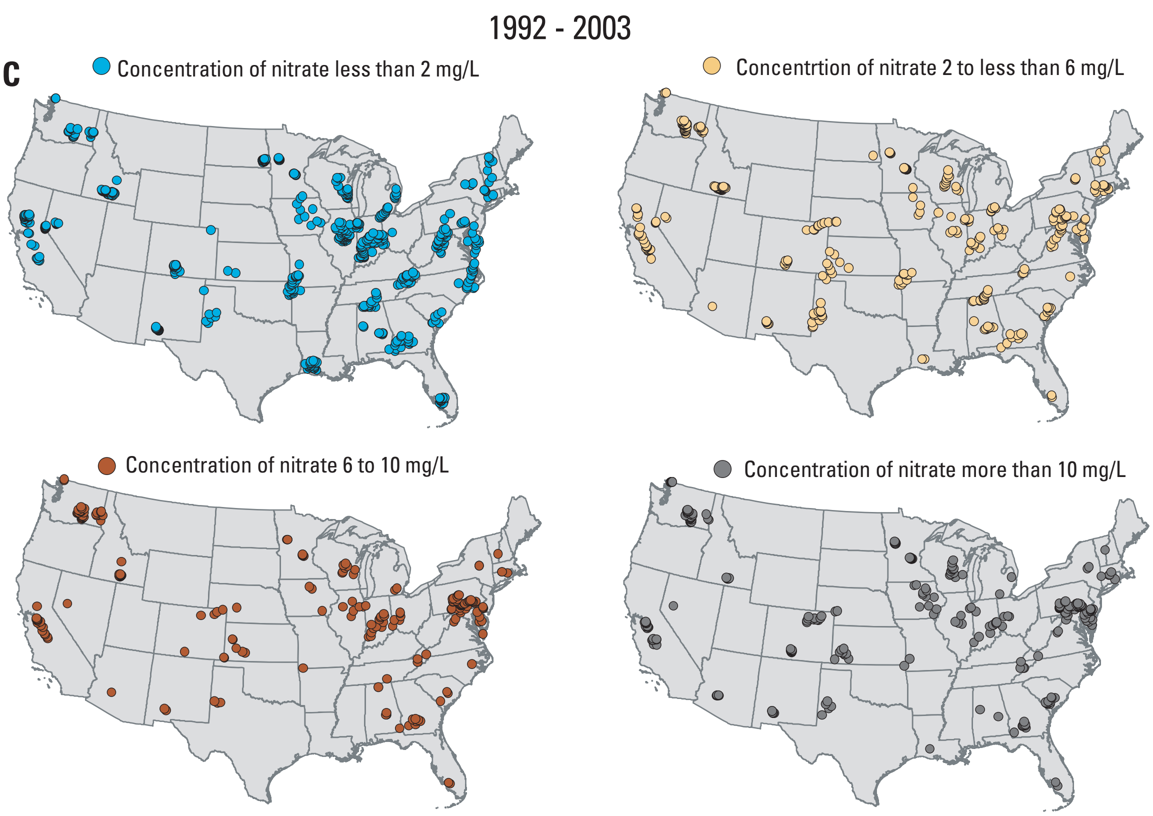


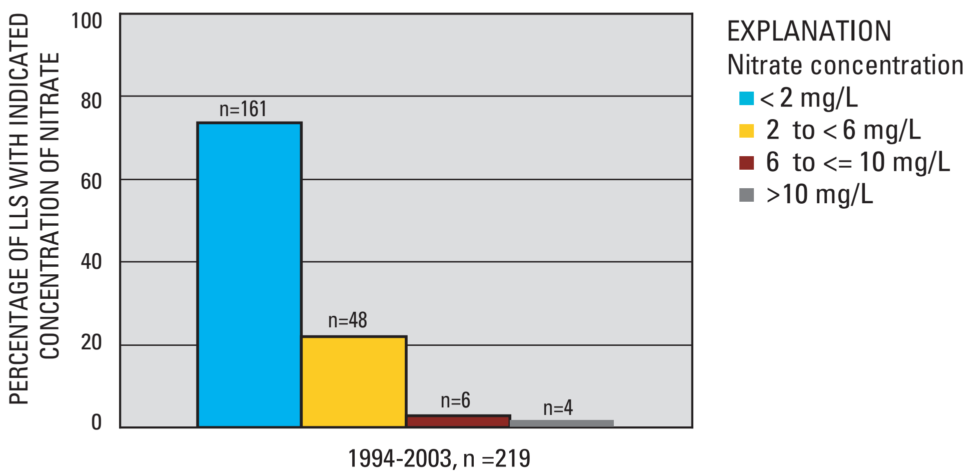
Figure 34. Concentration of nitrate in ground water of the *Farmlands* ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2003) editions of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of nitrate, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of nitrate for the two data sets, and (**C**) a map of the sites with the indicated concentration of nitrate for the 2007 edition.

A

SAMPLING PERIOD AND NUMBER OF SITES	PERCENTAGE[1] OF SITES WITH INDICATED CONCENTRATION OF NITRATE			
	< 2 mg/L	2 to < 6 mg/L	6 to <= 10 mg/L	> 10 mg/L
2007 report (1994-2003); 219 sites	73.5	21.9	2.8	1.8

[1]Percentages may be rounded to equal 100

B



C

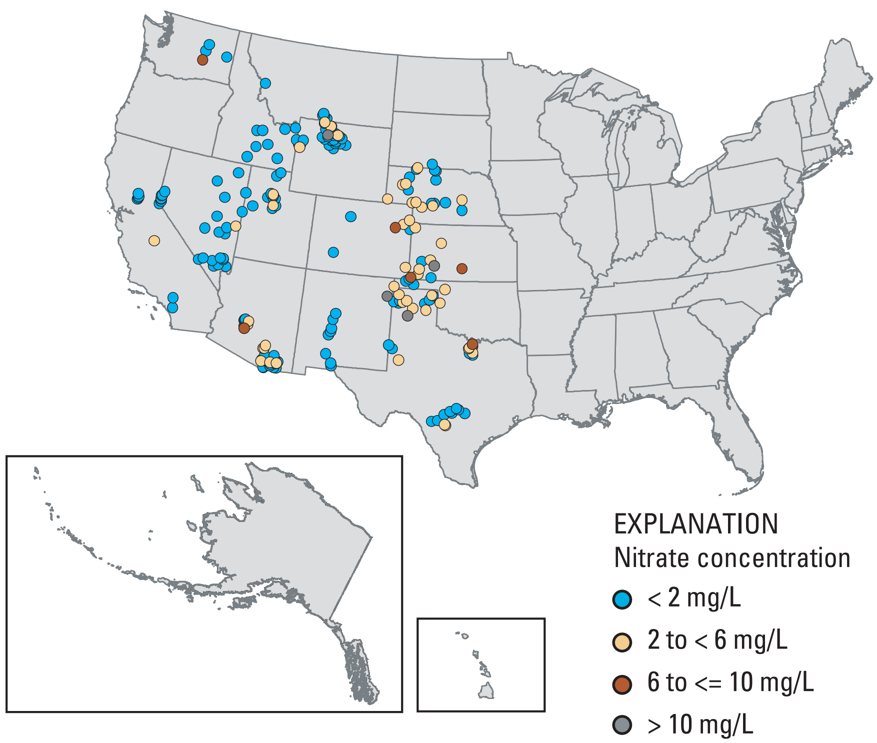


Figure 35. Concentration of nitrate in ground water of the *Grasslands and Shrublands* ecosystem compiled for the 2007 (1994–2003) edition of the Heinz Center report, showing (**A**) the percentage of sites with the indicated concentration of nitrate, (**B**) a graphical comparison of the percentage of sites with the indicated concentration of nitrate, and (**C**) a map of the sites with the indicated concentration of nitrate for the 2007 edition.

SAMPLING PERIOD	ECOSYSTEM	NUMBER OF SITES	PERCENTAGE OF SITES WITH INDICATED FLOW-WEIGHTED MEAN CONCENTRATION OF NITRATE			
			< 2 mg/L	2 to < 6 mg/L	6 to <= 10 mg/L	> 10 mg/L
2002 report (1992-1998)	Farmlands	1,222	43.8	21.0	14.6	20.6
	Forest	31	93.5	6.5	0.0	0.0
	Urban and Suburban	639	58.5	30.4	8.8	2.3
2007 report (1992-2003)	Farmlands	1,423	42.2	23.0	14.6	20.2
	Forest	34	94.1	5.9	0.0	0.0
	Urban and Suburban	861	58.1	28.3	10.2	3.4
	Grasslands and Shrublands	219	73.5	21.9	2.8	1.8

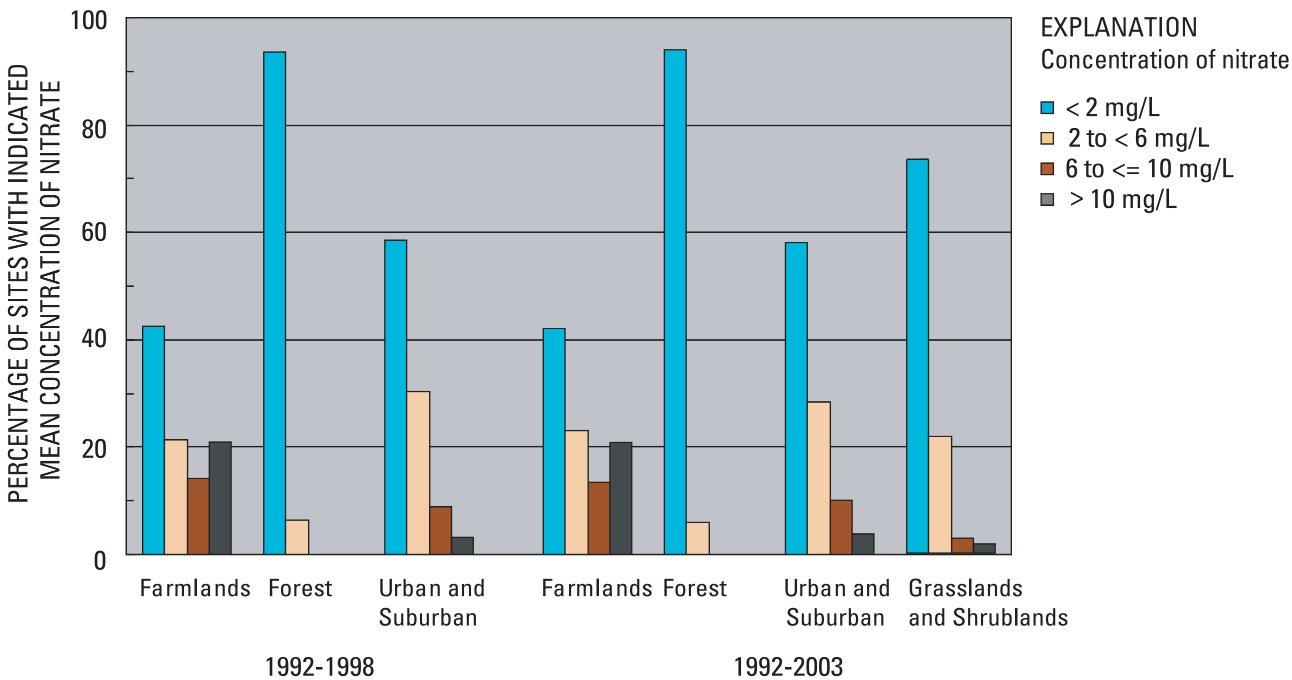


Figure 36. Comparison of mean concentration of nitrate in ground water by ecosystem compiled for the 2002 (1992–1998) and 2007 (1992–2003) editions of the Heinz Center report.

Summary

The USGS provided data and interpretations for a number of the water-quality indicators included in the Heinz Center's 2007 report on *The State of the Nation's Ecosystems*. The Heinz Center uses key indicators to report on the condition and use of ecosystems in the U.S. The USGS provided water-quality and streamflow data to the Heinz Center for documentation of these indicators including: *Core National* indicators and indicators for the *Farmlands*, *Forest*, *Freshwater*, *Grasslands and Shrublands*, and *Urban and Suburban* ecosystems. Data provided by the USGS for the *Core National* indicators included the delivery of nitrogen to streams and rivers (the *Movement of Nitrogen* indicator), and a national aggregation of water-quality data for streams, bed sediment, fish tissue, and ground water for the indicators of *Chemical Contamination*. Information on pesticides, nutrients, semivolatile organic compounds, total polychlorinated biphenyls, and trace elements were analyzed for frequency of detection and exceedance of benchmarks for the indicators of *Chemical Contamination*. Pesticide and nutrient data were analyzed in terms of frequency of detection, exceedance of benchmarks, and concentration in samples for indicators in the *Farmlands*, and *Urban and Suburban* ecosystems, and nutrient data were analyzed in terms of concentration in samples for indicators in the *Forest*, and *Grasslands and Shrublands* ecosystems. Concentrations of total phosphorus and streamflow were used to develop the *Phosphorus in Large Rivers* indicator of the *Freshwater* ecosystem.

The water-quality data used for the *Chemical Contamination* and indicators in the *Farmlands*, *Forest*, *Grasslands and Shrublands*, and *Urban and Suburban* ecosystems were collected from 1992 through 2003 as part of the USGS NAWQA Program. NAWQA data were collected throughout the U.S. in 51 major hydrologic systems referred to as study units. Streamflow and nutrient data were collected by USGS National Stream Water Quality Accounting Network and the Federal–State Cooperative Programs from 1996 through 2005 for the indicator *Delivery of Total Nitrogen to Streams and Rivers* and from 1955 through 2004 for the indicator *Nitrate Discharged to Coastal Waters*. Both of these individual indicators were used to develop the *Core National* indicator for the *Movement of Nitrogen*. Water-quality and streamflow data collected by the USGS from 1996 through 2005, and retrieved from the USGS National Water Information System, were used to develop the *Phosphorus in Large Rivers* indicator.

This report also documents changes to the data sets and interpretations between the 2002 and 2007 editions of the Heinz Center's report. Where possible, results from the 2002 analyses were included in the illustrations to show the changes that have occurred as a result of changing sample size, changes in the data selection or interpretations, and changes to the quantity and values of human-health and aquatic-life benchmarks. For some analyses, the 2007 suite of benchmarks has been applied to the 2002 data sets to illustrate how the frequency of benchmark exceedances have changed as a result of the new benchmark values rather than as a result of changing sample size.

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The authors are grateful for the technical reviews provided by David C. Reutter and Anne F. Choquette, 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. Charles G. Crawford provided National Water Information System retrievals for the comprehensive data sets used for the *Movement of Nitrogen* indicator and the *Total Phosphorus in Large Rivers* indicator. JoAnn M. Gronberg provided trace element data for ground-water samples. Stephen J. Kalkhoff wrote statistical scripts for the *Chemical Contamination* indicator of the 2002 Heinz Center report. These scripts were easily modified and used for counting detections and exceedances of contaminants in stream water, streambed sediment, and fish tissue for the 2007 Heinz Center report. Moon H. Kim retrieved total PCBs data from NAWQA's Data Warehouse for the 700 fish-tissue samples that had organochlorine pesticides data. Jeffrey D. Martin provided several data sets for pesticides in stream water related to work that was done by the Pesticides National Synthesis Project. Martin also provided data for nitrate samples in streams that corresponded to the pesticide samples. Members of the Nutrients National Synthesis Project provided data related to NAWQA Cycle I stream sites. David K. Mueller and Neil M. Dubrovsky provided land-use classifications for all of the stream-water sampling sites with nutrient data. Gregory M. Clark provided calculations of the acute ammonia criterion and the chronic ammonia criterion for all ammonia samples used in the section on *Chemical Contamination* in stream water. Bernard T. Nolan provided nutrient data for ground-water samples.

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Appendixes 1–25

1. Delivery of total nitrogen to streams and rivers from major watersheds: LOADEST model input parameters and model output total nitrogen yields
2. Annual nitrate load estimates for the Mississippi River for 1968–2004
3. Annual nitrate load estimates for the Mississippi River, Susquehanna River, St. Lawrence River and Columbia River
4. List of NAWQA Cycle 1 stream-water sampling sites with land-use classification used for the Heinz Center's report on *The State of the Nation's Ecosystems*
5. Water-quality data for pesticides and nutrients in stream-water samples collected by NAWQA
6. List of analytes sampled in stream water with human-health and aquatic-life benchmarks
7. Contaminant occurrence in national, farmland, and urban and suburban streams
8. Streambed-sediment quality data for organochlorine pesticide compounds, total PCBs, SVOCs, and trace elements in samples collected by NAWQA
9. List of analytes sampled in streambed sediment with aquatic-life benchmarks
10. Contaminant occurrence in streambed sediment
11. Fish-tissue data for organochlorine pesticide compounds and total PCBs in whole-fish samples collected by NAWQA
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13. Contaminant occurrence in fish tissue
14. Water-quality data for nutrients in ground-water samples collected by NAWQA
15. Compilation of water-quality data for contaminants in National ground water
16. List of analytes sampled in ground water with human-health benchmarks
17. Pesticide and nitrate exceedances of human-health benchmarks in stream water and time-weighted mean pesticide concentrations in stream water.
18. Aquatic-life criteria for ammonia, with exceedances of aquatic-life benchmarks for pesticides in streams
19. Exceedance of bed-sediment benchmarks for the protection of benthic aquatic organisms
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21. Water-quality data for trace elements in ground-water samples collected by NAWQA
22. Compilation of water-quality data for pesticides in farmlands ground water
23. Water-quality data for nitrate and total phosphorus in stream-water samples collected by NAWQA
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25. Compilation of water-quality data for nitrate in ground water