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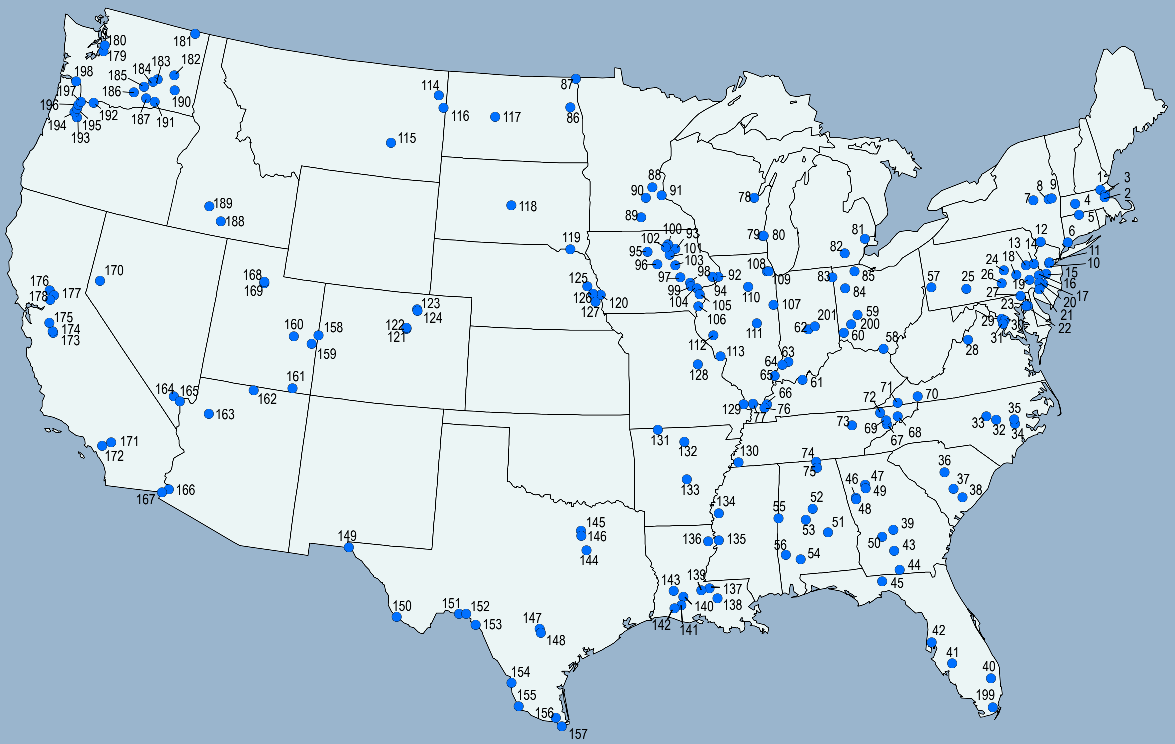
Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in Streams of the United States, 1992–2006



Scientific Investigations Report 2009–5062

U.S. Department of the Interior
U.S. Geological Survey

Cover image: Locations of stream-water sites selected for trend analysis in this study. (See figure 1 and accompanying text in report.)

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By Jeffrey D. Martin

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KEN SALAZAR, Secretary

U.S. Geological Survey
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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 groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, 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. During 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 groundwater. 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.

Matthew C. Larsen

Associate Director for Water

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Abbreviations

Pesticide concentrations are given in micrograms per liter (µg/L). Pore sizes of filters are given in micrometers (µM).

Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in Streams of the United States, 1992–2006

By Jeffrey D. Martin

Abstract

This report provides a water-quality data set of 44 commonly used pesticides and 8 pesticide degradates suitable for a national assessment of trends in pesticide concentrations in streams of the United States. Water-quality samples collected from January 1992 through August 2006 at stream-water sites of the U.S. Geological Survey National Water-Quality Assessment Program and the National Stream Quality Accounting Network Program were compiled, reviewed, selected, and prepared for trend analysis as described in this report. Samples analyzed at the U.S. Geological Survey National Water Quality Laboratory by a gas chromatography/mass spectrometry analytical method were the most extensive in time and space and were selected for national trend analysis. The selection criteria described in the report produced a trend data set of 16,869 pesticide samples at 201 stream and river sites.

Introduction

A primary goal of the National Water-Quality Assessment (NAWQA) Program is to assess and understand long-term trends in the quality of the Nation's streams and rivers, herein collectively referred to as streams. A key aspect of water quality that presents unique data-analysis problems for trend assessment is pesticide concentrations in stream water. Selective analyses to date (2009) have included assessment of trends in diazinon and other insecticides in urban streams of the northeastern and midwestern United States (Phillips and others, 2007) and of trends in major herbicides in agricultural streams of the Corn Belt (Gilliom and others, 2006, p. 132, 133). Data from NAWQA pesticide monitoring, supplemented by data from the National Stream Quality Accounting Network (NASQAN) Program, are now sufficiently extensive for a national assessment of trends in pesticide concentrations in streams. These data, however, require a number of specific preparation steps to address potential biases from differences in sampling strategies among sites, including different sampling periods and intensities, and changes over time in performance of the analytical method and changes in data-reporting practices. This report describes the steps taken to prepare data for trend analysis and provides the resulting trend data set.

Purpose and Scope

This report describes the procedures and criteria used to compile, review, select, and prepare pesticide-concentration data for trend analysis. The data are from water samples collected from January 1992 through August 2006 at stream-water sites of the NAWQA and NASQAN Programs. Water samples were analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) by a gas chromatography/mass spectrometry (GCMS) method for as many as 44 commonly used pesticides and 8 pesticide degradates. Stream-water sites with three or more years of data, each with six or more samples per year, were selected for pesticide trend analysis. These and other selection criteria described in the report yielded a data set of 16,869 pesticide samples at 201 sites that is suitable for a national assessment of trends in pesticide concentrations in streams of the United States.

Monitoring Programs for Pesticides

The NAWQA Program, which began monitoring pesticides in 1992, and the NASQAN Program, which began monitoring pesticides in 1995, are national USGS water-quality monitoring programs that collect data suitable for a national assessment of trends in pesticide concentrations in the Nation's streams.

National Water-Quality Assessment Program

Monitoring of streams for the NAWQA Program initially (1992–2001) focused on assessing water-quality conditions in 51 of the Nation's river basins and aquifers (referred to as Study Units). The 51 Study Units were assessed on a rotational schedule—20 Study Units during 1992–1995, 16 during

1996–1998, and 15 during 1998–2001 (Gilliom and others, 2006, p. 32). The number of stream-water sites monitored and the number of samples collected also followed a rotational schedule. After a 3- to 4-year period of active assessment, Study Units began a 6-year period of reduced scope, low-level monitoring until the next period of active assessment (Gilliom and others, 1995, p. 2–5).

"Pesticide samples" (water samples for analysis of pesticides) generally were collected at each site using a combination of fixed-interval and high-flow sampling (Gilliom and others, 1995, p. 16). Fixed-interval sampling (also called fixed-frequency sampling) is the collection of water samples at regular intervals of time and results in a timeseries of samples where the number of days between samples is approximately the same. For the fixed-interval sampling, two to four samples generally were collected each month during seasonal periods of high use and runoff of pesticides and one to two samples were collected each month during other periods. The intensive seasonal sampling period typically ranged from 3 to 9 months (Gilliom and others, 1995, p. 17). Additional samples were collected during periods of high streamflows. High-flow sampling is intended to supplement fixed-interval sampling by targeting hydrologic conditions that are important, but occur infrequently and, therefore, are unlikely to be sampled solely based on fixed-interval sampling. Some stream-water sites were intensively sampled for only 1 year, whereas most stream-water sites had multiple years of intensive data collection for pesticides. High-flow sampling generally was discontinued during the 6-year period of low-level monitoring that followed the 3- to 4-year period of active assessment. Design of the NAWQA Program was revised in 2001 (Gilliom and others, 2001); changes included a reduction in the number of long-term monitoring sites and an increased emphasis on regional assessments. Information on the USGS NAWQA Program is available at *http://water.usgs.gov/nawqa/.*

National Stream Quality Accounting Network Program

The NASQAN Program was redesigned in 1995 to estimate the mass flux of pesticides and other constituents at 41 monitoring sites in the drainage basins of four large river systems: the Mississippi, the Rio Grande, the Columbia, and the Colorado. The focus on estimating mass flux enables (1) a comparison of pesticide inputs and river outputs, (2) identification of sources and sinks of pesticides within subbasins of the drainage network, and (3) an estimate of mass loadings to receiving waters (Hooper and others, 2001, p. 1090). Monitoring sites were chosen at major nodes within the river basin primarily based on increased discharge, the location of large reservoirs that serve as sinks, and where tributaries were known or expected to have a disproportionate affect on mass flux (U.S. Geological Survey, 2006).

Pesticide samples generally were collected at each site using a combination of fixed-interval and high-flow sampling (Hooper and others, 2001, p. 1093). Similar to the NAWQA Program, the frequency of fixed-interval sampling typically changed seasonally, with more frequent samples during the peak pesticide-runoff periods. Sites located downstream of major reservoirs had a reduced frequency of sampling (typically 6 samples per year), whereas sites on free flowing reaches had 8 to 12 fixed-interval samples per year and 0 to 4 high-flow samples per year (Hooper and others, 2001, p. 1093; U.S. Geological Survey, 2006). The NASQAN Program sampling strategy was revised in 2000; changes included reduced monitoring in the Columbia and Colorado River Basins. Information on the USGS NASQAN Program is available at *http://water.usgs.gov/nasqan/.*

Methods of Sample Collection and Analysis

Although study objectives and sampling frequencies of the NAWQA and NASQAN Programs differ, both programs routinely collect water samples for pesticide analyses at a network of stream-water sites throughout the United States. Water samples are collected and processed using similar equipment and procedures, and pesticides and pesticide degradates (hereafter referred to as "pesticides" in this report) are analyzed by the same method and laboratory.

Sample Collection, Processing, and Field Quality-Control Program

Flow-weighted, depth- and width-integrated water samples for the analysis of pesticides were collected using Teflon-coated isokinetic samplers and processed following standard USGS methods (U.S. Geological Survey, variously dated; Shelton, 1994; Edwards and Glysson, 1999). Most water samples were collected from bridges or by wading but samples from large rivers were collected from boats or cableways. All sample-collection and processing equipment that came in contact with sample water was constructed of Teflon, glass, aluminum, or stainless steel. Equipment was cleaned with a dilute solution of phosphate-free detergent and rinsed with deionized water and pesticide-grade methanol. Water samples were filtered using pre-combusted glass-fiber filters with a nominal 0.7-µm pore diameter to remove suspended particulate matter and collected in baked amber glass bottles. Filtered samples were placed on ice in coolers and shipped to the NWQL in Denver, Colorado, for pesticide analysis.

The quality of the stream-water pesticide data collected for the NAWQA Program was monitored using quality-control (QC) procedures presented in Mueller and others (1997). The field QC program included the collection of field blank water samples to assess potential contamination, replicate water samples to assess variability, and field matrix spikes to assess bias from the analytical method, potential pesticide degradation, or matrix effects. Contamination in field blank water samples is summarized in Martin and others (1999). Variability in replicate water samples is summarized in Martin (2002). Pesticide recovery in laboratory reagent spikes and field matrix spikes is summarized in Martin (1999). The NASQAN Program followed similar QC procedures and collected the same types of field-submitted QC samples. The NASQAN QC program is summarized in Hooper and others (2001, p. 1095).

Pesticides, Analytical Method, Reporting Levels, and Laboratory Quality-Control Programs

The NAWQA Program has used many analytical methods and multiple laboratories to measure a wide variety of pesticides in water samples whereas the NASQAN Program primarily has used one analytical method and laboratory. Trend analysis of pesticide data analyzed by different analytical methods or different laboratories has the potential to identify trends caused solely by differences in the performance of the analytical methods. The water-quality data review and selection procedures described in subsequent sections of this report ultimately determined that only pesticide data from a single laboratory and analytical method commonly used by both programs were sufficiently extensive in time and space for a national assessment of trends (appendix 1). This gas chromatography/mass spectrometry analytical method (referred to as "GCMS" in this report) is described in this section.

All water-quality samples selected for trend analysis were analyzed by NWQL using the GCMS method. Pesticides are isolated from filtered water samples by solid-phase extraction and analyzed by capillary-column GCMS with selected-ion monitoring (Zaugg and others, 1995; Lindley and others, 1996; Madsen and others, 2003). The GCMS method provides low-level analyses of as many as 44 commonly used pesticides and 8 pesticide degradates[1] (table 1). The pesticide acetochlor was added to the GCMS method in 1994 (Lindley and others, 1996) and the pesticide fipronil and four degradates of fipronil were added to the GCMS method in 1999 (Madsen and others, 2003).

The GCMS analytical method does not have specified "detection limits" for each pesticide analyte. Compounds detected and conclusively identified by retention time and spectral characteristics are quantified and reported (Zaugg and others, 1995, p. 19-21). Nondetections of pesticides (analyses that do not meet identification criteria based on retention time and spectral characteristics) are reported as less than the "routine" reporting level (for example: < 0.005 µg/L). A small number of samples have "matrix effects" or other analytical difficulties that interfere with the measurement of pesticide retention time or spectral characteristics. Under conditions of interference, pesticides (1) cannot be identified/detected if they are present at concentrations less than the level of interference and (2) are reported as nondetections less than a "raised" reporting level (for example: < 0.03 µg/L; six times greater than the routine reporting level). Nondetections at raised reporting levels indicate the maximum possible concentration of the pesticide based on the magnitude of the interference. Raised reporting levels always are greater than routine reporting levels. Raised reporting levels are sample-specific and determined by the magnitude of the interference. Routine reporting levels are the same for all samples (for a given time period) that are not affected by interference.

The types and numerical values of routine reporting levels used to report nondetections analyzed by GCMS have changed over time. Prior to October 2000, GCMS reporting levels were minimum reporting levels (MRLs) that were statistically determined as a function of the standard deviation of seven replicate low-level measurements (Zaugg and others, 1995, p. 21–33; U.S. Geological Survey, 1994; Oblinger Childress and others, 1999, p. 2, 3). MRLs were assessed only during the initial stages of method development and were not reassessed annually. MRLs for a pesticide typically did not change during the pre-October 2000 period. Beginning in October 2000, GCMS MRLs were changed to laboratory reporting levels (LRLs) that were statistically determined as a (more complex) function of the standard deviation of at least 24 replicate low-level measurements. LRLs are reassessed annually, and LRLs for a single pesticide typically did change during the post-October 2000 period.

A concentration value of approximately three times the standard deviation of the replicate low-level measurements used to determine the LRL is known as the "long-term method detection level" (LT-MDL). The maximum value of the LT-MDL for water years 1994–2006 (table 1) is the concentration value used in a later section of this report to "reassign" the temporally inconsistent concentration value for routine nondetections to a uniform, temporally consistent concentration value for trend analysis. The types of reporting levels used by NWQL, procedures used to set reporting levels, and considerations for data analysis are discussed in Oblinger Childress and others (1999).

As previously explained, low-level detections of pesticides analyzed by GCMS are not censored at the reporting level. All detections meeting identification criteria are quantified and reported, although concentrations less than the routine reporting level are reported with an "E" remark to indicate that the concentration—but not the presence—is estimated.

[1]The actual number of pesticides analyzed by the GCMS method depends on the NWQL analytical "schedule" used to request a pesticide analysis. A schedule is a suite of pesticides to be measured by one or more analytical methods. Four NWQL schedules used the GCMS method for analysis: 2001, 2010, 2003, and 2033. Schedules 2001 and 2010 differ only in the location of pesticide extraction—2001 is extracted in the laboratory, whereas 2010 is extracted in the field (Zaugg and others, 1995, p. 43–45). Schedules 2003 and 2033 are extracted in the laboratory but, compared to schedules 2001 and 2010, have a reduced number of pesticides analyzed by GCMS (table 1). The NASQAN Program used schedule 2001 almost exclusively from 1995 through 2005 for pesticide analyses. The NAWQA Program used schedules 2001 and 2010 extensively from 1992 through 2004, used schedule 2003 extensively from 2003 through 2005, and used schedule 2033 extensively from 2004 through 2006.

Table 1. Pesticides selected for trend analysis.

[Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; CAS, Chemical Abstract Service (table contains CAS Registry Numbers®, a Registered Trademark of the American Chemical Society; CAS recommends the verification of CASRNs through CAS Client Services[SM]); LT-MDL, long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Pesticide	Param-eter code	CAS number	Pesticide class	Type of pesticide	Parent pesticide (if degradate)	Does the indicated National Water-Quality Laboratory analytical schedule analyze for the pesticide?				Maximum LT-MDL (µg/L)
						Schedule 2001	Schedule 2010	Schedule 2003	Schedule 2033	
Acetochlor	49260	34256-82-1	acetanilide	Herbicide	NA	Yes	Yes	Yes	Yes	0.003
Alachlor	46342	15972-60-8	acetanilide	Herbicide	NA	Yes	Yes	Yes	Yes	0.002
Atrazine	39632	1912-24-9	triazine	Herbicide	NA	Yes	Yes	Yes	Yes	0.004
Azinphos-methyl	82686	86-50-0	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.040
Benfluralin	82673	1861-40-1	dinitroaniline	Herbicide	NA	Yes	Yes	Yes	Yes	0.005
Butylate	04028	2008-41-5	thiocarbamate	Herbicide	NA	Yes	Yes	No	No	0.002
Carbaryl	82680	63-25-2	carbamate	Insecticide	NA	Yes	Yes	Yes	Yes	0.030
Carbofuran	82674	1563-66-2	carbamate	Insecticide	NA	Yes	Yes	No	Yes	0.010
Chlorpyrifos	38933	2921-88-2	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.003
Cyanazine	04041	21725-46-2	triazine	Herbicide	NA	Yes	Yes	No	Yes	0.009
Dacthal	82682	1861-32-1	chlorobenzoic acid ester	Herbicide	NA	Yes	Yes	Yes	Yes	0.002
p,p'-DDE	34653	72-55-9	organochlorine	Degradate	DDT	Yes	Yes	No	No	0.001
Deethylatrazine	04040	6190-65-4	triazine	Degradate	Atrazine	Yes	Yes	Yes	Yes	0.007
Desulfinylfipronil	62170	ND	phenyl pyrazole	Degradate	Fipronil	Yes	Yes	Yes	Yes	0.006
Desulfinylfipronil amide	62169	ND	phenyl pyrazole	Degradate	Fipronil	Yes	Yes	Yes	Yes	0.015
Diazinon	39572	333-41-5	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.003
Dieldrin	39381	60-57-1	organochlorine	Insecticide	NA	Yes	Yes	Yes	Yes	0.004
2,6-Diethylaniline	82660	579-66-8	aniline	Degradate	Alachlor	Yes	Yes	Yes	Yes	0.003
Disulfoton	82677	298-04-4	organothiophosphate	Insecticide	NA	Yes	Yes	No	Yes	0.011
EPTC	82668	759-94-4	thiocarbamate	Herbicide	NA	Yes	Yes	No	Yes	0.002
Ethalfluralin	82663	55283-68-6	dinitroaniline	Herbicide	NA	Yes	Yes	No	No	0.005

Ethoprophos	82672	13194-48-4	organothiophosphate	Insecticide	NA	Yes	Yes	No	Yes	0.006
Fipronil	62166	120068-37-3	phenyl pyrazole	Insecticide	NA	Yes	Yes	Yes	Yes	0.008
Fipronil sulfide	62167	120067-83-6	phenyl pyrazole	Degradate	Fipronil	Yes	Yes	Yes	Yes	0.006
Fipronil sulfone	62168	120068-36-2	phenyl pyrazole	Degradate	Fipronil	Yes	Yes	Yes	Yes	0.012
Fonofos	04095	944-22-9	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.003
alpha-HCH	34253	319-84-6	organochlorine	Degradate	*gamma*-HCH	Yes	Yes	No	No	0.002
gamma-HCH	39341	58-89-9	organochlorine	Insecticide	NA	Yes	Yes	No	No	0.002
Linuron	82666	330-55-2	urea	Herbicide	NA	Yes	Yes	No	No	0.030
Malathion	39532	121-75-5	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.014
Metolachlor	39415	51218-45-2	acetanilide	Herbicide	NA	Yes	Yes	Yes	Yes	0.006
Metribuzin	82630	21087-64-9	triazine	Herbicide	NA	Yes	Yes	Yes	Yes	0.014
Molinate	82671	2212-67-1	thiocarbamate	Herbicide	NA	Yes	Yes	No	Yes	0.002
Napropamide	82684	15299-99-7	amide	Herbicide	NA	Yes	Yes	No	No	0.009
Parathion	39542	56-38-2	organothiophosphate	Insecticide	NA	Yes	Yes	No	No	0.005
Parathion-methyl	82667	298-00-0	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.008
Pebulate	82669	1114-71-2	thiocarbamate	Herbicide	NA	Yes	Yes	No	No	0.002
Pendimethalin	82683	40487-42-1	dinitroaniline	Herbicide	NA	Yes	Yes	Yes	Yes	0.011
cis-Permethrin	82687	54774-45-7	pyrethroid	Insecticide	NA	Yes	Yes	Yes	Yes	0.005
Phorate	82664	298-02-2	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.027
Prometon	04037	1610-18-0	triazine	Herbicide	NA	Yes	Yes	Yes	Yes	0.007
Propachlor	04024	1918-16-7	acetanilide	Herbicide	NA	Yes	Yes	No	No	0.012
Propanil	82679	709-98-8	amide	Herbicide	NA	Yes	Yes	No	Yes	0.005
Propargite	82685	2312-35-8	sulfite ester	Acaricide	NA	Yes	Yes	No	Yes	0.011
Propyzamide	82676	23950-58-5	amide	Herbicide	NA	Yes	Yes	Yes	Yes	0.002
Simazine	04035	122-34-9	triazine	Herbicide	NA	Yes	Yes	Yes	Yes	0.006
Tebuthiuron	82670	34014-18-1	urea	Herbicide	NA	Yes	Yes	Yes	Yes	0.008
Terbacil	82665	5902-51-2	uracil	Herbicide	NA	Yes	Yes	No	No	0.020
Terbufos	82675	13071-79-9	organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.009
Thiobencarb	82681	28249-77-6	thiocarbamate	Herbicide	NA	Yes	Yes	No	Yes	0.005
Triallate	82678	2303-17-5	thiocarbamate	Herbicide	NA	Yes	Yes	No	No	0.003
Trifluralin	82661	1582-09-8	dinitroaniline	Herbicide	NA	Yes	Yes	Yes	Yes	0.005

In addition, concentrations less than the lowest calibration standard or concentrations extrapolated above the highest calibration standard also are remarked “E” (Oblinger Childress and others, 1999, p. 8–10). Any detection of the following five pesticides analyzed by GCMS (azinphos-methyl, carbaryl, carbofuran, deethylatrazine, or terbacil) are reported with an “E” remark, regardless of concentration, because these pesticides have lower or more variable recovery than other pesticides analyzed by the method (Zaugg and others, 1995, p. 35). Data users should infer that the uncertainty in the measured concentration (the precision of the concentration—not uncertainty in detection) for a concentration remarked “E” is expected to be greater than that for a concentration without an “E” remark.

QC procedures for analytical data produced by the NWQL are described at *http://nwql.usgs.gov/quality.shtml*. In addition to internal QC programs used by the NWQL, the quality of the analytical data produced by the NWQL is independently monitored by the USGS Branch of Quality Systems (BQS) [*http://bqs.usgs.gov/*]. Blind QC samples are made by BQS and submitted to the NWQL as routine environmental samples. The bias and variability of analytical results are reported for each pesticide by schedule [*http://bqs.usgs.gov/obsp/*]. The frequency and magnitude of contamination also is measured [*http://bqs.usgs.gov/bbp/*].

Sources of Water-Quality Data

Water-quality data collected for both the NAWQA and NASQAN Programs are stored in USGS National Water Information System (NWIS) data bases located in the individual State Water Science Centers (WSC). Water-quality data collected for the NAWQA Program are periodically retrieved from the individual NWIS systems and aggregated into the NAWQA Data Warehouse (DWH) located in the Wisconsin WSC [*http:/water.usgs.gov/nawqa/data*]. Water-quality data collected for the NASQAN Program are periodically retrieved from the individual NWIS systems and aggregated into a data set in the Oregon WSC. Data aggregations for both monitoring programs are subjected to program-specific automated data-checking routines intended to identify erroneous or incomplete coding and missing or unusual pesticide concentrations.

NAWQA water-quality data were provided by DWH data managers (Nathaniel L. Booth, U.S. Geological Survey, written commun., September 22, 2006). Any water-quality sample in the DWH with analyses of one or more pesticides of interest was retrieved along with selected supporting sample information. NASQAN water-quality data were provided by NASQAN data managers (Curt A. Hughes, U.S. Geological Survey, written commun., May 21, 2007). All available water-quality samples collected by the NASQAN Program since October 1, 1995, were provided.

Review, Selection, and Preparation of Water-Quality Data

The initial data-review procedures for the NAWQA and NASQAN data sets were done independently then merged for additional data processing and preparation for trend analysis. Initial data review involved a much broader suite of sites, sample types, and analytical methods than those ultimately selected for a national assessment of pesticide trends in streams. Most readers of this report will be interested in data-preparation procedures for trend analysis but few will be interested in the initial data-review procedures; thus, this section emphasizes data-preparation procedures for trend analysis. Data review procedures are briefly summarized in this section but presented in detail in appendix 1 for the benefit of data managers who may need to create data sets similar to this one.

Data Review

The principal steps in data review for trend analysis were to (1) identify analytical method and schedule, (2) verify sample-level coding, (3) exclude inappropriate samples or results, (4) review pesticide detections per sample, (5) review high pesticide concentrations, and (6) review the spatial and temporal extent of pesticide data and selection of analytical methods for trend analysis. Details of these procedures are provided in appendix 1.

Data Selection and Preparation for Trend Analysis

The principal steps in data preparation for trend analysis were to (1) select stream-water sites for trend analysis; (2) identify routine reporting levels used to report nondetections unaffected by matrix interference; (3) reassign the concentration value for routine nondetections to the maximum value of the long-term method detection level; (4) round concentrations to a consistent level of precision for the concentration range; (5) adjust concentrations to compensate for temporal changes in bias of recovery of the GCMS analytical method; and (6) identify samples considered inappropriate for trend analysis. Details of these procedures are provided in the following sections.

Selection of Stream-Water Sites for Trend Analysis

Only samples analyzed by the GCMS method at NWQL were selected for trend analysis (appendix 1). The NAWQA and NASQAN data sets were merged. Fifteen stream-water sites were common to both data sets; for these sites, unique (unmatched) samples in the NASQAN data set were merged

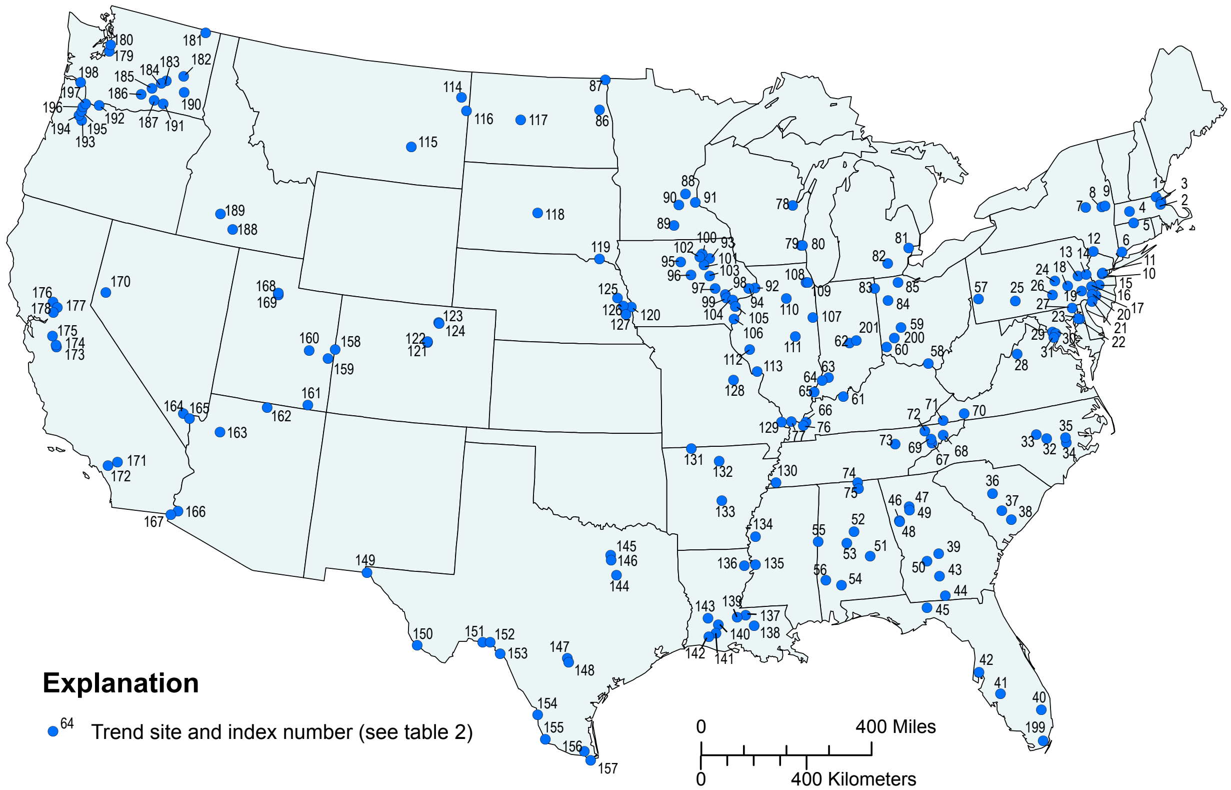

Figure 1. Locations of stream-water sites selected for trend analysis.

with the NAWQA site and samples. Stream-water sites with at least 3 water years[2] of data (and at least six GCMS samples per water year) were deemed the minimum data requirements to be potentially useful for pesticide trend analysis. The 201 stream-water sites that met these minimum data requirements are shown in figure 1 and listed in table 2. National Stream Quality Accounting Network Program or National Water-Quality Assessment Program Study Unit identifiers used in table 2 are explained in table 3.

Determination of Reporting Levels

The type and value of the routine reporting level in effect at the time of sample analysis has been recorded in the data transmitted to NWIS only since 2001. The need to distinguish between routine reporting levels for nondetections and raised reporting levels for nondetections caused by matrix interference was anticipated for some types of analysis activities. **In this report, the term "routine reporting level" refers to the "less than" concentration value used to report a pesticide nondetection in the absence of interference. The term "raised reporting level" is the "less than" concentration value used to report a pesticide nondetection in the presence of interference (see section "Pesticides, Analytical Method, Reporting Levels, and Laboratory Quality-Control Programs").** A raised reporting level is always greater than routine reporting level (for a given period of time).

The types and values of routine reporting levels and the effective dates of their use were obtained from NWQL (Stephen R. Glodt, U.S. Geological Survey, written commun., March 16, 2007). The values of the routine reporting levels provided by NWQL were joined to the trend data, nondetections in the trend data were classified as routine or raised, and timeseries plots of reporting levels for pesticide nondetections were examined. Several aspects of data reporting were observed to change over time: (1) rounding procedures, both in the trend data set and in the NWQL reporting level information, resulted in many routine reporting levels being misclassified (by computer programs) as raised reporting levels solely because of rounding; (2) no information was available on reporting levels used prior to December 1994; (3) a period of "overlap" as routine reporting levels changed; and (4) a few isolated reporting levels at concentration values less than routine reporting levels.

[2]A water year is the period October 1 though September 30 and is named for the year in which the water year ends.

Table 2. Stream-water sites selected for trend analysis.

[Drainage areas rounded to 1 square mile; agric, greater than 50 percent agricultural land and less than or equal to 5 percent urban land; undev, less than or equal to 25 percent agricultural land and less than or equal to 5 percent urban land; urban, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of land use]

Figure 1 index number	Station number	Study Unit abbreviation (explained in table 3)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
1	01100000	necb	mixed	4,627	Merrimack River below Concord River at Lowell, MA
2	01102500	necb	urban	23	Aberjona River at Winchester, MA
3	01104615	necb	urban	268	Charles River above Watertown Dam at Watertown, MA
4	01170970	conn	undev	1	Hatfield Reservoir near West Hatfield, MA
5	01184000	conn	mixed	9,672	Connecticut River at Thompsonville, CT
6	01209710	conn	urban	33	Norwalk River at Winnipauk, CT
7	01349150	hdsn	mixed	60	Canajoharie Creek near Canajoharie, NY
8	01356190	hdsn	urban	15	Lisha Kill near Niskayuna, NY
9	01357500	hdsn	mixed	3,519	Mohawk River at Cohoes, NY
10	01403300	linj	mixed	801	Raritan River at Queens Bridge at Bound Brook, NJ
11	01403900	linj	urban	49	Bound Brook at Middlesex, NJ
12	01434000	delr	undev	3,076	Delaware River at Port Jervis, NY
13	01451800	delr	mixed	52	Jordan Creek near Schnecksville, PA
14	01454700	delr	mixed	1,359	Lehigh River at Glendon, PA
15	01463500	delr	mixed	6,787	Delaware River at Trenton, NJ
16	01464907	delr	mixed	28	Little Neshaminy Creek at Valley Road near Neshaminy, PA
17	01467150	delr	urban	18	Cooper River at Haddonfield, NJ
18	01470779	delr	mixed	69	Tulpehocken Creek near Bernville, PA
19	01472157	delr	mixed	59	French Creek near Phoenixville, PA
20	01474500	delr	mixed	1,890	Schuylkill River at Philadelphia, PA
21	01477120	delr	mixed	26	Raccoon Creek near Swedesboro, NJ
22	01493112	podl	agric	7	Chesterville Branch near Crumpton, MD
23	01493500	podl	agric	13	Morgan Creek near Kennedyville, MD
24	01555400	lsus	mixed	45	East Mahantango Creek at Klingerstown, PA
25	01559795	lsus	undev	17	Bobs Creek near Pavia, PA
26	01571490	lsus	urban	13	Cedar Run at Eberlys Mill, PA
27	01578310	podl	mixed	27,067	Susquehanna River at Conowingo, MD
28	01621050	podl	mixed	14	Muddy Creek at Mount Clinton, VA
29	01645495	podl	mixed	11,464	Potomac River near Great Falls, VA
30	01646580	podl	mixed	11,583	Potomac River at Chain Bridge at Washington, DC
31	01654000	podl	urban	23	Accotink Creek near Annandale, VA
32	0208755215	albe	mixed	1,207	Neuse River above US 70 at Smithfield, NC
33	02087580	albe	urban	21	Swift Creek near Apex, NC
34	02089500	albe	mixed	2,711	Neuse River at Kinston, NC
35	02091500	albe	mixed	737	Contentnea Creek at Hookerton, NC
36	02169570	sant	urban	60	Gills Creek at Columbia, SC
37	02174250	sant	mixed	24	Cow Castle Creek near Bowman, SC
38	02175000	sant	mixed	2,732	Edisto River near Givhans, SC
39	02215100	gafl	mixed	162	Tucsawhatchee Creek near Hawkinsville, GA
40	02281200	sofl	agric	311	Hillsboro Canal at S-6 near Shawano, FL
41	02296750	sofl	mixed	1,327	Peace River at Arcadia, FL
42	02306774	gafl	urban	20	Rocky Creek at Highway 587 at Citrus Park, FL
43	02317797	gafl	mixed	129	Little River at Upper Ty Ty Road near Tifton, GA

Table 2. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 1 square mile; agric, greater than 50 percent agricultural land and less than or equal to 5 percent urban land; undev, less than or equal to 25 percent agricultural land and less than or equal to 5 percent urban land; urban, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of land use]

Figure 1 index number	Station number	Study Unit abbreviation (explained in table 3)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
44	02318500	gafl	mixed	1,492	Withlacoochee River at US 84 near Quitman, GA
45	02326838	gafl	urban	10	Lafayette Creek at Miccosukee Road at Tallahassee, FL
46	02335870	acfb	urban	31	Sope Creek near Marietta, GA
47	02336020	acfb	mixed	1,455	Intake on Chattahoochee River at Atlanta, GA
48	02337500	acfb	mixed	36	Snake Creek near Whitesburg, GA
49	02338000	acfb	urban	2,413	Chattahoochee River near Whitesburg, GA
50	02350080	acfb	mixed	62	Lime Creek near Cobb, GA
51	02419977	mobl	urban	9	Three Mile Branch at North Boulevard at Montgomery, AL
52	0242354750	mobl	urban	26	Cahaba Valley Creek at Cross Creek Road at Pelham, AL
53	02424000	mobl	mixed	1,026	Cahaba River at Centreville, AL
54	02429500	mobl	mixed	21,977	Alabama River at Claiborne, AL
55	02444490	mobl	agric	53	Bogue Chitto Creek near Memphis, AL
56	02469762	mobl	mixed	18,480	Tombigbee Riber below Coffeeville Dam near Coffeeville, AL
57	03086000	nasq	mixed	19,457	Ohio River at Sewickley, PA
58	03216600	nasq	mixed	61,528	Ohio River at Greenup Dam near Greenup, KY
59	03267900	whmi	mixed	310	Mad River at St. Paris Pike at Eagle City, OH
60	03274000	whmi	mixed	3,631	Great Miami River at Hamilton, OH
61	03303280	nasq	mixed	96,475	Ohio River at Cannelton Dam at Cannelton, IN
62	03353637	whmi	urban	17	Little Buck Creek near Indianapolis, IN
63	03360895	whmi	mixed	56	Kessinger Ditch near Monroe City, IN
64	03374100	whmi	mixed	11,309	White River at Hazleton, IN
65	03378500	nasq	mixed	29,303	Wabash River at New Harmony, IN
66	03438500	nasq	mixed	17,913	Cumberland River at Smithland, KY
67	03455000	tenn	mixed	1,853	French Broad River near Newport, TN
68	03466208	tenn	mixed	79	Big Limestone Creek near Limestone, TN
69	03467609	tenn	mixed	1,688	Nolichucky River near Lowland, TN
70	03474000	tenn	mixed	132	Middle Fork Holston River at Seven Mile Ford, VA
71	03526000	tenn	mixed	107	Copper Creek near Gate City, VA
72	03528000	tenn	mixed	1,473	Clinch River above Tazewell, TN
73	03539778	tenn	mixed	170	Clear Creek at Lilly Bridge near Lancing, TN
74	0357479650	tenn	mixed	29	Hester Creek at Buddy Williamson Road near Plevna, AL
75	03575100	tenn	mixed	374	Flint River at Brownsboro, AL
76	03609750	nasq	mixed	40,297	Tennessee River at Highway 60 near Paducah, KY
77	03612500	nasq	mixed	203,564	Ohio River at Dam 53 near Grand Chain, IL
78	04072050	wmic	mixed	95	Duck Creek at Seminary Road near Oneida, WI
79	040869415	wmic	urban	10	Lincoln Creek at 47th Street at Milwaukee, WI
80	04087000	wmic	mixed	697	Milwaukee River at Milwaukee, WI
81	04161820	leri	urban	310	Clinton River at Sterling Heights, MI
82	04175600	leri	mixed	128	River Raisin near Manchester, MI
83	04178000	leri	mixed	618	St. Joseph River near Newville, IN
84	04186500	leri	mixed	331	Auglaize River near Fort Jennings, OH
85	04193500	leri	mixed	6,336	Maumee River at Waterville, OH
86	05082625	redn	mixed	254	Turtle River at Turtle River State Park near Arvilla, ND

Table 2. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 1 square mile; agric, greater than 50 percent agricultural land and less than or equal to 5 percent urban land; undev, less than or equal to 25 percent agricultural land and less than or equal to 5 percent urban land; urban, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of land use]

Figure 1 index number	Station number	Study Unit abbreviation (explained in table 3)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
87	05102490	redn	agric	35,555	Red River of the North at Pembina, ND
88	05288705	umis	urban	28	Shingle Creek at Queen Avenue at Minneapolis, MN
89	05320270	umis	mixed	130	Little Cobb River near Beauford, MN
90	05330000	umis	mixed	16,232	Minnesota River near Jordan, MN
91	05331580	umis	mixed	37,049	Mississippi River below Lock and Dam 2 at Hastings, MN
92	05420500	nasq	mixed	85,779	Mississippi River at Clinton, IA
93	05420680	eiwa	mixed	346	Wapsipinicon River near Tripoli, IA
94	05422000	eiwa	mixed	2,336	Wapsipinicon River near De Witt, IA
95	05449500	eiwa	mixed	419	Iowa River near Rowan, IA
96	05451210	eiwa	mixed	224	South Fork Iowa River near New Providence, IA
97	05453100	eiwa	mixed	2,795	Iowa River at Marengo, IA
98	05455100	eiwa	mixed	201	Old Mans Creek near Iowa City, IA
99	05455570	eiwa	mixed	626	English River at Riverside, IA
100	05457750	eiwa	mixed	1,095	Cedar River near Carville, IA
101	05458900	eiwa	mixed	857	West Fork Cedar River at Finchford, IA
102	05461390	eiwa	mixed	124	Flood Creek near Powersville, IA
103	05464220	eiwa	mixed	299	Wolf Creek near Dysart, IA
104	05465000	eiwa	mixed	7,781	Cedar River near Conesville, IA
105	05465500	eiwa	mixed	12,496	Iowa River at Wapello, IA
106	05474000	eiwa	mixed	4,311	Skunk River at Augusta, IA
107	05525500	uirb	mixed	447	Sugar Creek at Milford, IL
108	05531500	uirb	urban	112	Salt Creek at Western Springs, IL
109	05532500	uirb	urban	631	Des Plaines River at Riverside, IL
110	05553500	uirb	mixed	10,938	Illinois River at Ottawa, IL
111	05572000	lirb	mixed	551	Sangamon River at Monticello, IL
112	05586100	lirb	mixed	26,705	Illinois River at Valley City, IL
113	05587455	nasq	mixed	172,483	Mississippi River below Grafton, IL
114	06185500	nasq	undev	92,569	Missouri River near Culbertson, MT
115	06295000	yell	undev	40,147	Yellowstone River at Forsyth, MT
116	06329500	yell	undev	69,085	Yellowstone River near Sidney, MT
117	06338490	nasq	undev	180,876	Missouri River at Garrison Dam, ND
118	06440000	nasq	undev	240,157	Missouri River at Pierre, SD
119	06467500	nasq	undev	279,498	Missouri River at Yankton, SD
120	06610000	nasq	undev	320,764	Missouri River at Omaha, NE
121	06713500	splt	mixed	411	Cherry Creek at Denver, CO
122	06714000	splt	mixed	3,866	South Platte River at Denver, CO
123	06753990	splt	undev	571	Lonetree Creek near Greeley, CO
124	06754000	splt	mixed	9,659	South Platte River near Kersey, CO
125	06800000	cnbr	agric	368	Maple Creek near Nickerson, NE
126	06800500	cnbr	agric	6,945	Elkhorn River at Waterloo, NE
127	06805500	cnbr	undev	85,293	Platte River at Louisville, NE
128	06934500	nasq	mixed	519,714	Missouri River at Hermann, MO
129	07022000	nasq	mixed	710,301	Mississippi River at Thebes, IL

Table 2. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 1 square mile; agric, greater than 50 percent agricultural land and less than or equal to 5 percent urban land; undev, less than or equal to 25 percent agricultural land and less than or equal to 5 percent urban land; urban, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of land use]

Figure 1 index number	Station number	Study Unit abbreviation (explained in table 3)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
130	07031692	mise	urban	30	Fletcher Creek at Sycamore View Road at Memphis, TN
131	07053250	ozrk	mixed	53	Yocum Creek near Oak Grove, AR
132	07060710	ozrk	undev	59	North Sylamore Creek near Fifty-Six, AR
133	07263620	nasq	mixed	157,610	Arkansas River at David Terry Dam below Little Rock, AR
134	07288650	mise	agric	502	Bogue Phalia near Leland, MS
135	07288955	mise	mixed	13,456	Yazoo River below Steele Bayou near Long Lake, MS
136	07369500	mise	agric	278	Tensas River at Tendal, LA
137	07373420	nasq	mixed	1,144,972	Mississippi River near St. Francisville, LA
138	07379960	acad	urban	15	Dawson Creek at Bluebonnet Boulevard near Baton Rouge, LA
139	07381495	nasq	undev	92,907	Atchafalaya River at Melville, LA
140	08010000	acad	mixed	142	Bayou Des Cannes near Eunice, LA
141	08012150	acad	mixed	1,381	Mermentau River at Mermentau, LA
142	08012470	acad	mixed	296	Bayou Lacassine near Lake Arthur, LA
143	08014500	acad	mixed	504	Whiskey Chitto Creek near Oberlin, LA
144	08057200	trin	urban	67	White Rock Creek at Greenville Avenue at Dallas, TX
145	08057410	trin	mixed	6,265	Trinity River below Dallas, TX
146	08064100	trin	mixed	825	Chambers Creek near Rice, TX
147	08178800	sctx	urban	195	Salado Creek at Loop 13 at San Antonio, TX
148	08181800	sctx	mixed	1,748	San Antonio River near Elmendorf, TX
149	08364000	riog	undev	33,385	Rio Grande at El Paso, TX
150	08374200	nasq	undev	72,975	Rio Grande below Rio Conchos near Presidio, TX
151	08377200	nasq	undev	95,115	Rio Grande at Foster Ranch near Langtry, TX
152	08447410	nasq	undev	44,174	Pecos River near Langtry, TX
153	08450900	nasq	undev	167,199	Rio Grande below Amistad Dam near Del Rio, TX
154	08459200	nasq	undev	177,073	Rio Grande at Pipeline Crossing below Laredo, TX
155	08461300	nasq	undev	206,916	Rio Grande below Falcon Dam, TX
156	08470400	nasq	mixed	272	Arroyo Colorado at Harlingen, TX
157	08475000	nasq	undev	214,604	Rio Grande near Brownsville, TX
158	09163500	ucol	undev	17,866	Colorado River near Colorado-Utah State Line
159	09180500	nasq	undev	23,973	Colorado River near Cisco, UT
160	09315000	nasq	undev	40,799	Green River at Green River, UT
161	09379500	nasq	undev	22,993	San Juan River near Bluff, UT
162	09380000	nasq	undev	108,137	Colorado River at Lees Ferry, AZ
163	09404200	nasq	undev	145,602	Colorado River above Diamond Creek near Peach Spring, AZ
164	094196783	nvbr	mixed	1,021	Las Vegas Wash below Flamingo Wash near Las Vegas, NV
165	09421500	nasq	undev	166,918	Colorado River below Hoover Dam, AZ-NV
166	09429490	nasq	undev	181,536	Colorado River above Imperial Dam, AZ-CA
167	09522000	nasq	undev	240,932	Colorado River at International Boundary above Morelos Dam, AZ
168	10168000	grsl	urban	45	Little Cottonwood Creek at Jordan River near Salt Lake City, UT
169	10171000	grsl	mixed	3,512	Jordan River at County Road 1700 South at Salt Lake City, UT
170	10350500	nvbr	mixed	1,664	Truckee River at Clark, NV
171	11060400	sana	urban	12	Warm Creek near San Bernardino, CA
172	11074000	sana	urban	2,261	Santa Ana River below Prado Dam, CA

Table 2. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 1 square mile; agric, greater than 50 percent agricultural land and less than or equal to 5 percent urban land; undev, less than or equal to 25 percent agricultural land and less than or equal to 5 percent urban land; urban, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of land use]

Figure 1 index number	Station number	Study Unit abbreviation (explained in table 3)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
173	11273500	sanj	undev	1,383	Merced River at River Road Bridge near Newman, CA
174	11274538	sanj	mixed	11	Orestimba Creek at River Road near Crows Landing, CA
175	11303500	sanj	undev	7,347	San Joaquin River near Vernalis, CA
176	11391100	sacr	mixed	1,285	Sacramento Slough near Knights Landing, CA
177	11447360	sacr	urban	31	Arcade Creek near Del Paso Heights, CA
178	11447650	sacr	undev	23,820	Sacramento River at Freeport, CA
179	12113390	pugt	mixed	461	Duwamish River at golf course at Tukwila, WA
180	12128000	pugt	urban	11	Thornton Creek near Seattle, WA
181	12400520	nasq	undev	60,373	Columbia River at Northport, WA
182	12464770	ccyk	agric	459	Crab Creek at Rocky Ford Road near Ritzville, WA
183	12471400	ccyk	agric	711	Lind Coulee Wasteway at State Road 17 near Warden, WA
184	12472380	ccyk	mixed	56	Crab Creek Lateral above Royal Lake near Othello, WA
185	12472900	nasq	undev	96,333	Columbia River at Vernita Bridge near Priest Rapid Dam, WA
186	12505450	ccyk	mixed	62	Granger Drain at Granger, WA
187	12510500	ccyk	undev	5,612	Yakima River at Kiona, WA
188	13092747	usnk	undev	257	Rock Creek above Highway 30/93 Crossing at Twin Falls, ID
189	13154500	usnk	undev	35,885	Snake River at King Hill, ID
190	13351000	ccyk	agric	2,463	Palouse River at Hooper, WA
191	13353200	nasq	undev	107,894	Snake River at Burbank, WA
192	14128910	nasq	undev	236,623	Columbia River at Warrendale, OR
193	14200400	will	undev	10	Little Abiqua Creek near Scotts Mills, OR
194	14201300	will	mixed	15	Zollner Creek near Mount Angel, OR
195	14202000	will	mixed	487	Pudding River at Aurora, OR
196	14206950	will	urban	31	Fanno Creek at Durham, OR
197	14211720	will	mixed	11,173	Willamette River at Portland, OR
198	14246900	nasq	undev	258,798	Columbia River at Beaver Army Terminal near Quincy, OR
199	252414-080333200	sofl	mixed	51	C-111 Canal 100 feet above S-177 near Homestead, FL
200	393944-084120700	whmi	urban	20	Holes Creek at Huffman Park at Kettering, OH
201	394340-085524601	whmi	mixed	95	Sugar Creek at County Road 400 South at New Palestine, IN

Table 3. National Stream Quality Accounting Network Program or National Water-Quality Assessment Program Study Unit identifiers.

Study Unit abbreviation	Study Unit name
acad	Acadian-Pontchartrain Drainages
acfb	Apalachicola-Chattahoochee-Flint River Basin
albe	Albemarle-Pamlico Drainage Basin
ccyk	Central Columbia Plateau-Yakima River Basin
cnbr	Central Nebraska Basins
conn	Connecticut, Housatonic, and Thames River Basins
delr	Delaware River Basin
eiwa	Eastern Iowa Basins
gafl	Georgia-Florida Coastal Plain
grsl	Great Salt Lake Basins
hdsn	Hudson River Basin
leri	Lake Erie-Lake Saint Clair Drainages
linj	Long Island-New Jersey Coastal Drainages
lirb	Lower Illinois River Basin
lsus	Lower Susquehanna River Basin
mise	Mississippi Embayment
mobl	Mobile River Basin
nasq	NASQAN Program
necb	New England Coastal Basins
nvbr	Las Vegas Valley Area and Carson and Truckee River Basins
ozrk	Ozark Plateaus
podl	Potomac River Basin and Delmarva Peninsula
pugt	Puget Sound Basin
redn	Red River of the North Basin
riog	Rio Grande Valley
sacr	Sacramento River Basin
sana	Santa Ana Basin
sanj	San Joaquin-Tulare Basins
sant	Santee River Basin and Coastal Drainages
sctx	South-Central Texas
sofl	Southern Florida
splt	South Platte River Basin
tenn	Tennessee River Basin
trin	Trinity River Basin
ucol	Upper Colorado River Basin
uirb	Upper Illinois River Basin
umis	Upper Mississippi River Basin
usnk	Upper Snake River Basin
whmi	White, Great Miami, and Little Miami River Basins
will	Willamette Basin
wmic	Western Lake Michigan Drainages
yell	Yellowstone River Basin

These issues were resolved as follows: (1) nondetections misclassified as raised reporting levels were reclassified as routine if the magnitude of difference in values was within the tolerances of rounding error (rounding is discussed in a subsequent section), (2) reporting levels for pre-December 1994 samples were inferred from the pattern and values of nondetections in the trend data for this period, (3) periods of overlapping routine reporting levels were identified by visual inspection of the timeseries plots and reporting levels misclassified as raised were manually corrected, and (4) unusually low reporting levels were attributed to data-management/data-editing errors and were changed to nondetections at routine reporting levels.

A timeseries plot of reporting levels for nondetections of simazine in the original concentration data provided by NAWQA and NASQAN data managers for all sites in the trend data set is shown in the first panel of figure 2. Timeseries plots of reporting levels for nondetections in the original concentration data for all GCMS pesticides are provided in first panels of the figures in appendix 2.

Reassigning the Concentration Value for Routine Nondetections

Temporal changes in the types and magnitude of reporting levels used to report routine nondetections have the potential to adversely affect trend analysis because they introduce a temporal "structure" to the timeseries of routine nondetections. The temporal structure of routine nondetections was removed for trend analysis by "reassigning" the temporally inconsistent concentration value to a uniform, temporally consistent concentration value. The concentration value of all pesticide nondetections at *routine* reporting levels was reassigned to a concentration value equal to the maximum value of the long-term method detection level for water years 1994–2006 (maxLT-MDL). Pesticide nondetections at *raised* reporting levels were *not* reassigned to maxLT-MDL. For most, but not all pesticides and time periods, reassigning the concentration value of routine nondetections to the maxLT-MDL resulted in an increase in the nondetected "less than" concentration (appendix 2).

The maxLT-MDL was determined from records provided by NWQL (Stephen R. Glodt, U.S. Geological Survey, written commun., March 16, 2007). It is anticipated that the maxLT-MDL will be used as a temporally consistent, conservatively high estimate of the detection limit for some types of trend-analysis activities. Data users are reminded that the reporting level is not a detection limit and that changes in the reporting level reflect changes in the variability/precision of low-level quantification or policy changes, not changes in detection capability.

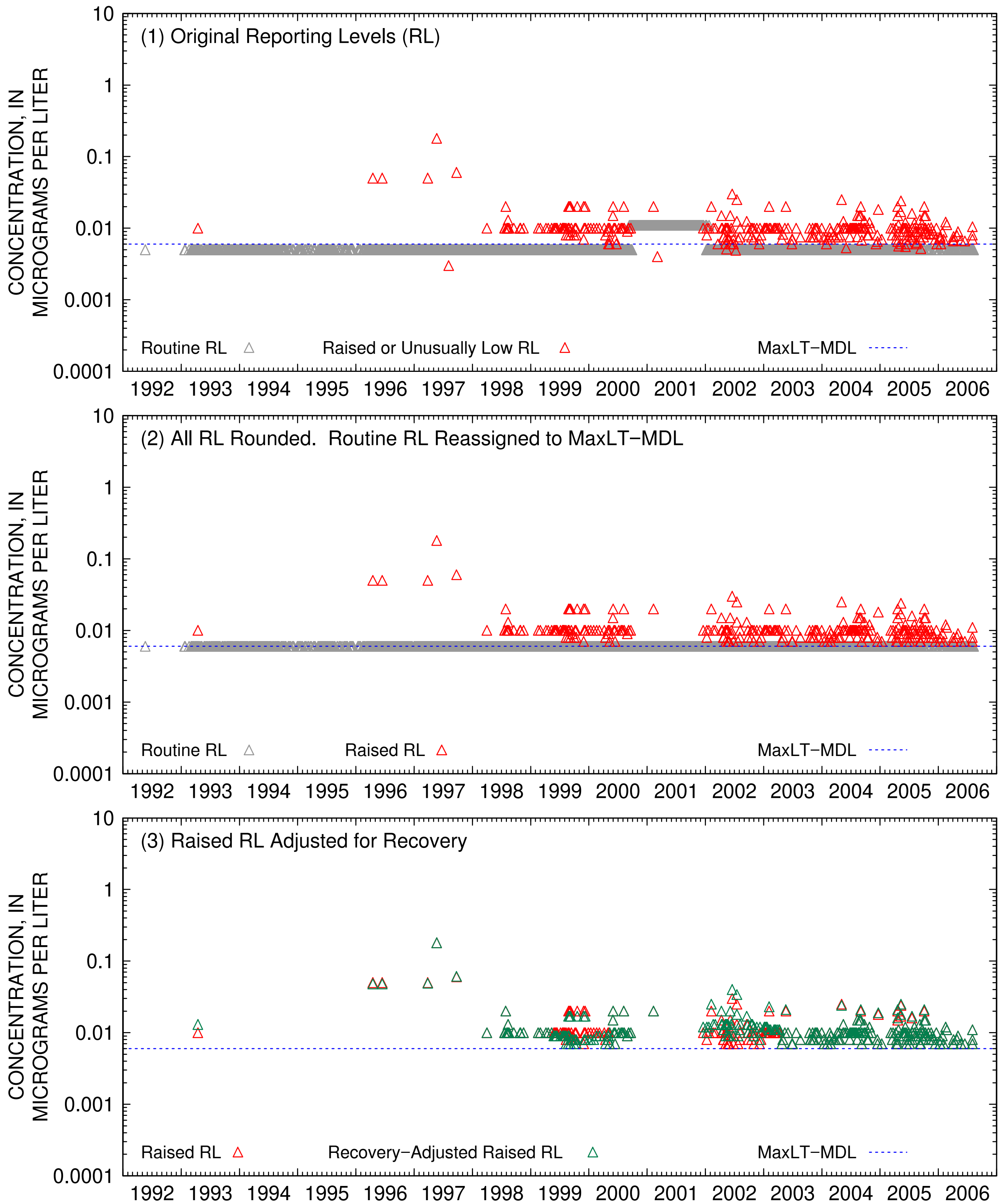

Figure 2. Timeseries plots of nondetections of simazine for all sites in the trend data set showing (1) original reporting levels; (2) rounded reporting levels and, for routine nondetections, reporting levels reassigned to the maximum value of the long-term method detection level (maxLT-MDL); and (3) raised reporting levels adjusted for temporal changes in recovery.

Precision and Rounding

Classification of reporting levels identified differences in the rounding of pesticide concentrations in the trend data set. Prior to April 1997, pesticide data reported by NWQL were rounded to a greater degree than data reported subsequently (U.S. Geological Survey, 1997a). In addition, nearly all NASQAN data less than 0.1 µg/L were rounded to a greater degree than the post-April 1997 NAWQA data. Differences in rounding between NASQAN and NAWQA data probably were caused by use of different rounding options during retrieval of data from NWIS or by software used to manage the concentration data. Inconsistent rounding has the potential to adversely affect trend analysis, especially for nonparametric trend approaches based on the ranks of the concentrations. Consequently, all pesticide concentrations in the trend data set were rounded to the degree used for the pre-April 1997 data (table 4). Thirty analytical results, originally reported as detections less than 0.0005 µg/L, rounded to 0.000 µg/L following the rules in this section. These results were changed to routine nondetections at a concentration value equal to maxLT-MDL.

A timeseries plot of reporting levels for nondetections of simazine reassigned to maxLT-MDL and rounded following the rules in this section for all sites in the trend data set is shown in the second panel of figure 2. A timeseries plot of rounded, detected concentrations of simazine in relation to maxLT-MDL for all sites in the trend data set is shown in the first panel of figure 3. Similar timeseries plots of rounded, detected concentrations for all GCMS pesticides are provided in the first panels of the figures in appendix 3.

Adjustment of Concentrations for Temporal Changes in Recovery

Temporal changes in the performance of the GCMS analytical method used to measure pesticide concentrations during 1992–2006 have the potential to mask true trends in environmental concentrations or to identify trends in environmental concentrations that are caused solely by trends in the performance of the GCMS method. Consequently, measured concentrations of pesticides were adjusted for temporal changes in analytical recovery. Data and procedures for modeling temporal changes in recovery bias are summarized below (Martin and others, 2009).

Recovery of a pesticide compound in the analytical process is measured by analysis of “spiked” QC samples. “Spikes” are water samples where a known amount of pesticide is added to the water sample. Recovery is the measured concentration of the pesticide divided by the expected concentration and is expressed as a percentage. Both bias in recovery and variability of recovery are characteristics of method performance. Bias is the systematic error in the measurement process and results in measurements that differ from the true (or expected) value in the same direction. Variability is the random error in the measurement process. Changes in the bias of recovery, however, were considered more important for trend analysis than changes in the variability of recovery.

Timeseries plots of pesticide recovery during 1992–2006 in 5,132 NWQL “reagent” spikes[3] and in 2,097 NAWQA “matrix” spikes[4] were visually examined for temporal changes in recovery bias. A locally weighted scatterplot smoothing procedure (lowess) was used to fit a center smooth to the timeseries of recoveries (Cleveland and McGill, 1985, p. 833; Helsel and Hirsch, 2002, p. 45–47). Lowess smooths were used to (1) model recovery as a function of time and (2) compare temporal changes in bias and the magnitude of bias among the different types of spiked QC samples. Temporal changes in lowess-modeled recovery of more than 50 percent were observed for some pesticides during 1992–2006. Temporal patterns in recovery were similar among NWQL

[3] Pesticides added to blank water.

[4] Pesticides added to stream-water or groundwater samples. Measured pesticide concentrations in spiked stream-water or groundwater samples were corrected for background pesticide concentrations by subtracting the pesticide concentration measured in a replicate, unspiked water sample.

Table 4. Precision of pesticide data.

[µg/L, microgram per liter; NASQAN, National Stream Quality Accounting Network Program; NAWQA, National Water-Quality Assessment Program; ND, no data]

Pesticide concentration (µg/L)	Precision of pesticide data (µg/L)			
	NASQAN data	NAWQA data prior to April 1997	NAWQA data during and after April 1997	Final rounding for trend analysis
< 0.001	0.001	0.001	0.0001	0.001
0.001 to < 0.01	0.001	0.001	0.0001	0.001
0.01 to < 0.1	0.001	0.001	0.0001	0.001
0.1 to < 1	0.001	0.01	0.001	0.01
1 to < 10	0.01	0.1	0.01	0.1
10 to < 100	0.1	1	0.1	1
100 to < 1000	ND	10	1	10

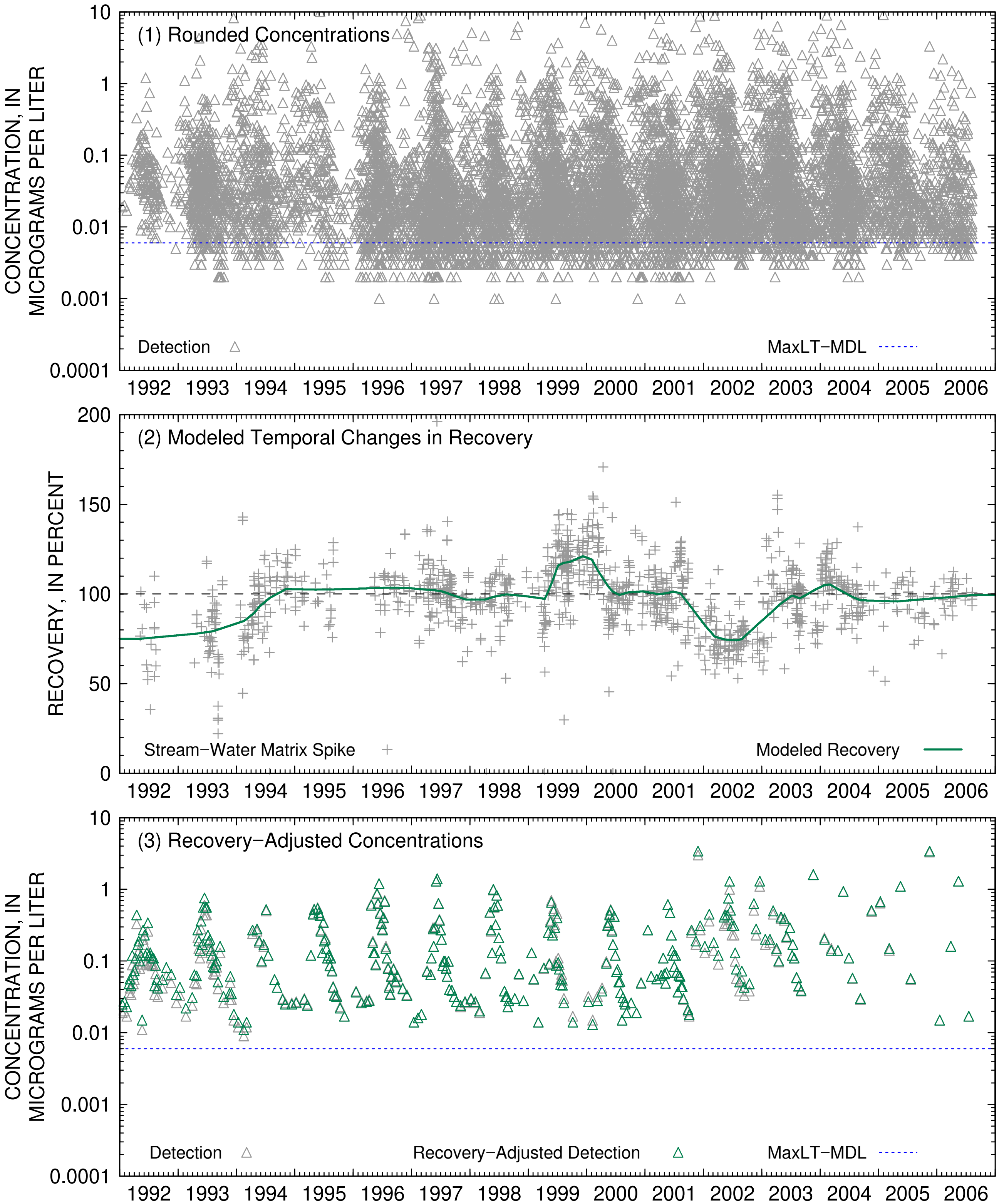

Figure 3. Timeseries plots of (1) rounded concentrations of simazine in relation to the maximum value of the long-term method detection level (maxLT-MDL) for all sites in the trend data set; (2) modeled temporal changes in recovery; and, (3) for detections at White River at Hazleton, IN, a comparison of recovery-adjusted versus unadjusted concentrations.

reagent spikes, NAWQA stream-water matrix spikes, and NAWQA groundwater matrix spikes (Martin and others, 2009). The similarity of temporal patterns among these three types of spikes supports the hypothesis that a temporal change in method performance (rather than a temporal change in the matrix of water samples spiked) is the primary cause of temporal change in recovery. For several pesticides, however, the magnitude of recovery (at any given time during 1992–2006) was 30 percent or greater in stream-water spikes than in the other spike types.

NAWQA stream-water matrix spikes are expected to more closely match the matrix of NAWQA stream-water samples to be analyzed for trends; therefore, temporal changes in recovery were modeled using as many as 1,234 NAWQA stream-water matrix spikes. Recovery for each day in the 1992–2006 period was modeled using the LOESS procedure of SAS/STAT version8 with a 10 percent smoothing window (SAS Institute Inc., undated). Measured concentrations of pesticides were adjusted to 100-percent recovery to compensate for changes in recovery over time. Concentrations were adjusted by dividing the measured concentration by the lowess-modeled recovery, where recovery was expressed as a fraction. Recovery-adjusted concentrations were rounded using the criteria in table 4. No concentrations were downward adjusted to the degree that a detected concentration rounded to 0.000 µg/L.

Concentrations of nondetections at *raised* reporting levels also were adjusted to 100-percent recovery (third panel of the figures in appendix 2). Some nondetections at raised reporting levels were downward adjusted to concentrations less than or equal to the maxLT-MDL. These recovery-adjusted nondetections were changed to routine nondetections at maxLT-MDL. *Routine* nondetections at maxLT-MDL were *not* adjusted for lowess-modeled recovery. Routine nondetections were not adjusted because adjustment would create a temporal structure to the timeseries of nondetections and defeat the original purpose of reassigning routine nondetections to the maxLT-MDL (see section “Reassign the Concentration Value for Routine Nondetections”).

Timeseries plots of recovery-adjusted *raised* reporting levels for nondetections of simazine compared to unadjusted raised reporting levels for all sites in the trend data set are shown in the third panel of figure 2; and for all GCMS pesticides in the third panels of the figures in appendix 2. Timeseries plots of recovery-adjusted concentrations of simazine at White River at Hazleton, IN, compared to unadjusted concentrations are shown in the third panel of figure 3; and for all GCMS pesticides in the third panels of the figures in appendix 3. Lowess-modeled recovery of simazine in stream-water matrix spikes is shown in the second panel of figure 3 and for all GCMS pesticides in the second panels of the figures in appendix 3 (Martin and others, 2009).

Identification of Samples Considered Inappropriate for Trend Analysis

Many trend-analysis approaches require the removal of samples collected too frequently in time. Samples collected too frequently in time typically have highly correlated, redundant information that is inappropriate for use in trend analyses. At some NAWQA sites, samples were frequently collected during periods of storm runoff to characterize changes in pesticide concentrations during storm runoff. This storm sampling strategy resulted in a series of samples at the site that, for some samples, differed only days, hours, or even minutes in time.

In view of the sampling strategies used by NAWQA and NASQAN since 1992, an approximately weekly sampling frequency was considered the maximum frequency for a national trend analysis of these data. All samples at a site were assigned to calendar weeks (Sunday through Saturday). If two or more samples were collected during the same calendar week, only the sample collected closest in time to noon Wednesday was retained for trend analysis. The procedure for identifying samples collected too frequently identified 827 samples that were considered inappropriate for trend analysis (table 5). *All samples, however, were retained in the trend data set* because they have uses beyond trend analysis (for example, load calculations or toxicity assessments). Samples considered appropriate for trend analysis are identified by the variable trend = KEEP in the data set (appendix 5).

Data Set for Trend Assessment

The site- and sample-selection criteria described in the preceding sections produced a trend data set of 16,869 pesticide samples at 201 stream-water sites (table 6, starting on p. 28). Tab-delimited American Standard Code for Information Interchange (ASCII) data files and metadata are provided in appendixes 4–6. Data for stream-water sites and their drainage basins are provided in appendix 4, data for pesticide concentrations in stream-water samples are provided in appendix 5, and data for pesticides selected for trend analysis are provided in appendix 6.

Table 5. Results of the procedure for identifying samples considered inappropriate for trend analysis.

[Sites are in descending ordered by number of samples not appropriate for trend analysis]

Station number	Study Unit abbreviation (explained in table 3)	Number of samples			Name of stream-water site
		Total	Appropriate for trend analysis?		
			No	Yes	
11303500	sanj	304	95	209	San Joaquin River near Vernalis, CA
11274538	sanj	276	81	195	Orestimba Creek at River Road near Crows Landing, CA
11273500	sanj	248	64	184	Merced River at River Road Bridge near Newman, CA
07369500	mise	126	63	63	Tensas River at Tendal, LA
394340085524601	whmi	291	38	253	Sugar Creek at County Road 400 South at New Palestine, IN
06800000	cnbr	236	36	200	Maple Creek near Nickerson, NE
06805500	cnbr	196	35	161	Platte River at Louisville, NE
01571490	lsus	99	33	66	Cedar Run at Eberlys Mill, PA
03353637	whmi	224	31	193	Little Buck Creek near Indianapolis, IN
01493500	podl	79	26	53	Morgan Creek near Kennedyville, MD
094196783	nvbr	170	25	145	Las Vegas Wash below Flamingo Wash near Las Vegas, NV
02326838	gafl	65	22	43	Lafayette Creek at Miccosukee Road at Tallahassee, FL
04072050	wmic	167	19	148	Duck Creek at Seminary Road near Oneida, WI
02350080	acfb	141	17	124	Lime Creek near Cobb, GA
02335870	acfb	176	16	160	Sope Creek near Marietta, GA
01349150	hdsn	183	14	169	Canajoharie Creek near Canajoharie, NY
05572000	lirb	135	12	123	Sangamon River at Monticello, IL
13351000	ccyk	146	11	135	Palouse River at Hooper, WA
01654000	podl	170	7	163	Accotink Creek near Annandale, VA
02317797	gafl	104	7	97	Little River at Upper Ty Ty Road near Tifton, GA
05553500	uirb	97	7	90	Illinois River at Ottawa, IL
06713500	splt	108	7	101	Cherry Creek at Denver, CO
05288705	umis	114	6	108	Shingle Creek at Queen Avenue at Minneapolis, MN
10168000	grsl	89	6	83	Little Cottonwood Creek at Jordan River near Salt Lake City, UT
12128000	pugt	112	6	106	Thornton Creek near Seattle, WA
01621050	podl	168	5	163	Muddy Creek at Mount Clinton, VA
0357479650	tenn	95	5	90	Hester Creek at Buddy Williamson Road near Plevna, AL
05082625	redn	66	5	61	Turtle River at Turtle River State Park near Arvilla, ND
01403900	linj	78	4	74	Bound Brook at Middlesex, NJ
01646580	podl	119	4	115	Potomac River at Chain Bridge at Washington, DC
03267900	whmi	107	4	103	Mad River at St. Paris Pike at Eagle City, OH
03374100	whmi	317	4	313	White River at Hazleton, IN
14211720	will	167	4	163	Willamette River at Portland, OR
252414080333200	sofl	107	4	103	C-111 Canal 100 feet above S-177 near Homestead, FL
01357500	hdsn	166	3	163	Mohawk River at Cohoes, NY
05531500	uirb	79	3	76	Salt Creek at Western Springs, IL
06714000	splt	66	3	63	South Platte River at Denver, CO
06934500	nasq	146	3	143	Missouri River at Hermann, MO
07031692	mise	59	3	56	Fletcher Creek at Sycamore View Road at Memphis, TN
07288650	mise	143	3	140	Bogue Phalia near Leland, MS
12113390	pugt	87	3	84	Duwamish River at golf course at Tukwila, WA
14206950	will	106	3	103	Fanno Creek at Durham, OR
01102500	necb	74	2	72	Aberjona River at Winchester, MA
01209710	conn	196	2	194	Norwalk River at Winnipauk, CT

Table 5. Results of the procedure for identifying samples considered inappropriate for trend analysis.—Continued

[Sites are in descending ordered by number of samples not appropriate for trend analysis]

Station number	Study Unit abbreviation (explained in table 3)	Number of samples			Name of stream-water site
		Total	Appropriate for trend analysis?		
			No	Yes	
01555400	lsus	94	2	92	East Mahantango Creek at Klingerstown, PA
03360895	whmi	55	2	53	Kessinger Ditch near Monroe City, IN
03575100	tenn	82	2	80	Flint River at Brownsboro, AL
04193500	leri	123	2	121	Maumee River at Waterville, OH
05102490	redn	76	2	74	Red River of the North at Pembina, ND
05331580	umis	91	2	89	Mississippi River below Lock and Dam 2 at Hastings, MN
05420500	nasq	127	2	125	Mississippi River at Clinton, IA
05525500	uirb	66	2	64	Sugar Creek at Milford, IL
05532500	uirb	55	2	53	Des Plaines River at Riverside, IL
08057200	trin	136	2	134	White Rock Creek at Greenville Avenue at Dallas, TX
09180500	nasq	49	2	47	Colorado River near Cisco, UT
09315000	nasq	48	2	46	Green River at Green River, UT
09404200	nasq	36	2	34	Colorado River above Diamond Creek near Peach Spring, AZ
09421500	nasq	37	2	35	Colorado River below Hoover Dam, AZ-NV
12472380	ccyk	38	2	36	Crab Creek Lateral above Royal Lake near Othello, WA
12510500	ccyk	80	2	78	Yakima River at Kiona, WA
13154500	usnk	120	2	118	Snake River at King Hill, ID
14201300	will	152	2	150	Zollner Creek near Mount Angel, OR
393944084120700	whmi	106	2	104	Holes Creek at Huffman Park at Kettering, OH
01356190	hdsn	93	1	92	Lisha Kill near Niskayuna, NY
01463500	delr	69	1	68	Delaware River at Trenton, NJ
01467150	delr	32	1	31	Cooper River at Haddonfield, NJ
01474500	delr	71	1	70	Schuylkill River at Philadelphia, PA
01477120	delr	31	1	30	Raccoon Creek near Swedesboro, NJ
01493112	podl	52	1	51	Chesterville Branch near Crumpton, MD
02169570	sant	98	1	97	Gills Creek at Columbia, SC
02174250	sant	125	1	124	Cow Castle Creek near Bowman, SC
0242354750	mobl	96	1	95	Cahaba Valley Creek at Cross Creek Road at Pelham, AL
02444490	mobl	74	1	73	Bogue Chitto Creek near Memphis, AL
03467609	tenn	104	1	103	Nolichucky River near Lowland, TN
03528000	tenn	28	1	27	Clinch River above Tazewell, TN
04087000	wmic	129	1	128	Milwaukee River at Milwaukee, WI
04186500	leri	92	1	91	Auglaize River near Fort Jennings, OH
05330000	umis	40	1	39	Minnesota River near Jordan, MN
05449500	eiwa	87	1	86	Iowa River near Rowan, IA
05451210	eiwa	105	1	104	South Fork Iowa River near New Providence, IA
05455100	eiwa	25	1	24	Old Mans Creek near Iowa City, IA
05461390	eiwa	22	1	21	Flood Creek near Powersville, IA
05464220	eiwa	53	1	52	Wolf Creek near Dysart, IA
05465000	eiwa	23	1	22	Cedar River near Conesville, IA
05465500	eiwa	136	1	135	Iowa River at Wapello, IA
06329500	yell	94	1	93	Yellowstone River near Sidney, MT
06753990	splt	84	1	83	Lonetree Creek near Greeley, CO
07022000	nasq	143	1	142	Mississippi River at Thebes, IL

Table 5. Results of the procedure for identifying samples considered inappropriate for trend analysis.—Continued

[Sites are in descending ordered by number of samples not appropriate for trend analysis]

Station number	Study Unit abbreviation (explained in table 3)	Number of samples			Name of stream-water site
		Total	Appropriate for trend analysis?		
			No	Yes	
07263620	nasq	105	1	104	Arkansas River at David Terry Dam below Little Rock, AR
08064100	trin	92	1	91	Chambers Creek near Rice, TX
08178800	sctx	97	1	96	Salado Creek at Loop 13 at San Antonio, TX
08181800	sctx	78	1	77	San Antonio River near Elmendorf, TX
08377200	nasq	90	1	89	Rio Grande at Foster Ranch near Langtry, TX
08470400	nasq	94	1	93	Arroyo Colorado at Harlingen, TX
09379500	nasq	42	1	41	San Juan River near Bluff, UT
10350500	nvbr	111	1	110	Truckee River at Clark, NV
11060400	sana	73	1	72	Warm Creek near San Bernardino, CA
12505450	ccyk	120	1	119	Granger Drain at Granger, WA
13353200	nasq	66	1	65	Snake River at Burbank, WA
14202000	will	33	1	32	Pudding River at Aurora, OR
14246900	nasq	109	1	108	Columbia River at Beaver Army Terminal near Quincy, OR
01100000	necb	23	0	23	Merrimack River below Concord River at Lowell, MA
01104615	necb	52	0	52	Charles River above Watertown Dam at Watertown, MA
01170970	conn	28	0	28	Hatfield Reservoir near West Hatfield, MA
01184000	conn	109	0	109	Connecticut River at Thompsonville, CT
01403300	linj	107	0	107	Raritan River at Queens Bridge at Bound Brook, NJ
01434000	delr	26	0	26	Delaware River at Port Jervis, NY
01451800	delr	32	0	32	Jordan Creek near Schnecksville, PA
01454700	delr	30	0	30	Lehigh River at Glendon, PA
01464907	delr	77	0	77	Little Neshaminy Creek at Valley Road near Neshaminy, PA
01470779	delr	51	0	51	Tulpehocken Creek near Bernville, PA
01472157	delr	60	0	60	French Creek near Phoenixville, PA
01559795	lsus	26	0	26	Bobs Creek near Pavia, PA
01578310	podl	58	0	58	Susquehanna River at Conowingo, MD
01645495	podl	25	0	25	Potomac River near Great Falls, VA
0208755215	albe	30	0	30	Neuse River above US 70 at Smithfield, NC
02087580	albe	61	0	61	Swift Creek near Apex, NC
02089500	albe	114	0	114	Neuse River at Kinston, NC
02091500	albe	123	0	123	Contentnea Creek at Hookerton, NC
02175000	sant	97	0	97	Edisto River near Givhans, SC
02215100	gafl	60	0	60	Tucsawhatchee Creek near Hawkinsville, GA
02281200	sofl	103	0	103	Hillsboro Canal at S-6 near Shawano, FL
02296750	sofl	30	0	30	Peace River at Arcadia, FL
02306774	gafl	49	0	49	Rocky Creek at Highway 587 at Citrus Park, FL
02318500	gafl	144	0	144	Withlacoochee River at US 84 near Quitman, GA
02336020	acfb	30	0	30	Intake on Chattahoochee River at Atlanta, GA
02337500	acfb	48	0	48	Snake Creek near Whitesburg, GA
02338000	acfb	105	0	105	Chattahoochee River near Whitesburg, GA
02419977	mobl	28	0	28	Three Mile Branch at North Boulevard at Montgomery, AL
02424000	mobl	40	0	40	Cahaba River at Centreville, AL
02429500	mobl	41	0	41	Alabama River at Claiborne, AL
02469762	mobl	52	0	52	Tombigbee Riber below Coffeeville Dam near Coffeeville, AL

Table 5. Results of the procedure for identifying samples considered inappropriate for trend analysis.—Continued

[Sites are in descending ordered by number of samples not appropriate for trend analysis]

Station number	Study Unit abbreviation (explained in table 3)	Number of samples: Total	Appropriate for trend analysis?: No	Appropriate for trend analysis?: Yes	Name of stream-water site
03086000	nasq	67	0	67	Ohio River at Sewickley, PA
03216600	nasq	125	0	125	Ohio River at Greenup Dam near Greenup, KY
03274000	whmi	35	0	35	Great Miami River at Hamilton, OH
03303280	nasq	133	0	133	Ohio River at Cannelton Dam at Cannelton, IN
03378500	nasq	124	0	124	Wabash River at New Harmony, IN
03438500	nasq	23	0	23	Cumberland River at Smithland, KY
03455000	tenn	28	0	28	French Broad River near Newport, TN
03466208	tenn	103	0	103	Big Limestone Creek near Limestone, TN
03474000	tenn	28	0	28	Middle Fork Holston River at Seven Mile Ford, VA
03526000	tenn	51	0	51	Copper Creek near Gate City, VA
03539778	tenn	28	0	28	Clear Creek at Lilly Bridge near Lancing, TN
03609750	nasq	82	0	82	Tennessee River at Highway 60 near Paducah, KY
03612500	nasq	131	0	131	Ohio River at Dam 53 near Grand Chain, IL
040869415	wmic	56	0	56	Lincoln Creek at 47th Street at Milwaukee, WI
04161820	leri	84	0	84	Clinton River at Sterling Heights, MI
04175600	leri	58	0	58	River Raisin near Manchester, MI
04178000	leri	78	0	78	St. Joseph River near Newville, IN
05320270	umis	109	0	109	Little Cobb River near Beauford, MN
05420680	eiwa	59	0	59	Wapsipinicon River near Tripoli, IA
05422000	eiwa	23	0	23	Wapsipinicon River near De Witt, IA
05453100	eiwa	23	0	23	Iowa River at Marengo, IA
05455570	eiwa	30	0	30	English River at Riverside, IA
05457750	eiwa	27	0	27	Cedar River near Carville, IA
05458900	eiwa	26	0	26	West Fork Cedar River at Finchford, IA
05474000	eiwa	22	0	22	Skunk River at Augusta, IA
05586100	lirb	122	0	122	Illinois River at Valley City, IL
05587455	nasq	100	0	100	Mississippi River below Grafton, IL
06185500	nasq	73	0	73	Missouri River near Culbertson, MT
06295000	yell	60	0	60	Yellowstone River at Forsyth, MT
06338490	nasq	48	0	48	Missouri River at Garrison Dam, ND
06440000	nasq	23	0	23	Missouri River at Pierre, SD
06467500	nasq	38	0	38	Missouri River at Yankton, SD
06610000	nasq	145	0	145	Missouri River at Omaha, NE
06754000	splt	120	0	120	South Platte River near Kersey, CO
06800500	cnbr	46	0	46	Elkhorn River at Waterloo, NE
07053250	ozrk	117	0	117	Yocum Creek near Oak Grove, AR
07060710	ozrk	33	0	33	North Sylamore Creek near Fifty-Six, AR
07288955	mise	158	0	158	Yazoo River below Steele Bayou near Long Lake, MS
07373420	nasq	145	0	145	Mississippi River near St. Francisville, LA
07379960	acad	69	0	69	Dawson Creek at Bluebonnet Boulevard near Baton Rouge, LA
07381495	nasq	143	0	143	Atchafalaya River at Melville, LA
08010000	acad	41	0	41	Bayou Des Cannes near Eunice, LA
08012150	acad	79	0	79	Mermentau River at Mermentau, LA
08012470	acad	72	0	72	Bayou Lacassine near Lake Arthur, LA

Table 5. Results of the procedure for identifying samples considered inappropriate for trend analysis.—Continued

[Sites are in descending ordered by number of samples not appropriate for trend analysis]

Station number	Study Unit abbreviation (explained in table 3)	Number of samples			Name of stream-water site
		Total	Appropriate for trend analysis?		
			No	Yes	
08014500	acad	37	0	37	Whiskey Chitto Creek near Oberlin, LA
08057410	trin	122	0	122	Trinity River below Dallas, TX
08364000	riog	121	0	121	Rio Grande at El Paso, TX
08374200	nasq	42	0	42	Rio Grande below Rio Conchos near Presidio, TX
08447410	nasq	87	0	87	Pecos River near Langtry, TX
08450900	nasq	57	0	57	Rio Grande below Amistad Dam near Del Rio, TX
08459200	nasq	71	0	71	Rio Grande at Pipeline Crossing below Laredo, TX
08461300	nasq	55	0	55	Rio Grande below Falcon Dam, TX
08475000	nasq	59	0	59	Rio Grande near Brownsville, TX
09163500	ucol	67	0	67	Colorado River near Colorado-Utah State Line
09380000	nasq	25	0	25	Colorado River at Lees Ferry, AZ
09429490	nasq	24	0	24	Colorado River above Imperial Dam, AZ-CA
09522000	nasq	36	0	36	Colorado River at International Boundary above Morelos Dam, AZ
10171000	grsl	68	0	68	Jordan River at County Road 1700 South at Salt Lake City, UT
11074000	sana	50	0	50	Santa Ana River below Prado Dam, CA
11391100	sacr	35	0	35	Sacramento Slough near Knights Landing, CA
11447360	sacr	94	0	94	Arcade Creek near Del Paso Heights, CA
11447650	sacr	120	0	120	Sacramento River at Freeport, CA
12400520	nasq	56	0	56	Columbia River at Northport, WA
12464770	ccyk	73	0	73	Crab Creek at Rocky Ford Road near Ritzville, WA
12471400	ccyk	55	0	55	Lind Coulee Wasteway at State Road 17 near Warden, WA
12472900	nasq	45	0	45	Columbia River at Vernita Bridge near Priest Rapid Dam, WA
13092747	usnk	171	0	171	Rock Creek above Highway 30/93 Crossing at Twin Falls, ID
14128910	nasq	45	0	45	Columbia River at Warrendale, OR
14200400	will	48	0	48	Little Abiqua Creek near Scotts Mills, OR

Summary

This report provides a water-quality data set of 44 commonly used pesticides and 8 pesticide degradates suitable for a national assessment of pesticide trends in streams and rivers of the United States. Water-quality samples collected from January 1992 through August 2006 at stream-water sites of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program and the National Stream Quality Accounting Network (NASQAN) Program were compiled, reviewed, selected, and prepared for trend analysis. The principal steps in data review for trend analysis were to (1) identify analytical schedule, (2) verify sample-level coding, (3) exclude inappropriate samples or results, (4) review pesticide detections per sample, (5) review high pesticide concentrations, and (6) review the spatial and temporal extent of NAWQA pesticide data and selection of analytical methods for trend analysis. The principal steps in data preparation for trend analysis were to (1) select stream-water sites for trend analysis, (2) identify routine reporting levels used to report nondetections unaffected by matrix interference, (3) reassign the concentration value for routine nondetections to the maximum value of the long-term method detection level, (4) round concentrations to a consistent level of precision for the concentration range, (5) adjust concentrations to compensate for temporal changes in bias of recovery of the gas chromatography/mass spectrometry (GCMS) analytical method, and (6) identify samples considered inappropriate for trend analysis.

Samples analyzed at the USGS National Water Quality Laboratory (NWQL) by the GCMS analytical method were the most extensive in time and space and, consequently, were selected for trend analysis. Stream-water sites with three or more water years of data with six or more samples per year were selected for pesticide trend analysis. The selection criteria described in the report produced a trend data set of 16,869 pesticide samples at 201 stream-water sites.

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Appendixes

Appendix 1, which consists of a narrative and a table, follows immediately in this document. The other appendixes are separate documents available for downloading from the indicated Web addresses. Appendixes 2 and 3 are series of graphs; appendixes 4 through 6 are data sets and accompanying metadata. Table 6 from the main text follows appendix 1.

Appendixes:

Appendix 1—Procedures Used to Review Water-Quality Data

The NASQAN data set contained pesticide data collected at stream-water sites and analyzed by a single analytical method. The NAWQA data set contained pesticide data collected at a variety of site types (for example, stream water, groundwater, lakes, and springs) and analyzed by a variety of analytical methods. Both data sets contained field-submitted QC samples (for example blanks, spikes, and replicates) as well as routine environmental samples. The primary responsibility for water-quality data review is at the Study Unit or State level by personnel knowledgeable about local conditions. After aggregation into national data bases, data are subjected to program-specific automated data-checking routines intended to identify erroneous or incomplete coding and missing or unusual concentrations. The principal additional steps in data review for trend analysis were to (1) identify analytical method and schedule, (2) verify sample-level coding, (3) exclude inappropriate samples or results, (4) review pesticide detections per sample, (5) review high pesticide concentrations, and (6) review the spatial and temporal extent of NAWQA pesticide data and selection of analytical methods for trend analysis. Details of these procedures are provided in the following sectionMuch of the following discussion uses terms relevant to the USGS NWIS data base (the data base used to store USGS site information and water-quality data). Information on the NWIS data base is contained in Gellenbeck and others (2006). Chapters 1 and 2 explain the structure of the data base and basic terminology (such as sample, result, parameter code, method code, site type code, and station number). Appendix A further explains codes of relevance to this report (medium code, sample type code, station (site) type code, remark code, and data-quality indicator code).

Identification of Analytical Method and Schedule

The first step in data review was to assign the analytical schedule(s) used to measure the pesticide concentrations in the water sample. Knowledge of the analytical schedule is important because it indicates the analytical method(s) and the suite of pesticides analyzed by the method(s). Knowledge of the suite of pesticides analyzed is critical for determining the number and percentage of pesticide detections per sample (statistics useful in data review).

Analytical schedule generally was determined by comparing NWIS parameter codes and method codes to reference lists. Some pesticides had missing or invalid method codes, and the analytical schedule for these pesticides was determined by review of analytical schedules of other pesticides in the sample or by review of the analytical schedule used for other samples collected at the site. Several analytical schedules, including the four ultimately selected for trend analysis, could not be determined from reference lists because the same parameter and method codes are used for multiple analytical schedules. For these schedules, a computer program was written that (1) counted the parameter code and method code combinations for each pesticide in the sample and compared the count to the expected count for each analytical schedule and (2) identified parameter code and method code combinations for at least one pesticide that were unique to a particular analytical schedule. Review of the computer program's schedule assignments indicated a high degree of confidence in the assignment of the analytical schedule. Further review of water-quality data was restricted to the 22 most commonly used analytical schedules (9 analytical methods).

Review of Sample Codes

Water-quality samples were reviewed for consistency among sample medium code, sample type code, and station (site) type codes. Samples with unusual or inappropriate combinations of codes were reviewed in detail (for example, a sample with a groundwater medium code collected at a stream-water site). Coding discrepancies were resolved and fixed or samples were deleted from the data set. Further review of water-quality data was restricted to water samples collected at stream-water sites or from wells [NWIS sample medium code equal to 9 (surface water), 6 (groundwater), Q (blank water), R (quality-assurance, surface water), or S (quality-assurance, groundwater)].

Exclusion of Samples or Selected Analytical Results

Some types of samples or analytical results were considered inappropriate for an assessment of trends and were deleted from the data set. Composite samples (multiple, individual samples collected over time and combined into a single sample) were deleted (NWIS sample type code equal to H or samples with populated values for NWIS sample end dates and end times). Analytical results of zero or null were deleted, as were results with NWIS remark code equal to V (contaminated). Analytical results remarked V (by Study Unit personnel after reviewing the field-submitted QC data) indicate that a result was affected by a significant amount of contamination (U.S. Geological Survey, 1997b). Analytical results with NWIS data-quality indicator code equal to Q or X were deleted (these codes indicate that Study Unit personnel reviewed and rejected the analytical result).

Subsequent to the deletions made for the reasons described previously, the percentage of pesticides with analytical results was calculated by analytical schedule for each sample. In general, if the percentage of pesticides in the schedule was less than 75 percent, all of the pesticides analyzed by that schedule were deleted from the sample (schedules with a small number of pesticides had a less rigorous threshold for deletion). This "completeness" criterion was selected by review of the distribution of the percent completeness for all samples analyzed by a schedule. Nearly all of the analytes removed by this criterion were from samples that had a low percentage of the number of analytes expected for the schedule. Schedules with a low percentage of analytes were attributed to data-management/data-editing errors. Application of this completeness criterion facilitated review of percent detections by analytical schedule and eliminated samples that are inappropriate for some types of water-quality assessments that depend on a complete suite of analytes (such as pesticide toxicity indexes).

Review of Detections by Analytical Schedule

The percentage of pesticide detections was calculated by analytical schedule for each sample. The purpose of reviewing percent detections was to identify samples with an unusually large or small number of detections. Samples with an unusual number of detections usually are the result of natural hydrologic variability but also may arise when sample bottles are misidentified, incorrectly labeled, or otherwise inadvertently switched between sampling sites or between environmental samples and field-submitted QC samples. Misidentification can occur in either the field or the laboratory.

Some types of misidentification were easily determined, particularly for samples collected during the same site visit. Field spikes, for example, were easily distinguished from all other samples because all or nearly all of the pesticides were detected and all at approximately the same concentration. Field blanks generally have no detected pesticides and easily can be identified when switched with an environmental sample at a stream-water site that routinely has pesticides. Although some types of misidentifications are easily determined, others are more subtle and require an experienced data reviewer.

Selected samples were identified for additional review if they had an unusual number (percentage) of pesticide detections: more that 10 percent in groundwater samples, more than 30 percent in stream-water samples, more than 5 percent in field blank samples, and less than 90 percent in field spike samples. These samples and other samples collected on the same day for a Study Unit were reviewed for possible misidentification. In addition, timeseries of sample detections (environmental and field QC samples) were reviewed by stream-water site. Most errors identified by this review step involved field-submitted QC samples; few environmental samples were misidentified. NWIS medium codes and sample type codes were corrected, and data-checking routines were rerun.

Review of Large Concentrations

The 50 detections with the largest concentrations were plotted versus ranked concentration for each pesticide separately for stream-water samples, groundwater samples, and field blank samples. Concentrations were reviewed to determine if any concentration was unreasonably large in comparison to other high-concentration samples; one detection of *alpha*-HCH (1.88 µg/L) in stream water was deleted as a result of this review. This *alpha*-HCH concentration was nine times greater than the second ranked concentration and also was not detected in a field replicate water sample collected during the same site visit.

Review of the Spatial and Temporal Extent of NAWQA Pesticide Data and Selection of Analytical Methods for Trend Analysis

Water-quality samples and analytical results meeting the criteria described in the preceding sections were reviewed for potential use in a national assessment of pesticides in streams. Pesticide data from 23,867 stream-water samples (NWIS sample medium code equal to 9) collected at NAWQA stream-water sites were summarized by analytical method, site, and water year. Based on this review of NAWQA samples, and the extensive number of NASQAN samples analyzed by the GCMS method, only pesticide data from stream-water samples analyzed by the GCMS method at NWQL were considered sufficiently extensive in time and space for a national assessment of pesticide trends in streams (table A1).

Table A1. NAWQA stream-water pesticide samples by analytical method and water year.

[NAWQA, National Water-Quality Assessment Program; GCMS, Common pesticides and selected degradates by gas chromatography/mass spectrometry; HPLC, Pesticides and selected degradates by high-performance liquid chromatography/photodiode-array detection; GCM2, Moderate-use pesticides and selected degradates by gas chromatography/mass spectrometry; LCMS, Polar pesticides and selected degradates by high-performance liquid chromatography/mass spectrometry; LCAA, Chloroacetanilide herbicide degradates by high-performance liquid chromatography/mass spectrometry; GCS, Triazine and chloroacetanilide herbicides by gas chromatography/mass spectrometry; GCR, Rice and cotton herbicides by high-performance liquid chromatography/mass spectrometry; HPAA, Chloroacetanilide herbicide degradates by high-performance liquid chromatography/diode-array detection; LCGY, Glyphosate, Glufosinate, and AMPA by gas chromatography/mass spectrometry; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory; OGRL, Organic Geochemistry Research Laboratory]

Analytical method for pesticides	USGS laboratory	Number of samples	Number of samples in indicated water year (October 1 through September 30)														
			1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
GCMS	NWQL	21,854	324	1,077	2,319	1,252	947	2,063	1,365	1,905	2,323	2,144	1,644	1,890	1,422	641	538
HPLC	NWQL	5,713	0	890	1,920	573	405	1,279	392	216	32	6	0	0	0	0	0
GCM2	NWQL	3,128	0	0	0	0	0	0	0	177	199	71	20	962	534	627	538
LCMS	NWQL	2,777	0	0	0	0	0	0	0	654	629	228	715	158	39	208	146
LCAA	OGRL	1,534	0	0	0	0	0	1	5	111	189	142	375	310	259	90	52
GCS	OGRL	1,017	66	113	140	35	120	224	187	61	26	42	3	0	0	0	0
GCR	OGRL	695	0	0	0	53	161	342	82	35	22	0	0	0	0	0	0
HPAA	OGRL	547	0	0	0	0	97	225	169	22	34	0	0	0	0	0	0
LCGY	OGRL	493	0	0	0	0	0	0	0	0	0	0	23	365	40	65	0
LCGY	NWQL	93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	93

Table 6. Stream-water sites and samples selected for trend analysis.

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
01100000	Merrimack River below Concord River at Lowell, MA	necb	23	41	9
01102500	Aberjona River at Winchester, MA	necb	72	14	3
01104615	Charles River above Watertown Dam at Watertown, MA	necb	52	28	6
01170970	Hatfield Reservoir near West Hatfield, MA	conn	28	22	5
01184000	Connecticut River at Thompsonville, CT	conn	109	28	5
01209710	Norwalk River at Winnipauk, CT	conn	194	14	4
01349150	Canajoharie Creek near Canajoharie, NY	hdsn	169	21.5	5
01356190	Lisha Kill near Niskayuna, NY	hdsn	92	28	6
01357500	Mohawk River at Cohoes, NY	hdsn	163	26	4
01403300	Raritan River at Queens Bridge at Bound Brook, NJ	linj	107	29	5
01403900	Bound Brook at Middlesex, NJ	linj	74	27	6
01434000	Delaware River at Port Jervis, NY	delr	26	34	7
01451800	Jordan Creek near Schnecksville, PA	delr	32	28	5
01454700	Lehigh River at Glendon, PA	delr	30	29	8
01463500	Delaware River at Trenton, NJ	delr	68	34	9
01464907	Little Neshaminy Creek at Valley Road near Neshaminy, PA	delr	77	22.5	5
01467150	Cooper River at Haddonfield, NJ	delr	31	30	4
01470779	Tulpehocken Creek near Bernville, PA	delr	51	15	5
01472157	French Creek near Phoenixville, PA	delr	60	29	5
01474500	Schuylkill River at Philadelphia, PA	delr	70	25	7
01477120	Raccoon Creek near Swedesboro, NJ	delr	30	31	9
01493112	Chesterville Branch near Crumpton, MD	podl	51	27	4
01493500	Morgan Creek near Kennedyville, MD	podl	53	12.5	5
01555400	East Mahantango Creek at Klingerstown, PA	lsus	92	14	5
01559795	Bobs Creek near Pavia, PA	lsus	26	29	14
01571490	Cedar Run at Eberlys Mill, PA	lsus	66	13	5
01578310	Susquehanna River at Conowingo, MD	podl	58	34	14
01621050	Muddy Creek at Mount Clinton, VA	podl	163	18	3
01645495	Potomac River near Great Falls, VA	podl	25	30.5	14

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	0	0	0	0	0	0	0	0	0	8	7	8	0	0
0	0	0	0	0	0	0	22	26	0	8	8	8	0	0
0	0	0	0	0	0	0	9	11	0	8	8	8	5	3
0	0	0	0	0	0	0	0	0	0	0	11	7	9	1
0	0	5	0	0	5	11	12	12	12	18	18	8	6	2
0	26	32	0	0	10	17	17	18	13	28	18	8	5	2
0	0	14	22	10	10	20	18	18	11	8	8	7	6	17
0	0	15	21	0	0	0	0	0	11	8	8	8	6	15
0	0	14	20	12	11	17	16	17	12	8	8	9	6	13
0	0	0	0	6	16	5	10	12	12	9	9	8	6	14
0	0	0	0	14	21	5	0	0	8	9	9	8	0	0
0	0	0	0	0	0	0	8	11	7	0	0	0	0	0
0	0	0	0	0	0	0	11	14	7	0	0	0	0	0
0	0	0	0	0	0	0	10	13	7	0	0	0	0	0
0	0	0	0	0	0	0	10	13	8	9	9	8	6	5
0	0	0	0	0	0	0	23	20	8	9	9	8	0	0
0	0	0	0	0	0	0	10	12	9	0	0	0	0	0
0	0	0	0	0	0	0	24	20	7	0	0	0	0	0
0	0	0	0	0	0	0	11	15	9	9	8	8	0	0
0	0	0	0	0	0	0	17	19	8	10	8	8	0	0
0	0	0	0	0	0	0	10	12	8	0	0	0	0	0
0	0	0	0	0	0	0	16	11	12	12	0	0	0	0
0	0	0	0	0	0	0	0	1	0	22	21	9	0	0
0	23	20	1	0	12	12	12	12	0	0	0	0	0	0
0	0	0	1	0	6	7	6	6	0	0	0	0	0	0
0	23	21	21	0	1	0	0	0	0	0	0	0	0	0
0	0	1	0	0	9	5	6	6	7	8	9	7	0	0
0	21	10	3	0	12	13	13	16	12	26	18	8	6	5
0	0	0	0	0	0	0	0	0	0	0	6	8	11	0

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
01646580	Potomac River at Chain Bridge at Washington, DC	podl	115	28	4
01654000	Accotink Creek near Annandale, VA	podl	163	15	5
0208755215	Neuse River above US 70 at Smithfield, NC	albe	30	29	7
02087580	Swift Creek near Apex, NC	albe	61	21	5
02089500	Neuse River at Kinston, NC	albe	114	29	7
02091500	Contentnea Creek at Hookerton, NC	albe	123	23	5
02169570	Gills Creek at Columbia, SC	sant	97	14.5	4
02174250	Cow Castle Creek near Bowman, SC	sant	124	15	4
02175000	Edisto River near Givhans, SC	sant	97	28	7
02215100	Tucsawhatchee Creek near Hawkinsville, GA	gafl	60	8	5
02281200	Hillsboro Canal at S-6 near Shawano, FL	sofl	103	28	4
02296750	Peace River at Arcadia, FL	sofl	30	39	14
02306774	Rocky Creek at Highway 587 at Citrus Park, FL	gafl	49	14	5
02317797	Little River at Upper Ty Ty Road near Tifton, GA	gafl	97	28	4
02318500	Withlacoochee River at US 84 near Quitman, GA	gafl	144	28	6
02326838	Lafayette Creek at Miccosukee Road at Tallahassee, FL	gafl	43	15.5	4
02335870	Sope Creek near Marietta, GA	acfb	160	19	4
02336020	Intake on Chattahoochee River at Atlanta, GA	acfb	30	26	4
02337500	Snake Creek near Whitesburg, GA	acfb	48	34	9
02338000	Chattahoochee River near Whitesburg, GA	acfb	105	30	7
02350080	Lime Creek near Cobb, GA	acfb	124	14	4
02419977	Three Mile Branch at North Boulevard at Montgomery, AL	mobl	28	33	14
0242354750	Cahaba Valley Creek at Cross Creek Road at Pelham, AL	mobl	95	25.5	5
02424000	Cahaba River at Centreville, AL	mobl	40	16	7
02429500	Alabama River at Claiborne, AL	mobl	41	36	10
02444490	Bogue Chitto Creek near Memphis, AL	mobl	73	22.5	4
02469762	Tombigbee Riber below Coffeeville Dam near Coffeeville, AL	mobl	52	45	8
03086000	Ohio River at Sewickley, PA	nasq	67	23	5

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	0	2	0	4	7	12	13	11	12	17	18	8	6	5
0	0	22	13	0	12	14	13	18	7	27	18	8	6	5
0	0	0	0	0	0	0	0	0	0	0	13	7	10	0
0	0	0	0	0	0	0	0	0	0	25	17	8	6	5
0	0	2	2	0	8	12	12	12	11	17	18	8	6	6
0	0	2	2	0	8	12	7	18	12	24	18	8	6	6
0	0	0	0	33	9	0	0	0	11	8	8	8	6	14
0	0	0	0	33	5	1	14	15	12	8	8	8	6	14
0	0	0	0	15	2	1	11	12	12	9	8	8	6	13
0	30	15	12	3	0	0	0	0	0	0	0	0	0	0
0	0	0	0	2	31	12	12	7	6	8	8	8	6	3
0	0	0	0	0	0	1	0	0	5	8	8	8	0	0
0	0	0	0	0	0	0	0	0	0	25	14	9	1	0
0	14	13	7	1	5	3	6	6	7	11	16	8	0	0
0	19	11	12	4	6	5	8	12	11	18	17	10	5	6
0	16	14	9	4	0	0	0	0	0	0	0	0	0	0
0	24	23	8	0	6	6	11	11	10	24	19	8	6	4
0	0	0	0	0	0	0	0	0	0	0	12	8	10	0
0	0	3	0	0	5	6	12	11	11	0	0	0	0	0
0	0	3	2	1	5	6	12	12	11	18	18	8	6	3
0	25	25	6	0	0	0	0	0	8	25	18	8	6	3
0	0	0	0	0	0	0	7	9	12	0	0	0	0	0
0	0	0	0	0	0	0	31	17	13	8	8	8	6	4
0	0	0	0	0	0	0	17	15	8	0	0	0	0	0
0	0	0	0	0	0	0	2	7	8	8	8	8	0	0
0	0	0	0	0	0	0	25	12	13	7	8	8	0	0
0	0	0	0	0	0	0	3	7	8	8	8	8	6	4
0	0	0	0	0	0	0	0	0	12	13	15	15	12	0

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
03216600	Ohio River at Greenup Dam near Greenup, KY	nasq	125	21	5
03267900	Mad River at St. Paris Pike at Eagle City, OH	whmi	103	15	5
03274000	Great Miami River at Hamilton, OH	whmi	35	16	4
03303280	Ohio River at Cannelton Dam at Cannelton, IN	nasq	133	21.5	6
03353637	Little Buck Creek near Indianapolis, IN	whmi	193	14	4
03360895	Kessinger Ditch near Monroe City, IN	whmi	53	14	6
03374100	White River at Hazleton, IN	whmi	313	8	4
03378500	Wabash River at New Harmony, IN	nasq	124	21	5
03438500	Cumberland River at Smithland, KY	nasq	23	57	28
03455000	French Broad River near Newport, TN	tenn	28	25	6
03466208	Big Limestone Creek near Limestone, TN	tenn	103	23.5	5
03467609	Nolichucky River near Lowland, TN	tenn	103	25	3
03474000	Middle Fork Holston River at Seven Mile Ford, VA	tenn	28	28	13
03526000	Copper Creek near Gate City, VA	tenn	51	8	4
03528000	Clinch River above Tazewell, TN	tenn	27	31.5	13
03539778	Clear Creek at Lilly Bridge near Lancing, TN	tenn	28	29	6
0357479650	Hester Creek at Buddy Williamson Road near Plevna, AL	tenn	90	27	5
03575100	Flint River at Brownsboro, AL	tenn	80	28	5
03609750	Tennessee River at Highway 60 near Paducah, KY	nasq	82	32	5
03612500	Ohio River at Dam 53 near Grand Chain, IL	nasq	131	21	6
04072050	Duck Creek at Seminary Road near Oneida, WI	wmic	148	15	4
040869415	Lincoln Creek at 47th Street at Milwaukee, WI	wmic	56	20	4
04087000	Milwaukee River at Milwaukee, WI	wmic	128	27	4
04161820	Clinton River at Sterling Heights, MI	leri	84	28	4
04175600	River Raisin near Manchester, MI	leri	58	29	7
04178000	St. Joseph River near Newville, IN	leri	78	28	5
04186500	Auglaize River near Fort Jennings, OH	leri	91	28	4
04193500	Maumee River at Waterville, OH	leri	121	28	4

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	0	0	0	0	14	14	12	11	15	15	15	15	14	0
0	0	0	0	0	0	0	20	20	12	25	18	8	0	0
0	0	0	0	0	0	0	14	13	8	0	0	0	0	0
0	0	0	0	11	13	13	12	12	15	15	15	15	12	0
20	28	16	13	13	8	12	8	12	14	24	17	8	0	0
0	23	15	15	0	0	0	0	0	0	0	0	0	0	0
31	28	17	26	27	27	23	23	26	26	22	19	8	5	5
0	0	0	0	0	15	14	12	10	15	14	14	16	14	0
0	0	0	0	0	0	0	0	0	0	6	6	6	5	0
0	0	0	0	7	12	9	0	0	0	0	0	0	0	0
0	0	0	1	28	18	8	8	6	10	8	8	8	0	0
0	0	0	0	28	18	10	9	6	10	7	8	7	0	0
0	0	0	1	7	13	7	0	0	0	0	0	0	0	0
0	0	0	1	28	15	7	0	0	0	0	0	0	0	0
0	0	0	1	7	12	7	0	0	0	0	0	0	0	0
0	0	0	0	0	8	12	0	0	7	1	0	0	0	0
0	0	0	0	0	0	0	26	18	11	9	9	8	6	3
0	0	0	0	0	0	0	18	17	12	8	8	8	6	3
0	0	0	0	0	14	12	12	12	10	6	5	6	5	0
0	0	0	0	7	14	14	11	13	15	15	13	15	14	0
0	19	16	3	0	10	11	10	15	13	25	18	8	0	0
0	0	0	0	0	0	0	0	0	5	24	18	9	0	0
0	16	17	0	1	5	12	11	11	11	18	18	8	0	0
0	0	0	0	8	25	4	0	0	7	7	8	8	5	12
0	0	0	0	8	15	4	0	0	7	8	8	8	0	0
0	0	0	0	8	22	14	5	0	6	7	7	9	0	0
0	0	0	0	8	22	7	0	0	7	7	8	9	4	19
0	0	0	0	9	18	14	13	13	12	7	8	8	5	14

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
05082625	Turtle River at Turtle River State Park near Arvilla, ND	redn	61	19	4
05102490	Red River of the North at Pembina, ND	redn	74	27	5
05288705	Shingle Creek at Queen Avenue at Minneapolis, MN	umis	108	27	2
05320270	Little Cobb River near Beauford, MN	umis	109	22	4
05330000	Minnesota River near Jordan, MN	umis	39	23.5	6
05331580	Mississippi River below Lock and Dam 2 at Hastings, MN	umis	89	32	7
05420500	Mississippi River at Clinton, IA	nasq	125	22	5
05420680	Wapsipinicon River near Tripoli, IA	eiwa	59	30.5	7
05422000	Wapsipinicon River near De Witt, IA	eiwa	23	28.5	7
05449500	Iowa River near Rowan, IA	eiwa	86	28	6
05451210	South Fork Iowa River near New Providence, IA	eiwa	104	29	3
05453100	Iowa River at Marengo, IA	eiwa	23	28.5	8
05455100	Old Mans Creek near Iowa City, IA	eiwa	24	28	8
05455570	English River at Riverside, IA	eiwa	30	28	14
05457750	Cedar River near Carville, IA	eiwa	27	33	9
05458900	West Fork Cedar River at Finchford, IA	eiwa	26	33	12
05461390	Flood Creek near Powersville, IA	eiwa	21	31	15
05464220	Wolf Creek near Dysart, IA	eiwa	52	15	5
05465000	Cedar River near Conesville, IA	eiwa	22	30	12
05465500	Iowa River at Wapello, IA	eiwa	135	28	4
05474000	Skunk River at Augusta, IA	eiwa	22	28	7
05525500	Sugar Creek at Milford, IL	uirb	64	28	3
05531500	Salt Creek at Western Springs, IL	uirb	76	29	5
05532500	Des Plaines River at Riverside, IL	uirb	53	31.5	7
05553500	Illinois River at Ottawa, IL	uirb	90	28	5
05572000	Sangamon River at Monticello, IL	lirb	123	11.5	4
05586100	Illinois River at Valley City, IL	lirb	122	28	5
05587455	Mississippi River below Grafton, IL	nasq	100	27	5
06185500	Missouri River near Culbertson, MT	nasq	73	27.5	8
06295000	Yellowstone River at Forsyth, MT	yell	60	27	5
06329500	Yellowstone River near Sidney, MT	yell	93	27	7

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	16	10	1	0	6	8	11	9	0	0	0	0	0	0
0	17	11	7	5	5	9	9	11	0	0	0	0	0	0
0	0	0	0	2	28	14	7	4	7	9	8	9	5	15
0	0	0	0	8	29	13	9	4	6	7	7	6	6	14
0	0	0	0	8	16	15	0	0	0	0	0	0	0	0
0	0	0	0	9	14	14	8	10	11	8	7	8	0	0
0	0	0	0	12	13	13	13	11	14	12	12	13	12	0
0	0	0	0	7	7	8	1	0	9	10	9	8	0	0
0	0	0	0	8	7	7	0	1	0	0	0	0	0	0
0	0	0	0	7	27	16	0	0	9	10	9	8	0	0
0	0	0	0	7	6	8	9	12	12	10	9	8	6	17
0	0	0	0	8	7	8	0	0	0	0	0	0	0	0
0	0	0	0	8	7	8	0	1	0	0	0	0	0	0
0	0	0	0	7	12	11	0	0	0	0	0	0	0	0
0	0	0	0	6	10	11	0	0	0	0	0	0	0	0
0	0	0	0	6	9	11	0	0	0	0	0	0	0	0
0	0	0	0	8	6	6	1	0	0	0	0	0	0	0
0	0	0	0	7	28	16	0	1	0	0	0	0	0	0
0	0	0	0	7	8	6	1	0	0	0	0	0	0	0
0	0	0	0	8	28	15	12	12	11	10	9	8	9	13
0	0	0	0	7	6	8	0	1	0	0	0	0	0	0
0	0	0	0	0	0	0	16	17	6	8	8	8	1	0
0	0	0	0	0	0	0	21	13	6	8	8	8	6	6
0	0	0	0	0	0	0	12	11	6	8	8	8	0	0
0	0	0	0	7	18	19	7	8	7	8	8	8	0	0
0	0	0	0	1	32	32	0	0	7	8	8	8	6	21
0	0	0	0	5	20	21	12	12	10	8	7	7	6	14
0	0	0	0	0	11	15	14	13	15	11	0	9	12	0
0	0	0	0	0	9	9	9	8	8	7	8	8	7	0
0	0	0	0	0	0	0	16	14	12	8	8	2	0	0
0	0	0	0	5	11	12	17	16	12	8	8	2	2	0

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
06338490	Missouri River at Garrison Dam, ND	nasq	48	53	15
06440000	Missouri River at Pierre, SD	nasq	23	55.5	27
06467500	Missouri River at Yankton, SD	nasq	38	42	20
06610000	Missouri River at Omaha, NE	nasq	145	18	4
06713500	Cherry Creek at Denver, CO	splt	101	22.5	3
06714000	South Platte River at Denver, CO	splt	63	16	5
06753990	Lonetree Creek near Greeley, CO	splt	83	15.5	4
06754000	South Platte River near Kersey, CO	splt	120	28	6
06800000	Maple Creek near Nickerson, NE	cnbr	200	14	5
06800500	Elkhorn River at Waterloo, NE	cnbr	46	21	10
06805500	Platte River at Louisville, NE	cnbr	161	26	3
06934500	Missouri River at Hermann, MO	nasq	143	21	3
07022000	Mississippi River at Thebes, IL	nasq	142	21	5
07031692	Fletcher Creek at Sycamore View Road at Memphis, TN	mise	56	29	5
07053250	Yocum Creek near Oak Grove, AR	ozrk	117	21	6
07060710	North Sylamore Creek near Fifty-Six, AR	ozrk	33	29	21
07263620	Arkansas River at David Terry Dam below Little Rock, AR	nasq	104	30	6
07288650	Bogue Phalia near Leland, MS	mise	140	16	4
07288955	Yazoo River below Steele Bayou near Long Lake, MS	mise	158	22	5
07369500	Tensas River at Tendal, LA	mise	63	17	4
07373420	Mississippi River near St. Francisville, LA	nasq	145	20	4
07379960	Dawson Creek at Bluebonnet Boulevard near Baton Rouge, LA	acad	69	21	4
07381495	Atchafalaya River at Melville, LA	nasq	143	21	7
08010000	Bayou Des Cannes near Eunice, LA	acad	41	22	6
08012150	Mermentau River at Mermentau, LA	acad	79	29.5	8
08012470	Bayou Lacassine near Lake Arthur, LA	acad	72	28	4
08014500	Whiskey Chitto Creek near Oberlin, LA	acad	37	28	12
08057200	White Rock Creek at Greenville Avenue at Dallas, TX	trin	134	22	4
08057410	Trinity River below Dallas, TX	trin	122	29	5
08064100	Chambers Creek near Rice, TX	trin	91	26	6

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	0	0	0	0	4	6	6	6	5	6	6	5	4	0
0	0	0	0	0	6	5	6	6	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	7	8	8	8	7	0
0	0	0	0	13	15	15	14	14	15	15	15	15	14	0
0	14	14	3	0	0	0	0	0	7	25	18	8	6	6
0	0	13	3	0	8	12	12	12	3	0	0	0	0	0
0	17	18	0	0	0	0	0	0	8	22	10	8	0	0
0	0	12	0	0	5	11	12	12	12	18	18	8	6	6
16	7	6	0	0	11	19	17	17	12	25	29	30	6	5
0	2	0	0	0	0	0	0	0	0	18	18	8	0	0
17	8	6	0	5	13	16	14	15	11	18	18	8	6	6
0	0	0	0	15	15	15	14	14	14	13	14	15	14	0
0	0	0	0	15	15	14	14	14	13	15	14	14	14	0
0	0	0	0	0	23	0	0	0	6	10	9	8	0	0
0	0	21	5	0	9	12	11	11	8	8	7	8	13	4
0	0	1	3	0	5	6	4	6	8	0	0	0	0	0
0	0	0	0	12	13	10	11	10	10	10	10	10	8	0
0	0	0	0	17	36	15	11	4	8	7	8	7	21	6
0	0	0	0	16	26	14	12	12	11	10	12	11	18	16
0	0	0	0	8	27	13	11	4	0	0	0	0	0	0
0	0	0	0	14	15	14	15	14	15	15	15	14	14	0
0	0	0	0	0	0	1	16	29	4	8	8	3	0	0
0	0	0	0	13	15	14	15	13	14	15	15	15	14	0
0	0	0	0	0	0	1	16	15	9	0	0	0	0	0
0	0	0	0	0	0	1	16	17	9	8	8	8	6	6
0	0	0	0	0	0	1	16	17	14	8	8	8	0	0
0	0	0	0	0	0	1	15	12	9	0	0	0	0	0
0	0	0	5	0	7	16	16	15	12	24	18	10	6	5
0	3	2	11	0	5	11	12	12	12	17	18	8	6	5
0	4	17	11	0	0	0	0	0	7	21	14	8	6	3

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
08178800	Salado Creek at Loop 13 at San Antonio, TX	sctx	96	27	5
08181800	San Antonio River near Elmendorf, TX	sctx	77	33.5	6
08364000	Rio Grande at El Paso, TX	riog	121	30	5
08374200	Rio Grande below Rio Conchos near Presidio, TX	nasq	42	35	7
08377200	Rio Grande at Foster Ranch near Langtry, TX	nasq	89	34	5
08447410	Pecos River near Langtry, TX	nasq	87	34	3
08450900	Rio Grande below Amistad Dam near Del Rio, TX	nasq	57	49	20
08459200	Rio Grande at Pipeline Crossing below Laredo, TX	nasq	71	33.5	6
08461300	Rio Grande below Falcon Dam, TX	nasq	55	49.5	15
08470400	Arroyo Colorado at Harlingen, TX	nasq	93	29.5	5
08475000	Rio Grande near Brownsville, TX	nasq	59	39	14
09163500	Colorado River near Colorado-Utah State Line	ucol	67	36.5	7
09180500	Colorado River near Cisco, UT	nasq	47	28	8
09315000	Green River at Green River, UT	nasq	46	28	8
09379500	San Juan River near Bluff, UT	nasq	41	29	7
09380000	Colorado River at Lees Ferry, AZ	nasq	25	59	7
09404200	Colorado River above Diamond Creek near Peach Spring, AZ	nasq	34	28	7
094196783	Las Vegas Wash below Flamingo Wash near Las Vegas, NV	nvbr	145	16	6
09421500	Colorado River below Hoover Dam, AZ-NV	nasq	35	50	7
09429490	Colorado River above Imperial Dam, AZ-CA	nasq	24	62	21
09522000	Colorado River at International Boundary above Morelos Dam, AZ	nasq	36	79	21
10168000	Little Cottonwood Creek at Jordan River near Salt Lake City, UT	grsl	83	29	5
10171000	Jordan River at County Road 1700 South at Salt Lake City, UT	grsl	68	29	5
10350500	Truckee River at Clark, NV	nvbr	110	28	9
11060400	Warm Creek near San Bernardino, CA	sana	72	28	3
11074000	Santa Ana River below Prado Dam, CA	sana	50	36	27
11273500	Merced River at River Road Bridge near Newman, CA	sanj	184	14	4

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
0	0	0	0	0	25	7	0	0	11	8	8	8	24	5
0	0	0	0	0	14	7	9	12	10	8	9	8	0	0
0	0	6	5	7	12	10	8	10	12	8	9	8	14	12
0	0	0	0	0	0	0	4	8	5	4	6	8	7	0
0	0	0	0	13	11	9	9	9	8	9	6	8	7	0
0	0	0	0	13	11	9	8	8	8	8	7	8	7	0
0	0	0	0	5	6	6	6	6	6	6	5	6	5	0
0	0	0	0	0	0	8	12	10	9	10	8	8	6	0
0	0	0	0	5	4	7	6	6	5	6	6	6	4	0
0	0	0	0	9	11	10	10	10	10	10	8	8	7	0
0	0	0	0	9	6	9	6	4	1	2	7	8	7	0
0	0	0	0	0	6	3	6	9	11	7	8	8	6	3
0	0	0	0	5	12	10	10	10	0	0	0	0	0	0
0	0	0	0	4	12	10	10	10	0	0	0	0	0	0
0	0	0	0	2	12	9	9	9	0	0	0	0	0	0
0	0	0	0	3	4	6	6	6	0	0	0	0	0	0
0	0	0	0	0	9	8	9	8	0	0	0	0	0	0
0	10	24	7	0	0	12	10	12	12	24	18	6	6	4
0	0	0	0	11	6	6	6	6	0	0	0	0	0	0
0	0	0	0	1	5	6	6	6	0	0	0	0	0	0
0	0	0	0	2	3	6	6	6	3	2	3	2	3	0
0	0	0	0	0	0	0	22	14	12	8	8	8	6	5
0	0	0	0	0	0	0	20	12	12	8	8	8	0	0
0	0	8	0	0	4	12	12	12	12	18	17	8	6	1
0	0	0	0	0	0	0	16	21	11	8	8	8	0	0
0	0	0	0	0	0	0	0	3	11	8	8	8	6	6
0	25	12	0	0	10	15	15	18	32	18	21	8	5	5

Table 6. Stream-water sites and samples selected for trend analysis.—Continued

Station number	Name of stream-water site	Study Unit abbreviation (explained in table 3)	Number of samples	Median number of days between samples	Minimum number of days between samples
11274538	Orestimba Creek at River Road near Crows Landing, CA	sanj	195	14	3
11303500	San Joaquin River near Vernalis, CA	sanj	209	14	4
11391100	Sacramento Slough near Knights Landing, CA	sacr	35	35	20
11447360	Arcade Creek near Del Paso Heights, CA	sacr	94	21	4
11447650	Sacramento River at Freeport, CA	sacr	120	28	10
12113390	Duwamish River at golf course at Tukwila, WA	pugt	84	30	6
12128000	Thornton Creek near Seattle, WA	pugt	106	28	4
12400520	Columbia River at Northport, WA	nasq	56	29	12
12464770	Crab Creek at Rocky Ford Road near Ritzville, WA	ccyk	73	28.5	6
12471400	Lind Coulee Wasteway at State Road 17 near Warden, WA	ccyk	55	15	8
12472380	Crab Creek Lateral above Royal Lake near Othello, WA	ccyk	36	14	4
12472900	Columbia River at Vernita Bridge near Priest Rapid Dam, WA	nasq	45	38	9
12505450	Granger Drain at Granger, WA	ccyk	119	8	4
12510500	Yakima River at Kiona, WA	ccyk	78	27	6
13092747	Rock Creek above Highway 30/93 Crossing at Twin Falls, ID	usnk	171	21	5
13154500	Snake River at King Hill, ID	usnk	118	30	6
13351000	Palouse River at Hooper, WA	ccyk	135	28	3
13353200	Snake River at Burbank, WA	nasq	65	23.5	8
14128910	Columbia River at Warrendale, OR	nasq	45	28.5	6
14200400	Little Abiqua Creek near Scotts Mills, OR	will	48	34	19
14201300	Zollner Creek near Mount Angel, OR	will	150	21	5
14202000	Pudding River at Aurora, OR	will	32	29	4
14206950	Fanno Creek at Durham, OR	will	103	25	4
14211720	Willamette River at Portland, OR	will	163	28	3
14246900	Columbia River at Beaver Army Terminal near Quincy, OR	nasq	108	29	5
252414080333200	C-111 Canal 100 feet above S-177 near Homestead, FL	sofl	103	28	5
393944084120700	Holes Creek at Huffman Park at Kettering, OH	whmi	104	15	3
394340085524601	Sugar Creek at County Road 400 South at New Palestine, IN	whmi	253	14	3

Number of samples in indicated water year (October 1 through September 30)														
1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
20	27	3	1	0	10	14	16	17	33	19	16	8	6	5
19	26	16	8	0	9	11	12	17	35	19	20	7	5	5
0	0	0	0	0	2	0	0	0	9	8	9	7	0	0
0	0	0	0	0	21	9	0	0	9	9	9	8	23	6
0	0	0	0	0	15	11	12	12	12	8	9	9	16	16
0	0	0	0	10	11	0	12	12	12	9	9	9	0	0
0	0	0	0	14	19	9	0	0	8	9	9	9	24	5
0	0	0	0	14	12	10	10	10	0	0	0	0	0	0
0	10	9	2	0	4	6	6	6	6	8	8	8	0	0
0	0	5	2	1	12	11	12	12	0	0	0	0	0	0
0	18	11	6	0	1	0	0	0	0	0	0	0	0	0
0	0	0	0	4	11	10	10	10	0	0	0	0	0	0
0	0	0	0	0	0	0	19	6	8	25	31	30	0	0
0	0	0	0	0	0	0	10	4	9	18	18	8	6	5
0	19	14	10	0	10	10	18	18	18	8	11	8	23	4
0	0	2	2	4	8	12	11	12	12	8	11	8	18	10
0	12	13	8	1	11	12	12	12	11	17	18	8	0	0
0	0	0	0	15	14	12	12	12	0	0	0	0	0	0
0	0	0	0	0	15	10	10	10	0	0	0	0	0	0
0	1	0	2	0	6	6	6	6	11	10	0	0	0	0
0	8	13	7	0	7	11	11	12	14	30	17	8	6	6
0	7	13	8	0	4	0	0	0	0	0	0	0	0	0
0	9	11	7	0	0	0	0	0	8	30	18	9	6	5
0	1	10	8	15	12	15	15	13	11	16	18	11	12	6
0	0	0	0	13	15	11	13	11	7	8	8	11	11	0
0	0	0	0	2	30	11	12	13	11	8	8	8	0	0
0	0	0	0	0	0	0	21	21	11	25	18	8	0	0
17	28	16	16	27	21	15	12	12	15	25	20	18	6	5

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