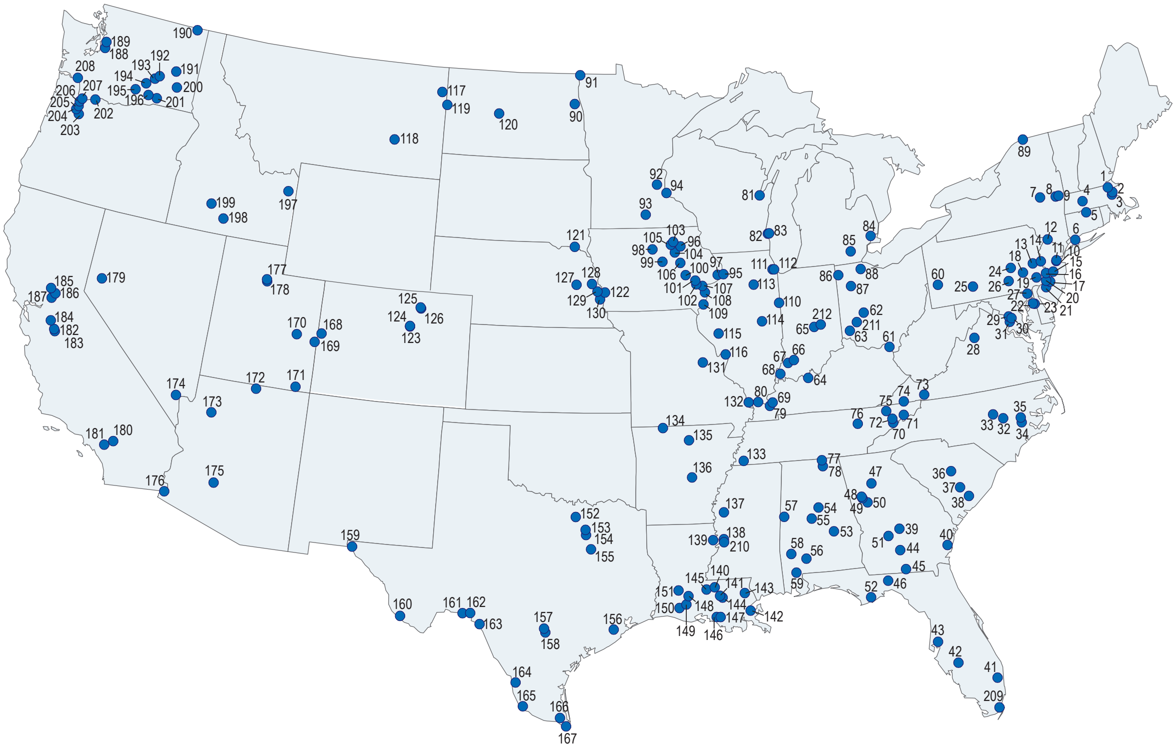
National Water-Quality Assessment Program

Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in Streams of the United States, 1992–2010



Data Series 655

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 and tables in report.)

Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in Streams of the United States, 1992–2010

By Jeffrey D. Martin, Michael Eberle, and Naomi Nakagaki

National Water-Quality Assessment Program

Data Series 655

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

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit http://www.usgs.gov or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit http://www.usgs.gov/pubprod

To order this and other USGS information products, visit http://store.usgs.gov

Suggested citation:
Martin, J.D.; Eberle, Michael; and Nakagaki, Naomi, 2011, Sources and preparation of data for assessing trends in concentrations of pesticides in streams of the United States, 1992–2010: U.S. Geological Survey Data Series 655, 23 p., 5 app.

Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable 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, 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 quality 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. From 1991 to 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/studies/study_units.html*).

National and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are selectively reassessed. These assessments extend the findings in the Study Units by determining water-quality 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 studies 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. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, 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.

William H. Werkheiser
USGS Associate Director for Water

Contents

Figures

Tables

Abbreviations

ASCII	American Standard Code for Information Interchange
BQS	Branch of Quality Systems
DWH	(National Water-Quality Assessment Program) Data Warehouse
GCMS	gas chromatography/mass spectrometry
lowess	locally weighted scatterplot smoothing
LRL	laboratory reporting level
LT-MDL	long-term method detection level
maxLT-MDL	maximum value of the long-term method detection level
MRL	minimum reporting level
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
QC	quality control
USGS	U.S. Geological Survey
µm	micrometer
µg/L	microgram per liter
<	less than

Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in Streams of the United States, 1992–2010

By Jeffrey D. Martin, Michael Eberle, and Naomi Nakagaki

Abstract

This report updates a previously published water-quality dataset 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 September 2010 at stream-water sites of the U.S. Geological Survey National Water-Quality Assessment Program and the National Stream Quality Accounting Network 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 dataset of 21,144 pesticide samples at 212 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, hereafter 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. Analyses to date by the U.S. Geological Survey (USGS) have included assessments of trends in diazinon and other insecticides in urban streams of the northeastern and midwestern United States (Phillips and others, 2007), trends in major herbicides in agricultural streams of the Corn Belt (Sullivan and others, 2009; Vecchia and others, 2009), and trends in selected herbicides and insecticides in urban streams of the United States (Ryberg and others, 2010). Pesticide data from NAWQA and the National Stream Quality Accounting Network (NASQAN) were used for these trend assessments. These data, however, require several 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.

A previous report (Martin, 2009) described the steps taken to prepare data for trend analysis and provided the resulting trend dataset for the period 1992–2006. In January 2011, similar procedures were used to obtain, screen, and prepare pesticide data for the period 1992–2010.[1]

Purpose and Scope

This report updates previous datasets published in Martin (2009) and briefly 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 September 2010 at NAWQA and NASQAN stream-water sites. Water samples were analyzed at the USGS National Water Quality Laboratory

---

[1] Although water-quality data for the period 1992–2006 were previously compiled and prepared for trend analysis by Martin (2009), this report repeats the compilation and preparation process for the entire period 1992–2010 rather than just for the recent, "updated" period 2007–10. This was done for several reasons related to data management and the development and application of recovery models used to prepare the data.

The database used to store USGS water-quality data is a dynamic database. Data and coding of samples and sites may be updated by local data managers as needed. For example, site identification numbers, concentration data, or codes used to indicate data quality might change through time. Data for the entire period were recompiled to ensure that the most up-to-date information was used. In addition, recovery models must be modeled as a single time series. It would be inappropriate to merge recovery-adjusted data from Martin (2009) for 1992–2006 with recovery-adjusted data on the basis of a model for the period 2007–10.

The data user should note that some of the samples and sites in Martin (2009) are not in this report, most likely because of changes to site or sample coding. In addition, the recovery-adjusted concentrations reported in Martin (2009) often are different than the recovery-adjusted concentrations in this report. The differences are small and result from small changes in the recovery models, particularly for the period 2005–6. Differences in trend results for similar time periods using data from Martin (2009) and data from this report have not been investigated but are expected to be negligible.

(NWQL) by a gas chromatography/mass spectrometry (GCMS) method for as many as 44 commonly used pesticides and 8 pesticide degradates (hereafter referred to collectively as "pesticides"). Stream-water sites with 3 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 dataset of 21,144 pesticide samples[2] at 212 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 for pesticides in 1992, and NASQAN, which began monitoring for 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. Details about the NAWQA and NASQAN monitoring approaches can be found in Martin (2009); a brief summary of those approaches follows.

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," on a rotational schedule—20 Study Units during 1992–95, 16 during 1996–98, and 15 during 1998–2001 (Gilliom and others, 2006, p. 32). The number of stream-water sites monitored and the number of pesticide samples[3] collected also followed a rotational schedule of heavier sampling during a 3- to 4-year period of active assessment followed by a 6-year period of reduced sampling until the next period of active assessment (Gilliom and others, 1995, p. 2–5). Pesticide samples generally were collected at each site by using a combination of fixed-interval and high-flow sampling (Gilliom and others, 1995, p. 16). The active-assessment sampling involved a combination of fixed-interval or fixed-frequency sampling—collection of water samples at regular intervals, yielding a time where the number of days between samples is about the same—and additional samples collected during periods of high streamflows. For the fixed-interval sampling, two to four samples generally were collected each month during seasonal periods of high use and runoff of pesticides (typically 3 to 9 months) and one to two samples a month during other periods. 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 (Gilliom and others, 2001). Changes to the design of the NAWQA Program in 2001 included 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

NASQAN was redesigned in 1995 to estimate the mass flux of pesticides and other constituents at 41 monitoring sites in the drainage basins of 4 large river systems: the Mississippi, the Rio Grande, the Columbia, and the Colorado. As in the NAWQA sampling, pesticide samples generally were collected at each site by using a combination of fixed-interval and high-flow sampling (Hooper and others, 2001, p. 1093). Also similar to the NAWQA Program, the frequency of fixed-interval sampling typically changed seasonally, with more frequent samples during the peak pesticide-runoff periods. Sampling frequency at sites downstream of major reservoirs was reduced (typically 6 samples per year), whereas the frequency at sites on free-flowing reaches was 8 to 12 fixed-interval samples per year, plus 0 to 4 high-flow samples per year (Hooper and others, 2001, p. 1093; U.S. Geological Survey, 2006). The NASQAN sampling strategy was revised in 2000 (U.S. Geological Survey, 2010); changes included reduced monitoring in the Columbia and Colorado River Basins. Information on the USGS NASQAN is available at *http://water.usgs.gov/nasqan/*.

Sample Collection, Processing, and Field Quality Control

NAWQA and NASQAN water samples for pesticide analyses are collected and processed by use of similar equipment and procedures. Flow-weighted, depth- and width-integrated water samples for the analysis of pesticides were collected with Teflon-coated isokinetic samplers and processed in accordance with standard USGS methods (U.S. Geological Survey, variously dated; Shelton, 1994; Edwards and Glysson, 1999). Equipment that came in contact with sample water was constructed of Teflon, glass, aluminum, or stainless steel and was cleaned with a dilute solution of phosphate-free detergent and rinsed with deionized water and pesticide-grade methanol. Water samples were filtered through pre-combusted glass-fiber filters with a nominal 0.7-micrometer (µm) pore diameter to remove suspended particulate matter, collected in baked amber glass bottles, 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 by 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

---

[2] The dataset provided in appendix 4 comprises 21,988 samples, 844 of which are considered inappropriate for trend analysis but are included in the dataset for uses other than trend analysis.

[3] That is, water samples for analysis of pesticides.

(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), Martin and others (2009), and Martin and Eberle (2011). NASQAN 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 NASQAN 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 Martin (2009, appendix 1) ultimately determined that only pesticide data from a single laboratory (NWQL) and analytical method commonly used by both programs (GCMS) were sufficiently extensive in time and space for a national assessment of trends. The analytical method, GCMS, is described in this section.

All water-quality samples selected for trend analysis were analyzed by NWQL personnel 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[4] (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 microgram per liter (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; 6 times 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 routine 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 routine reporting levels were changed from MRLs 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 (Oblinger Childress and others, 1999). LRLs are reassessed annually, and LRLs for a single pesticide typically did change during the post-October 2000 period.

A concentration value of approximately 3 times the standard deviation of the 24 (or more) 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[5] 1994–2010 (maxLT-MDL, 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.[6] 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).

---

[4] 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). NASQAN used schedules 2001 and 2010 exclusively from 1995 through October 2007 and used schedule 2033 extensively from November 2007 through 2010. The NAWQA Program used schedules 2001 and 2010 extensively from 1992 through October 2004, used schedule 2003 extensively from November 2004 through May 2005, and used schedule 2033 extensively from June 2005 through 2010. The pesticides "selected" for trend analysis are those measured in schedules 2001 and 2010.

[5] A water year is the period October 1 through September 30 and is named for the year in which it ends.

[6] The maxLT-MDL reported in table 1 is rounded according to the rules given later in the report.

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; CASRN, Chemical Abstract Service Registry Number; maxLT-MDL, maximum value of the long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Pesticide	Parameter code	CASRN[1]	Pesticide class	Type of pesticide	Parent pesticide (if degradate)	Does the indicated National Water-Quality Laboratory analytical schedule analyze for the pesticide?				maxLT-MDL (µg/L)
						Schedule 2001	Schedule 2010	Schedule 2003	Schedule 2033	
Acetochlor	49260	34256-82-1	Acetanilide	Herbicide	NA	Yes	Yes	Yes	Yes	0.005
Alachlor	46342	15972-60-8	Acetanilide	Herbicide	NA	Yes	Yes	Yes	Yes	0.004
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	0.060
Benfluralin	82673	1861-40-1	Dinitroaniline	Herbicide	NA	Yes	Yes	Yes	Yes	0.007
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	0.10
Carbofuran	82674	1563-66-2	Carbamate	Insecticide	NA	Yes	Yes	No	Yes	0.030
Chlorpyrifos	38933	2921-88-2	Organothiophosphate	Insecticide	NA	Yes	Yes	Yes	Yes	0.005
Cyanazine	04041	21725-46-2	Triazine	Herbicide	NA	Yes	Yes	No	Yes	0.020
Dacthal®	82682	1861-32-1	Chlorobenzoic acid ester	Herbicide	NA	Yes	Yes	Yes	Yes	0.004
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	0.020
EPTC	82668	759-94-4	Thiocarbamate	Herbicide	NA	Yes	Yes	No	Yes	0.003
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	0.008
Fipronil	62166	120068-37-3	Phenyl pyrazole	Insecticide	NA	Yes	Yes	Yes	Yes	0.020
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	0.005
alpha-HCH	34253	319-84-6	Organochlorine	Degradate	*gamma*-HCH	Yes	Yes	No	No	0.004
gamma-HCH	39341	58-89-9	Organochlorine	Insecticide	NA	Yes	Yes	No	No	0.007
Linuron	82666	330-55-2	Urea	Herbicide	NA	Yes	Yes	No	No	0.030

Table 1. Pesticides selected for trend analysis.—Continued

[Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; CASRN, Chemical Abstract Service Registry Number; maxLT-MDL, maximum value of the long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Pesticide	Parameter code	CASRN[1]	Pesticide class	Type of pesticide	Parent pesticide (if degradate)	Does the indicated National Water-Quality Laboratory analytical schedule analyze for the pesticide?				maxLT-MDL (µg/L)
						Schedule 2001	Schedule 2010	Schedule 2003	Schedule 2033	
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	0.010
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	0.010
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	0.008
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	0.007
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	0.007
Propargite	82685	2312-35-8	Sulfite ester	Acaricide	NA	Yes	Yes	No	Yes	0.020
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	0.014
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	0.008
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	0.009

[1] This report contains CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. CAS recommends the verification of CASRNs through CAS Client Services^{SM}.

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. 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 pesticides 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*. Laboratory quality-control charts and statistics for the pesticide data provided in this report (since 2001) are available at *http://nwql.usgs.gov/Public/PublicQAQC/AggregatedCharts.html*. 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 Program and NASQAN are stored in USGS National Water Information System (NWIS) databases and are periodically aggregated into the NAWQA Data Warehouse (DWH) (*http:/water.usgs.gov/nawqa/data*). 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.

Water-quality data were provided by the DWH (Jessica L. Thompson, Information Technology Specialist, U.S. Geological Survey, written commun., January 19, 2011). Any water-quality sample in the DWH with analyses of one or more pesticides of interest was retrieved along with selected supporting sample information.

Review, Selection, and Preparation of Water-Quality Data

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. A detailed discussion of data-review procedures is provided in Martin (2009, appendix 1).

The principal steps in data preparation for trend analysis were to (1) select stream-water sites for trend analysis, (2) round concentrations to a consistent level of precision for the concentration range, (3) identify routine reporting levels used to report nondetections unaffected by matrix interference, (4) reassign the concentration value for routine nondetections to the maxLT-MDL, (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

As stated previously, only samples analyzed by the GCMS method at NWQL were selected for trend analysis (Martin 2009, appendix 1). Stream-water sites with at least 3 water years 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 212 stream-water sites[7] that met these minimum data requirements are shown in figure 1 and listed in table 3. NAWQA Program Study-Unit identifiers used in table 3 are explained in table 2.

---

[7] The NAWQA DWH is a dynamic database. Data and coding for samples and sites may be updated by local data managers as needed. Five sites identified as having sufficient data for trend analysis by Martin (2009) no longer have sufficient data for this report. The reason for the decrease in the number of samples is not known but likely is the result of changes to sample coding or other data-management activities. Similarly, data for certain individual samples in the 2009 report may not be included in the data appendixes in this report, and vice versa.

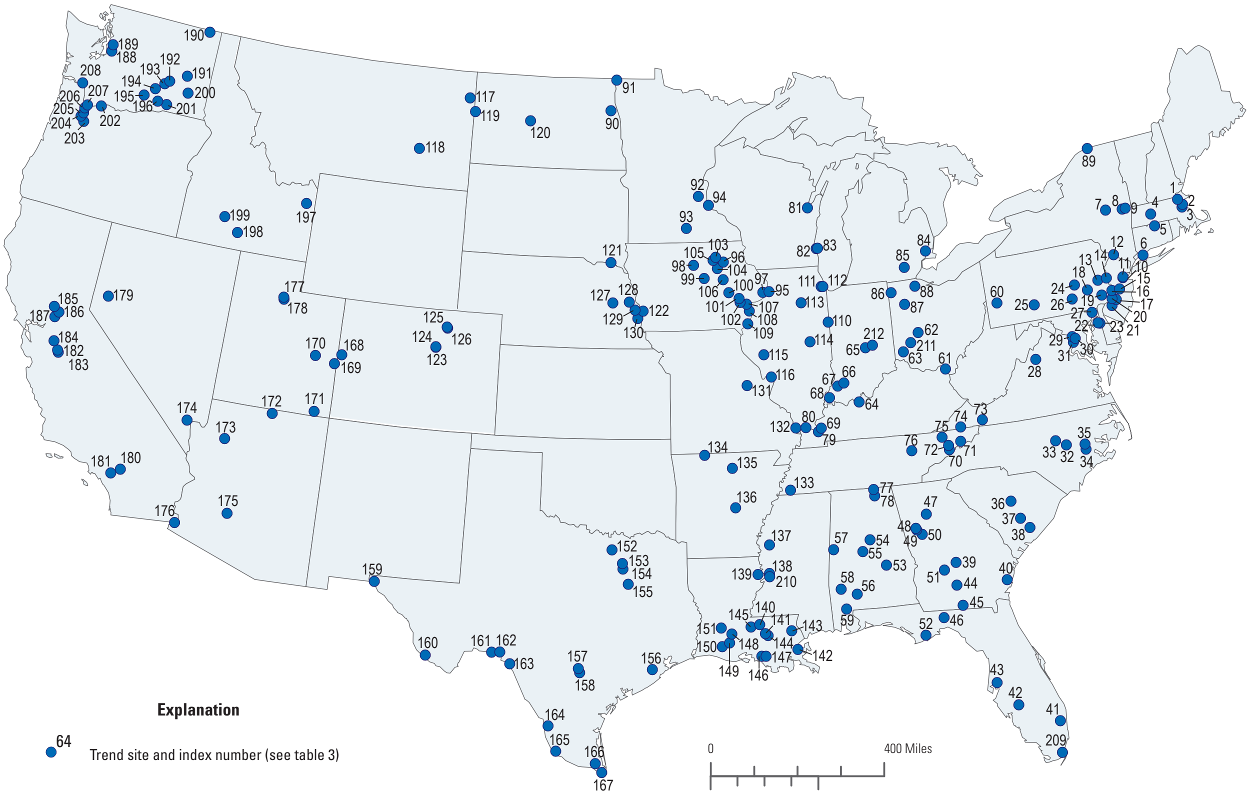


Figure 1. Locations of stream-water sites selected for trend analysis.

Table 2. National Water-Quality Assessment Program Study-Unit identifiers (NASQAN sites are coded as "NSQN.")

Identifier	Study Unit name	Identifier	Study Unit name
ACAD	Acadian-Pontchartrain Drainages	PODL	Potomac River Basin and Delmarva Peninsula
ACFB	Apalachicola-Chattahoochee-Flint River Basin	PUGT	Puget Sound Basin
ALBE	Albemarle-Pamlico Drainage Basin	REDN	Red River of the North Basin
CAZB	Central Arizona Basins	RIOG	Rio Grande Valley
CCYK	Central Columbia Plateau-Yakima River Basin	SACR	Sacramento River Basin
CNBR	Central Nebraska Basins	SANA	Santa Ana Basin
CONN	Connecticut, Housatonic, and Thames River Basins	SANJ	San Joaquin-Tulare Basins
DELR	Delaware River Basin	SANT	Santee River Basin and Coastal Drainages
EIWA	Eastern Iowa Basins	SCTX	South-Central Texas
GAFL	Georgia-Florida Coastal Plain	SOFL	Southern Florida
GRSL	Great Salt Lake Basins	SPLT	South Platte River Basin
HDSN	Hudson River Basin	TENN	Tennessee River Basin
LERI	Lake Erie-Lake Saint Clair Drainages	TRIN	Trinity River Basin
LINJ	Long Island-New Jersey Coastal Drainages	UCOL	Upper Colorado River Basin
LIRB	Lower Illinois River Basin	UIRB	Upper Illinois River Basin
LSUS	Lower Susquehanna River Basin	UMIS	Upper Mississippi River Basin
MISE	Mississippi Embayment	USNK	Upper Snake River Basin
MOBL	Mobile River Basin	WHMI	White, Great Miami, and Little Miami River Basins
NECB	New England Coastal Basins	WILL	Willamette Basin
NVBR	Las Vegas Valley Area and Carson and Truckee River Basins	WMIC	Western Lake Michigan Drainages
OZRK	Ozark Plateaus	YELL	Yellowstone River Basin

Table 3. Stream-water sites selected for trend analysis.

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
1	01100000	NECB	23	mixed	4,626.8	tot	Merrimack River below Concord River at Lowell, MA
2	01102500	NECB	72	urb	23.1	con	Aberjona River at Winchester, MA
3	01104615	NECB	72	urb	271.4	tot	Charles River above Watertown Dam at Watertown, MA
4	01170970	CONN	31	undev	0.9	both	Hatfield Reservoir near West Hatfield, MA
5	01184000	CONN	126	mixed	9,671.7	both	Connecticut River at Thompsonville, CT
6	01209710	CONN	214	urb	32.9	both	Norwalk River at Winnipauk, CT
7	01349150	HDSN	197	mixed	59.8	both	Canajoharie Creek near Canajoharie, NY
8	01356190	HDSN	134	urb	15.4	both	Lisha Kill near Niskayuna, NY
9	01357500	HDSN	180	mixed	3,518.7	both	Mohawk River at Cohoes, NY
10	01403300	LINJ	183	urb	800.9	both	Raritan River at Queens Bridge at Bound Brook, NJ
11	01403900	LINJ	93	urb	48.5	both	Bound Brook at Middlesex, NJ
12	01434000	DELR	26	undev	3,076.3	both	Delaware River at Port Jervis, NY
13	01451800	DELR	32	mixed	52.4	both	Jordan Creek near Schnecksville, PA
14	01454700	DELR	30	mixed	1,358.7	both	Lehigh River at Glendon, PA
15	01463500	DELR	107	mixed	6,786.6	both	Delaware River at Trenton, NJ
16	01464907	DELR	93	urb	27.9	both	Little Neshaminy Creek at Valley Road near Neshaminy, PA
17	01467150	DELR	31	urb	18.1	both	Cooper River at Haddonfield, NJ
18	01470779	DELR	51	mixed	69.2	both	Tulpehocken Creek near Bernville, PA
19	01472157	DELR	78	mixed	58.8	both	French Creek near Phoenixville, PA
20	01474500	DELR	69	mixed	1,890.3	both	Schuylkill River at Philadelphia, PA
21	01477120	DELR	30	mixed	26	both	Raccoon Creek near Swedesboro, NJ
22	01493112	PODL	51	ag	6.6	both	Chesterville Branch near Crumpton, MD
23	01493500	PODL	52	ag	12.8	both	Morgan Creek near Kennedyville, MD
24	01555400	LSUS	92	mixed	44.7	both	East Mahantango Creek at Klingerstown, PA
25	01559795	LSUS	26	undev	16.7	both	Bobs Creek near Pavia, PA
26	01571490	LSUS	66	urb	12.6	both	Cedar Run at Eberlys Mill, PA
27	01578310	PODL	93	mixed	27,086.4	both	Susquehanna River at Conowingo, MD
28	01621050	PODL	186	mixed	14.4	both	Muddy Creek at Mount Clinton, VA
29	01645495	PODL	24	mixed	11,464.4	both	Potomac River near Great Falls, VA

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
30	01646580	PODL	181	mixed	11,570.4	both	Potomac River at Chain Bridge at Washington, DC
31	01654000	PODL	207	urb	23.4	both	Accotink Creek near Annandale, VA
32	0208755215	ALBE	30	mixed	1,206.7	both	Neuse River above US 70 at Smithfield, NC
33	02087580	ALBE	109	urb	20.8	both	Swift Creek near Apex, NC
34	02089500	ALBE	183	mixed	2,711	both	Neuse River at Kinston, NC
35	02091500	ALBE	146	mixed	736.9	both	Contentnea Creek at Hookerton, NC
36	02169570	SANT	116	urb	59.6	both	Gills Creek at Columbia, SC
37	02174250	SANT	144	mixed	23.8	both	Cow Castle Creek near Bowman, SC
38	02175000	SANT	117	mixed	2,732.5	both	Edisto River near Givhans, SC
39	02215100	GAFL	60	mixed	162.3	both	Tucsawhatchee Creek near Hawkinsville, GA
40	02226160	GAFL	37	mixed	14,111.2	both	Altamaha River near Everett City, GA
41	02281200	SOFL	124	ag	311.3	unk	Hillsboro Canal at S-6 near Shawano, FL
42	02296750	SOFL	30	mixed	1,326.6	both	Peace River at Arcadia, FL
43	02306774	GAFL	67	urb	20.4	con	Rocky Creek at Highway 587 at Citrus Park, FL
44	02317797	GAFL	108	mixed	129.3	both	Little River at Upper Ty Ty Road near Tifton, GA
45	02318500	GAFL	160	mixed	1,491.8	both	Withlacoochee River at US 84 near Quitman, GA
46	02326838	GAFL	43	urb	9.7	con	Lafayette Creek at Miccosukee Road at Tallahassee, FL
47	02335870	ACFB	227	urb	30.7	both	Sope Creek near Marietta, GA
48	02337500	ACFB	48	mixed	35.6	both	Snake Creek near Whitesburg, GA
49	02338000	ACFB	178	urb	2,413.4	both	Chattahoochee River near Whitesburg, GA
50	02344797	ACFB	25	urb	43.5	both	White Oak Creek at Cannon Road near Raymond, GA
51	02350080	ACFB	151	mixed	62.4	both	Lime Creek near Cobb, GA
52	02359170	ACFB	32	mixed	19,202.4	both	Apalachicola River near Sumatra, FL
53	02419977	MOBL	28	urb	9	both	Three Mile Branch at North Boulevard at Montgomery, AL
54	0242354750	MOBL	142	urb	25.5	both	Cahaba Valley Creek at Cross Creek Road at Pelham, AL
55	02424000	MOBL	62	mixed	1,025.7	both	Cahaba River at Centreville, AL
56	02429500	MOBL	41	mixed	21,977.2	both	Alabama River at Claiborne, AL
57	02444490	MOBL	73	ag	52.6	both	Bogue Chitto Creek near Memphis, AL
58	02469762	MOBL	72	mixed	18,479.6	both	Tombigbee River below Coffeeville Dam near Coffeeville, AL

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
59	02470500	NSQN	35	mixed	42,816.1	both	Mobile River at Mount Vernon, AL
60	03086000	NSQN	88	mixed	19,457.5	both	Ohio River at Sewickley, PA
61	03216600	NSQN	148	mixed	61,527.6	both	Ohio River at Greenup Dam near Greenup, KY
62	03267900	WHMI	126	mixed	309.8	both	Mad River at St. Paris Pike at Eagle City, OH
63	03274000	WHMI	35	mixed	3,630.8	both	Great Miami River at Hamilton, OH
64	03303280	NSQN	188	mixed	96,492.4	both	Ohio River at Cannelton Dam at Cannelton, IN
65	03353637	WHMI	193	urb	17.2	both	Little Buck Creek near Indianapolis, IN
66	03360895	WHMI	53	mixed	56.2	both	Kessinger Ditch near Monroe City, IN
67	03374100	WHMI	381	mixed	11,303.1	both	White River at Hazleton, IN
68	03378500	NSQN	182	mixed	29,300.8	both	Wabash River at New Harmony, IN
69	03438500	NSQN	33	mixed	17,913.4	both	Cumberland River at Smithland, KY
70	03455000	TENN	28	mixed	1,853	both	French Broad River near Newport, TN
71	03466208	TENN	127	mixed	79.1	both	Big Limestone Creek near Limestone, TN
72	03467609	TENN	124	mixed	1,688.5	both	Nolichucky River near Lowland, TN
73	03474000	TENN	28	mixed	132	both	Middle Fork Holston River at Seven Mile Ford, VA
74	03526000	TENN	51	mixed	106.8	both	Copper Creek near Gate City, VA
75	03528000	TENN	27	mixed	1,473.3	both	Clinch River above Tazewell, TN
76	03539778	TENN	28	mixed	170.3	both	Clear Creek at Lilly Bridge near Lancing, TN
77	0357479650	TENN	117	mixed	29.3	both	Hester Creek at Buddy Williamson Road near Plevna, AL
78	03575100	TENN	106	mixed	374	both	Flint River at Brownsboro, AL
79	03609750	NSQN	124	mixed	40,325.3	both	Tennessee River at Highway 60 near Paducah, KY
80	03612500	NSQN	193	mixed	203,639.6	both	Ohio River at Dam 53 near Grand Chain, IL
81	04072050	WMIC	164	mixed	95.4	both	Duck Creek at Seminary Road near Oneida, WI
82	040869415	WMIC	90	urb	10	both	Lincoln Creek at 47th Street at Milwaukee, WI
83	04087000	WMIC	128	mixed	697	both	Milwaukee River at Milwaukee, WI
84	04161820	LERI	107	urb	310	both	Clinton River at Sterling Heights, MI
85	04175600	LERI	78	mixed	127.7	both	River Raisin near Manchester, MI
86	04178000	LERI	78	mixed	617.8	both	St. Joseph River near Newville, IN
87	04186500	LERI	118	mixed	331.4	both	Auglaize River near Fort Jennings, OH

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
88	04193500	LERI	142	mixed	6,335.7	both	Maumee River at Waterville, OH
89	04264331	NSQN	45	undev	297,954.7	both	St. Lawrence River at Cornwall, Ontario, near Massena, NY
90	05082625	REDN	61	mixed	254.2	unk	Turtle River at Turtle River State Park near Arvilla, ND
91	05102490	REDN	74	ag	35,554.6	unk	Red River of the North at Pembina, ND
92	05288705	UMIS	146	urb	28.2	both	Shingle Creek at Queen Avenue at Minneapolis, MN
93	05320270	UMIS	127	mixed	129.7	both	Little Cobb River near Beauford, MN
94	05331580	UMIS	97	mixed	37,049.2	both	Mississippi River below Lock and Dam 2 at Hastings, MN
95	05420500	NSQN	177	mixed	85,883.5	both	Mississippi River at Clinton, IA
96	05420680	EIWA	83	mixed	346.3	both	Wapsipinicon River near Tripoli, IA
97	05422000	EIWA	23	mixed	2,335.5	both	Wapsipinicon River near De Witt, IA
98	05449500	EIWA	86	mixed	418.5	both	Iowa River near Rowan, IA
99	05451210	EIWA	168	mixed	224.1	both	South Fork Iowa River near New Providence, IA
100	05453100	EIWA	23	mixed	2,794.6	both	Iowa River at Marengo, IA
101	05455100	EIWA	24	mixed	201.4	both	Old Mans Creek near Iowa City, IA
102	05455570	EIWA	30	mixed	626.3	both	English River at Riverside, IA
103	05457750	EIWA	27	mixed	1,095	both	Cedar River near Carville, IA
104	05458900	EIWA	26	mixed	857.4	both	West Fork Cedar River at Finchford, IA
105	05461390	EIWA	21	mixed	124	both	Flood Creek near Powersville, IA
106	05464220	EIWA	52	mixed	299.3	both	Wolf Creek near Dysart, IA
107	05465000	EIWA	22	mixed	7,781.4	both	Cedar River near Conesville, IA
108	05465500	EIWA	156	mixed	12,500.2	both	Iowa River at Wapello, IA
109	05474000	EIWA	22	mixed	4311	both	Skunk River at Augusta, IA
110	05525500	UIRB	63	mixed	447.4	both	Sugar Creek at Milford, IL
111	05531500	UIRB	99	urb	112.2	both	Salt Creek at Western Springs, IL
112	05532500	UIRB	76	urb	631	both	Des Plaines River at Riverside, IL
113	05553500	UIRB	90	mixed	10,938.2	both	Illinois River at Ottawa, IL
114	05572000	LIRB	149	mixed	550.8	both	Sangamon River at Monticello, IL
115	05586100	LIRB	168	mixed	26,673.4	both	Illinois River at Valley City, IL
116	05587455	NSQN	141	mixed	172,536.2	both	Mississippi River below Grafton, IL

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
117	06185500	NSQN	84	undev	92,569.3	both	Missouri River near Culbertson, MT
118	06295000	YELL	69	undev	39,456.3	con	Yellowstone River at Forsyth, MT
118	06295000	YELL	69	undev	40,147.2	tot	Yellowstone River at Forsyth, MT
119	06329500	YELL	102	undev	68,393.8	con	Yellowstone River near Sidney, MT
119	06329500	YELL	102	undev	69,084.7	tot	Yellowstone River near Sidney, MT
120	06338490	NSQN	58	undev	180,876	both	Missouri River at Garrison Dam, ND
121	06467500	NSQN	63	undev	278,656.4	both	Missouri River at Yankton, SD
122	06610000	NSQN	190	undev	321,075.8	both	Missouri River at Omaha, NE
123	06713500	SPLT	142	mixed	410.5	both	Cherry Creek at Denver, CO
124	06714000	SPLT	63	mixed	3,865.7	both	South Platte River at Denver, CO
125	06753990	SPLT	83	undev	570.6	both	Lonetree Creek near Greeley, CO
126	06754000	SPLT	137	mixed	9,658.6	both	South Platte River near Kersey, CO
127	06795500	CNBR	37	ag	294.1	both	Shell Creek near Columbus, NE
128	06800000	CNBR	243	ag	368.3	both	Maple Creek near Nickerson, NE
129	06800500	CNBR	63	ag	6,945.5	tot	Elkhorn River at Waterloo, NE
130	06805500	CNBR	212	undev	8,5329	tot	Platte River at Louisville, NE
131	06934500	NSQN	188	mixed	519,408.5	both	Missouri River at Hermann, MO
132	07022000	NSQN	189	mixed	710,440.6	both	Mississippi River at Thebes, IL
133	07031692	MISE	56	urb	30.5	both	Fletcher Creek at Sycamore View Road at Memphis, TN
134	07053250	OZRK	135	mixed	52.6	both	Yocum Creek near Oak Grove, AR
135	07060710	OZRK	36	undev	58.6	both	North Sylamore Creek near Fifty-Six, AR
136	07263620	NSQN	153	mixed	157,786.9	tot	Arkansas River at David D Terry Lock and Dam below Little Rock, AR
137	07288650	MISE	173	ag	502.4	both	Bogue Phalia near Leland, MS
138	07288955	MISE	234	mixed	13,414.3	both	Yazoo River below Steele Bayou near Long Lake, MS
139	07369500	MISE	63	ag	284.3	both	Tensas River at Tendal, LA
140	07373420	NSQN	209	mixed	1,144,886	both	Mississippi River near St. Francisville, LA
141	07374000	NSQN	91	mixed	1,145,342.5	both	Mississippi River at Baton Rouge, LA
142	07374525	NSQN	59	mixed	1,145,457.4	tot	Mississippi River at Belle Chasse, LA
143	07375050	ACAD	46	undev	141.2	both	Tchefuncte River near Covington, LA

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
144	07379960	ACAD	86	urb	15.1	both	Dawson Creek at Bluebonnet Boulevard near Baton Rouge, LA
145	07381495	NSQN	207	mixed	93,510.9	both	Atchafalaya River at Melville, LA
146	07381590	NSQN	55	mixed	2,178	unk	Wax Lake Outlet at Calumet, LA
147	07381600	NSQN	65	mixed	94,620.9	unk	Atchafalaya River at Morgan City, LA
148	08010000	ACAD	41	mixed	142.4	both	Bayou Des Cannes near Eunice, LA
149	08012150	ACAD	97	mixed	1,380.8	both	Mermentau River at Mermentau, LA
150	08012470	ACAD	72	mixed	296	both	Bayou Lacassine near Lake Arthur, LA
151	08014500	ACAD	40	mixed	503.9	both	Ouiska Chitto Creek near Oberlin, LA
152	08051500	TRIN	50	undev	294.8	both	Clear Creek near Sanger, TX
153	08057200	TRIN	174	urb	66.8	both	White Rock Creek at Greenville Avenue at Dallas, TX
154	08057410	TRIN	193	mixed	6,265.2	both	Trinity River below Dallas, TX
155	08064100	TRIN	91	mixed	807	both	Chambers Creek near Rice, TX
156	08116650	NSQN	32	mixed	45,415	tot	Brazos River near Rosharon, TX
157	08178800	SCTX	117	urb	195.3	both	Salado Creek at Loop 13 at San Antonio, TX
158	08181800	SCTX	77	urb	1,748.4	both	San Antonio River near Elmendorf, TX
159	08364000	RIOG	159	undev	29,939.1	con	Rio Grande at El Paso, TX
159	08364000	RIOG	159	undev	33,385.2	tot	Rio Grande at El Paso, TX
160	08374200	NSQN	56	undev	72,974.7	both	Rio Grande below Rio Conchos near Presidio, TX
161	08377200	NSQN	102	undev	95,115.4	both	Rio Grande at Foster Ranch near Langtry, TX
162	08447410	NSQN	101	undev	44,173.8	tot	Pecos River near Langtry, TX
163	08450900	NSQN	57	undev	167,199.3	both	Rio Grande below Amistad Dam near Del Rio, TX
164	08459200	NSQN	83	undev	177,072.8	both	Rio Grande at Pipeline Crossing below Laredo, TX
165	08461300	NSQN	55	undev	206,915.7	both	Rio Grande below Falcon Dam, TX
166	08470400	NSQN	106	mixed	345.4	both	Arroyo Colorado at Harlingen, TX
167	08475000	NSQN	102	undev	215,270.8	both	Rio Grande near Brownsville, TX
168	09163500	UCOL	79	undev	17,866.5	both	Colorado River near Colorado-Utah State Line
169	09180500	NSQN	47	undev	23,973.1	both	Colorado River near Cisco, UT
170	09315000	NSQN	46	undev	40,799.4	both	Green River at Green River, UT
171	09379500	NSQN	41	undev	22,993.1	both	San Juan River near Bluff, UT

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
172	09380000	NSQN	25	undev	108,137	both	Colorado River at Lees Ferry, AZ
173	09404200	NSQN	33	undev	145,602.4	con	Colorado River above Diamond Creek near Peach Spring, AZ
174	094196783	NVBR	180	mixed	1,028.5	both	Las Vegas Wash below Flamingo Wash near Las Vegas, NV
175	09517000	CAZB	52	undev	1,536.8	both	Hassayampa River near Arlington, AZ
176	09522000	NSQN	76	undev	249,077.6	both	Colorado River at N. International Boundary above Morelos Dam, AZ
177	10168000	GRSL	110	urb	45.1	both	Little Cottonwood Creek at Jordan River near Salt Lake City, UT
178	10171000	GRSL	79	mixed	3,510.7	tot	Jordan River at County Road 1700 South at Salt Lake City, UT
179	10350500	NVBR	111	mixed	1,600.8	both	Truckee River at Clark, NV
180	11060400	SANA	71	urb	11.9	both	Warm Creek near San Bernardino, CA
181	11074000	SANA	120	urb	1,438.8	con	Santa Ana River below Prado Dam, CA
181	11074000	SANA	120	urb	2,261.4	tot	Santa Ana River below Prado Dam, CA
182	11273500	SANJ	212	undev	1,383	both	Merced River at River Road Bridge near Newman, CA
183	11274538	SANJ	211	mixed	10.8	con	Orestimba Creek at River Road near Crows Landing, CA
183	11274538	SANJ	211	undev	203.6	tot	Orestimba Creek at River Road near Crows Landing, CA
184	11303500	SANJ	297	undev	7,347.5	con	San Joaquin River near Vernalis, CA
184	11303500	SANJ	297	mixed	13,511.3	tot	San Joaquin River near Vernalis, CA
185	11391100	SACR	35	mixed	1,285.5	unk	Sacramento Slough near Knights Landing, CA
186	11447360	SACR	112	urb	31.5	both	Arcade Creek near Del Paso Heights, CA
187	11447650	SACR	171	undev	23,723.9	unk	Sacramento River at Freeport, CA
188	12113390	PUGT	84	urb	461.1	both	Duwamish River at golf course at Tukwila, WA
189	12128000	PUGT	125	urb	11.3	both	Thornton Creek near Seattle, WA
190	12400520	NSQN	56	undev	60,373.2	both	Columbia River at Northport, WA
191	12464770	CCYK	91	ag	458.8	both	Crab Creek at Rocky Ford Road near Ritzville, WA
192	12471400	CCYK	55	ag	710.8	both	Lind Coulee Wasteway at State Road 17 near Warden, WA
193	12472380	CCYK	36	mixed	56.2	both	Crab Creek Lateral above Royal Lake near Othello, WA
194	12472900	NSQN	45	undev	96,333	both	Columbia River at Vernita Bridge near Priest Rapid Dam, WA

Table 3. Stream-water sites selected for trend analysis.—Continued

[Drainage areas rounded to 0.1 square mile; ag, 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; urb, greater than 25 percent urban land and less than or equal to 25 percent agricultural land; mixed, all other combinations of agricultural, urban, and undeveloped land; tot, total drainage basin; con, contributing drainage basin; both, total and contributing drainage basins are the same; unk, the type of drainage basin is not known. See appendix 3 for additional site and basin information.]

Fig. 1 index number	Station number	Study Unit[1] abbreviation (explained in table 2)	Number of samples considered appropriate for trend analysis	Drainage basin land-use class	Drainage area (square miles)	Type of drainage basin	Name of stream-water site
195	12505450	CCYK	130	mixed	61.7	con	Granger Drain at Granger, WA
196	12510500	CCYK	92	mixed	5,612.5	both	Yakima River at Kiona, WA
197	13055000	USNK	42	mixed	885.9	both	Teton River near St. Anthony, ID
198	13092747	USNK	187	undev	256.5	both	Rock Creek above Highway 30/93 Crossing at Twin Falls, ID
199	13154500	USNK	131	undev	35,885.3	both	Snake River at King Hill, ID
200	13351000	CCYK	135	ag	2462.9	both	Palouse River at Hooper, WA
201	13353200	NSQN	65	undev	107,893.7	both	Snake River at Burbank, WA
202	14128910	NSQN	45	undev	236,623.4	both	Columbia River at Warrendale, OR
203	14200400	WILL	48	undev	9.8	both	Little Abiqua Creek near Scotts Mills, OR
204	14201300	WILL	171	mixed	15	both	Zollner Creek near Mount Angel, OR
205	14202000	WILL	32	mixed	487.1	both	Pudding River at Aurora, OR
206	14206950	WILL	147	urb	31.2	both	Fanno Creek at Durham, OR
207	14211720	WILL	232	mixed	11,172.6	both	Willamette River at Portland, OR
208	14246900	NSQN	156	undev	258,696.9	both	Columbia River at Beaver Army Terminal near Quincy, OR
209	252414080333200	SOFL	103	mixed	51	unk	C-111 Canal 100 feet above S-177 near Homestead, FL
210	322023090544500	NSQN	30	mixed	1,123,967	unk	Mississippi River at mile 438 above Vicksburg, MS
211	393944084120700	WHMI	104	urb	20	both	Holes Creek at Huffman Park at Kettering, OH
212	394340085524601	WHMI	299	mixed	95.1	both	Sugar Creek at County Road 400 South at New Palestine, IN

[1] NASQAN sites are coded “NSQN.”

Precision and Rounding

Water-quality data from different periods of time are rounded differently. Prior to April 1997, pesticide data reported by NWQL were rounded to a greater degree than data reported subsequently (U.S. Geological Survey, 1997). 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 dataset were rounded to the degree used for the pre-April 1997 data (table 4). The same rounding rules also were applied to the maxLT-MDL for water years 1994–2010 (table 1).

Determination of Reporting Levels

The types and values of the routine reporting level in effect at the time of sample analysis have 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 internal NWQL files. The values of the routine reporting levels used by NWQL were rounded to the precision listed in table 4 and joined to the trend data, nondetections in the trend data were classified as routine or raised, and time-series plots of reporting levels for pesticide nondetections were examined. Several aspects of data reporting were observed to change over time: (1) prior to December 1994, no information on reporting levels used; (2) a period of "overlap" as routine reporting levels changed; and (3) a few isolated reporting levels at concentration values less than routine reporting levels.

These issues were resolved as follows: (1) reporting levels for pre-December 1994 samples were inferred from the pattern and values of nondetections in the trend data for this period; (2) periods of overlapping routine reporting levels were identified by visual inspection of the time-series plots, and reporting levels misclassified as raised were manually corrected; and (3) unusually low reporting levels were attributed to data-management/data-editing errors and were changed to nondetections at routine reporting levels.

A time-series plot of reporting levels for nondetections of simazine in the original concentration data provided for all sites in the trend dataset is shown in the first panel of figure 2. Time-series 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 1.

Table 4. Precision of pesticide data reported by the National Water Quality Laboratory (U.S. Geological Survey, 1997).

[µg/L, microgram per liter; <, less than]

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

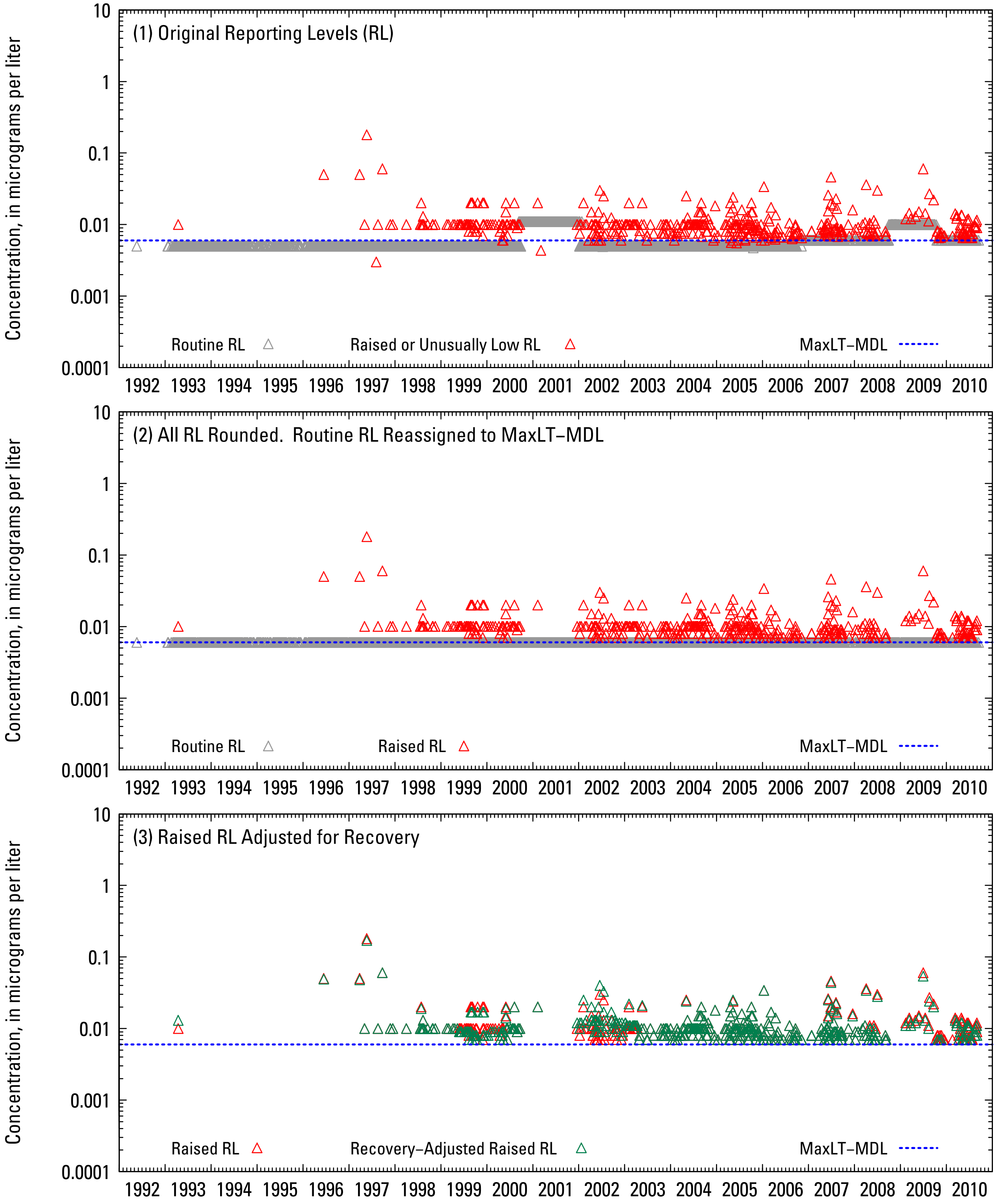


Figure 2. Example time-series plots of nondetections (of simazine) for all sites in the trend dataset showing (1) original reporting levels; (2) rounded reporting levels and, for routine nondetections, reporting levels reassigned to the maximum value of the long-term method detection level (maxLT-MDL);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

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 time series 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 maxLT-MDL for water years 1994–2010 (table 1). 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 1).

The maxLT-MDL was determined from records provided by NWQL (*http://nwql.cr.usgs.gov/usgs/ltmdl/ltmdl.cfm*). It is expected 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. A time-series plot of reporting levels for nondetections of simazine reassigned to maxLT-MDL and rounded according to the rules in this section for all sites in the trend dataset is shown in the second panel of figure 2.

Adjustment of Concentrations for Temporal Changes in Recovery

Temporal changes in the performance of the GCMS analytical method used to measure pesticide concentrations during 1992–2010 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 (Martin and Eberle, 2011). Data and procedures for modeling temporal changes in recovery bias are summarized below.

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.

A locally weighted scatterplot smoothing (lowess) procedure was used to fit a center smooth (Cleveland and McGill, 1985, p. 833; Helsel and Hirsch, 2002, p. 45–47) to a time series of pesticide recovery for 1,819 stream-water matrix spikes collected between 1992 and 2010. Temporal changes in lowess-modeled recovery of more than 50 percent were observed for 18 pesticides (Martin and Eberle, 2011, table 2). 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.

Concentrations of nondetections at **raised** reporting levels also were adjusted to 100 percent recovery (third panel of fig. 2 and the figures in appendix 1). 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 time series of nondetections and defeat the original purpose of reassigning routine nondetections to the maxLT-MDL (see section “Reassigning the Concentration Value for Routine Nondetections”).

Time-series plots of recovery-adjusted **raised** reporting levels for nondetections of simazine compared to unadjusted raised reporting levels for all sites in the trend dataset are shown in the third panel of figure 2 and for all GCMS pesticides in the third panels of the figures in appendix 1. A time-series plot of rounded, detected concentrations of simazine in relation to maxLT-MDL for all sites in the trend dataset is shown in the first panel of figure 3. Similar time-series plots of rounded, detected concentrations for all GCMS pesticides are provided in the first panels of the figures in appendix 2. 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 2. Time-series plots of recovery-adjusted concentrations of simazine at White River at Hazleton, Indiana, 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 2.

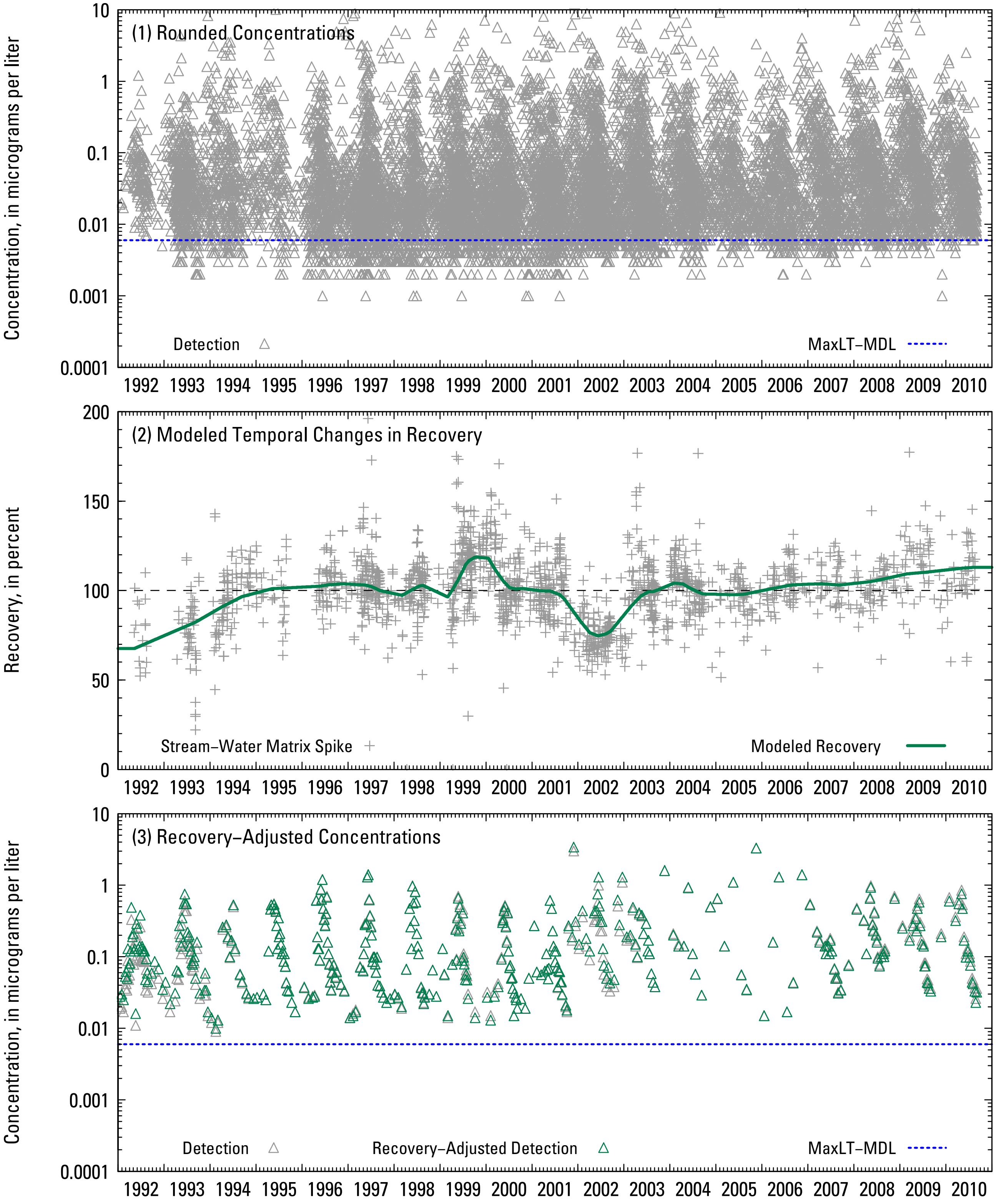


Figure 3. Example time-series plots of (1) rounded concentrations (of simazine) in relation to the maximum value of the long-term method detection level (maxLT-MDL) for all sites in the trend dataset; (2) modeled temporal changes in recovery; and, (3) for detections at White River at Hazleton, IN, a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

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 sites, samples were collected frequently 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 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. This procedure identified 844 samples that were collected too frequently and, hence, are considered inappropriate for trend analysis. *All samples, however, were retained in the trend dataset* 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 dataset (appendix 4).

Dataset for Trend Assessment

The site- and sample-selection criteria described in the preceding sections produced a dataset of 21,988 pesticide samples at 212 stream-water sites (table 3). Only 21,144 pesticide samples, however, are considered appropriate for trend analysis. Tab-delimited American Standard Code for Information Interchange (ASCII) data files and metadata are provided in appendixes 3–5. Data for stream-water sites and their drainage basins are provided in appendix 3, data for pesticide concentrations in stream-water samples are provided in appendix 4, and data for pesticides selected for trend analysis[8] are provided in appendix 5.

Summary

This report provides a water-quality dataset 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 September 2010 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) 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) round concentrations to a consistent level of precision for the concentration range, (3) identify routine reporting levels used to report nondetections unaffected by matrix interference, (4) reassign the concentration value for routine nondetections to the maximum value of the long-term method detection level (maxLT-MDL), (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 3 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 dataset of 21,988 pesticide samples at 212 stream-water sites. Only 21,144 pesticide samples, however, are considered appropriate for trend analysis.

Acknowledgments

Many USGS employees contributed to this report: Jessica L. Thompson provided water-quality data from the NAWQA Data Warehouse; Sonja R. Abney, Jana Iverson, Leslie K. Kanagy, Janece C. Koleis, Chris E. Lindley, James E. Madsen, Dennis J. Markovchick, Lucinda K. Murtagh, Mary C. Olson, Scott D. Oppenheimer, Carmen G. Reed-Parker, Rhiannon C. Revello, Steven G. Smith, Max E. Stroppel, and Frank W. Wiebe analyzed the water samples for pesticide concentrations; Jonathon C. Scott provided software and programming support; David L. Lorenz, Aldo V. Vecchia, Dennis R. Helsel, Robert J. Gilliom, and Charles G. Crawford consulted on data-preparation procedures for trend analysis; Wesley W. Stone and Karen R. Ryberg provided technical reviews of early drafts of the report; and Bonnie Stich Fink edited the report.

---

[8] The pesticides “selected” for trend analysis are those measured by the GCMS analytical method in schedules 2001 and 2010 (table 1). Martin (2009, appendix 1) determined that only pesticides analyzed by the GCMS analytical method were sufficiently extensive in time and space for a national assessment of trends.

References Cited

Cleveland, W.S., and McGill, Robert, 1985, Graphical perception and graphical methods for analyzing scientific data: Science, v. 229, p. 828–833.

Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p. Available at *http://pubs.usgs.gov/twri/twri3-c2/.*

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p. Available at *http://water.usgs.gov/pubs/circ/circ1112/.*

Gilliom, R.J.; Barbash, J.E.; Crawford, C.G.; Hamilton, P.A.; Martin, J.D.; Nakagaki, Naomi; Nowell, L.H.; Scott, J.C.; Stackelberg, P.E.; Thelin, G.P.; and Wolock, D.M., 2006, The quality of our Nation's waters—Pesticides in the Nation's streams and ground water, 1992–2001: U.S. Geological Survey Circular 1291, 172 p. Available at *http://pubs.usgs.gov/circ/2005/1291/.*

Gilliom, R.J., Hamilton, P.A., and Miller, T.L., 2001, The National Water-Quality Assessment Program—Entering a new decade of investigations: U.S. Geological Survey Fact Sheet 071–01, 6 p. Available at *http://pubs.usgs.gov/fs/fs-071-01/.*

Helsel, D.R., and Hirsch R.M., 2002, Statistical methods in water resources: U.S. Geological Survey Techniques of Water-Resources Investigations, book 4, chap. A3, 510 p. Available at *http://water.usgs.gov/pubs/twri/twri4a3/.*

Hooper, R.P., Aulenbach, B.T., and Kelly, V.J., 2001, The National Stream Quality Accounting Network—A flux-based approach to monitoring the water quality of large rivers: Hydrological Processes, v. 15, p. 1089–1106, accessed April 1, 2008, at *http://www3.interscience.wiley.com/journal/82002952/issue*.

Lindley, C.E., Stewart, J.T., and Sandstrom, M.W., 1996, Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass-selective detection: Journal of the AOAC International, v. 79, no. 4, p. 962–966.

Madsen, J.E., Sandstrom, M.W., and Zaugg, S.D., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—A method supplement for the determination of fipronil and degradates in water by gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02–462, 11 p. Available at *http://nwql.usgs.gov/Public/pubs/OFR02-462/OFR02-462.html.*

Martin, J.D., 1999, Quality of pesticide data for environmental water samples collected for the National Water-Quality Assessment Program, 1992–96, and examples of the use of quality-control information in water-quality assessments, accessed February 20, 2008, at *http://water.usgs.gov/nawqa/pnsp/pubs/qcsummary.html*.

Martin, J.D., 2002, Variability of pesticide detections and concentrations in field replicate water samples collected for the National Water-Quality Assessment Program, 1992–97: U.S. Geological Survey Water-Resources Investigations Report 01–4178, 84 p. Available at *http://pubs.usgs.gov/wri/2001/wri01_4178/.*

Martin, J.D., 2009, Sources and preparation of data for assessing trends in concentrations of pesticides in streams of the United States, 1992–2006: U.S. Geological Survey Scientific Investigations Report 2009–5062, 41 p. Available at *http://pubs.usgs.gov/sir/2009/5062/.*

Martin, J.D., and Eberle, Michael, 2011, Adjustment of pesticide concentrations for temporal changes in analytical recovery, 1992–2010: U.S. Geological Survey Data Series 630, 11 p., 5 app. Available at *http://pubs.usgs.gov/ds/630/*.

Martin, J.D., Gilliom, R.J., and Schertz, T.J., 1999, Summary and evaluation of pesticides in field blanks collected for the National Water-Quality Assessment Program, 1992–95: U.S. Geological Survey Open-File Report 98–412, 102 p. Available at *http://water.usgs.gov/nawqa/pnsp/pubs/files/ofr98412.pdf*.

Martin, J.D., Stone, W.W., Wydoski, D.S., and Sandstrom, M.W., 2009, Adjustment of pesticide concentrations for temporal changes in analytical recovery, 1992–2006: U.S. Geological Survey Scientific Investigations Report 2009–5189, 23 p., 9 app. Available at *http://pubs.usgs.gov/sir/2009/5189/.*

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97–223, 17 p. Available at *http://pubs.usgs.gov/of/1997/223/.*

Oblinger Childress, C.J., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p. Available at *http://water.usgs.gov/owq/OFR_99-193/index.html*.

Phillips, P.J., Ator, S.W., and Nystrom, E.A., 2007, Temporal changes in surface-water insecticide concentrations after the phaseout of diazinon and chlorpyrifos: Environmental Science & Technology, v. 41, no. 12, p. 4246–4251.

Ryberg, K.R., Vecchia, A.V., Martin, J.D., and Gilliom, R.J., 2010, Trends in pesticide concentrations in urban streams in the United States, 1992–2008: U.S. Geological Survey Scientific Investigations Report 2010–5139, 101 p. Available at *http://pubs.usgs.gov/sir/2010/5139/*.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–455, 42 p. Available at *http://pubs.usgs.gov/of/1994/0455/report.pdf*.

Sullivan, D.J., Vecchia, A.V., Lorenz, D.L., Gilliom, R.J., and Martin, J.D., 2009, Trends in pesticide concentrations in corn-belt streams, 1996–2006: U.S. Geological Survey Scientific Investigations Report 2009–5132, 75 p. Available at *http://pubs.usgs.gov/sir/2009/5132/*.

U.S. Geological Survey [variously dated], National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, accessed April 1, 2008, at *http://water.usgs.gov/owq/FieldManual/*.

U.S. Geological Survey, 1994, Description and guide for interpreting low-level data supplied by the NWQL for schedules 2001, 2010, 2050, and 2051: National Water Quality Laboratory Technical Memorandum 94–12, accessed April 1, 2008, at *http://nwql.usgs.gov/Public/tech_memos/nwql.94-12.html*.

U.S. Geological Survey, 1997, Changes to the NWQL's data formatting and transmittal software: National Water Quality Laboratory Technical Memorandum 97–08, accessed April 1, 2008, at *http://nwql.usgs.gov/Public/tech_memos/nwql.97-08.html.*

U.S. Geological Survey, 2006, National Stream Water Quality Accounting Network (NASQAN)—Station selection for fiscal years (FY) 1996–2000, accessed February 20, 2008, at *http://water.usgs.gov/nasqan/progdocs/statables.html*.

U.S. Geological Survey, 2010, NASQAN National Stream Water Quality Accounting Network, 2001–2007 NASQAN design information, accessed September 15, 2011, at *http://water.usgs.gov/nasqan/2001_2007_design_info.html*.

Vecchia, A.V., Gilliom, R.J., Sullivan, D.J., Lorenz, D.L., and Martin, J.D., 2009, Trends in concentration and use of agricultural herbicides for corn belt rivers, 1996–2006: Environmental Science & Technology, v. 43, no. 24, p. 9096–9102.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 49 p. Available at *http://wwwnwql.cr.usgs.gov/Public/pubs/OFR95-181/OFR95-181.html.*

Appendixes

The appendixes are separate documents, available for downloading at—

http://pubs.usgs.gov/ds/655/

Appendixes 1 and 2 are series of graphs; appendixes 3 through 5 are datasets and accompanying metadata.

Appendixes:

1. Time-series plots of nondetections of pesticides for all sites in the trend dataset 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.
2. Time-series plots of (1) rounded concentrations of pesticides in relation to the maximum value of the long-term method detection level (maxLT-MDL) for all sites in the trend dataset; (2) modeled temporal changes in recovery; and, (3) for detections at White River at Hazleton, IN, a comparison of recovery-adjusted versus unadjusted concentrations.
3. Data file of stream-water sites selected for trend analysis.
4. Data files of pesticide concentrations in stream-water samples.
5. Data file of pesticides selected for trend analysis.

Martin and others—**Sources and Preparation of Data for Assessing Trends in Concentrations of Pesticides in U.S. Streams, 1992–2010**—Data Series 655