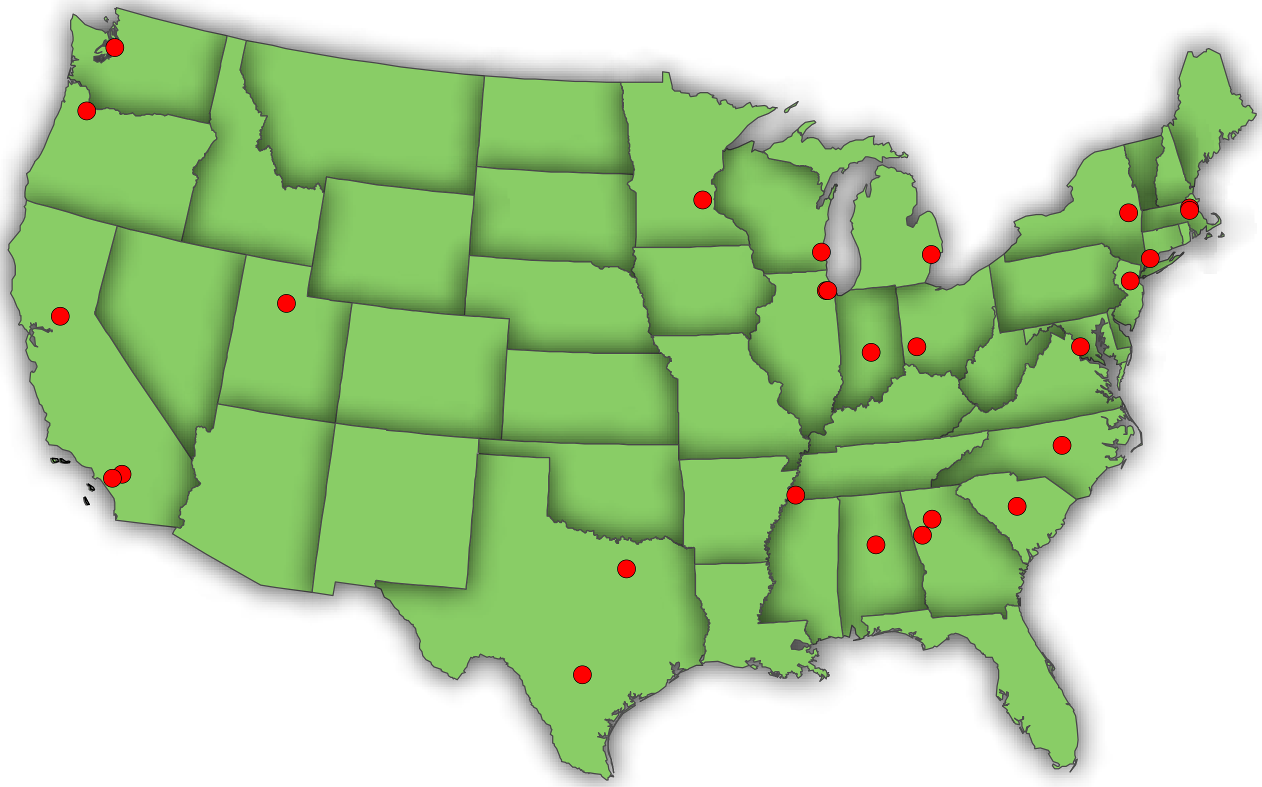
NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Trends in Pesticide Concentrations in Urban Streams in the United States, 1992–2008



Scientific Investigations Report 2010–5139

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

Trends in Pesticide Concentrations in Urban Streams in the United States, 1992–2008

By Karen R. Ryberg, Aldo V. Vecchia, Jeffrey D. Martin, and Robert J. Gilliom

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Scientific Investigations Report 2010–5139

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

Suggested citation:
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.

Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
	Length	
micrometer (µm)	0.00003937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
	Area	
square kilometer (km^2)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L).

Trends in Pesticide Concentrations in Urban Streams in the United States, 1992–2008

By Karen R. Ryberg, Aldo V. Vecchia, Jeffrey D. Martin, and Robert J. Gilliom

Abstract

Pesticide concentration trends in streams dominated by urban land use were assessed using data from 27 urban streams sampled as part of the U.S. Geological Survey National Water-Quality Assessment Program. The sites were divided into four regions, Northeast, South, Midwest, and West, to examine possible regional patterns. Three partially overlapping 9-year periods (1992–2000, 1996–2004, and 2000–2008) were examined for eight herbicides and one degradation product (simazine, prometon, atrazine, deethylatrazine, metolachlor, trifluralin, pendimethalin, tebuthiuron, and Dacthal), and five insecticides and two degradation products (chlorpyrifos, malathion, diazinon, fipronil, fipronil sulfide, desulfinylfipronil, and carbaryl). The data were analyzed for trends in concentration using a parametric regression model with seasonality, flow-related variability, and trend, called SEAWAVE-Q. The SEAWAVE-Q model also was used to generate estimated daily concentration percentiles for each analysis period to provide a summary of concentration magnitudes.

For herbicides, the largest 90th percentiles of estimated concentrations for simazine were in the South, prometon at some sites in all of the regions, atrazine and deethylatrazine in the South and Midwest, metolachlor in the Midwest and a few sites in the South, pendimethalin at scattered sites in all of the regions, and tebuthiuron in the South and a few sites in the Midwest and West. For insecticides, the largest 90th percentiles of estimated concentrations for diazinon and carbaryl were distributed among various sites in all regions (especially during 1996–2004), and fipronil at isolated sites in all of the regions during 2000–2008.

Trend analysis results for the herbicides indicated many significant trends, both upward and downward, with varying patterns depending on period, region, and herbicide. Overall, deethylatrazine showed the most consistent pattern of upward trends, especially in the Northeast (2000–2008), South (1996–2004 and 2000–2008), and Midwest (1996–2004 and 2000–2008). Other herbicides showed less consistent upward trends, including simazine in the South (1996–2004), prometon in the Midwest (2000–2008), and atrazine in the South (1996–2004). The most consistent downward trends were for simazine in the Northeast and Midwest (1996–2004), prometon in the Northeast and Midwest (1996–2004) and West (1996–2004 and 2000–2008), and tebuthiuron in the South (1996–2004 and 2000–2008) and West (2000–2008).

Strong similarity existed between the trends for atrazine and deethylatrazine during 1996–2004. During 2000–2008, however, there were mixed upward and downward trends in atrazine and predominantly upward trends in deethylatrazine. Ten sites with a downward trend in atrazine were paired with an upward trend in deethylatrazine and for three of these sites (1 in the South and 2 in the Midwest) both opposing trends were significant. Opposing trends showing a decrease in atrazine and an increase in deethylatrazine may indicate that decreases in atrazine from surface runoff are being offset in some cases by increases in deethylatrazine from groundwater for the latter analysis period.

Trend results for insecticides indicated widespread significant downward trends for chlorpyrifos (especially 1996–2004), diazinon (1996–2004 and 2000–2008), and malathion (especially 1996–2004); widespread significant upward trends for fipronil and its degradation products (2000–2008); and mostly nonsignificant trends for carbaryl (1996–2004 and 2000–2008). The downward trends for chlorpyrifos and diazinon were consistent with the regulatory phaseout of residential uses of these insecticides and the upward trends for fipronil and its degradation products were consistent with its introduction in 1996 and subsequent increasing use as a possible substitute for chlorpyrifos and diazinon. The downward trends in malathion may be caused by voluntary substitution of pyrethroids or fipronil for malathion. Although carbaryl trends were mostly nonsignificant, most of the trends for 1996–2004 were upward and four of the upward trends were significant. The upward tendency in carbaryl concentrations during that time may indicate some substitution of carbaryl for chlorpyrifos and diazinon. For 2000–2008, carbaryl trends were mixed upward and downward and the trends were mostly nonsignificant. Despite voluntary cancellation of some residential uses of carbaryl beginning in about 2000, there were only four significant downward trends during 2000–2008 and two significant upward trends during that time. Voluntary cancellations of some carbaryl uses may not have decreased overall carbaryl

usage in some areas, or decreases in some uses may have been offset by substitution of carbaryl for chlorpyrifos and diazinon.

Introduction

More than 450 million kilograms (kg) of pesticides are used each year in the United States to control weeds, insects, and other pests in agricultural areas, urban areas, and a variety of other land-use settings (Gilliom and others, 2006). The use of pesticides has resulted in a range of benefits, including increased food production and a decrease in insect-borne disease. However, the use of pesticides also raises questions about possible adverse effects on the environment, including water quality. Once released into the environment, pesticides can move through the hydrologic system to streams and groundwater, where they may have unintended effects on humans, aquatic life, or wildlife (Gilliom and others, 2006).

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) has conducted a series of regional and national assessments of pesticide trends for streams with a variety of land use, geographic, and hydrologic settings throughout the country. Information is needed that focuses on pesticide trends in streams dominated by urban land use. To address this need, the USGS analyzed pesticide data from 27 urban streams, sampled throughout the United States as part of NAWQA studies, for trends in the concentrations of the most frequently detected pesticides for the sampling period 1992–2008.

The use of pesticides in urban settings changes over time in response to changes in factors such as land use, pesticide effectiveness, regulations, market forces, and development of new pesticides. Unlike agricultural uses for which pesticide use can be reasonably estimated for a particular basin and year (Sullivan and others, 2009), the amount of a pesticide applied in an urban setting is virtually impossible to estimate because few records of use are available. In addition to urban uses, some of the urban streams included in the study have some agricultural land in their drainage basins, which could contribute some pesticides, and some of the streams are in agricultural regions, which may contribute pesticides to urban areas by atmospheric deposition.

Evaluation of trends in pesticide concentrations in urban streams provides valuable insight for understanding how concentrations of individual pesticides may be changing in relation to potential causal mechanisms, such as changes in use of pesticides because of factors ranging from national scale changes (including mandated phasing out of pesticides, voluntary cancellation of uses, and substitution of new pesticides for phased-out pesticides) to localized factors (including increases in urbanization). Although quantitative estimates of pesticide usage in urban settings are not readily available, qualitative information regarding changes in regulation and phase out of pesticides is. By identifying the directions, periods, and statistical significance of past trends, in context with regulation changes, the study described in this report provides a step toward achieving the goal of definitive attribution of trends in urban-stream pesticide detection.

Purpose and Scope

The purpose of this report is to assess trends in the concentrations of commonly detected pesticides in streams dominated by urban land use and, to the extent possible, interpret the trends in relation to available information on pesticide uses and regulations during 1992–2008. Concentration trends were assessed for eight herbicides and one degradation product (simazine, prometon, atrazine, deethylatrazine, metolachlor, trifluralin, pendimethalin, tebuthiuron, and Dacthal) and five insecticides and two degradation products (chlorpyrifos, malathion, diazinon, fipronil, fipronil sulfide, desulfinylfipronil, and carbaryl). An overview of concentration patterns is also provided as context for the trend analysis. All of these most commonly detected herbicides and insecticides have known nonagricultural uses, although not well quantified, and some pesticides may be contributed to the streams from nearby agricultural usage.

Data from 27 urban-stream sites sampled throughout the United States were used in the assessment, including sites from each of 4 regional groupings—Northeast, South, Midwest, and West (fig. 1). Pesticide concentrations for these 27 sites were analyzed for trends during each of three partially overlapping 9-year periods: 1992–2000, 1996–2004, and 2000–2008. Depending on minimum data requirements for assessing trends as described in the Selection of Pesticides and Time Periods for Trend Analysis section, different subsets of the sites were included for each period and pesticide.

Acknowledgments

The authors thank Naomi Nakagaki, who provided basin characteristics and population data and guidance in understanding the data and their sources, and Jack Barbash, who provided detailed chemical property information for fipronil, fipronil sulfide, and desulfinylfipronil. Thanks also to Dave Lorenz and Dennis Helsel, who provided valuable input on the methods for handling low-level detections, and to Charlie Crawford and Wes Stone, who provided guidance on the statistical methods and interpretation of trend results. Finally, the authors acknowledge improvements made to the manuscript thanks to the reviews done by Patrick Phillips and Joseph Domagalski.

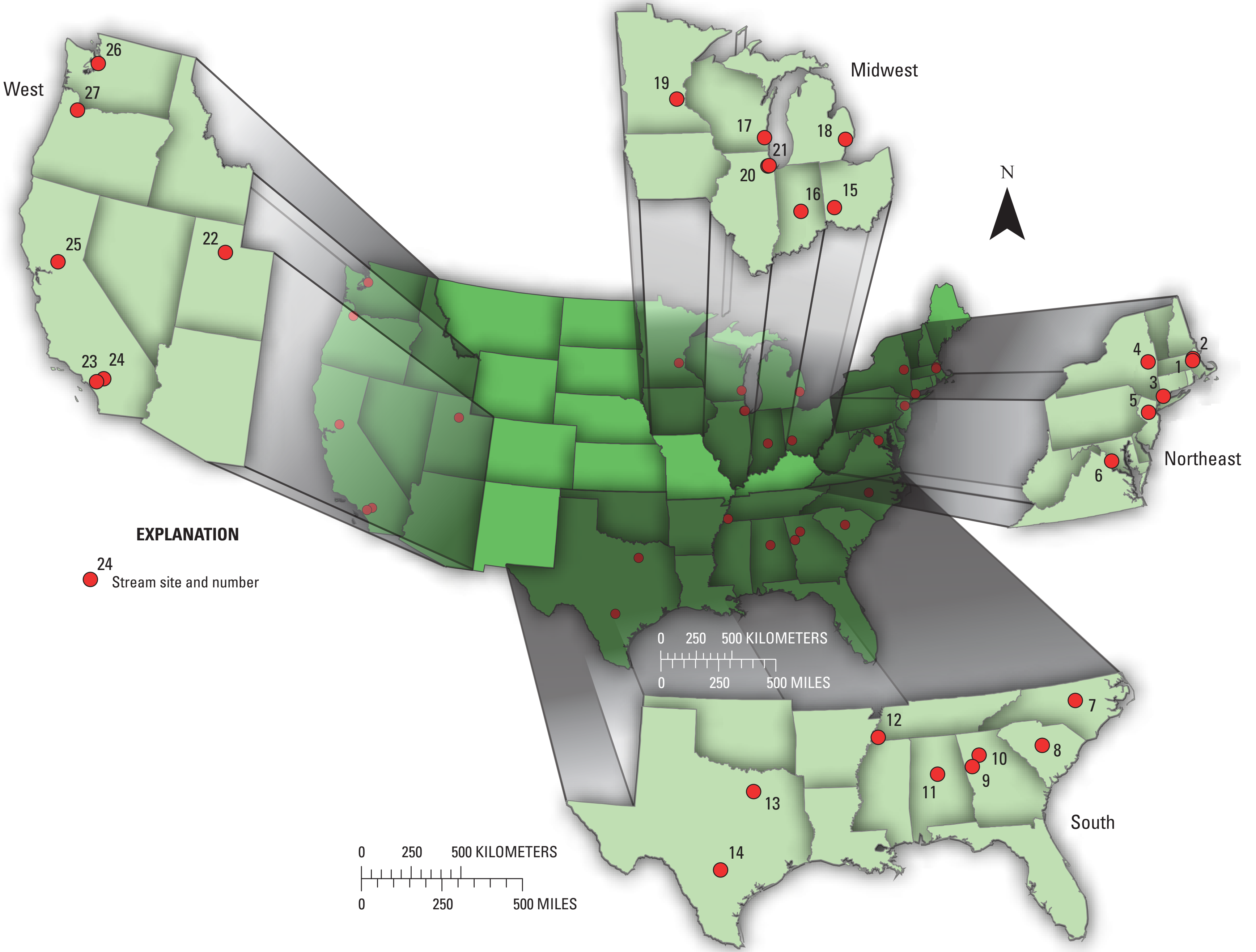


Figure 1. Stream sites dominated by urban land use and selected for pesticide trend analysis, 1992–2008.

Study Design and Methods

Site Selection

The 27 stream sites analyzed in this study (table 1; fig. 1) are a subset of 201 sites that were sampled as part of NAWQA studies and the USGS National Stream Quality Accounting Network (NASQAN), and which were selected as part of a national set of sites that have adequate pesticide data for trend analysis (Martin, 2009). The 27 sites were those classified as "urban," based on the criteria of greater than 25 percent of the drainage basin in urban land use and agricultural land use of no more than 25 percent (Martin, 2009). The land use was determined from drainage basin boundaries provided by NAWQA (as of March 11, 2009) overlain with 30-meter (m) resolution National Land Cover Database (NLCD) land-cover data (Martin, 2009, appendix 4; Homer and others, 2004). Drainage areas for the sites range from 26.0 to 6,250 square kilometers (km^2; median 80.7 km^2); urban land use in 2001 ranged from 27.6 to 100 percent of the drainage areas (median 73.9 percent); and population density in 2000 ranged from 275 to 2,364 people per km^2 (median 847 people per km^2). In addition to the land-use requirements, each of the 27 sites had at least 5 years of concentration data and concurrent daily streamflow data.

Sample Collection, Processing, and Field Quality-Control Program

Sampling strategies varied by site and among some years, but followed guidelines established by the NAWQA Program (Crawford, 2004; Gilliom and others, 1995). Samples were collected using a combination of fixed-interval and high-flow sampling procedures. The fixed-interval sampling was more frequent during the times of year when pesticide concentrations usually were greatest, typically during the growing season. The typical frequency of sampling ranged from four times per month to once a month or once every other month, depending on the time of the year.

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. All sample-collection and processing equipment that came in contact with sample water were 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-micrometer (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 National Water Quality Laboratory (NWQL) in Denver, Colorado, for pesticide analysis.

The quality of the stream-water pesticide data 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 field replicate water samples is summarized in Martin (2002). Pesticide recovery in laboratory reagent spikes and field matrix spikes is summarized in Martin and others (2009). QC data are stored in the NAWQA Data Warehouse, *http://water.usgs.gov/nawqa/data*.

Analytical Method for Pesticides

All water-quality samples for pesticide trend analysis were analyzed by NWQL using a gas chromatography/mass spectrometry (GCMS) method. Pesticides were 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). This method is available from the National Environmental Methods Index (*http://www.nemi.gov/*) as USGS-NWQL method O–1126–95. The GCMS method provides low-level analyses of as many as 44 commonly used pesticides and 8 pesticide degradates. 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 conclusively identified (detected) 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 reporting level (for example: <0.005 µg/L [less than 0.005 micrograms per liter]). The types and numerical values of reporting levels used to report nondetections of pesticides analyzed by GCMS have changed through time. Martin (2009) has additional information on reporting procedures for GCMS analytical data.

Sources and Preparation of Concentration Data for Trend Analysis

For the trend analyses in this report, the pesticide data set (1992–2006) provided in Martin (2009, Appendix 5a) was extended with approximately 2 additional years of data (through summer 2008) obtained from NAWQA Data Warehouse data managers (Jessica L. Thompson, U.S. Geological Survey, written commun., November 5, 2008). Pesticide

Table 1. Selected information for stream sites dominated by urban land use and selected for pesticide trend analysis, 1992–2008.

[USGS, U.S. Geological Survey; km^2, square kilometers; basins were delineated by a number of USGS hydrologists and geographers in National Water-Quality Assessment Program study units using a variety of methods using data sources at multiple scales and were current as of December 2009 (N. Nakagaki, U.S. Geological Survey, 2009, written commun.); NLCD, National Landcover Database, U.S. Geological Survey, 2007, and Fry and others, 2009; population data based on 1990 and 2000 population counts (U.S. Bureau of the Census, 1992, and Geolytics, Inc., 2001) and 1990 and 2000 census block group boundaries (U.S. Bureau of the Census, 2001a and 2001b)]

					Percent land use			Population density		
Site number (fig. 1)	Site short name	USGS station number	Site name	Drainage area (km^2)	Urban 2001 from NLCD Change Product	Urban 1992 from NLCD Change Product	Urban land use, percent change in total from 1992 to 2001	2000 (People per km^2)	1990 (People per km^2)	Percent change from 1990 to 2000
			Northeast							
1	ABERJ	01102500	Aberjona River at Winchester, Mass.	59.8	79.3	78.0	1.7	1,141	1,126	1.3
2	CHRLS	01104615	Charles River above Watertown Dam at Watertown, Mass.	695	41.2	40.1	2.7	571	534	6.9
3	NRWLK	01209710	Norwalk River at Winnipauk, Conn.	85.1	27.6	27.1	1.7	281	255	10.2
4	LISHA	01356190	Lisha Kill near Niskayuna, N.Y.	40.0	51.2	49.3	3.9	552	524	5.3
5	BOUND	01403900	Bound Brook at Middlesex, N.J.	126	61.2	60.3	1.6	1,391	1,292	7.7
6	ACCOT	01654000	Accotink Creek near Annandale, Va.	60.7	61.8	59.0	4.8	1,610	1,440	11.8
			South							
7	SWIFT	02087580	Swift Creek near Apex, N.C.	53.9	73.9	64.4	14.8	726	489	48.5
8	GILLS	02169570	Gills Creek at Columbia, S.C.	154	51.8	50.7	2.2	481	445	8.1
9	SOPEC	02335870	Sope Creek near Marietta, Ga.	79.5	74.4	68.3	9.0	902	793	13.7
10	CHATT	02338000	Chattahoochee River near Whitesburg, Ga.	6,250	28.8	25.4	13.3	311	231	34.6
11	CAHAB	0242354750	Cahaba Valley Creek at Cross Creek Road at Pelham, Ala.	66.1	30.2	28.4	6.4	275	216	27.3
12	FLTCH	07031692	Fletcher Creek at Sycamore View Road at Memphis, Tenn.	79.0	85.0	70.7	20.3	847	442	91.6
13	WHITE	08057200	White Rock Creek at Greenville Avenue at Dallas, Tex.	173	91.2	77.1	18.2	1,510	987	53.0
14	SALAD	08178800	Salado Creek at Loop 13 at San Antonio, Tex.	506	53.7	46.1	16.6	624	508	22.8
			Midwest							
15	HOLES	393944084120700	Holes Creek at Huffman Park at Kettering, Ohio	51.9	85.5	82.4	3.8	650	572	13.6
16	LBUCK	03353637	Little Buck Creek near Indianapolis, Ind.	44.6	86.9	71.9	20.9	749	572	30.9
17	LINCO	040869415	Lincoln Creek at 47th Street at Milwaukee, Wis.	26.0	91.6	91.0	.7	2,222	2,184	1.7
18	CLINT	04161820	Clinton River at Sterling Heights, Mich.	803	48.5	46.6	4.1	469	413	13.6
19	SHING	05288705	Shingle Creek at Queen Avenue at Minneapolis, Minn.	73.0	78.4	76.3	2.7	1,093	1,045	4.6
20	SALTC	05531500	Salt Creek at Western Springs, Ill.	291	90.7	87.0	4.3	1,183	1,116	6.0
21	DPLAI	05532500	Des Plaines River at Riverside, Ill.	1,630	63.0	60.0	5.0	868	780	11.3
			West							
22	LCOTT	10168000	Little Cottonwood Creek at Jordan River near Salt Lake City, Utah	117	29.0	28.1	3.3	493	473	4.2
23	WARMC	11060400	Warm Creek near San Bernardino, Calif.	30.9	96.1	95.6	.5	1,900	1,887	.7
24	SANTA	11074000	Santa Ana River below Prado Dam, Calif.	3,730	39.1	37.5	4.2	539	451	19.5
25	ARCAD	11447360	Arcade Creek near Del Paso Heights, Calif.	81.5	100.0	97.9	2.1	2,034	1,986	2.4
26	THORN	12128000	Thornton Creek near Seattle, Wash.	29.2	95.8	95.7	.1	2,364	2,205	7.2
27	FANNO	14206950	Fanno Creek at Durham, Oreg.	80.7	87.0	85.2	2.1	1,502	1,202	25.0

data analyzed by the GCMS method for the 201 stream sites selected by Martin (2009, table 2) were identified and samples collected prior to September 1, 2005, from Martin (2009) were merged with samples collected on or after September 1, 2005, from the November 2008 data retrieval.

Pesticide concentration data were prepared for trend analysis using the approach presented in Martin (2009). The principal steps in data preparation were to (1) identify routine reporting levels used to report nondetections; (2) reassign the concentration value for routine nondetections to the maximum value of the long-term method detection level; (3) round concentrations to a consistent level of precision for the concentration range; (4) adjust concentrations to compensate for temporal changes in bias of recovery of the GCMS analytical method; and (5) identify and remove samples collected too frequently in time for trend analysis. In addition to the procedures used by Martin (2009), at selected sites with sufficient low-level pesticide detections, the concentration for routine nondetections was lowered from the maximum of the long-term method detection level (maxLT-MDL) to the median concentration of the low-level detections (qlow50). These data-preparation steps are further described in appendix 1 (at the back of this report).

Selection of Pesticides and Time Periods for Trend Analysis

Of the 52 pesticide compounds included in the USGS GCMS method described in the Analytical Methods for Pesticides section, 16 compounds with the highest overall rates of detection (based on initial exploratory data analysis and the data requirements for trend analysis) for the 27 urban sites were selected for trend analysis (table 2), including 9 herbicides and degradates and 7 insecticides and degradates. The 16 compounds span a considerable range of characteristics and factors that can affect trends and a considerable range of relative importance among urban and agricultural applications.

The two considerations that determined the time periods for trend analysis and interpretation for each pesticide were: (1) the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period being assessed and (2) there needed to be at least 10 uncensored concentrations (detections at or above the censoring level) for a particular site-pesticide combination. The first consideration, representative sample coverage, is illustrated by the example in table 3, which shows for

Table 2. Pesticides and degradates selected for 1992–2008 urban-stream trend analysis.

[Sorted by U.S. Geological Survey (USGS) parameter code with the exception of degradation products which are listed after parent product regardless of parameter code; DCPA, dimethyl tetrachloroterephthalate; CAS, Chemical Abstracts Service; year registered from U.S. Environmental Protection Agency (USEPA) registration and reregistration documents (variously dated); --, not defined or not applicable]

Pesticide compound (synonym)	USGS parameter code	CAS number[a]	Pesticide class (subclass)	Parent pesticide, if degradate	Year first registered for use by USEPA
			Herbicides and degradates		
Simazine	04035	122-34-9	Triazine (chlorotriazine)	--	1984
Prometon	04037	1610-18-0	Triazine (methoxytriazine)	--	1959
Atrazine	39632	1912-24-9	Triazine (chlorotriazine)	--	1958
Deethylatrazine	04040	6190-65-4	degradate	Atrazine	--
Metolachlor	39415	51218-45-2	Amide (chloroacetanilide)	--	1976
Trifluralin	82661	1582-09-8	Dinitroaniline	--	1963
Pendimethalin	82683	40487-42-1	Dinitroaniline	--	1974
Tebuthiuron	82670	34014-18-1	Urea (thiadiazolylurea)	--	1974
Dacthal (DCPA)	82682	1861-32-1	Chlorobenzoic acid ester/organochlorine	--	1958
			Insecticides and degradates		
Chlorpyrifos	38933	2921-88-2	Organophosphate (pyridine organothiophosphate)	--	1965
Malathion	39532	121-75-5	Organophosphate (aliphatic organothiophosphate)	--	1956
Diazinon	39572	333-41-5	Organophosphate (pyrimidine organothiophosphate)	--	1956
Fipronil	62166	120068-37-3	Pyrazole (phenylpyrazole)	--	1996
Fipronil sulfide	62167	120067-83-6	degradate	Fipronil	--
Desulfinylfipronil	62170	--	degradate	Fipronil	--
Carbaryl	82680	63-25-2	Carbamate	--	1959

[a] This report contains CAS Registry Numbers®, which is a registered trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services℠.

selected sites the number of carbaryl concentration values that were available for trend analysis for each year, regardless of whether or not the values were censored. The sample sizes for the other pesticides analyzed, except fipronil and its degradates, were similar to carbaryl (fipronil and its degradates were not analyzed before 1999). The years in which samples were collected varied considerably from site to site (table 3). Therefore, to facilitate comparisons among trends from different sites, the entire sampling interval (1992–2008) was split into three partially overlapping 9-year periods: 1992–2000, 1996–2004, and 2000–2008.

The minimum sampling criteria for a particular site to be considered adequately representative of a particular 9-year trend assessment period were (1) at least 2 years with four or more samples collected during the first 5 years of the assessment period and (2) at least 2 years with four or more samples collected during the last 5 years of the assessment period. For the sites shown in table 3 and the first assessment period (1992–2000), only two sites (3, NRWLK and 16, LBUCK) met these criteria. Two sites (4, LISHA and 27, FANNO) did not have enough samples during the last part of the period (1996–2000), three sites (8, BOUND; 10, CHATT; and 12, FLTCH) did not have enough samples during the first part (1992–96), and one site (7, SWIFT) did not have any samples during 1992–2000. For the 1996–2004 assessment period, all of the sites in table 3 except 4, LISHA; 7, SWIFT; and 27, FANNO met the criteria and for the 2000–2008 period, all of the sites except 12, FLTCH and 16, LBUCK met the criteria.

The sites and pesticides that satisfied the minimum sampling criteria for each trend assessment period are shown in table 4. Sites not listed for an assessment period were not representative of the given period, regardless of the pesticide being considered. In the trend results described the Trends in Pesticide Concentration section, such cases will be referred to as “NR” for “not representative” of the trend assessment period. Unshaded cells in the table indicate cases where there were enough samples collected for that site, but for which the data were too highly censored to analyze trends for the given pesticide (except for fipronil and its degradates, which were not collected for the first two assessment periods).

Table 3. Annual sample sizes for carbaryl for selected urban-stream sites, 1992–2008.

[Yellow bar indicates that carbaryl samples at particular sites were sufficient for analysis for the 1992–2000 period; green bar indicates that carbaryl samples at particular sites were sufficient for analysis for the 1996–2004 period; blue bar indicates that carbaryl samples at particular sites were sufficient for analysis for the 2000–2008 period.]

Site number (fig. 1)	Site short name	Number of samples used for trend assessment																
		1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
3	NRWLK	0	32	26	0	0	13	17	17	17	13	28	16	8	4	6	0	0
		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
4	LISHA	0	0	18	18	0	0	0	0	3	10	8	8	8	7	19	2	11
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
8	BOUND	0	0	0	0	18	19	3	0	0	10	9	8	7	0	3	16	0
						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
7	SWIFT	0	0	0	0	0	0	0	0	0	8	22	14	8	6	10	18	0
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
10	CHATT	0	0	3	3	0	8	5	12	12	13	16	17	7	6	9	18	9
						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
12	FLTCH	0	0	0	0	4	19	0	0	0	8	9	9	7	0	0	0	0
						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
16	LBUCK	23	29	14	11	13	9	11	8	13	19	22	14	7	0	0	0	0
		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
27	FANNO	0	13	9	5	0	0	0	0	0	18	25	13	10	6	9	17	0
										🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦

Table 4. Number of uncensored concentrations for pesticides in urban-stream samples, 1992–2008.

[Shaded cells indicate site/pesticide samples with at least 10 uncensored concentrations during the trend assessment period; DCPA, dimethyl tetrachloroterephthalate; --, indicates that fipronil and its degradates were not considered for trend analysis in the first two periods because samples were not analyzed for fipronil and its degradates until 1999]

Trend assessment period	Site number (fig. 1)	Site short name	Number of uncensored concentrations								
			Simazine	Prometon	Atrazine	Deethylatrazine	Metolachlor	Trifluralin	Pendimethalin	Tebuthiuron	Dacthal (DCPA)
1992–2000	3	NRWLK	43	97	80	42	32	10	1	0	11
	6	ACCOT	76	78	64	48	74	11	29	6	21
	9	SOPEC	78	39	75	36	9	8	23	61	5
	16	LBUCK	113	118	118	112	118	29	21	46	47
1996–2004	1	ABERJ	21	51	40	17	28	16	7	9	0
	2	CHRLS	5	14	29	8	3	0	1	0	4
	3	NRWLK	28	112	88	58	42	13	0	1	1
	5	BOUND	45	66	67	58	52	16	13	28	20
	6	ACCOT	104	112	88	64	99	25	30	10	12
	8	GILLS	77	71	76	68	19	0	4	74	1
	9	SOPEC	92	57	88	64	5	11	23	90	7
	10	CHATT	88	67	87	43	13	1	4	60	2
	11	CAHAB	86	30	85	82	6	12	10	12	0
	12	FLTCH	56	43	54	51	54	13	20	19	2
	13	WHITE	120	114	120	120	117	11	66	37	16
	14	SALAD	43	70	70	65	15	0	3	69	2
	15	HOLES	74	99	104	94	73	27	23	0	0
	16	LBUCK	96	116	116	110	112	11	13	8	8
	18	CLINT	58	60	69	63	63	6	4	1	7
	19	SHING	6	82	73	51	56	8	4	32	19
	20	SALTC	44	59	66	63	54	11	5	2	5
	21	DPLAI	30	50	53	51	48	9	3	25	3
	22	LCOTT	11	68	54	45	0	7	17	39	26
	23	WARMC	42	36	2	2	2	0	0	18	25
	25	ARCAD	50	69	16	0	48	18	13	23	41
	26	THORN	30	68	17	0	0	6	0	1	1
2000–2008	2	CHRLS	4	13	38	15	7	0	1	0	0
	3	NRWLK	10	73	54	37	20	8	0	1	0
	4	LISHA	8	39	29	16	33	1	3	0	0
	5	BOUND	20	45	48	37	34	5	4	14	3
	6	ACCOT	85	93	70	51	78	17	21	7	4
	7	SWIFT	83	74	69	36	44	7	9	8	1
	8	GILLS	56	53	58	52	23	0	0	53	1
	9	SOPEC	109	82	106	85	4	9	24	105	5
	10	CHATT	106	82	105	69	23	2	5	76	5
	11	CAHAB	81	24	81	78	5	9	7	6	0
	13	WHITE	107	92	107	107	96	9	60	13	8
	14	SALAD	59	80	80	77	9	3	8	76	7
	17	LINCO	24	64	70	63	51	1	11	60	3
	18	CLINT	37	44	53	47	47	3	2	1	1
	19	SHING	2	67	59	44	45	1	3	26	6
	20	SALTC	37	62	75	72	63	11	6	2	2
	22	LCOTT	7	62	49	47	0	7	12	39	24
	24	SANTA	83	69	59	37	16	1	2	6	48
	25	ARCAD	53	76	12	2	60	20	26	17	44
	26	THORN	22	61	7	0	0	11	0	1	6
	27	FANNO	87	71	83	43	48	24	6	57	2

Table 4. Number of uncensored concentrations for pesticides in urban-stream samples, 1992–2008.—Continued

[Shaded cells indicate site/pesticide samples with at least 10 uncensored concentrations during the trend assessment period; DCPA, dimethyl tetrachloroterephthalate; --, indicates that fipronil and its degradates were not considered for trend analysis in the first two periods because samples were not analyzed for fipronil and its degradates until 1999]

Trend assessment period	Site number (fig. 1)	Site short name	Number of uncensored concentrations						
			Chlorpyrifos	Malathion	Diazinon	Fipronil	Fipronil sulfide	Desulfinyl-fipronil	Carbaryl
1992–2000	3	NRWLK	2	2	30	--	--	--	26
	6	ACCOT	41	11	75	--	--	--	49
	9	SOPEC	39	10	70	--	--	--	33
	16	LBUCK	64	26	109	--	--	--	36
1996–2004	1	ABERJ	3	0	55	--	--	--	38
	2	CHRLS	0	0	21	--	--	--	13
	3	NRWLK	3	1	36	--	--	--	28
	5	BOUND	24	7	59	--	--	--	37
	6	ACCOT	25	11	105	--	--	--	69
	8	GILLS	32	32	63	--	--	--	21
	9	SOPEC	20	5	76	--	--	--	30
	10	CHATT	9	3	81	--	--	--	44
	11	CAHAB	22	2	60	--	--	--	15
	12	FLTCH	30	25	47	--	--	--	37
	13	WHITE	54	22	120	--	--	--	55
	14	SALAD	12	9	52	--	--	--	24
	15	HOLES	18	8	90	--	--	--	36
	16	LBUCK	18	12	111	--	--	--	34
	18	CLINT	8	1	51	--	--	--	17
	19	SHING	1	4	54	--	--	--	19
	20	SALTC	2	6	54	--	--	--	26
	21	DPLAI	1	3	41	--	--	--	21
	22	LCOTT	1	11	64	--	--	--	29
	23	WARMC	5	3	40	--	--	--	5
	25	ARCAD	42	33	71	--	--	--	58
	26	THORN	3	6	55	--	--	--	15
2000–2008	2	CHRLS	0	0	12	11	19	16	19
	3	NRWLK	1	1	24	0	4	2	18
	4	LISHA	1	1	31	0	1	1	31
	5	BOUND	3	0	30	13	16	19	18
	6	ACCOT	6	8	69	36	21	27	52
	7	SWIFT	4	0	50	52	49	52	39
	8	GILLS	3	15	31	16	18	19	16
	9	SOPEC	15	4	58	43	42	40	35
	10	CHATT	5	2	62	49	40	41	55
	11	CAHAB	17	1	31	31	31	27	20
	13	WHITE	30	26	87	48	36	46	49
	14	SALAD	3	7	32	16	20	26	26
	17	LINCO	0	2	45	0	1	5	16
	18	CLINT	1	0	28	6	1	1	20
	19	SHING	0	2	36	4	8	17	19
	20	SALTC	9	5	33	33	24	29	29
	22	LCOTT	1	3	46	0	1	1	26
	24	SANTA	3	9	39	23	31	41	23
	25	ARCAD	39	35	77	58	50	56	60
	26	THORN	0	1	21	5	4	16	22
	27	FANNO	17	2	61	22	26	30	62

Such cases will be referred to as "HC" for too "highly censored" to analyze trends. Shaded cells indicate cases where the data were sufficient for reporting trend results.

Statistical Method for Analyzing Trends in Pesticide Concentrations

Sullivan and others (2009) compared several methods for analyzing trends in pesticide concentrations for 31 sites and 11 pesticides, including several of the pesticides analyzed in this report. The methods compared included the seasonal Kendall (SEAKEN) test for non-flow-adjusted concentrations, a parametric regression model with seasonality and trend called SEAWAVE, and a parametric regression model with seasonality, flow-related variability, and trend, called SEAWAVE-Q. The best approach in terms of maximizing the number of sites and pesticides that could be assessed and accounting for variable streamflow conditions when comparing trends for multiple sites and pesticides was determined to be the SEAWAVE-Q model. Based on those results (Sullivan and others, 2009), the SEAWAVE-Q model was selected as the statistical tool for analyzing trends for this study.

The SEAWAVE-Q model is a parametric regression model specifically designed for analyzing seasonal- and flow-related variability and trends in pesticide concentrations. The model is expressed as follows,

$$Log\ C(t) = \beta_0 + \beta_1 W(t) + \beta_2 LTFA(t) + \beta_3 MTFA(t) + \beta_4 STFA(t) + \beta_5 t + \eta(t) \quad (1)$$

where

Log denotes the base-10 logarithm;

t is decimal time, in years, with respect to an arbitrary time origin;

C is pesticide concentration, in micrograms per liter;

W is a seasonal wave representing intra-annual variability in concentration;

$LTFA$, $MTFA$, and $STFA$ are dimensionless flow anomalies computed from daily streamflow (described later in this section);

$\beta_0, \beta_1, \ldots,$ are regression coefficients; and

$\eta(t)$ is the model error.

The seasonal wave is a dimensionless, periodic function of time with an annual cycle, similar to a mixture of sine and cosine functions often used to model seasonality in concentration data. However, the seasonal wave is better suited for modeling seasonal behavior of pesticide data than a mixture of sines and cosines. The seasonal wave is a periodic (with a period of 1 year) solution to the following differential equation (Vecchia and others, 2008):

$$\frac{d}{dt}W(t) = \lambda(t+s^*) - \varphi W(t) \quad (2)$$

where

$\lambda(.)$ is a pulse input function with $\lambda(.) > 0$ during specified application season(s) and $\lambda(.)=0$ otherwise;

s^* is a seasonal shift that determines the time at which W reaches its maximum; and

φ is a "decay rate" corresponding with an approximate half-life of $12/\varphi$ months.

As in Sullivan and others (2009, appendix 2), the pulse input function is selected from a menu of 14 choices with either one or two distinct application seasons (when pesticides may be transported to the stream) of lengths from 1 to 6 months and the half-life is selected from four choices (1, 2, 3, or 4 months). The half-life is referred to as a model half-life when discussing model results to distinguish it from the chemical half-life of pesticides. Thus, 56 (14x4) choices for the wave function are available. As described in Sullivan and others (2009, appendix 2), the observed concentration data were used to select the best wave function and to estimate the seasonal shift (s*) through a combination of graphical and maximum likelihood techniques.

Three dimensionless flow anomalies were included in the SEAWAVE-Q model to help account for flow-related variability in pesticide concentrations. The anomalies were computed using log-transformed daily flow aggregated over various time scales. The first anomaly represented short-term (day-to-day) flow variability, and was defined as

$$STFA(t) = X(t) - X_{10}(t) \quad (3)$$

where

$STFA$ is the short-term flow anomaly (dimensionless);

$X(t)$ is log-transformed daily flow in cubic meters per second; and

$X_{10}(t)$ is the average of log-transformed daily flow for 10 days up to and including time t.

Large positive values of STFA and associated increases in pesticide concentrations tended to occur near the beginning of a substantial rainfall-runoff event, whereas negative values of STFA and associated decreases in pesticide concentrations tended to occur after the event passes. The second flow anomaly represents mid-term (10- to 100-day) flow variability and was defined as

$$MTFA(t) = X_{10}(t) - X_{100}(t) \quad (4)$$

where

$MTFA$ is the mid-term flow anomaly (dimensionless); and

$X_{100}(t)$ is the average of log-transformed daily flow for 100 days up to and including time t.

The third flow variable added to the model represented long-term (greater than 100-day) flow variability and was defined as

$$LTFA(t) = X_{100}(t) - X_* \quad (5)$$

where

LTFA is the long-term flow anomaly (dimensionless); and

X_* is the average of log-transformed daily flow for the specified trend assessment period (either 1992–2000, 1996–2004, or 2000–2008).

Unlike STFA, which tends to affect pesticide concentrations in a relatively consistent manner among different sites and pesticides, MTFA and LTFA can affect pesticide concentrations in different ways and to different degrees depending on the type of pesticide, the size of the basin, and the climatic and hydrologic properties of the basin. For example, for a relatively large basin with substantial non-urban runoff, higher-than-normal seasonal flow conditions (as indicated by a positive value for LTFA) can cause decreased pesticide concentrations because of more dilution from non-urban runoff.

The SEAWAVE-Q model (eq. 1) was fitted to the pesticide data using maximum likelihood methods for censored data, as described in Sullivan and others (2009), using the statistical software R and the survival package for R (R Development Core Team, 2010; Therneau, 2009). The flow anomalies used in this report, although defined in a manner similar to that used in Sullivan and others (2009), are not identical. The time scales used to define the anomalies can be changed depending on the sites and pesticides being considered for analysis. In this report, the sites analyzed generally were much smaller in drainage area than the corn-belt sites analyzed in Sullivan and others (2009). Therefore, the shorter time scales (10- and 100-day) used here to define the anomalies produced better results for these sites as compared to the longer time scales (30- and 365-day) used for the previous report.

Statistical significance was determined using the t-test (Neter and others, 1996) of significance of the model coefficients, (β_1-β_5, eq. 1). A p-value greater than or equal to 0.10 indicated that a model variable or trend was not statistically significant. A p-value less than 0.10 indicated a statistically significant model variable or an upward or downward trend. A p-value of less the 0.01 also was used to indicate highly significant upward or downward trends.

To illustrate the SEAWAVE-Q model, results for three of the pesticides for site 9 (SOPEC) and the 2000–2008 trend assessment period are provided. Daily streamflow for this site is shown in figure 2 along with the flow anomalies. The flow anomalies partition the variability of log-transformed daily flows around their mean into orthogonal (uncorrelated) components representing short-, mid-, and long-term variability. This site has a small drainage basin (79.5 km^2) and is dominated by storm runoff, thus the short-term variability (STFA) is particularly strong (STFA has a higher degree of variability than LTFA and MTFA, extending further on the y-axis, and STFA has a greater frequency than the other anomalies with more frequent changes between positive and negative values).

The fitted (estimated) and observed concentrations for simazine, pendimethalin, and carbaryl (fig. 3) show distinct patterns of seasonality, flow-related variability, and trend. There was a very small and nonsignificant upward trend for simazine (1.1 percent per year [pct/yr], p-value=0.681), a highly significant downward trend for pendimethalin (-9.3 pct/yr, p-value=0.005), and a nonsignificant upward trend for carbaryl (6.7 pct/yr, p-value=0.160). The fitted values for the seasonal wave plus the trend (the estimated values for $\beta_0 + \beta_1 W(t) + \beta_5 t$, eq. 1) are shown in figure 4 for each pesticide. The optimal seasonal wave for simazine had a 3-month application season extending from mid-September to mid-December and a 4-month model half-life. The optimal seasonal wave for pendimethalin had two applications seasons—a 2-month season extending from mid-January to mid-March and a less intensive 2-month application season from mid-August to mid-October—and a 4-month model half-life. The optimal seasonal wave for carbaryl had a 3-month application season extending from early April to early July and a 2-month model half-life.

The fitted values for the flow-related variability plus the trend (the estimated values for $\beta_0 + \beta_2\, LTFA(t) + \beta_3\, MTFA(t) + \beta_4\, STFA(t) + \beta_5 t$; eq. 1), similar to the seasonal waves, differed substantially among the three compounds (fig. 5). Simazine did not have much flow-related variability and the variability consisted primarily of mid-frequency variability. Only the coefficient for MTFA (0.55, p-value<0.001) was significant for that compound. Pendimethalin had more flow-related variability than simazine and the variability consisted of both mid-frequency and high-frequency variability. Both the coefficients for MTFA (0.90, p-value<0.001) and STFA (0.50, p-value<0.001) were significant for pendimethalin. Carbaryl also had more flow-related variability than simazine and was dominated by high-frequency variability. Only the coefficient for STFA (0.73, p-value <0.001) was significant for that compound.

Use and Properties of Pesticides

Eight herbicides, one herbicide degradation product, five insecticides, and two insecticide degradation products were analyzed at the urban sites (table 2). The general use characteristics and properties of the 16 pesticide compounds evaluated are described in this section as background information for understanding the trend analysis results. In describing pesticide properties, mobility is discussed in relation to movement in dissolved forms. Thus, pesticides with a relatively low organic carbon-water partition coefficient are more mobile than those with a high coefficient.

Herbicides

Three of the herbicides, simazine, prometon, and atrazine, as well as the degradation product of atrazine, deethyl-atrazine, are triazine compounds. Triazines inhibit photosynthesis in susceptible plants and the class has a wide

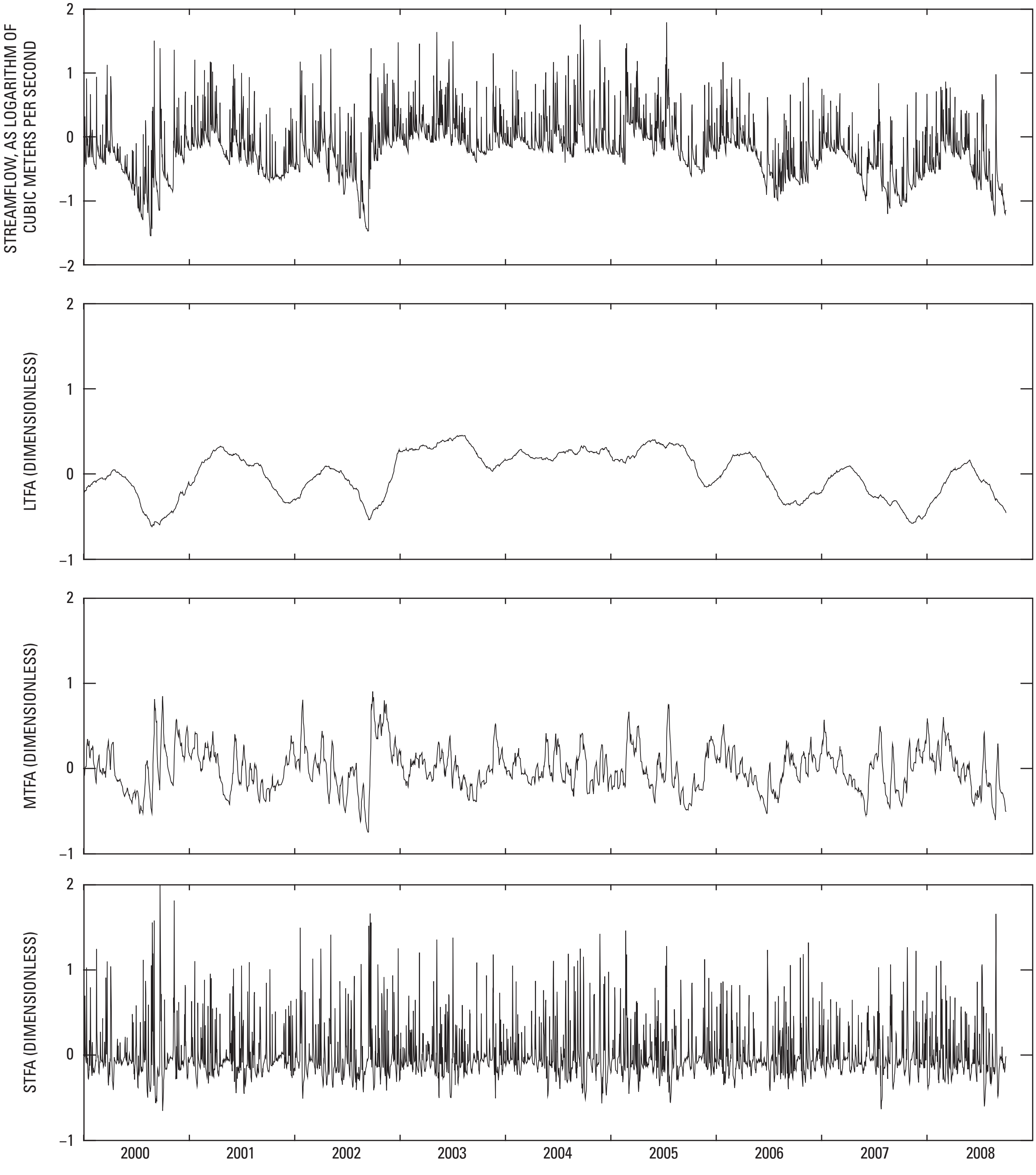


Figure 2. Daily streamflow and dimensionless long-term (LTFA), mid-term (MTFA), and short-term (STFA) flow anomalies for site 9 (SOPEC) for the 2000–2008 period.

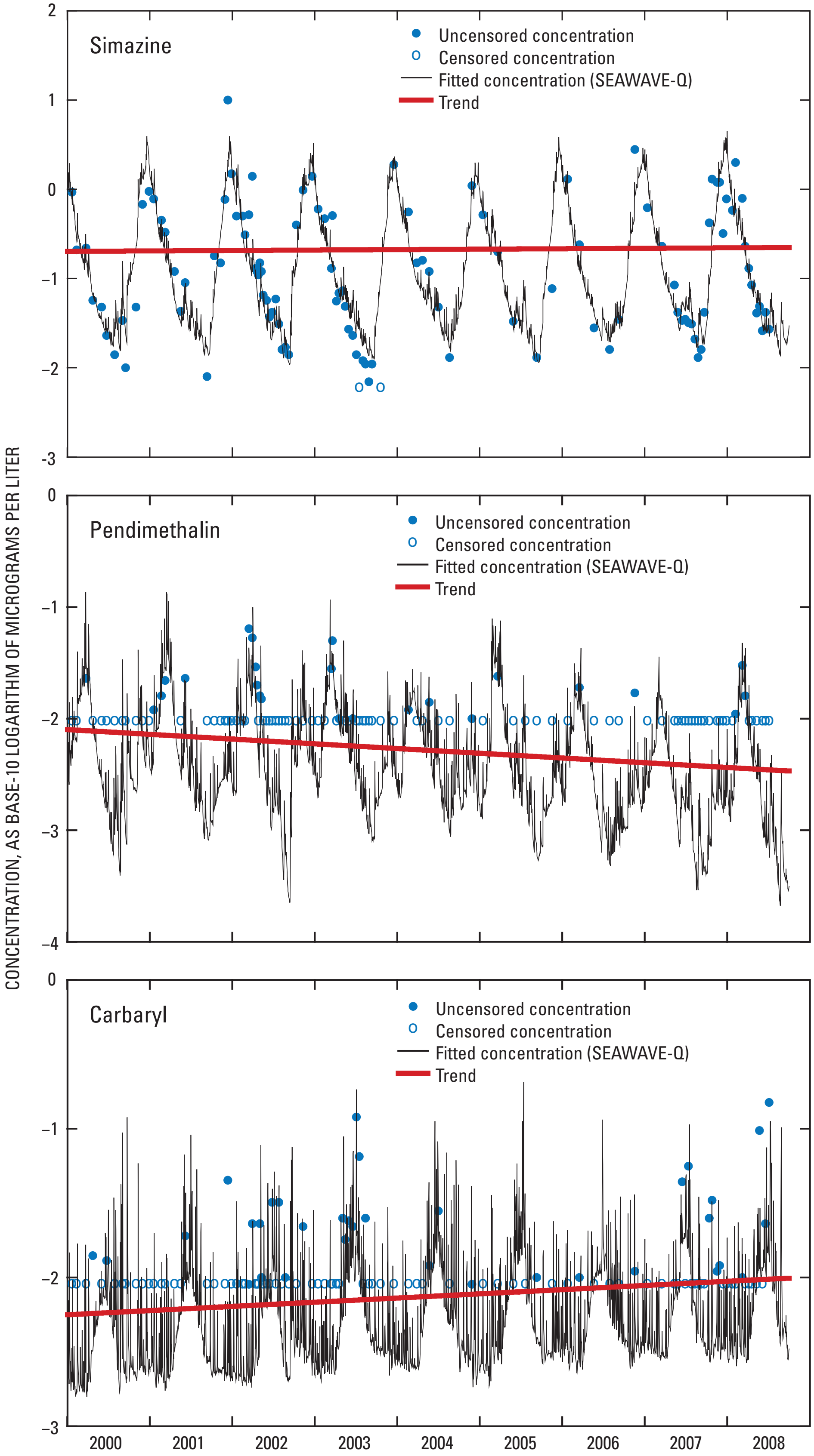


Figure 3. SEAWAVE-Q model results for simazine, pendimethalin, and carbaryl for site 9 (SOPEC) for the 2000–2008 period.

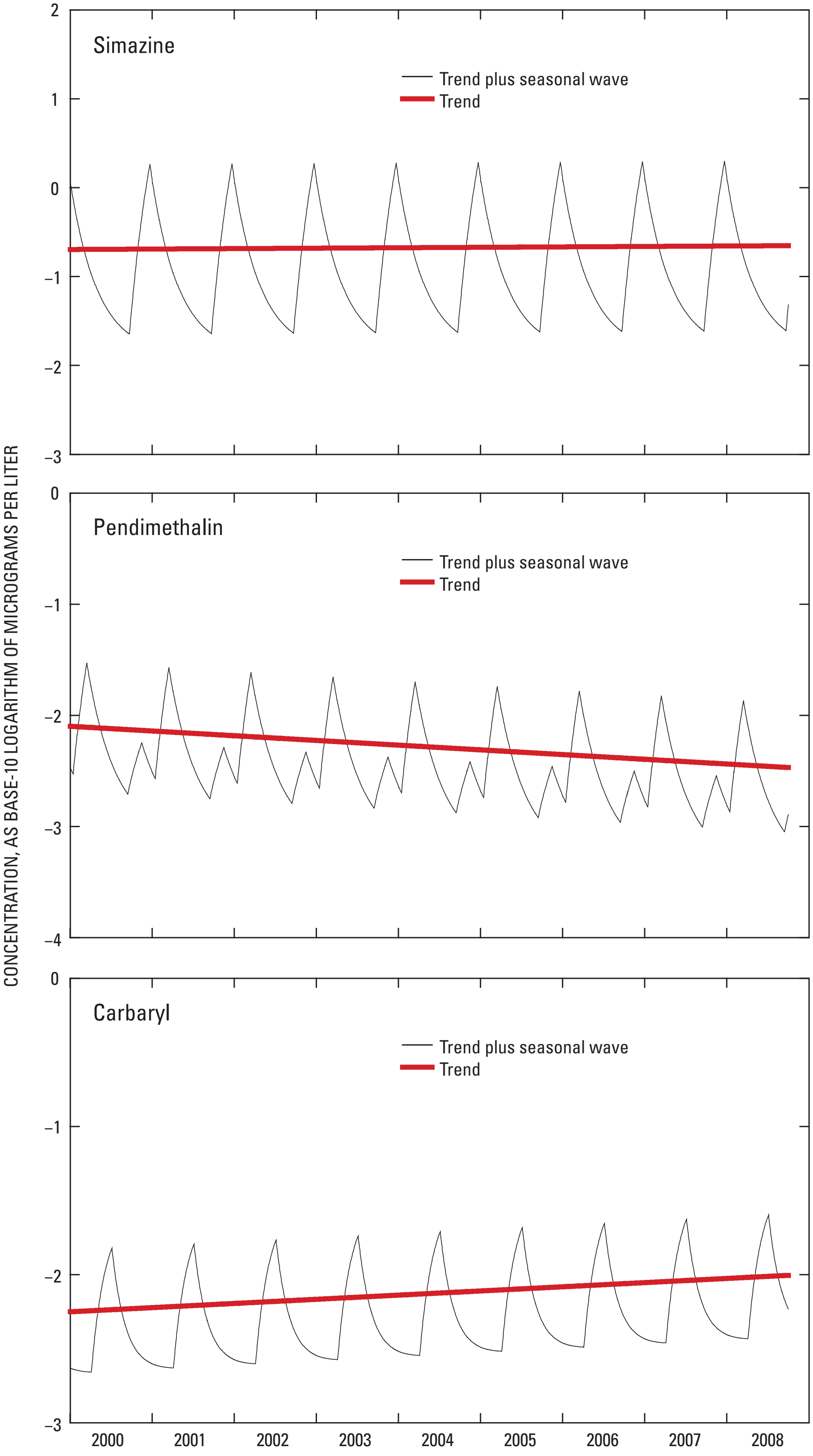


Figure 4. Fitted seasonal waves for simazine, pendimethalin, and carbaryl for site 9 (SOPEC) for the 2000–2008 period.

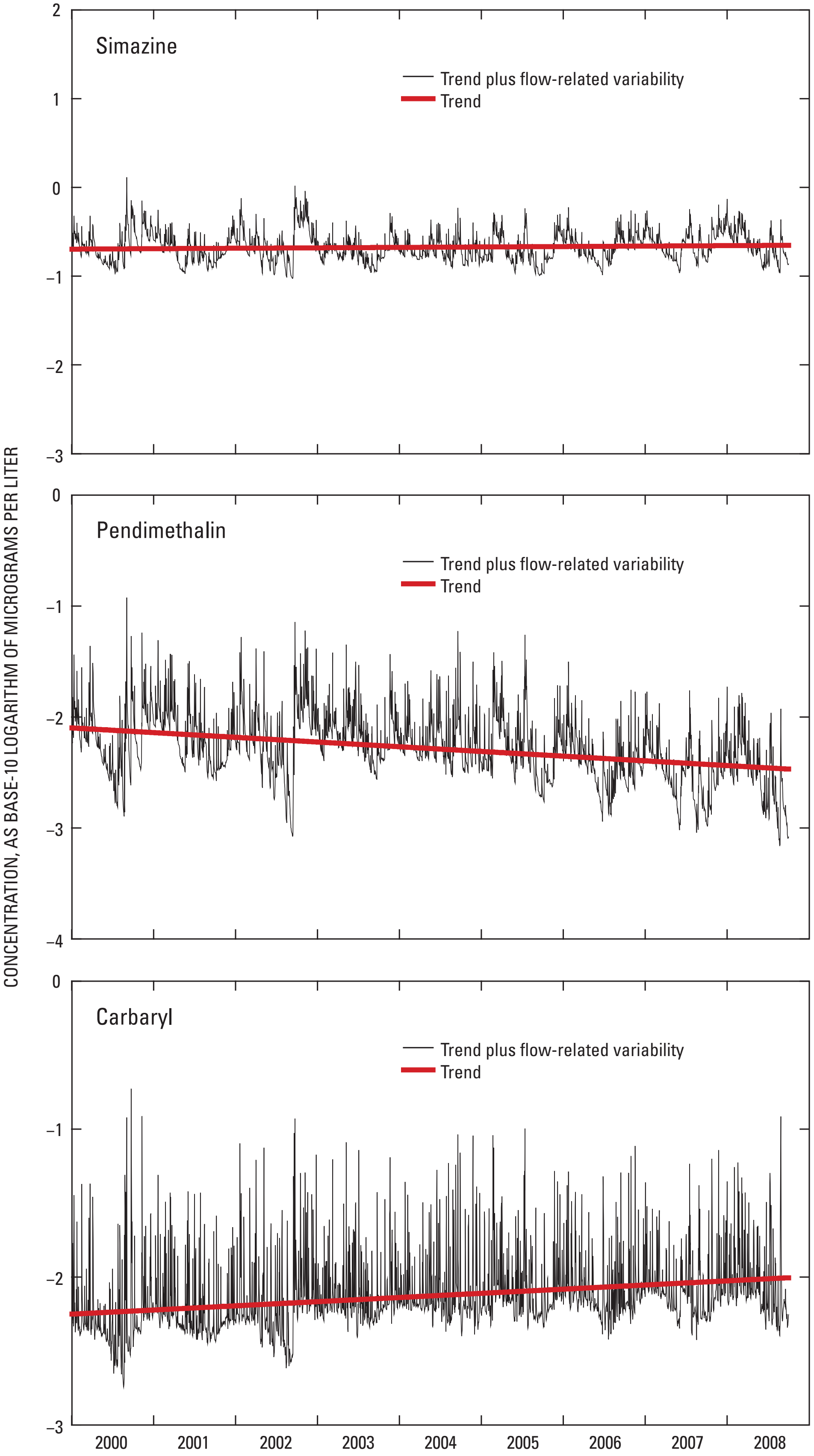


Figure 5. Fitted flow-related variability for simazine, pendimethalin, and carbaryl for site 9 (SOPEC) for the 2000–2008 period.

range of uses. Triazines have been used for many years, with research on triazines for weed control beginning in the 1950s (Fishel, 2006).

Simazine is applied as a pre- or post-emergent herbicide that is absorbed through leaves and roots and selectively controls annual grasses and broadleaf weeds (U.S. Environmental Protection Agency, 2006d). Uses of simazine include weed control in turfgrass grown for commercial sod, weed control in right-of-way or industrial sites, commercial and residential use on lawns and golf courses, and as an algaecide in ornamental ponds and aquariums less than 1,000 gallons. Simazine is used in a number of agricultural applications as well, including weed control for fruits, nuts, and corn (U.S. Environmental Protection Agency, 2006d). Simazine is relatively persistent in soil (as indicated by a 91-day chemical half-life; table 5) and mobile (as indicated by a low soil organic carbon-water partition coefficient; table 5), indicating that it could be transported to surface water during runoff events while dissolved in water (U.S. Environmental Protection Agency, 2006d). Runoff and detection in surface water has been related to the seasonal application of simazine (Gunasekara, 2004).

Prometon is a non-selective herbicide that is used as a pre- or post-emergent herbicide for total vegetation control. Prometon is persistent in soil (932-day half-life; table 5) and, therefore, weed control, resulting in bare ground, may last for a year or more (U.S. Environmental Protection Agency, 2008c). According to U.S. Environmental Protection Agency (USEPA) data collected for reregistration (2008c; reregistration is an USEPA program for reviewing previously registered pesticides), approximately 60 percent of prometon use is for vegetation control along building perimeters and fencerows, 30 percent is for vegetation control in industrial sites, and less than 10 percent is for right-of-way areas. Geographically, the greatest use occurs in the Midwest, South, and Southeast. One common use is to extend the life of asphalt pavement by preventing vegetation from emerging through the pavement (Capel and others, 1999). Prometon use is restricted in Colorado, Texas, and Washington (U.S. Environmental Protection Agency, 2008c).

Atrazine is a selective pre- or post-emergent herbicide that is used to control broadleaf weeds and some grassy weeds and is one of the most widely used agricultural pesticides in the United States. Although urban use of atrazine is limited compared to agricultural use, atrazine was one of the most widely detected herbicides for the predominantly urban streams analyzed in this report and thus was included in the analysis. Based on use estimates from 1990 to 1997, less than 2 percent of atrazine is applied to forestry, turf, or other non-agricultural uses. Much of the use on golf courses and residential lawns is confined to Florida and the Southeast (U.S. Environmental Protection Agency, 2006a). Atrazine is "mobile and persistent in the environment" and, therefore, is expected to be present in surface water (U.S. Environmental Protection Agency, 2006a). Numerous changes to atrazine regulation have occurred during the study period. In the early 1990s, the USEPA's Office of Water began to regulate atrazine under the Safe Drinking Water Act (the maximum contaminant level for atrazine in drinking water is 3 μg/L; U.S. Environmental Protection Agency, 2009). In addition, in the early 1990s, risk reduction measures were instituted to address concerns about surface-water contamination. Measures included a decrease in application rates for corn and sorghum, a decrease in maximum application rates for non-crop land use, deletion of uses for total vegetation control, well-head protection requiring 15-meter setbacks around wells when workers mix and load atrazine-containing products, a 61-meter application setback around lakes and reservoirs, and classification of all atrazine-containing products (except those for lawn and turf care and conifers) as restricted-use pesticides (RUPs). In 2003, the USEPA found that registered uses for atrazine were eligible for interim reregistration (use for cotton being phased out over 5 years), with a number of label changes and risk management measures, further explained in the Interim Reregistration Eligibility Decision for Atrazine (U.S. Environmental Protection Agency, 2006a). Atrazine has four hydroxyatrazine compounds and three chlorinated atrazine compounds as degradation products. This study included one of the chlorinated degradation products, deethylatrazine (also known as desethylatrazine). Metabolic activity of soil fungi and bacteria is the primary converter of atrazine to deethylatrazine. This process can be useful in determining the source of contamination by evaluating the atrazine/deethylatrazine ratio. In nonpoint-source contamination, atrazine likely has more contact with soil microorganisms that would degrade atrazine to deethylatrazine, whereas in point-source contamination, atrazine would have much less contact with soil microorganisms and would be less likely to degrade to deethylatrazine (Scribner and others, 2005).

Metolachlor is a broad-spectrum chloroacetanilide pre-emergent herbicide used for general weed control. Metolachlor works by inhibiting seedling development. It was first registered for use on turf, but now is also registered for use on food and feed crops, including corn, alfalfa, sorghum, and trees and shrubs. In 1995, the USEPA determined that all uses of metolachlor were eligible for reregistration, except for potatoes, soybeans, and peanuts. Metolachlor is persistent and mobile in the environment and "substantial amounts of metolachlor could be available for runoff to surface water for several months post-application" (U.S. Environmental Protection Agency, 1995). A reformulation of metolachlor, called S-metolachlor, was introduced in 1996 and resulted in a decrease in the amount of metolachlor required for effective weed control (Sullivan and others, 2009).

Trifluralin is a dinitroaniline herbicide that inhibits microtubules by entering plants through developing roots and stopping plant cells from dividing and elongating. Trifluralin may be used alone or in pesticide mixtures with multiple active ingredients, including two pesticides in this study, tebuthiuron and chlorpyrifos. In pesticide products with multiple active ingredients, trifluralin also can be used as an acaricide (miticide) and an insecticide. Trifluralin is used for a wide range of

Table 5. Properties affecting the transport and fate of selected pesticides.

[All values obtained from Gilliom and others (2006), unless otherwise noted; additional information about how the values in Gilliom and others (2006) were obtained is available at *http://water.usgs.gov/nawqa/pnsp/pubs/circ1291/appendix2.html*; all values measured at (or estimated for) 25°C (degrees Celsius), unless otherwise noted; numbers of significant figures are identical to those given in original sources. K_{OC}, soil organic carbon-water partition coefficient; S_W, water solubility; K_H, Henry's law constant; mL/g, milliliters per gram; mg/L, milligrams per liter; Pa•m³/mol, pascal-cubic meters per mole; --, data not available; >, greater than; T, temperature]

Pesticide compound (synonym)	log K_{oc} (K_{oc} in mL/g)		S_w (mg/L)		log K_H (K_H in Pa•m³/mol)		Half-life for non-photolytic transformation (days)			
							In aerobic soil		In water	
	Value	Source/ remarks	Value	Source/ remarks	Value	Source/ remarks	Value	Source/ remarks	Value	Source/ remarks
Herbicides and degradates										
Simazine	2.11		5		-3.46		91		>32	
Prometon	2.54		750		-4.05		932		>200	
Atrazine	2.00		30		-3.54		146		742	
Deethylatrazine	1.90		2,700		-4.12		170		--	
Metolachlor	2.26		430		-2.63		26		410	
Trifluralin	4.14		.5		1.00		169		>32	
Pendimethalin	4.13		.0275		.0899		1,300		>200	
Tebuthiuron	2.10		2,400		-4.88		1,050		>2,700	
Dacthal (DCPA)	3.75		.5		-.66		16		>200	
Insecticides and degradates										
Chlorpyrifos	3.78		0.73		0.0374		30.5		29	
Malathion	3.26		145		-2.64		<1		6.3	
Diazinon	2.76		60		-1.39		39		140	
Fipronil	2.76	a	2.2	b (T=20°C)	-10.19	c (T=24°C)	9.72	d	1,390	e (pH 7.1; 22°C)
Fipronil sulfide	3.59	a	.54	f	-5.99	g (T=24°C)	229	a (T=20°C) z, d	--	
Desulfinylfipronil	3.26	h	2.8	f	-4.41	g (T=24°C)	662	i (T not given)	--	
Carbaryl	2.36		120		-4.35		17		11	

[a] Verified value from the FOOTPRINT Pesticide Properties Database (PPDB; *http://sitem.herts.ac.uk/aeru/footprint/en/*), accessed February 4, 2010.

[b] Tomlin, 2008; value given is the average of values measured at pH 5 (1.9) and 9 (2.4) at 20°C.

[c] Ngim and Crosby, 2001; "Desthiofipronil" appears to be identical to desulfinylfipronil.

[d] Measured in a clay loam soil (weight fraction of organic carbon, f_{oc} = 0.0197) by Zhu and others (2004). Value for fipronil consistent with the half-life of 5 days cited by Gunasekara and others (2007). Value for fipronil sulfide (from FOOTPRINT PPDB) was consistent with results from a study by Zhu and others (2004), who observed no discernible disappearance of the degradate over 35 days.

[e] Ramesh and Balasudramanian, 1999; cited by Connelly, 2001.

[f] Obtained by scaling S_w value measured for parent using ratio of S_w values estimated for degradate and parent from octanol water partition coefficient, K_{ow}, molecular weight and structure with WsKow v.1.41, EPI (estimation program interface) Suite v.4.0.

[g] Obtained by scaling K_H value measured for parent using ratio of K_H values estimated for degradate and parent from structure with HenryWin v.3.20, EPI Suite v.4.0.

[h] Obtained by scaling K_{oc} value reported for fipronil sulfide using the ratio of K_{oc} values estimated from structure and K_{ow} for desulfinylfipronil and fipronil sulfide with KocWin v.2.00, EPI Suite v.4.0. Resulting value is in close agreement (within 30 percent) with those from other studies cited by Gunasekara and others (2007).

[i] Rhône-Poulenc, 1998, in Gunasekara and others, 2007. Value given is midpoint of range cited by Gunasekara and others, 2007 (630–693 days).

non-food and outdoor residential uses, including right of way maintenance, forestry and ornamental maintenance, as well as on a wide range of food and feed crops (U.S. Environmental Protection Agency, 1996b). Trifluralin is moderately persistent (half-life of 169 days; table 5) and non-mobile (highest soil organic carbon-water partition coefficient in this report) in soil (table 5; U.S. Environmental Protection Agency, 1996b). In 1996, the USEPA determined that trifluralin was eligible for reregistration for all uses except for nongrass forage/fodder/straw/hay and dill.

Pendimethalin is a selective pre- and post-emergent dinitroaniline herbicide for control of broadleaf weeds and grassy weed species. It inhibits microtubules, stopping plant cells from dividing and elongating. Pendimethalin is used for turf, outdoor residential sites, Christmas trees, right-of-way maintenance, and food and feed crops. Transport of pendimethalin to surface water during runoff occurring soon after application could be “considerable” because of pendimethalin’s “persistence and extensive use” (U.S. Environmental Protection Agency, 1997). Pendimethalin is persistent (half-life of 1,300 days) and non-mobile (second highest soil organic carbon-water partition coefficient in this report) in soil (table 5). In 1996, the USEPA determined that pendimethalin was eligible for reregistration for all uses.

Tebuthiuron is a “relatively nonselective” herbicide that is soil activated and absorbed through plant roots (U.S. Environmental Protection Agency, 1994). Tebuthiuron is used to control broadleaf and woody weeds, grasses, and brush on non-food crops and non-agricultural sites such as rights-of-way, industrial areas, and under asphalt and concrete (U.S. Environmental Protection Agency, 1994). Tebuthiuron is persistent and mobile (table 5) and is “resistant to biological and chemical degradation under environmental conditions” (U.S. Environmental Protection Agency, 1994). The 1987 registration standard included use for aquatic non-food/ditch-bank sites, but the manufacturer dropped their support of this use in 1992 (U.S. Environmental Protection Agency, 1994).

Dacthal is the trade name for DCPA, or dimethyl tetrachloroterephthalate, a pre-emergent chlorobenzoic acid ester herbicide used to control annual grasses and broadleaf weeds. Dacthal is used on outdoor residential sites and on food and feed crops. Dacthal itself is not very mobile, but its degradation products are highly mobile in soils. Biodegradation and volatilization are primary dissipation routes for Dacthal and drift may contaminate areas where Dacthal was not applied (U.S. Environmental Protection Agency, 1998).

Insecticides

Chlorpyrifos, malathion, and diazinon are all organophosphate insecticides (table 2). Organophosphates are widely used and largely replaced organochlorines because of their relatively fast degradation. Organophosphates affect insects and other animals by phosphorylation of an enzyme necessary for controlling nerve impulse transmission between nerve fibers. Loss of this enzyme function causes an accumulation of acetylcholine, which causes unregulated nerve impulses (Fishel, 2005).

Chlorpyrifos is an insecticide and acaricide (miticide) used on golf courses, cattle ear tags, and Christmas tree farms; as a structural treatment for termites; in ship holds, box cars, and industrial plants; for fire ant control; and as an adult mosquitocide (U.S. Environmental Protection Agency, 2002b). It also is used to control foliage and soil-borne insects on a variety of food and feed cops (U.S. Environmental Protection Agency, 2002a). Chlorpyrifos is one of the least mobile pesticides in this study (table 5). Chlorpyrifos regulation changed during data collection for this report. In 1997, the technical registrants, in an agreement with the USEPA, eliminated indoor broadcast treatments and aerosols, direct application to pets, and use as a paint additive to decrease indoor exposure to chlorpyrifos. Then, in 2000, the technical registrants, in an agreement with the USEPA, eliminated and phased out (sales stopped December 31, 2001) almost all home uses that result in residential exposures. Use was stopped for tomatoes and post-bloom apples on December 31, 2000. Application rates for outdoor areas where children will not be exposed, such as road medians, industrial sites, and golf-course turf, were decreased, effective December 1, 2000. Use for structural control of termites was also phased out, effective December 31, 2005. Based on pesticide usage information for 1987–98, approximately 9.5 million kg of chlorpyrifos were used annually (for all uses including urban and agriculture; U.S. Environmental Protection Agency, 2002b). Because of the eliminated residential uses and phase out of termite uses, approximately 4.5 million kg of chlorpyrifos were expected to be phased out of the market (U.S. Environmental Protection Agency, 2002b).

Malathion is a broad-spectrum organophosphate insecticide and miticide with numerous industrial, governmental (mosquito, bollworm, and fruit fly eradication programs), homeowner, and agricultural uses, ranging from pharmaceutical use for treatment of head lice to use on food and feed crops. Malathion has the highest water solubility of the insecticides in this report and can be highly mobile in soil, although is generally nonpersistent, with the shortest soil and water half-lives of the pesticides in this study (table 5; Newhart, 2006; U.S. Environmental Protection Agency, 2006c).

Diazinon is an insecticide, acaricide, and nematicide and has been one of the mostly widely used insecticides in the United States. It is used to control foliage and soil-borne insects of numerous fruit, nut, vegetable, and ornamental crops and is used in cattle ear tags (U.S. Environmental Protection Agency, 2006b; 2008b). In a December 2000 agreement, all indoor and outdoor residential uses were phased out and cancelled. Retail sales of indoor residential products ended December 31, 2002, and retail sales of outdoor residential products ended December 31, 2004 (U.S. Environmental

Protection Agency, 2006b; 2008b). Diazinon is moderately persistent and mobile in the environment (table 5).

Fipronil is a broad-spectrum phenylpyrazole insecticide that is relatively new compared to most in this study (table 2)—first registered for use in the United States in 1996 (U.S. Environmental Protection Agency, 1996a). Fipronil targets the gamma-aminobutyric acid (GABA) receptor system of insects (National Pesticide Information Center, 2009) and provides an alternative to phyrethroid, organophosphate, and carbamate insecticides, to which insects have developed resistance (Gunasekara and others, 2007). Fipronil is used as a granular turf product, as a topical pet care product for control of fleas and ticks, as a liquid termiticide, and in agriculture (seed treatment for rice; National Pesticide Information Center, 2009). Various reactions degrade fipronil to fipronil amide, fipronil sulfide, fipronil sulfone, and desulfinylfipronil (Gunasekara and others, 2007). Two of these degradation products (fipronil sulfide and desulfinylfipronil) are included in this study.

Fipronil sulfide primarily is the result of reduction and is the major degradation product in soil (Gunasekara and others, 2007), where it has a much longer half-life than fipronil (table 5). Fipronil sulfide is 1.9 times more toxic to freshwater invertebrates than fipronil (U.S. Environmental Protection Agency, 1996a). Fipronil readily degrades to desulfinylfipronil when exposed to sunlight either when it is on the soil or on foliage after crops have been treated with fipronil (Gunasekara and others, 2007). Desulfinylfipronil also has a longer half-life than fipronil in soil (table 5). Compared to fipronil, desulfinylfipronil has decreased selectivity between insects and humans (Gunasekara and others, 2007; National Pesticide Information Center, 2009).

Carbaryl is a carbamate insecticide. Carbaryl's primary mode of action is cholinesterase inhibition. Carbaryl is used for professional turf management, ornamental production, residential lawn care and gardening, pet care, and on agricultural sites (fruit and nut trees, fruits, vegetables, and grain crops). Most agricultural use during 1992 through 2001 was in California, Michigan, Indiana, Illinois, Ohio, Texas, Georgia, Oklahoma, Mississippi, and Arkansas (U.S. Environmental Protection Agency, 2004). Carbaryl is moderately mobile and is one of the least persistent pesticides in this study (table 5). Carbaryl usage and regulation have changed during data collection for this report. In the Interim Reregistration Eligibility Document (IRED; U.S. Environmental Protection Agency, 2004), the USEPA indicated a decline in agricultural usage. The IRED also required risk mitigation measures and label changes. In March 2005, the USEPA issued a cancellation order for the liquid broadcast of carbaryl on residential turf and issued data call-ins (DCIs) for additional studies and data related to carbaryl. "In response to the DCIs, many carbaryl registrants chose to voluntarily cancel their carbaryl products, rather than revise their labels or conduct studies to support these products. Approximately two-thirds of all of the carbaryl products registered at the time of the carbaryl IRED (June 2003) have been canceled through this process" (U.S. Environmental Protection Agency, 2007). The 2008 Amended Registration Eligibility Decision (RED) for carbaryl, indicated that in response to the 2005 DCIs, "approximately 80 percent of all of the carbaryl end-use products registered at the time of the 2003 IRED have since been canceled through this process or other voluntary cancellations" (U.S. Environmental Protection Agency, 2008a). The amended RED required additional worker risk mitigation measures and label amendments.

Overview of Pesticide Concentration Patterns

As context for evaluating trends in pesticide concentrations, a statistical overview of concentration magnitudes and geographic patterns is provided for the sites and pesticides evaluated. Where possible, the results are related to qualitative information on use or regulation, or both, although in many cases the results are not easily explained by the available ancillary information.

Site and regional patterns in pesticide concentrations were evaluated using estimated daily pesticide concentrations generated using the SEAWAVE-Q model. The estimated daily concentrations from the model for the respective trend analysis periods were detrended and the 90th percentiles of the detrended concentrations were computed. The detrended concentrations are defined as

$$[Log\ C(t)]_{DT} = Log\ C(t) - \hat{\beta}_5(t - t_{mid}) \qquad (6)$$

where

$[Log\ C(t)]_{DT}$ is the detrended concentration at time *t*,
$C(t)$ is the concentration at time *t,*
$\hat{\beta}_5$ is the estimated trend coefficient (eq. 1), and
t_{mid} is the midpoint of the trend analysis interval.

Using the entire 9-year period to calculate the percentiles essentially "averages out" the flow-related variability among the years. The 90th percentile is thus an estimate of the concentration that is exceeded 10 percent of the time (about 36 days) in a "typical" year. These percentiles should not be confused with the sample percentiles computed using the discrete concentration samples collected at each site. The sample percentiles are affected by the annual frequency and timing of the samples; because the samples do not represent a random sampling of days within each year, the sample percentiles cannot be directly related to any particular duration of exceedance. The emphasis in this section is on spatial comparisons among the various sites. Therefore, the earliest assessment period (1992–2000), which had only four sites with sufficient data for analysis, is not included.

Herbicides

Star plots of the estimated 90th percentile concentrations for the herbicides in the latter two assessment periods are shown in figures 6 and 7. The same scale is used for all sites, herbicides, and periods, with the largest segment size representing a concentration of 10 µg/L and segment sizes decreasing in proportion to the base-10 logarithm of concentration to the smallest segment size representative of concentrations of 0.01 µg/L or less. The smallest segment size (0.01 µg/L) was chosen as a conservative upper bound for the 90th percentiles for all pesticide/site combinations for which the data were too highly censored to estimate daily concentrations using the SEAWAVE-Q model (table 4, unshaded cells).

The 90th percentile concentrations for the herbicides generally were similar for both the 1996–2004 and 2000–2008 assessment periods. The similarity between the two periods generally is consistent with the lack of major changes in use or regulation for most herbicides during 1996–2008. Only atrazine (numerous regulation changes) and metolachlor (introduction of S-metolachlor) were subject to documented changes, and these changes did not cause major decreases in the 90th percentile concentrations for the sites analyzed in the two periods (at least at the scale of the graphs shown in figures 6 and 7). The following discussion therefore will refer to overall patterns for both figures.

Simazine concentrations were by far the largest for streams in the South, with many sites in that region having 90th percentile concentrations between about 1 and 10 µg/L. Simazine concentration percentiles for the remaining regions, though occasionally above 0.01 µg/L, generally were much lower than concentrations in the South. The relatively high concentrations in the South evidently reflected a combination of high simazine use in that region, relatively high persistence and mobility of simazine, and rainfall-runoff conditions that favor simazine transport to streams during or shortly after the application season.

Prometon concentrations were much more uniform across regions and sites compared with simazine concentrations. Elevated 90th percentile concentrations for prometon (between about 0.05 and 0.5 µg/L) were observed for many sites scattered across all of the regions. Except for the South, where simazine concentrations were much higher than prometon concentrations, the prometon concentration percentiles tended to be higher than those for simazine. The elevated prometon concentration percentiles probably indicated a combination of the high persistence and mobility of prometon and the relatively uniform and widespread use among the urban sites analyzed. According to the U.S. Environmental Protection Agency (2008c), the areas with the greatest prometon use are the Midwest, South, and Southeast and use is restricted in Texas, Colorado, and Washington. However, prometon 90th percentile concentrations are relatively similar in all of the regions, including both Texas sites (13, WHITE and 14, SALAD) and the Washington site (26, THORN).

The highest atrazine concentrations were in the South and Midwest, where most of the sites analyzed had 90th percentile concentrations between about 0.1 and 1 µg/L. Concentrations for the remaining regions generally were low (90th percentiles less than about 0.02 µg/L). The relatively high atrazine concentrations in urban streams in the South and Midwest are noteworthy because atrazine predominately is an agricultural herbicide. Many of the sites in those regions had high 90th percentile concentrations despite having some of the largest urban land-use percentages of any of the sites (more than 85 percent urban land use; table 1). Either atrazine runoff from agricultural sources is high for these basins, or atmospheric deposition of atrazine from neighboring agricultural areas is occurring, or there is significant nonagricultural use, such as on turf, or some combination of these sources. Deethylatrazine concentrations in the South and Midwest regions, though generally lower than atrazine, also were elevated (90th percentiles generally between about 0.01 and 0.1 µg/L).

Metolachlor concentrations also were highest in the South and Midwest regions, though generally not as high as atrazine or deethylatrazine—90th percentile metolachlor concentrations for several sites in those regions ranged from about 0.02 to 0.2 µg/L. Metolachlor concentration percentiles for the remaining regions generally were low (less than about 0.02 µg/L).

Concentrations for the remaining herbicides were relatively low (90th percentiles less than about 0.02 µg/L), except for pendimethalin and tebuthiuron, which had elevated 90th percentile concentrations (between about 0.02 and 0.2 µg/L) for several sites in the South and scattered sites in the remaining regions.

Insecticides

The 90th percentiles for the estimated daily insecticide concentrations for the latter two assessment periods are shown in figures 8 and 9. The same small segment size used for herbicides (less than 0.01 µg/L) is used for the insecticides, but the largest segment size for insecticides is 0.4 µg/L.

For the 1996–2004 period, diazinon had relatively high 90th percentile concentrations (greater than about 0.02 µg/L) for 20 of 22 sites analyzed (fig. 8). Carbaryl had relatively high 90th percentile concentrations for 10 of 22 sites, including 4 of 5 sites in the Northeast and 5 of 7 sites in the South. The percentiles for chlorpyrifos were relatively low for all sites and the percentiles for malathion were relatively low except for three sites (two in the South and one in the West).

Compared with the earlier analysis period, the diazinon concentration percentiles were much lower for 2000–2008 (fig. 9). However, a few sites still had relatively high diazinon concentration percentiles, including three sites each in the South, Midwest, and West. As discussed in the Use and Properties of Pesticides section, residential uses of diazinon were phased out beginning in 2000, and this probably caused the

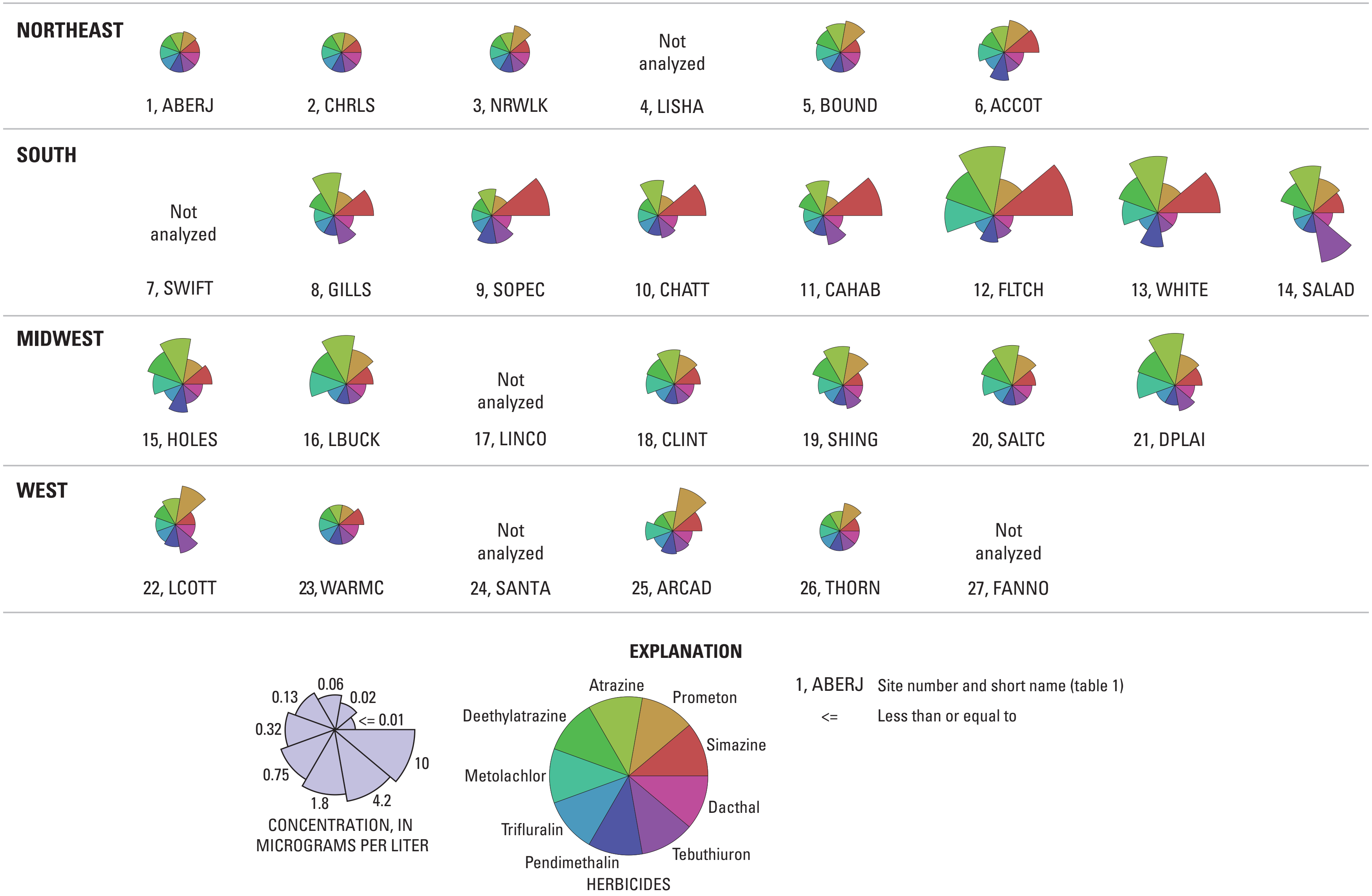


Figure 6. Star plots of 90th percentiles of estimated concentrations for herbicides at urban-stream sites, 1996–2004.

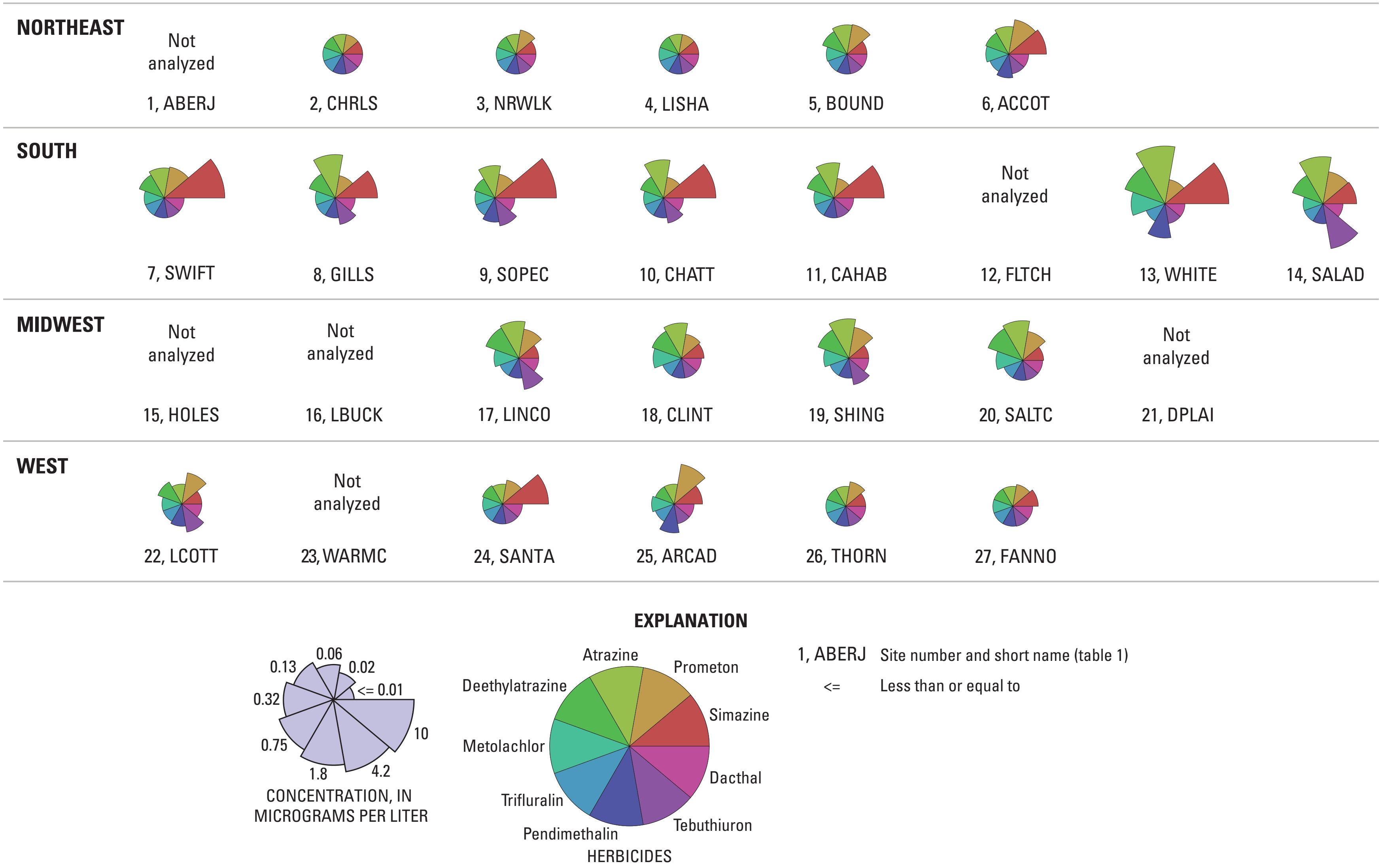


Figure 7. Star plots of 90th percentiles of estimated concentrations for herbicides at urban-stream sites, 2000–2008.

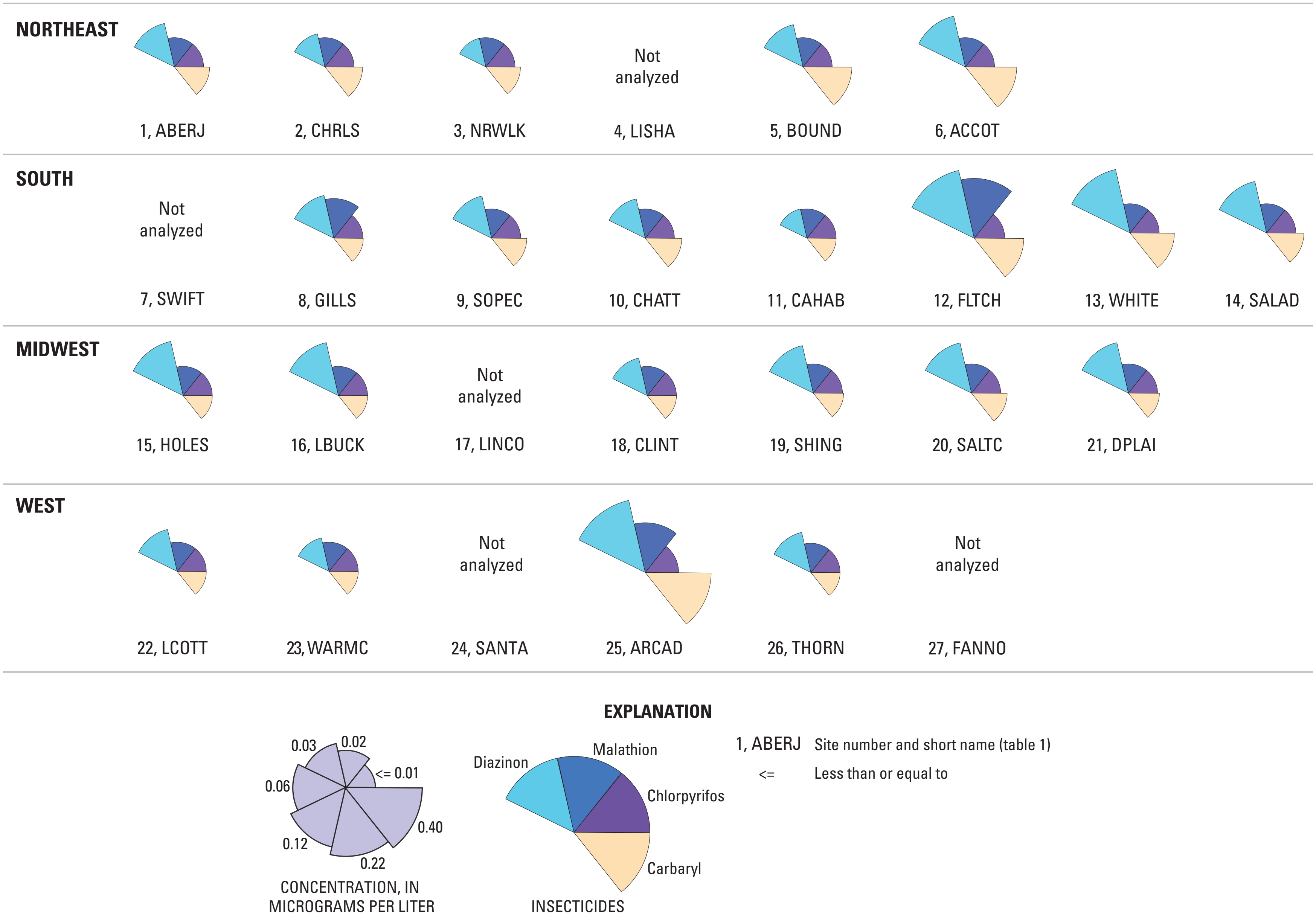


Figure 8. Star plots of 90th percentiles of estimated concentrations for insecticides at urban-stream sites, 1996–2004.

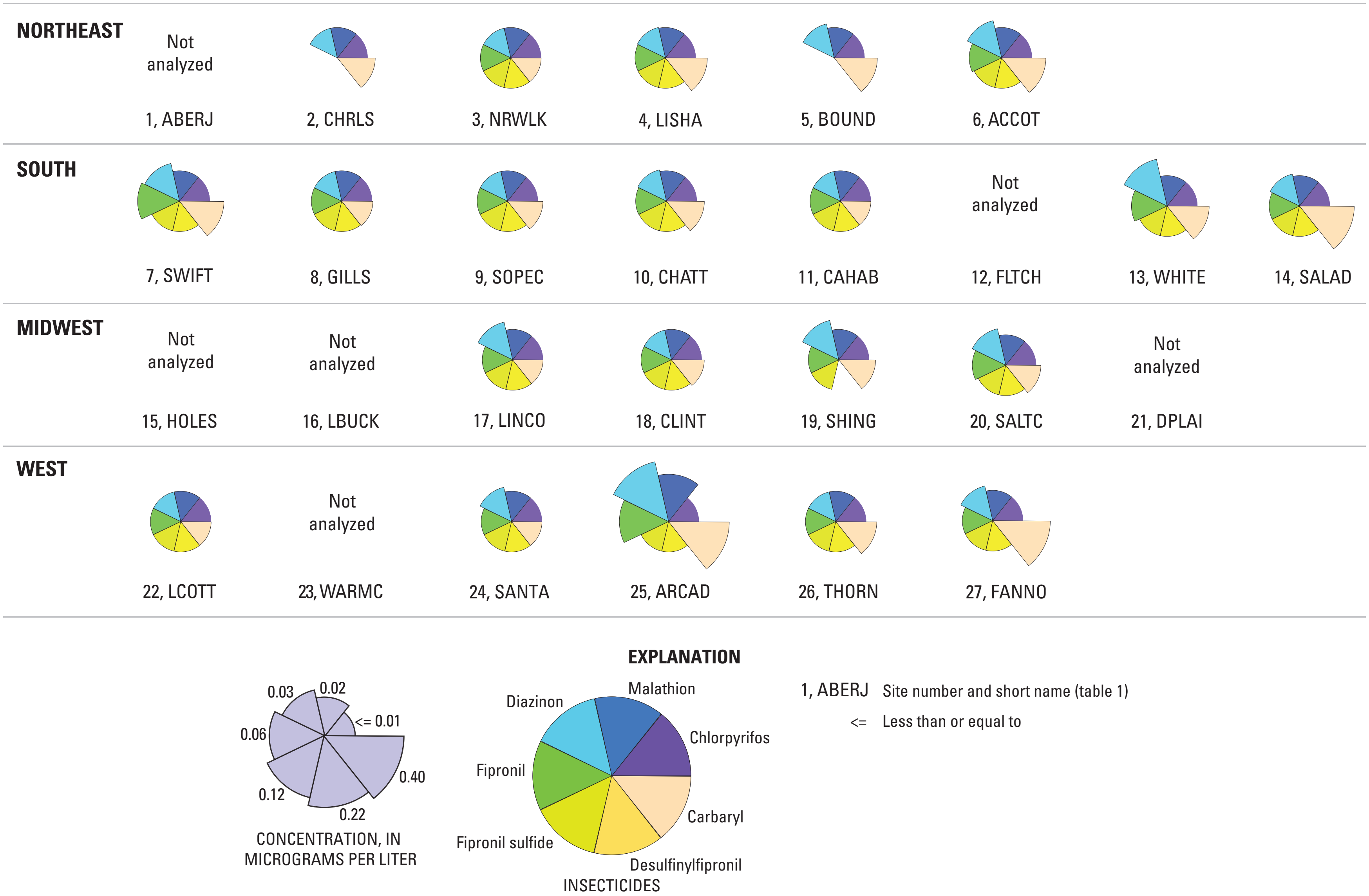


Figure 9. Star plots of 90th percentiles of estimated concentrations for insecticides at urban-stream sites, 2000–2008.

large decrease in the percentiles for the latter period. Carbaryl concentration percentiles for 2000–2008 were somewhat higher compared to the percentiles for the earlier period, with 15 of 21 sites having relatively high percentiles, including most sites in all of the regions. Chlorpyrifos and malathion concentration percentiles were relatively low for all sites for the latter period, except for a relatively high percentile for malathion at one site in the West. Fipronil and its degradates, which were not analyzed for the earlier period, had relatively low percentiles except relatively high fipronil percentiles for 5 of the 21 sites spread over all regions.

The insecticide concentration percentiles generally were consistent with the available information for pesticide properties and use. Diazinon, fipronil, and carbaryl are widely used in urban areas and all are relatively mobile compared with the other insecticides; consequently, those pesticides have the largest concentrations. Chlorpyrifos and the fipronil byproducts are relatively immobile in dissolved forms and had relatively low concentration percentiles. Malathion, despite its short half-life (<1 day in soil, 6.3 days in water, table 5), showed elevated concentrations at a few sites.

Insecticide concentration patterns, compared to herbicides, were more similar among regions, but more different between the 1996–2004 and 2000–2008 periods. During 1996–2004, diazinon or carbaryl—sometimes both—had the largest concentrations in 21 of 22 streams in the four regions. During 2000–2008, concentrations of diazinon were markedly lower in all regions and carbaryl concentrations were relatively similar to the previous period.

Pesticide Concentration Trends

Temporal trends in pesticide concentrations were evaluated for each site-pesticide combination with adequate data using the SEAWAVE-Q model. For pesticides that have had no apparent change in nonagricultural use due to regulations, the trend results for urban streams are an indicator of changing use due to uncontrolled factors, such as market or land-use changes. For pesticides that had changes in regulations intended to decrease or eliminate use, the trend results serve to evaluate the effectiveness and temporal distribution of the changes in affecting stream concentrations.

Herbicides

Trends in herbicide concentrations for the three analysis periods are given in table 6. For the earliest period (1992–2000), only four sites could be analyzed. Most of the significant trends for these four sites were downward trends. The Midwest site (site 16, LBUCK) had significant downward trends in all nine herbicides. The only significant upward trends during 1992–2000 were in the Northeast for metolachlor (site 3, NRWLK) and trifluralin (site 6, ACCOT).

For the 1996–2004 analysis period, there were many significant trends both upward and downward, and the patterns in trend directions varied depending on the herbicide and region (table 6). In the Northeast, many more significant downward trends (14) were determined than upward trends (4). Herbicides with the largest number of significant downward trends were prometon and metolachlor (three sites each) followed by simazine and Dacthal (two sites each). The largest number of significant upward trends was for atrazine (two sites). In the South, there were fewer significant downward trends (9) than upward trends (16). Herbicides with the largest number of significant downward trends were tebuthiuron (three sites) and prometon (two sites). The largest number of significant upward trends was for deethylatrazine (six sites) followed by simazine (four sites) and atrazine (three sites). In the Midwest, significant trends were fairly evenly mixed between downward trends (10) and upward trends (9). The largest number of significant downward trends was three sites each for simazine and prometon and the largest number of significant upward trends was for deethylatrazine (four sites), followed by atrazine (two sites). In the West, significant trends also were mixed between downward (four) and upward (three) trends. The largest number of significant downward trends was for prometon (two sites) and none of the herbicides had more than one site with a significant upward trend.

For the 2000–2008 period, patterns in trend results also varied depending on herbicide and region. In the Northeast, significant trends were mixed between downward trends (three) and upward trends (five). No site had more than one significant downward trend and the largest number of significant upward trends was for deethylatrazine (four sites). In the South, significant trends were mixed between downward (12) and upward (13) trends. The largest number of significant downward trends was three sites each for simazine and prometon and the largest number of significant upward trends was for deethylatrazine (six sites), followed by atrazine (three sites). In the Midwest, there were six significant downward trends and eight significant upward trends. The largest number of significant downward trends was for atrazine (two sites) and the largest number of significant upward trends was three sites each for prometon and deethylatrazine. In the West, there were eight significant downward trends and five significant upward trends. The largest number of downward trends was for tebuthiuron (three sites), followed by prometon and atrazine (two sites each). None of the herbicides had more than one significant upward trend.

Table 6. Trends, in percent per year, for herbicides at urban-stream sites, 1992–2008.

[DCPA, dimethyl tetrachloroterephthalate; trend results in **bold** type are significant at the p<0.10 level; HC, too “highly censored” to analyze trends]

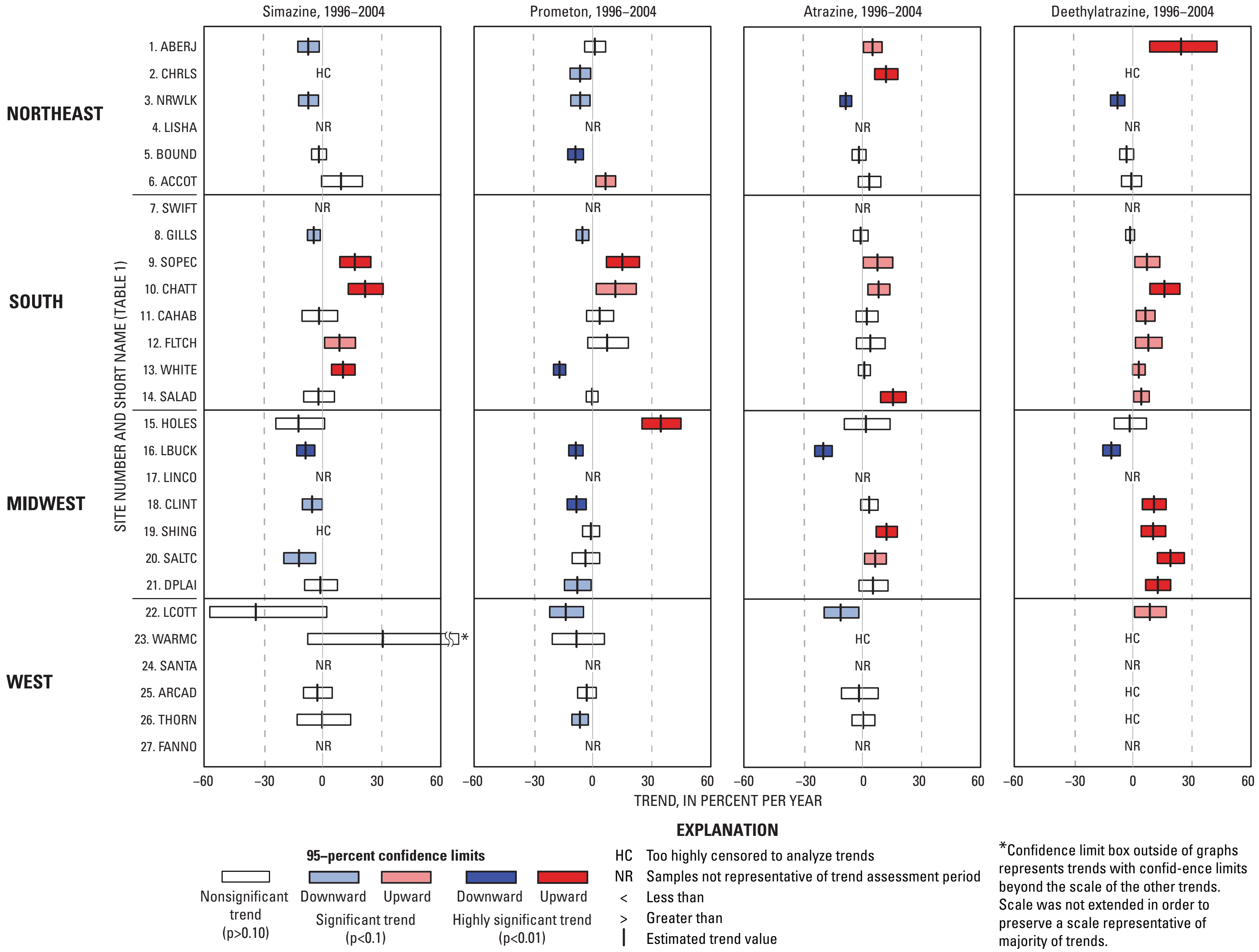
Site number (fig. 1)	Site short name	Simazine	Prometon	Atrazine	Deethyl-atrazine	Metolachlor	Trifluralin	Pendimethalin	Tebuthiuron	Dacthal (DCPA)
1992–2000 trend result (percent per year)										
Northeast										
3	NRWLK	**-10.3**	**-4.6**	-1.1	1.5	**11.5**	9.4	HC	HC	**-14.8**
6	ACCOT	**-33.9**	**-20.8**	-3.4	-1.6	-2.9	**36.8**	**-13.5**	HC	-10.3
South										
9	SOPEC	**-9.4**	-4.0	**-10.0**	3.1	HC	HC	-5.9	2.4	HC
Midwest										
16	LBUCK	**-22.2**	**-7.3**	**-10.3**	**-10.9**	**-8.3**	**-21.5**	**-14.0**	**-22.7**	**-25.2**
1996–2004 trend result (percent per year)										
Northeast										
1	ABERJ	**-7.2**	1.2	**5.2**	**24.5**	3.0	-14.0	HC	HC	HC
2	CHRLS	HC	**-6.3**	**12.0**	HC	HC	HC	HC	HC	HC
3	NRWLK	**-7.1**	**-6.2**	**-8.4**	**-7.7**	**-13.6**	**-15.9**	HC	HC	HC
5	BOUND	-1.8	**-8.6**	-1.7	-3.1	**-8.3**	-3.5	-4.3	0.0	**-26.1**
6	ACCOT	9.4	**6.6**	3.6	-.7	**-8.5**	-7.1	**-16.2**	.5	**-49.4**
South										
8	GILLS	**-4.4**	**-5.1**	-0.8	-1.3	-2.3	HC	HC	**-7.4**	HC
9	SOPEC	**16.4**	**15.2**	**7.7**	**7.3**	HC	0.9	**-14.2**	-2.3	HC
10	CHATT	**21.6**	**11.6**	**8.3**	**16.1**	**25.6**	HC	HC	3.6	HC
11	CAHAB	-1.7	3.7	2.3	**6.5**	HC	-13.7	-.6	**-48.7**	HC
12	FLTCH	**8.6**	7.4	4.1	**8.0**	**-34.3**	-9.3	-19.2	-10.9	HC
13	WHITE	**10.4**	**-16.7**	1.0	**3.1**	-6.3	**-15.6**	.1	**-24.4**	2.0
14	SALAD	-2.0	-.2	**15.6**	**4.4**	-5.1	HC	HC	-3.9	HC
Midwest										
15	HOLES	-12.1	**34.6**	1.9	-1.5	-11.2	-0.4	0.7	HC	HC
16	LBUCK	**-8.5**	**-8.4**	**-19.8**	**-10.8**	**-19.5**	-5.0	6.6	HC	HC
18	CLINT	**-5.2**	**-8.1**	3.5	**10.8**	-.1	HC	HC	HC	HC
19	SHING	HC	-.8	**12.3**	**10.4**	4.8	HC	HC	-0.8	**-12.2**
20	SALTC	**-11.9**	-3.6	**6.6**	**19.2**	4.6	-1.8	HC	HC	HC
21	DPLAI	-1.0	**-7.7**	5.4	**12.8**	**20.5**	HC	HC	**21.6**	HC
West										
22	LCOTT	-33.8	**-13.5**	**-10.9**	**8.7**	HC	HC	5.8	-1.7	**13.7**
23	WARMC	30.6	-8.1	HC	HC	HC	HC	HC	2.2	1.8
25	ARCAD	-2.6	-2.9	-1.6	HC	-5.1	1.7	-2.0	**14.9**	**-5.7**
26	THORN	-.2	**-6.4**	.4	HC	HC	HC	HC	HC	HC

Table 6. Trends, in percent per year, for herbicides at urban-stream sites, 1992–2008.—Continued

[DCPA, dimethyl tetrachloroterephthalate; trend results in **bold** type are significant at the p<0.10 level; HC, too "highly censored" to analyze trends]

Site number (fig. 1)	Site short name	Simazine	Prometon	Atrazine	Deethyl-atrazine	Metolachlor	Trifluralin	Pendi-methalin	Tebuthiuron	Dacthal (DCPA)
2000–2008 trend result (percent per year)										
Northeast										
2	CHRLS	HC	-4.5	-1.2	9.3	HC	HC	HC	HC	HC
3	NRWLK	-7.0	**-10.5**	-2.7	**8.4**	4.4	HC	HC	HC	HC
4	LISHA	HC	3.0	7.5	**19.1**	5.3	HC	HC	HC	HC
5	BOUND	-3.9	-1.9	2.3	**9.3**	4.7	HC	HC	**-24.0**	HC
6	ACCOT	3.9	2.8	**9.8**	**7.8**	-2.3	-10.6	**-6.1**	HC	HC
South										
7	SWIFT	**-17.3**	**-10.5**	**-11.5**	-2.1	-0.9	HC	HC	HC	HC
8	GILLS	**-16.7**	**10.1**	-1.3	**17.2**	7.8	HC	HC	5.0	HC
9	SOPEC	1.1	**8.6**	**20.0**	**23.0**	HC	HC	**-9.3**	-.7	HC
10	CHATT	**5.7**	.7	**12.1**	**19.2**	11.4	HC	HC	1.6	HC
11	CAHAB	-2.7	.1	**4.0**	**11.9**	HC	HC	HC	HC	HC
13	WHITE	**-9.0**	**-8.5**	-2.5	**3.2**	**-8.9**	HC	-3.3	**-46.0**	HC
14	SALAD	**27.9**	**-7.5**	**-10.8**	**5.4**	HC	HC	HC	**-15.2**	HC
Midwest										
17	LINCO	**20.9**	**17.3**	-2.7	**7.7**	4.7	HC	**-17.0**	**-13.1**	HC
18	CLINT	7.7	**11.9**	**-9.0**	**10.9**	**11.8**	HC	HC	HC	HC
19	SHING	HC	**8.3**	-3.2	2.0	8.9	HC	HC	3.7	HC
20	SALTC	-2.7	-3.1	**-4.7**	**8.1**	**-6.2**	**-21.5**	HC	HC	HC
West										
22	LCOTT	HC	**-13.0**	**-11.6**	3.9	HC	HC	-1.9	**-8.7**	4.3
24	SANTA	3.9	.1	**5.6**	2.1	-0.9	HC	HC	HC	24.8
25	ARCAD	3.2	**-10.5**	**-15.1**	HC	**7.0**	6.6	**8.1**	**-33.0**	4.5
26	THORN	**-17.7**	-2.3	HC	HC	HC	3.4	HC	HC	HC
27	FANNO	**15.2**	-.8	2.0	4.6	4.3	**9.3**	HC	**-10.2**	HC

Trends for the three most prevalent herbicides, simazine, prometon, and atrazine, as well as deethylatrazine, are shown in more detail in figs. 10 and 11. During 1996–2004 (fig. 10), there were predominantly downward trends in simazine (14 downward trends, with 6 significant, for 20 streams with adequate data) and prometon (15 downward trends, with 10 significant, for 22 streams) and upward trends in atrazine (15 upward trends, with 7 significant, for 21 streams) and deethylatrazine (12 upward trends, all significant, for 18 streams). For the 2000–2008 analysis period (fig. 11), trends in simazine, prometon, and atrazine were more equally mixed between upward and downward trends. However, deethylatrazine continued to have mostly upward trends. Simazine and prometon had generally similar trends for both periods.



*Confidence limit box outside of graphs represents trends with confid-ence limits beyond the scale of the other trends. Scale was not extended in order to preserve a scale representative of majority of trends.

Figure 10. Trends, in percent per year, for simazine, prometon, atrazine, and deethylatrazine for the 1996–2004 period.

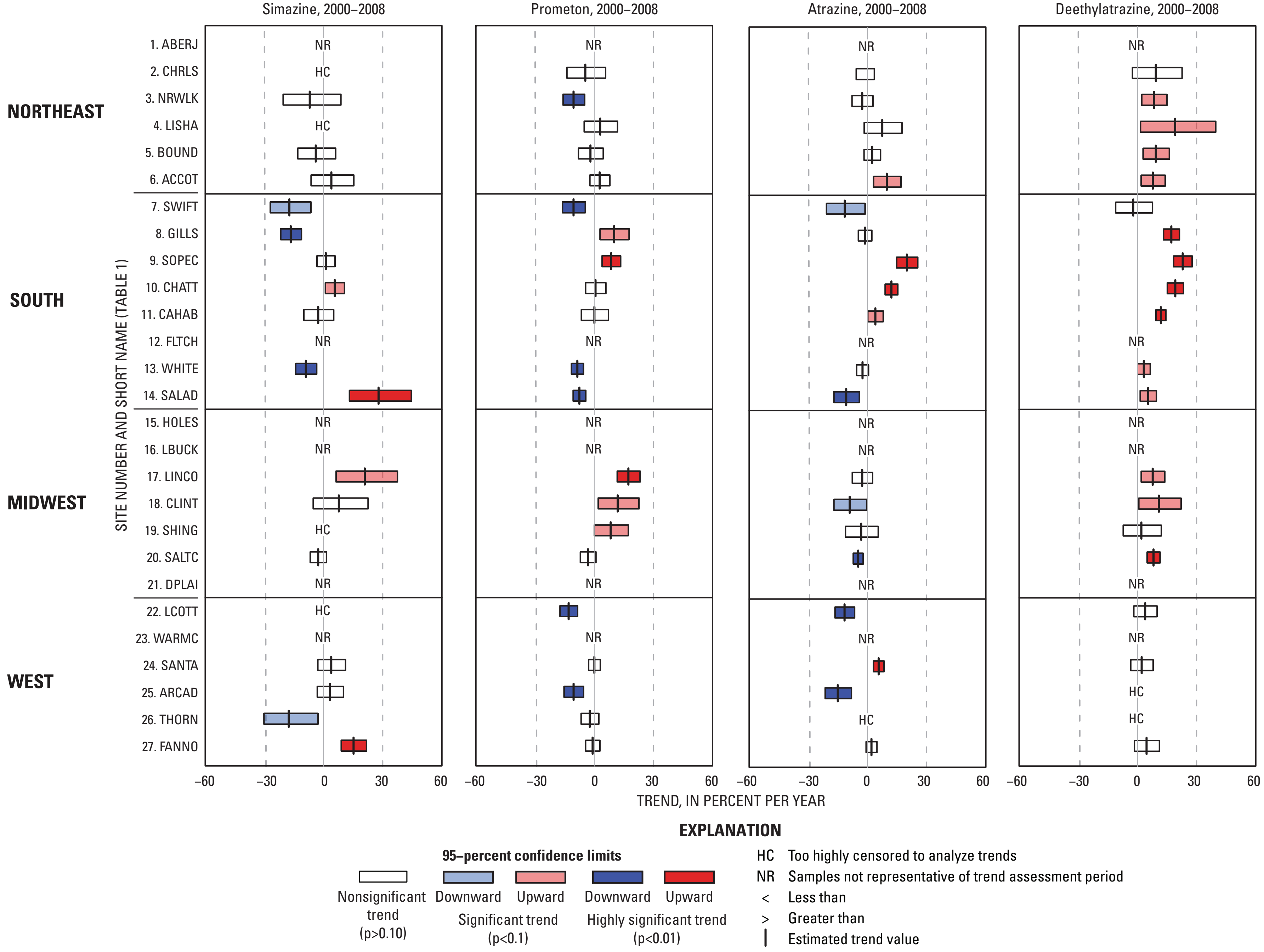


Figure 11. Trends, in percent per year, for simazine, prometon, atrazine, and deethylatrazine for the 2000–2008 period.

Simazine and Prometon

Simazine concentration trends in streams in the Northeast and West, where concentrations were generally low compared to concentrations in the South and Midwest (figs. 6 and 7), generally were nonsignificant or indeterminable during both 1996–2004 and 2000–2008 (figs. 10 and 11). Streams in the South mostly had upward trends during 1996–2004, with four of seven sites having significant upward trends in the range of 9 to 22 pct/yr. This shifted to a mixed pattern during 2000–2008, when there were three significant downward trends and two significant upward trends. The pattern was opposite for streams in the Midwest, where all five sites with adequate data for 1996–2004 had downward trends, with three significant. During the second analysis period, only three sites had data suitable for analysis, for which there were two nonsignificant trends and one significant upward trend.

Trends in prometon concentrations in streams of the Northeast, Midwest, and West were mostly downward or nonsignificant during 1996–2004 and were similar among the three regions, with significant downward trends all within a range of 6 to 14 pct/yr (table 6). This pattern remained essentially the same during 2000–2008 for streams in the Northeast and West, but the Midwest shifted to upward trends, with three of four sites analyzed having significant upward trends in the range of 8 to 17 pct/yr (table 6). Streams in the South, in contrast to the other regions, had a relatively even mix of upward and downward trends during 1996–2004, with two each of significant upward and downward trends and three nonsignificant trends. This pattern generally continued during 2000–2008 for the streams in the South, with two significant upward trends and three significant downward trends. Significant downward trends in the South were in the range of 5 to 17 pct/yr and significant upward trends were in the range of 9 to 15 pct/yr, for the nine significant trends across both analysis periods.

Trends for simazine and prometon indicated predominately downward trends during 1996–2004 except for significant upward trends in both simazine and prometon for two sites in the South, significant upward trends in simazine for two additional sites in the South, and significant upward trends for prometon for one site in the Northeast and one site in the Midwest. There was strong similarity between the trends for simazine and prometon for 1996–2004. There was only one site for which there were conflicting significant trends (one up, the other down) in simazine and prometon. During 2000–2008, there were mixed upward and downward trends in simazine and prometon and the trends for the two herbicides were not as similar as during the earlier period. Simazine had the most significant downward trends in the South (three sites) and the most significant upward trends in the South (two sites). Prometon had the most significant downward trends in the South (three sites) and West (two sites) and the most significant upward trends in the Midwest (three sites) and South (two sites).

Atrazine and Deethylatrazine

Trends in atrazine and deethylatrazine generally were consistent with each other, but followed somewhat different patterns in each of the four regions (figs. 10 and 11). Overall, urban streams in the South and Midwest, where concentrations generally were the largest (figs. 6 and 7), had the most distinct patterns in trends, with mostly upward trends during 1996–2004 and more evenly mixed upward and downward during 2000–2008. Streams in the Northeast and West, which generally had lower concentrations (figs. 6 and 7), had more mixed trend directions and a higher proportion of site-period combinations with inadequate data for analysis.

In the Northeast, atrazine trends were mixed during both analysis periods, with two significant upward trends, one significant downward trend, and two nonsignificant trends during 1996–2004, and one significant upward trend and four nonsignificant trends during 2000–2008. Deethylatrazine trends in the Northeast were generally similar to atrazine during 1996–2004, but more broadly upward during 2000–2008; all five streams had upward trends, four of the five significant.

Streams in the South all had nonsignificant trends or significant upward trends in atrazine concentrations during 1996–2004, and a more mixed combination of two nonsignificant trends, three significant upward trends, and two significant downward trends during 2000–2008. During 1996–2004, deethylatrazine trends were consistent with the directions and magnitudes of atrazine trends, but more were significant, with six significant upward trends among the seven sites evaluated. Atrazine and deethylatrazine trends also generally were consistent with each other during 2000–2008, although one stream (site 14, SALAD) had a highly significant downward trend in atrazine and a significant upward trend in deethylatrazine.

In Midwest urban streams, atrazine concentration trends generally were upward during 1996–2004, as they were in the South, but during 2000–2008 the Midwest had more downward trends, with two significant downward trends and two nonsignificant downward trends for the four sites evaluated. Deethylatrazine trends were similar to atrazine trends during 1996–2004, although more were significant similar to that observed for streams in the South. During 2000–2008, however, two streams (sites 18, CLINT, and 20, SALTC) had significant downward trends in atrazine, but significant upward trends in deethylatrazine.

Urban streams in the West, as a group, had the lowest atrazine and deethylatrazine concentrations and a number of site-analysis period combinations had inadequate data for analysis of trends for both compounds. During 1996–2004, atrazine had two nonsignificant trends and one significant downward trend and during 2000–2008 one nonsignificant trend, two significant downward trends, and one significant upward trend. Deethylatrazine trends were inconsistent with atrazine trends at one site (22, LCOTT) during 1996–2004, which had a significant downward trend in atrazine and a significant upward trend in deethylatrazine.

Trends for atrazine and deethylatrazine indicated predominately upward trends in both herbicides during 1996–2004 except for significant downward trends in both herbicides for one site in the Northeast and one in the Midwest and a significant downward trend for atrazine for one site in the West. There was strong similarity between the trends for the two herbicides during 1996–2004. During 2000–2008, there were mixed upward and downward trends in atrazine and predominately upward trends in deethylatrazine. There were 10 sites for which a downward trend in atrazine was paired with an upward trend in deethylatrazine, and for 3 of these sites (one in the South and 2 in the Midwest) both opposing trends were significant. Opposing trends showing a decrease in atrazine and an increase in deethylatrazine may indicate that decreases in atrazine from surface runoff are being offset in many cases by increases in atrazine from groundwater for the latter analysis period. Risk reduction measures for atrazine have included setbacks and reduced application rates; therefore, less atrazine may reach surface water directly, whereas the remaining atrazine degrades to deethylatrazine, which can eventually reach groundwater.

Other Herbicides

For the remaining herbicides (metolachlor, trifluralin, pendimethalin, tebuthiuron, and Dacthal), many of the trends could not be estimated because the data were too highly censored and many of the trends that could be estimated were not significant (table 6). Consequently, regional patterns were more difficult to identify. However, a few observations were noted for these herbicides. Five sites had significant downward trends in metolachlor concentration during 1996–2004, including three sites in the Northeast and one site each in the South and Midwest. Metolachlor downward trends were determined in an earlier study of streams in the corn belt (Sullivan and others, 2009) for a similar period (1996–2002) and those trends were attributed to a reformulation of metolachlor (S-metolachlor), introduced in 1996, which decreased the amount of chemical required for effective weed control. The metolachlor downward trends in this study may be related to this change. However, two significant metolachlor upward trends were determined during 1996–2004 (sites 10, CHATT, and 21, DPLAI) despite the reformulation to a more effective compound. For trifluralin, four significant downward trends and two significant upward trends were determined; significant upward trends occurred in trifluralin for one site in the Northeast (6, ACCOT) during 1992–2000 and one site in the West (27, FANNO) during 2000–2008. Pendimethalin had seven significant downward trends and one significant upward trend in the West (25, ARCAD). For tebuthiuron, there were 11 significant downward trends, including 3 sites in the south during 1996–2004 and 3 sites in the West during 2000–2008, and only 2 significant upward trends. The only significant upward trends were for one site in the Midwest (21, DPLAI) and one site in the West (25, ARCAD) during 1996–2004. For Dacthal, there were six significant downward trends during 1992–2000 and 1996–2004 and only one significant upward trend for a site in the West (22, LCOTT) during 1996–2004.

Insecticides

Trends in insecticide concentrations for the three analysis periods are given in table 7. For the earliest analysis period (1992–2000), all of the significant trends for the four sites were downward, including significant downward trends for chlorpyrifos for three sites, and for malathion, diazinon and carbaryl for one site each.

For the 1996–2004 analysis period, the organophosphates chlorpyrifos and diazinon trended strongly downward for all regions (table 7 and fig. 12). All 11 sites analyzed for chlorpyrifos had downward trends (10 significant), and 21 of 22 sites analyzed for diazinon had downward trends (18 significant). No significant upward trends were determined for either insecticide. Malathion concentrations were too highly censored to analyze trends for most sites, but those that could be analyzed were all downward trends, including two significant downward trends (table 7). In contrast to the other insecticides, carbaryl had fewer downward trends (6) than upward trends (15). Although most of the carbaryl trends were not significant, there were two significant downward trends (sites 5, BOUND, and 25, ARCAD) and four significant upward trends (sites 1, ABERJ; 12, FLTCH; 19, SHING; and 26, THORN).

For the 2000–2008 period, diazinon trended even more strongly downward than it did during the earlier period (fig. 13; table 7), corresponding with the phaseout of several diazinon uses. All 21 sites analyzed for diazinon had highly significant downward trends during 2000–2008 and these trends generally were larger in magnitude than during the first period. Although chlorpyrifos and malathion were too highly censored to analyze trends for most sites, there were no significant upward trends and three significant downward trends (all in the South) for these two insecticides (table 7). Carbaryl trends were mixed and mostly nonsignificant during 2000–2008 (fig. 13). However, there were four significant downward trends and two significant upward trends during 2000–2008 compared with two significant downward trends and four significant upward trends during the earlier analysis period. Fipronil and its degradates trended strongly upward during 2000–2008 (fig. 14). Only one site each in the Northeast (site 6, ACCOT) and Midwest (site 20, SALTC) were not too highly censored to analyze and both of those sites had highly significant upward trends in fipronil and both degradates. In the south, five of seven sites analyzed had significant upward trends in fipronil and seven of seven sites had significant upward trends in both degradates. Three of three sites analyzed in the West had significant upward trends in fipronil and both degradates. One site in the South (7, SWIFT) had a significant downward trend in fipronil and significant upward trends in both degradates. This site had the only significant downward trend in fipronil for any of the sites.

Table 7. Trends, in percent per year, for insecticides at urban-stream sites, 1992–2008.

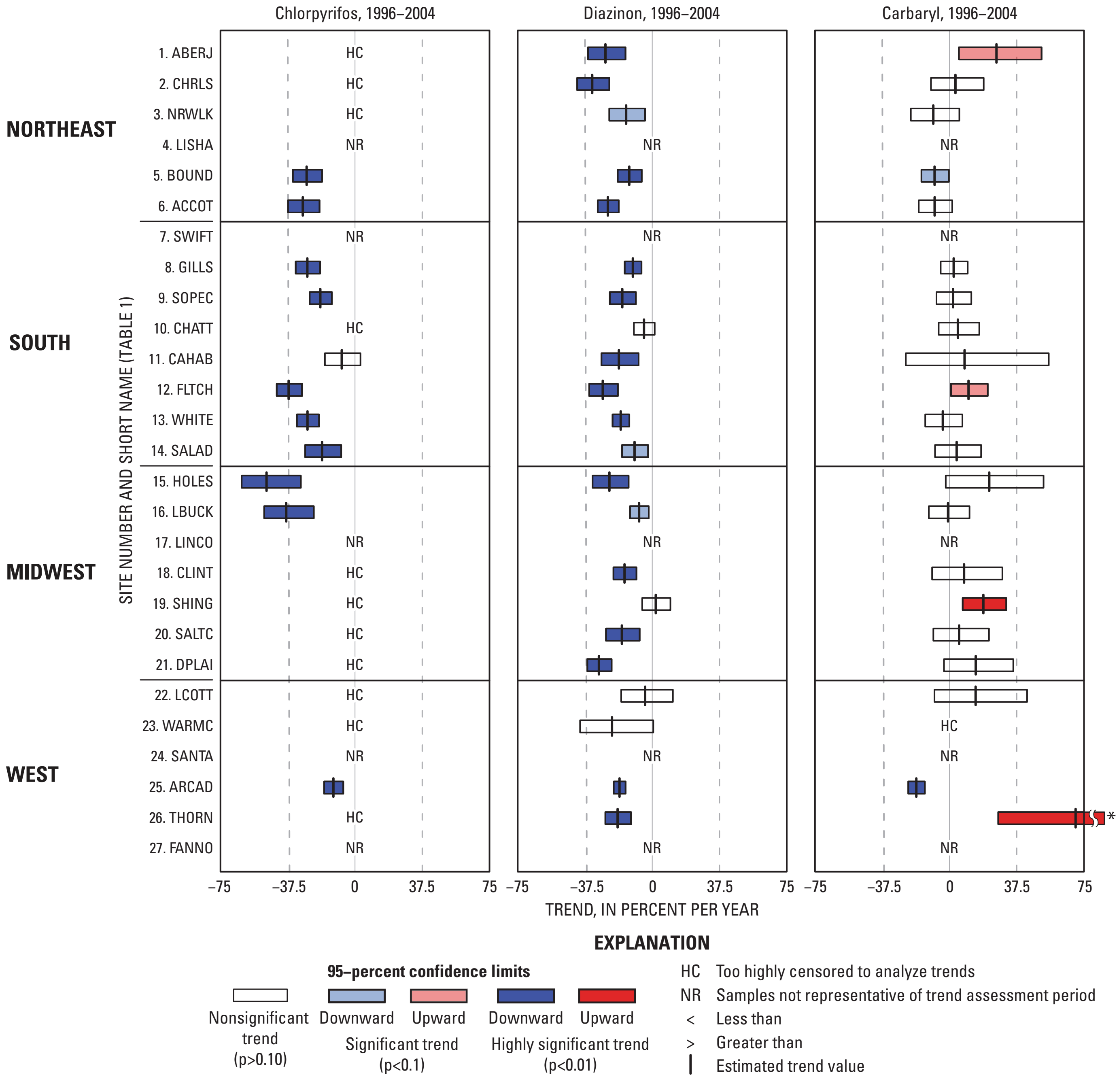
[Trend results in **bold** type are significant at the p<0.10 level; HC, too "highly censored" to analyze trends; --, no data; NR, samples "not representative" of trend assessment period]

Site number (fig. 1)	Site short name	Chlorpyrifos	Malathion	Diazinon	Fipronil	Fipronil sulfide	Desulfinyl-fipronil	Carbaryl
1992–2000 trend result (percent per year)								
Northeast								
3	NRWLK	HC	HC	-7.8	--	--	--	3.6
6	ACCOT	**-12.3**	-4.6	-5.2	--	--	--	-10.9
South								
9	SOPEC	**-8.7**	-18.9	**-8.3**	--	--	--	**-14.9**
Midwest								
16	LBUCK	**-24.5**	**-25.7**	.6	--	--	--	-5.7
1996–2004 trend result (percent per year)								
Northeast								
1	ABERJ	HC	HC	**-26.1**	--	--	--	**26.2**
2	CHRLS	HC	HC	**-33.5**	--	--	--	3.3
3	NRWLK	HC	HC	**-14.5**	--	--	--	-9.0
5	BOUND	**-27.0**	HC	**-12.8**	--	--	--	**-8.3**
6	ACCOT	**-29.1**	-1.5	**-24.8**	--	--	--	-8.3
South								
8	GILLS	**-26.6**	-9.4	**-10.8**	--	--	--	2.3
9	SOPEC	**-19.3**	HC	**-16.7**	--	--	--	2.0
10	CHATT	HC	HC	-4.6	--	--	--	4.7
11	CAHAB	-7.4	HC	**-18.6**	--	--	--	8.4
12	FLTCH	**-37.0**	-.4	**-27.6**	--	--	--	**10.6**
13	WHITE	**-26.5**	-10.4	**-17.6**	--	--	--	-3.7
14	SALAD	**-18.3**	HC	**-9.9**	--	--	--	4.0
Midwest								
15	HOLES	**-49.3**	HC	**-23.9**	--	--	--	22.2
16	LBUCK	**-38.3**	**-24.2**	**-7.3**	--	--	--	-.8
18	CLINT	HC	HC	**-15.5**	--	--	--	8.1
19	SHING	HC	HC	2.0	--	--	--	**18.9**
20	SALTC	HC	HC	**-16.9**	--	--	--	5.4
21	DPLAI	HC	HC	**-29.7**	--	--	--	14.6
West								
22	LCOTT	HC	**-32.9**	-4.0	--	--	--	14.6
23	WARMC	HC	HC	-22.5	--	--	--	HC
25	ARCAD	**-12.0**	-7.6	**-18.3**	--	--	--	**-18.5**
26	THORN	HC	HC	**-19.3**	--	--	--	**70.3**

Table 7. Trends, in percent per year, for insecticides at urban-stream sites, 1992–2008.—Continued

[Trend results in **bold** type are significant at the p<0.10 level; HC, too "highly censored" to analyze trends; --, no data; NR, samples "not representative" of trend assessment period]

Site number (fig. 1)	Site short name	Chlorpyrifos	Malathion	Diazinon	Fipronil	Fipronil sulfide	Desulfinyl-fipronil	Carbaryl
2000–2008 trend result (percent per year)								
Northeast								
2	CHRLS	HC	HC	**-42.2**	NR	NR	NR	2.6
3	NRWLK	HC	HC	**-46.3**	HC	HC	HC	-11.7
4	LISHA	HC	HC	**-50.4**	HC	HC	HC	-10.1
5	BOUND	HC	HC	**-29.7**	NR	NR	NR	.6
6	ACCOT	HC	HC	**-43.2**	**20.1**	**13.6**	**21.4**	**-9.9**
South								
7	SWIFT	HC	HC	**-50.1**	**-11.0**	**17.4**	**10.5**	**-9.3**
8	GILLS	HC	**-31.3**	**-46.8**	**22.0**	**53.2**	**33.3**	**17.3**
9	SOPEC	**-12.1**	HC	**-39.2**	**10.5**	**25.6**	**12.0**	6.7
10	CHATT	HC	HC	**-33.3**	**9.7**	**19.0**	**16.1**	-.6
11	CAHAB	-7.7	HC	**-42.3**	**19.4**	**37.9**	**26.3**	4.5
13	WHITE	**-18.8**	5.9	**-46.1**	**15.7**	**38.1**	**22.5**	-2.0
14	SALAD	HC	HC	**-55.4**	12.9	**13.2**	**3.6**	**-14.6**
Midwest								
17	LINCO	HC	HC	**-35.7**	HC	HC	HC	-2.2
18	CLINT	HC	HC	**-35.6**	HC	HC	HC	-1.2
19	SHING	HC	HC	**-34.1**	HC	HC	NR	-10.0
20	SALTC	HC	HC	**-42.4**	**14.2**	**16.4**	**20.8**	1.4
West								
22	LCOTT	HC	HC	**-36.9**	HC	HC	HC	-5.0
24	SANTA	HC	HC	**-39.8**	**33.4**	**10.3**	**16.0**	3.0
25	ARCAD	-1.3	-9.9	**-43.1**	**10.7**	**26.7**	**16.8**	.4
26	THORN	HC	HC	**-43.1**	HC	HC	**15.4**	**-19.3**
27	FANNO	.1	HC	**-19.4**	**97.0**	**33.0**	**37.9**	**20.3**



*Confidence limit box outside of graphs represents trends with confidence limits beyond the scale of the other trends. Scale was not extended in order to preserve a scale representative of majority of trends.

Figure 12. Trends, in percent per year, for chlorpyrifos, diazinon, and carbaryl for the 1996–2004 period.

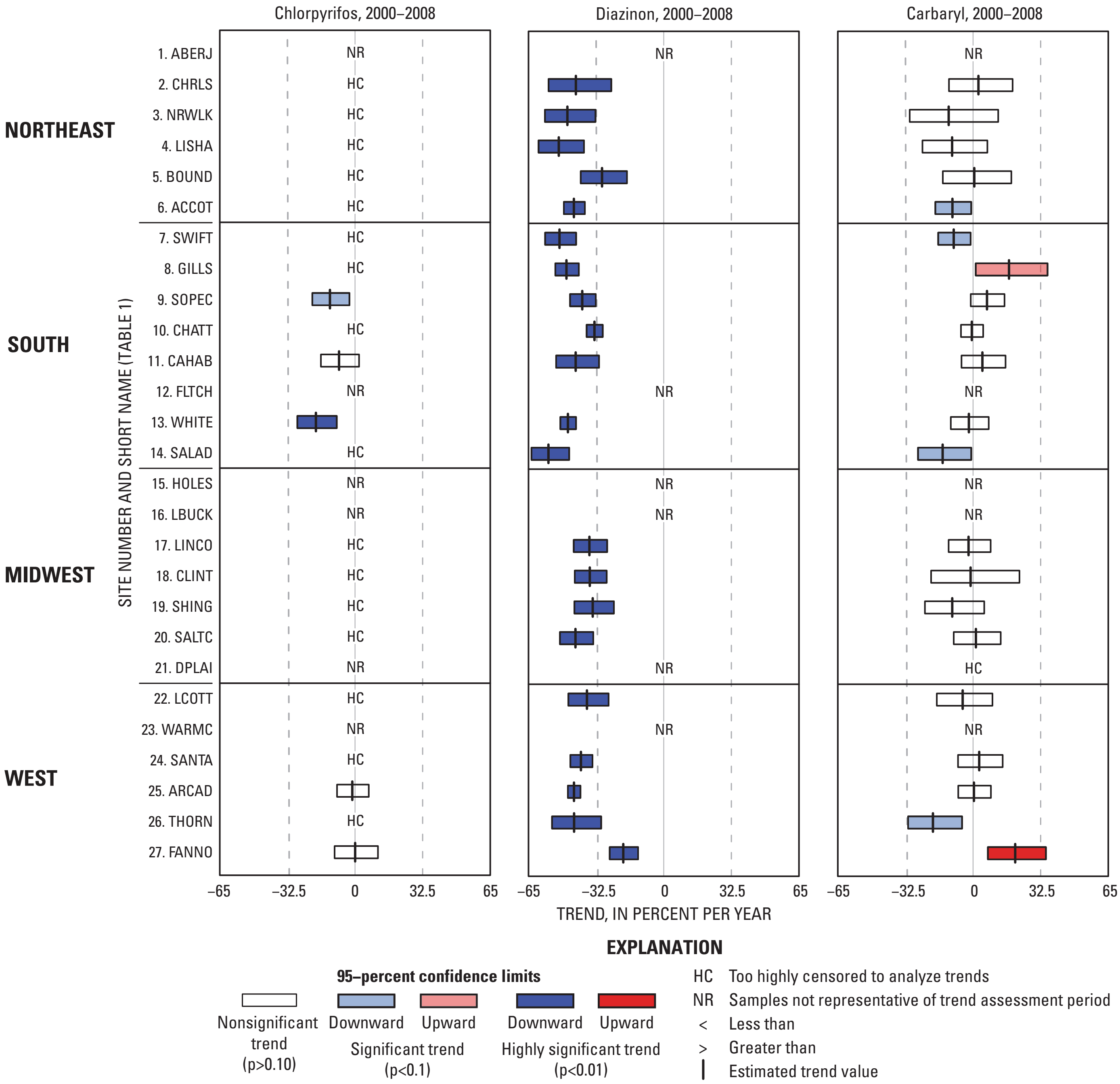


Figure 13. Trends, in percent per year, for chlorpyrifos, diazinon, and carbaryl for the 2000–2008 period.

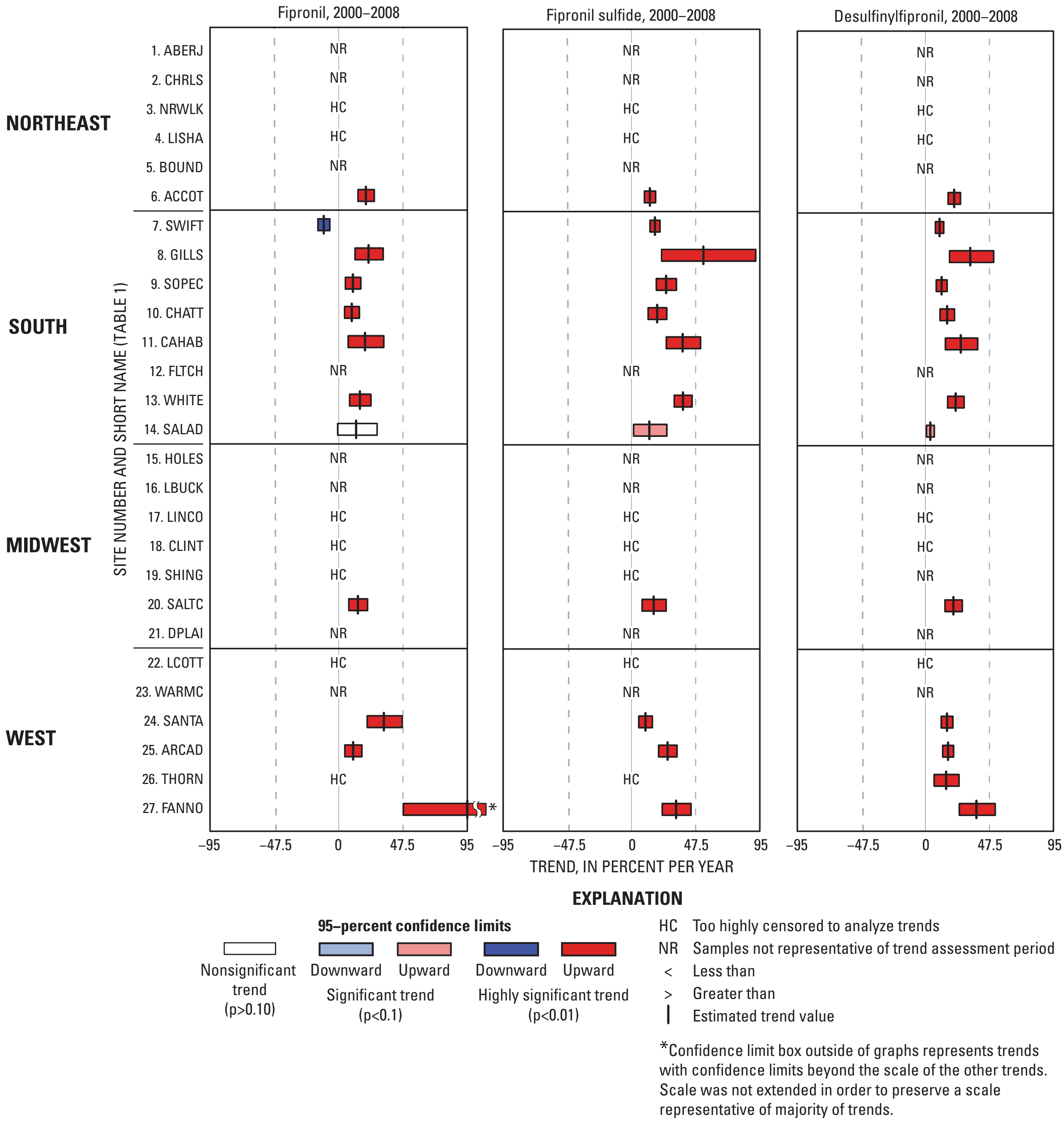


Figure 14. Flow-adjusted trends, in percent per year, for fipronil, fipronil sulfide, and desulfinylfipronil for the 2000–2008 period.

Chlorpyrifos

Chlorpyrifos trends were not assessable at most sites, particularly during 2000–2008, because of generally low and declining detection frequencies. Although quantities used in each basin are not known, chlorpyrifos has a combination of hydophobicity, low water solubility, and short half-life (table 5) that decreases its occurrence in filtered water samples compared to other insecticides evaluated. Most of the streams with adequate data for analysis had significant downward trends in concentrations, with 10 of 11 sites having significant downward trends during 1996–2004 and 2 of 5 sites having significant downward trends during 2000–2008. This general pattern was distributed across all regions, but most sites with adequate data were in the South. Significant downward trends ranged from 9 to 49 pct/yr (table 7). Many indoor and outdoor residential uses of chlorpyrifos were phased out or eliminated at various times during 1997–2001, which is consistent with the highly significant chlorpyrifos downward trends during the 1996–2004 analysis period and the substantially decreased chlorpyrifos concentrations in urban streams. By the 2000–2008 period, most measured chlorpyrifos concentrations were below detection limits (table 4). Only 5 sites had more than 10 detections during the latter period (all in the South and West), and chlorpyrifos concentrations for 2 of those sites (sites 9, SOPEC, and 13, FLTCH) continued to decline significantly. However, there were no significant downward trends for the remaining three sites (11, CAHAB; 25, ARCAD; 27, FANNO) during the latter period. Further investigation may be warranted to determine why chlorpyrifos concentrations for some sites did not continue to decline.

Malathion

No major changes in malathion regulation were identified in the U.S. Environmental Protection Agency reregistration document (2006c) that might explain the malathion downward trends for the few sites that could be analyzed. It is possible that voluntary changes occurred from malathion use to pyrethroid (not included in this study) use, fipronil use, or both. Fipronil, first available in the United States in 1996, is effective on insects that have become resistant to organophosphates (a class of pesticides including chlorpyrifos, malathion, and diazinon). Because the USGS did not begin analyzing samples for fipronil until 1999, data were highly censored, and sampling was not always representative of analysis periods, few direct comparisons can be made between malathion and fipronil concentrations. In the two cases where comparisons can be made, downward trends in malathion concentration occurred with upward trends in fipronil concentration (sites 8, GILLS, and 25, ARCAD; table 7).

Diazinon

Diazinon trends, which followed a strong and consistent pattern across all regions, were almost entirely significant downward, with the magnitudes of downward trends and the proportion that were highly significant, increasing markedly from the 1996–2004 period to 2000–2008. For 1996–2004, only four sites had nonsignificant trends. For 2000–2008, all 21 assessable trends were highly significant downward trends, and all but one was in the range of about 30 to 55 pct/yr (table 7). These downward trends in diazinon were consistent with the recent history of regulatory changes. All indoor and outdoor residential uses of diazinon were phased out beginning in 2002; retail sales of indoor residential products ended December 2002; retail sales of outdoor residential products ended December 31, 2004. Phillips and others (2007) also noted decreases in diazinon concentrations in urban streams of the Northeast.

Carbaryl

In contrast to the predominant downward trends for chlorpyrifos and diazinon, carbaryl concentration trends were mostly nonsignificant during both analysis periods: 15 of 21 sites during 1996–2004 and 15 of 21 sites during 2000–2008. Significant trends were mixed. Mostly upward trends occurred for carbaryl during 1996–2004 (though many were not significant; fig. 12). The upward trends in carbaryl during that time may be due at least in part to replacement of chlorpyrifos and diazinon with carbaryl. Although a number of restrictions and labeling changes for carbaryl were designed to decrease use, most of the changes did not take effect until after 2003 and thus may not have affected the trends for 1996–2004 substantially. Two sites (5, BOUND and 25, ARCAD) had significant downward trends in carbaryl during 1996–2004. Schreder and Dickey (2005) indicated that carbaryl might have replaced chlorpyrifos and diazinon in the Pacific Northwest for treating lawn insects. They analyzed 1996–2002 USGS NAWQA data for sites 26, THORN, and 27, FANNO, and noted decreases in diazinon concentration and increases in carbaryl concentration. For the similar period in this report, 1996–2004, the data at site 27, FANNO, were not used because of gaps in the data collection. However, site 26, THORN, was analyzed and results show a 19.3 pct/yr downward trend in diazinon with a 70.3 pct/yr upward trend in carbaryl. Schreder and Dickey (2005) stated that the increase in carbaryl corresponding to a decrease in diazinon has not been shown in other regions of the country. Phillips and others (2007) detected no significant step trends in summer carbaryl concentration at Northeastern and Midwestern sites, but did detect significant downward step trends for summer diazinon concentrations (study period 1992–2004). For the period 2000–2008, in this report carbaryl trends were mixed (upward and downward) and mostly nonsignificant (fig. 13). Carbaryl concentrations in this period may be affected both by the phase out of chlorpyrifos and diazinon, which would tend to cause upward trends, and the voluntary cancellation of registration for most of carbaryl products during the 2000–2008 period (see Use and Properties of Pesticides section), which would tend to cause downward trends. For sites 8, GILLS, and 27, FANNO, with significant upward trends in carbaryl during 2000–2008, the former (replacement of diazinon or chlorpyrifos, or both) may be the dominant cause and for sites 6, ACCOT; 7, SWIFT; 14, SALAD; and 26, THORN, with significant downward trends, the latter (voluntary cancellation and reduction of use) may be the dominant cause. Mostly nonsignificant carbaryl trends may have occurred either because the two causes cancelled each other or because carbaryl concentrations in the stream were not sensitive to either of the changes.

Fipronil and its Degradates

Because of the phaseout of chlorpyrifos and diazinon, the use of other insecticides may have increased in response. The most common replacement insecticides include fipronil, imidacloprid, and pyrethroids (Phillips and others, 2007). Replacement of chlorpyrifos and diazinon with fipronil may partly explain the preponderance of upward trends in fipronil and its degradation products during 2000–2008. Significant upward trends were noted at 10 sites for fipronil and both degradation products. There was one anomalous case (site 7, SWIFT) where there was a statistically significant downward trend in fipronil but statistically significant upward trends in both degradation products fipronil sulfide and desulfinylfipronil. The two degradation products have longer half-lives in soil (table 5) and Demcheck and Skrobialowski (2003) showed that the maximum concentration of fipronil sulfide tended to lag behind fipronil and that fipronil sulfide and desulfinylfipronil accumulated in bed sediment, whereas fipronil did not. For these reasons, it is possible that a decrease in fipronil use or a decrease in fipronil transport to the stream has occurred, but a corresponding decrease in degradation products will take longer to be detected. The cause for the single anomalous decrease in fipronil concentration for site 7 is not known.

Summary

Pesticide data from 27 urban streams sampled as part of the U.S. Geological Survey National Water-Quality Assessment Program were analyzed for trends in the concentrations of the most frequently detected pesticides for three partially overlapping 9-year periods: 1992–2000, 1996–2004, and 2000–2008. The sites were divided into four regions, Northeast, South, Midwest, and West, to examine possible regional patterns. The pesticides included nine herbicides and degradation products (simazine, prometon, atrazine, deethylatrazine, metolachlor, trifluralin, pendimethalin, tebuthiuron, and Dacthal) and seven insecticides and degradation products (chlorpyrifos, malathion, diazinon, fipronil, fipronil sulfide, desulfinylfipronil, and carbaryl).

The data required numerous preparatory steps for use in trend analysis and were analyzed for trends in concentration using a parametric regression model with seasonality, flow-related variability, and trend, called SEAWAVE-Q. The SEAWAVE-Q model was also used to generate 90th percentiles of the estimated daily concentrations for each analysis period to provide a summary of concentration magnitudes in addition to concentration trends.

There were some distinct patterns in concentrations among pesticides and geographic regions. For herbicides, the largest 90th percentiles of estimated concentrations for simazine were in the South, prometon at some sites in all of the regions, atrazine and deethylatrazine in the South and Midwest, metolachlor in the Midwest and a few sites in the South, pendimethalin at scattered sites in all of the regions, and tebuthiuron in the South and a few sites in the Midwest and West. All of these herbicides are relatively mobile and persistent. The remaining herbicides (trifluralin and Dacthal) are less mobile and the 90th percentiles for all sites were relatively low (less than 0.01 microgram per liter). For insecticides, the largest 90th percentiles of estimated concentrations for diazinon and carbaryl were distributed among various sites in all regions (especially during 1996–2004), and fipronil at isolated sites in all of the regions during 2000–2008.

Trend results for the herbicides indicated many significant trends, both upward and downward, with varying patterns depending on period, region, and herbicide. Overall, for all of the herbicides and periods, deethylatrazine showed the most consistent pattern of upward trends in concentrations, especially in the Northeast (2000–2008), South (1996–2004 and 2000–2008), and Midwest (1996–2004 and 2000–2008). Other herbicides showed less consistent increases, including simazine in the South (1996–2004), prometon in the Midwest (2000–2008), and atrazine in the South (1996–2004). The most consistent downward trends were for simazine in the Northeast and Midwest (1996–2004), prometon in the Northeast and Midwest (1996–2004) and West (1996–2004 and 2000–2008), and tebuthiuron in the South (1996–2004 and 2000–2008) and West (2000–2008).

Trends for simazine and prometon indicated predominately downward trends during 1996–2004 except for significant upward trends in both simazine and prometon for two sites in the South, significant upward trends in simazine for two additional sites in the South, and significant upward trends for prometon for one site in the Northeast and one site in the Midwest. There was strong similarity between the trends for simazine and prometon for 1996–2004. There was only one site for which there were conflicting significant trends (one up, the other down) in simazine and prometon. During 2000–2008, there were mixed upward and downward trends in simazine and prometon and the trends for the two herbicides were not as similar as during the earlier period. Simazine had the most significant downward trends in the South (three sites) and the most significant upward trends in the South (two sites). Prometon had the most significant downward trends in the South (three sites) and West (two sites) and the most significant upward trends in the Midwest (three sites) and South (two sites).

Trends for atrazine and deethylatrazine indicated predominately upward trends in both herbicides during 1996–2004 except for significant downward trends in both herbicides for one site in the Northeast and one in the Midwest and a significant downward trend for atrazine for one site in the West. There was strong similarity between the trends for the two herbicides during 1996–2004. During 2000–2008, however, there were mixed upward and downward trends in atrazine and predominately upward trends in deethylatrazine. There were 10 sites for which a downward trend in atrazine was paired with an upward trend in deethylatrazine, and for 3 of these sites (one in the South and 2 in the Midwest) both opposing trends were significant. Opposing trends showing a decrease in atrazine and an increase in deethylatrazine may indicate that decreases in atrazine from surface runoff are being offset in some cases by increases in deethylatrazine from groundwater for the latter analysis period. Risk reduction measures for atrazine have included setbacks and reduced application rates; therefore, less atrazine may reach surface water directly, whereas the remaining atrazine degrades to deethylatrazine, which can eventually reach groundwater.

Metolachlor trends were mostly nonsignificant, but there were five sites with significant downward trends during 1996–2004 and these trends may be related to the introduction of S-metolachlor in 1996. However, there also were two significant upward trends in metolachlor during the same period. Although trifluralin and pendimethalin were too highly censored to analyze trends for most sites and periods, there were 11 significant downward trends between the two pesticides for various regions and times. However, there also were three significant upward trends (two for trifluralin and one for pendimethalin). For tebuthiuron, there were 11 significant downward trends including 3 sites in the South during 1996–2004 and 3 sites in the West during 2000–2008. However, there also were two sites with significant upward trends during 1996–2004. Dacthal was too highly censored to analyze trends for most sites and periods, but there were six significant downward trends during the 1992–2000 and 1996–2004 analysis periods and only one significant upward trend during 1996–2004.

Trend results for two organophosphate insecticides, chlorpyrifos and diazinon, were consistent with known decreases in urban uses of these chemicals. Many residential uses of chlorpyrifos were phased out or eliminated at various times during 1997–2001, which is consistent with highly significant chlorpyrifos downward trends during 1996–2004 and substantially decreased chlorpyrifos concentrations in urban streams. Diazinon trended strongly downward during both the 1996–2004 and 2000–2008 analysis periods, which is consistent with various changes in regulation that reduced or eliminated most residential uses of diazinon during 2000–2004.

Malathion, another organophosphate insecticide, was too highly censored for trend analysis at most sites. However, most of the trends that could be analyzed were downward, four of which were significant. The downward trends in malathion may be caused by voluntary substitution of pyrethroids or fipronil for malathion.

The insecticide carbaryl had mostly upward trends during 1996–2004, although only four of the upward trends were significant. The upward trends in carbaryl during that time may be due at least in part to replacement of chlorpyrifos and diazinon with carbaryl. However, there were two sites with significant downward trends in carbaryl during the same period. For the 2000–2008 analysis period, carbaryl trends were mixed upward and downward and were mostly nonsignificant. Despite voluntary cancellation of many residential uses of carbaryl beginning in about 2000, there were only four significant downward trends during 2000–2008 and two significant upward trends during that time.

Trends in the insecticide fipronil and its degradation products fipronil sulfide and desulfinylfipronil were analyzed only for the analysis period 2000–2008. Fipronil was introduced in 1996 and concentrations were analyzed by the U.S. Geological Survey beginning in 1999. For 13 sites that were not too highly censored to analyze trends, fipronil and both degradation products trended strongly upward. Significant upward trends were noted at 10 sites for fipronil and both degradation products. One anomalous site had a significant downward trend in fipronil and highly significant upward trends in both degradation products. The strong upward trends in fipronil and its degradates are consistent with expected increasing use after its introduction, in 1996, particularly as a substitute for organophosphate insecticides.

References Cited

Capel, P.D., Spexet, A.H., and Larson, S.J., 1999, Occurrence and behavior of the herbicide prometon in the hydrologic system: Environmental Science and Technology, v. 33, no. 5, p. 674–680.

Connelly, Pete, 2001, Environmental fate of fipronil: Sacramento, California Department of Pesticide Regulation, 17 p.

Crawford, C.G., 2004, Sampling strategies for estimating acute and chronic exposures of pesticides in streams: Journal of the American Water Resources Association, v. 40, no. 2, p. 485–502.

Demcheck, D.K., and Skrobialowski, S.C., 2003, Fipronil and degradation products in the rice-producing areas of the Mermentau River Basin, Louisiana, February–September 2000: U.S. Geological Survey Fact Sheet FS–010–03, 6 p. (Also available at *http://pubs.er.usgs.gov/publication/fs01003*.)

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, chapter C2, 89 p. (Also available at *http://pubs.er.usgs.gov/usgspubs/twri/twri03C2*.)

Fishel, F.M., 2005, Pesticide toxicity profile—Organophosphate pesticides: University of Florida Institute of Food and Agricultural Sciences Pesticide Information Office PI-50, 3 p., accessed December 14, 2009, at *http://edis.ifas.ufl.edu/pdffiles/PI/PI08700.pdf*.

Fishel, F.M., 2006, Pesticide toxicity profile: triazine pesticides: University of Florida Institute of Food and Agricultural Sciences Pesticide Information Office PI-121, 3 p., accessed December 8, 2009, at *http://edis.ifas.ufl.edu/pi158*.

Fry, J.A., Coan, M.J., Homer, C.G., Meyer, D.K., and Wickham, J.D., 2009, Completion of the National Land Cover Database (NLCD) 1992–2001 Land Cover Change Retrofit product: U.S. Geological Survey Open-File Report 2008–1379, 18 p.

Geolytics, Inc., 2001, Census CD 2000 Short Form Blocks, digital files on CD-ROM, East Brunswick, N.J.

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. (Also 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.

Gunasekara, A.S., 2004, Environmental fate of simazine: California Department of Pesticide Regulation, Environmental Monitoring Branch, 35 p., accessed December 8, 2009, at *http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/simazine.pdf*.

Gunasekara, A.S., Truong, Tresca, Kean, S.G., Spurlock, Frank, and Tjeerdema, R.S., 2007, Environmental fate and toxicology of fipronil: Journal of Pesticide Science, v. 32, no. 3, p. 189–199.

Hahn, G.J. and Meeker, W.Q., 1991, Statistical intervals—A guide for practitioners: New York, John Wiley & Sons, 392 p.

Homer, Collin, Huang, Chengquan, Yang, Limin, Wylie, Bruce, and Coan, Michael, 2004, Development of a 2001 National Land Cover Database for the United States: Photogrammetric Engineering and Remote Sensing v. 70, no. 7, p. 829–840. (Also available at *http://www.mrlc.gov/pdf/July_PERS.pdf*.)

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399, 113 p.

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 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. (Also available at *http://nwql.usgs.gov/Public/pubs/OFR02-462/OFR02-462.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. (Also available at *http://in.water.usgs.gov/newreports/martin-pest.pdf*.)

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. (Also available at *http://pubs.usgs.gov/sir/2009/5062/*.)

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. (Also 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., plus appendixes. (Also 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. (Also available at *http://pubs.usgs.gov/of/1997/223/*.)

National Pesticide Information Center, 2009, Fipronil: technical fact sheet, 11 p., accessed September 17, 2009, at *http://npic.orst.edu/factsheets/fiptech.pdf*

Neter, John, Kutner, M.H., Nachtsheim, C.J., and Wasserman, William, 1996, Applied linear statistical models (4th ed.): Boston, Mass., WCB/McGraw-Hill, 1,408 p.

Newhart, KayLynn, 2006, Environmental fate of malathion: California Department of Pesticide Regulation, Environmental Monitoring Branch, 20 p., accessed December 11, 2009, at *http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/efate_malathion.pdf*.

Ngim, K.K., and Crosby, D.G., 2001, Abiotic processes influencing fipronil and desthiofipronil dissipation in California, USA, rice fields: Environmental Toxicology and Chemistry, v. 20, no. 5, p. 972–977.

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. (Also 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 and Technology, v. 41, no. 12, p. 4,246–4,251.

R Development Core Team, 2010, R: A language and environment for statistical computing: R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL *http://www.R-project.org*.

Ramesh, Atmakuru, and Balasudramanian, Muthukrishnan, 1999, Kinetics and hydrolysis of fenamiphos, fipronil, and trifluralin in aqueous buffer solutions: Journal of Agricultural and Food Chemistry, v. 47, p. 3,367–3,371.

Schreder, Erika, and Dickey, Philip, 2005, Toxic tradeoff: Exit diazinon, enter carbaryl—Phaseout leads to risky replacement: Seattle, Washington Toxics Coalition Report, 29 p., accessed April 8, 2010, at *http://watoxics.org/files/toxictradeoff.pdf*.

Scribner, E.A., Thurman, E.M., Goolsby, D.A., Meyer, M.T., Battaglin, W.A., and Kolpin, D.W., 2005, Summary of significant results from studies of triazine herbicides and their degradation products in surface water, ground water, and precipitation in the Midwestern United States during the 1990s: U.S. Geological Survey Scientific Investigations Report 2005–5094, 27 p. (Also available at *http://pubs.usgs.gov/sir/2005/5094/*.)

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.

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. (Also available at *http://pubs.usgs.gov/sir/2009/5132/*.)

Therneau, Terry (original R port by Thomas Lumley), 2009, survival: Survival analysis, including penalised likelihood: R package version 2.35-8. *http://CRAN.R-project.org/package=survival*

Tomlin, C., ed., 2008, The e-pesticide manual, version 4.1, Thornton Heath, United Kingdom: British Crop Production Council.

U.S. Bureau of the Census, 1992, Census of population and housing, 1990—Summary Tape file 3A, U.S. Bureau of the Census, Washington, D.C.

U.S. Bureau of the Census, 2001a, 1990 Census block group cartographic boundary files: U.S. Census Bureau, Geography Division, Cartographic Products Management Branch, rev. April 22, 2005, accessed October 25, 2007, at *http://www.census.gov/geo/www/cob/bg1990.html*.

U.S. Bureau of the Census, 2001b, 2000 Census block group cartographic boundary files: U.S. Census Bureau, Geography Division, Cartographic Products Management Branch, rev. April 22, 2005, accessed October 25, 2007, at *http://www.census.gov/geo/www/cob/bg2000.html*.

U.S. Environmental Protection Agency, 1994, Reregistration decision tebuthiuron, 205 p., accessed December 11, 2009, at *http://www.epa.gov/oppsrrd1/REDs/old_reds/tebuthiuron.pdf*

U.S. Environmental Protection Agency, 1995, Reregistration eligibility decision (RED) – metolachlor, 228 p., plus appendix, accessed December 10, 2009, at *http://www.epa.gov/oppsrrd1/REDs/0001.pdf*.

U.S. Environmental Protection Agency, 1996a, New pesticide fact sheet: EPA-737-F-96-005, 10 p., accessed December 15, 2009, at *http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1001KCY.txt*.

U.S. Environmental Protection Agency, 1996b, Reregistration eligibility decision (RED) – trifluralin, 221 p., accessed December 10, 2009, at *http://www.epa.gov/oppsrrd1/REDs/0179.pdf*.

U.S. Environmental Protection Agency, 1997, Reregistration eligibility decision (RED) pendimethalin, 223 p., accessed December 10, 2009, at *http://www.epa.gov/oppsrrd1/REDs/0187red.pdf*.

U.S. Environmental Protection Agency, 1998, Reregistration eligibility decision (RED) DCPA, 199 p., accessed December 11, 2009, at *http://www.epa.gov/oppsrrd1/REDs/0270red.pdf*.

U.S. Environmental Protection Agency, 2002a, Chlorpyrifos facts: U.S. Environmental Protection Agency, EPA 738-F-01-006, accessed December 11, 2009, at *http://www.epa.gov/oppsrrd1/REDs/factsheets/chlorpyrifos_fs.htm*.

U.S. Environmental Protection Agency, 2002b, Interim Reregistration Eligibility Decision for Chlorpyrifos, EPA 738-R-01-007, 235 p., accessed December 11, 2009, at *http://www.epa.gov/pesticides/reregistration/REDs/chlorpyrifos_ired.pdf*.

U.S. Environmental Protection Agency, 2004, Interim reregistration eligibility decision for carbaryl, 289 p., accessed January 11, 2010, at *http://www.epa.gov/oppsrrd1/REDs/carbaryl_ired.pdf*.

U.S. Environmental Protection Agency, 2006a, Decision documents for atrazine, 323 p., accessed December 8, 2009, at *http://www.epa.gov/oppsrrd1/REDs/atrazine_combined_docs.pdf*.

U.S. Environmental Protection Agency, 2006b, Reregistration eligibility decision for diazinon, 112 p., accessed December 14, 2009, at *http://www.epa.gov/pesticides/reregistration/REDs/diazinon_red.pdf*.

U.S. Environmental Protection Agency, 2006c, Reregistration eligibility decision (RED) for malathion, 188 p., accessed December 14, 2009, at *http://www.epa.gov/pesticides/reregistration/REDs/malathion_red.pdf*.

U.S. Environmental Protection Agency, 2006d, Reregistration eligibility decision for simazine, 266 p., accessed December 8, 2009, at *http://www.epa.gov/pesticides/reregistration/REDs/simazine_red.pdf*.

U.S. Environmental Protection Agency, 2007, Reregistration eligibility decision (RED) for carbaryl, accessed January 11, 2010, at *http://www.epa.gov/oppsrrd1/REDs/carbaryl_red.pdf*.

U.S. Environmental Protection Agency, 2008a, Amended reregistration eligibility decision (RED) for carbaryl, 43 p., accessed January 11, 2010, at *http://www.epa.gov/oppsrrd1/REDs/carbaryl-red-amended.pdf*.

U.S. Environmental Protection Agency, 2008b, Diazinon: Phase out of all residential uses of the insecticide, accessed December 11, 2009, at *http://www.epa.gov/opp00001/factsheets/chemicals/diazinon-factsheet.htm*.

U.S. Environmental Protection Agency, 2008c, Reregistration eligibility decision for prometon, 50 p., accessed December 8, 2009, at *http://www.epa.gov/pesticides/reregistration/REDs/prometon-red.pdf*.

U.S. Environmental Protection Agency, 2009, National Primary Drinking Water Regulations, EPA 816-F-09-004, 6 p., accessed August 4, 2010, at *http://www.epa.gov/safewater/consumer/pdf/mcl.pdf*.

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, 2007, National Land Cover Database (NLCD) 1992/2001 retrofit land cover change product multi-zone download site, [digital files], accessed December 11, 2007 at *http://www.mrlc.gov/mrlc2k_multizone.asp*.

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/*.

Vecchia, A.V., Gilliom, R.J., Sullivan, D.J., Lorenz, D.L., and Martin, J.D., 2009, Trends in concentrations and use of agricultural herbicides for Corn Belt rivers, 1996–2006: Environmental Science and Technology, v. 43, p. 9,096–9,102.

Vecchia, A.V., Martin, J.D., and Gilliom, R.J., 2008, Modeling variability and trends in pesticide concentrations in streams: Journal of the American Water Resources Association, v. 44, no. 5, p. 1,308–1,324.

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.

Zhu, Guonian, Wu, Huiming, Guo, Jiangfeng, and Kimaro, F.M.E., 2004, Microbial degradation of fipronil in clay loam soil: Water, Air, and Soil Pollution, v. 153, p. 35–44.

Appendixes

Appendix 1. Preparation of Concentration Data for Trend Analysis

Pesticide concentration data were prepared for trend analysis using the approach presented in Martin (2009). The principal steps in data preparation were to (1) identify routine reporting levels used to report nondetections; (2) reassign the concentration for routine nondetections to the maximum concentration of the long-term method detection level; (3) round concentrations to a consistent level of precision for the concentration range; (4) adjust concentrations to compensate for temporal changes in bias of recovery of the gas chromatography/mass spectrometry (GCMS) analytical method; and (5) identify and remove samples collected too frequently in time for trend analysis. In addition, at selected sites with sufficient low-level pesticide detections, the concentration for routine nondetections was lowered from the maximum concentration of the long-term method detection level to the median concentration of the low-level detections. These steps are further described in this appendix.

Identification of Reporting Levels

Two types of reporting levels were identified for the purposes of trend analysis: routine and raised. Nondetections of pesticides are reported as less than the "routine" reporting level (for example, <0.005 µg/L [less than 0.005 micrograms per liter]). 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 cannot be identified/detected if they are present at concentrations less than the level of interference and 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 (for a given period). 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 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. The concentration of the routine reporting level in effect for a given time period was determined from U.S. Geological Survey (USGS) National Water-Quality Laboratory (NWQL) records and from review of the data set.

Reassignment of 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 censored values (the "less-than" values) assigned to nondetections to a uniform, temporally consistent censored value. Thus, all pesticide nondetections at routine reporting levels were censored at a concentration equal to the maximum concentration of the long-term method detection level (maxLT-MDL) for water years 1994–2008 (the 1994 water year is the period from October 1, 1993 through September 30, 1994). Pesticide nondetections at raised reporting levels were treated as missing values and thus not used for trend assessment. For most, but not all pesticides and periods, reassigning the censored concentration of routine nondetections to the maxLT-MDL resulted in an increase in the nondetected "less than" concentration (Martin, 2009, appendix 2). The reporting level is not a detection limit for pesticides analyzed by GCMS and changes in the reporting level reflect changes in the quantitation variability of low-level concentrations or policy changes, not changes in detection capability.

Rounding of Concentrations to a Consistent Level of Precision

The precision of pesticide data compiled for trend analysis has changed through time. Prior to April 1997, pesticide data reported by NWQL were rounded to a greater degree than data reported subsequently (U.S. Geological Survey, 1997). Concentration data were rounded consistently for various concentration ranges for trend analysis (Martin, 2009, table 4).

Adjustment of Concentrations for Temporal Changes in Recovery

Temporal changes in the performance of the GCMS analytical method used to measure pesticide concentrations during 1992–2008 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. Measured concentrations of pesticides were adjusted for temporal changes in analytical recovery using the approach presented in Martin and others (2009) and summarized below.

Recovery of a pesticide compound is measured by analysis of "spiked" quality-control (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. Recovery measures bias in the analytical method—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.

Data for recovery of pesticides in stream-water matrix spikes is provided in Martin and others (2009, appendix 3). That recovery data set was extended with approximately two additional years of data (through summer 2008) following similar procedures used to extend the pesticide concentration data set described previously (merging data before and after September 1, 2005). Lowess smooths were used to model temporal changes in the recovery of pesticides in stream-water matrix spikes. A 10-percent smoothing window was selected to model 6- to 12-month time-scale temporal changes in recovery (because of a much shorter period of record, a 25-percent smoothing window was used for fipronil and the two degradates of fipronil). Temporal changes in lowess-modeled recovery of more than 50 percent were observed for some pesticides during 1992–2006 (Martin and others, 2009, appendixes 4 and 5).

Detected concentrations of pesticides were adjusted to 100-percent recovery by dividing the measured concentration by the lowess-modeled recovery, where recovery was expressed as a fraction. Routine nondetections at maxLT-MDL were not adjusted for 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 “Reassignment of the Concentration Value for Routine Nondetections”). Recovery-adjusted concentrations were rounded consistently as discussed previously.

Deletion of Samples Considered Inappropriate for Trend Analysis

Samples collected too frequently in time typically have highly correlated, redundant information that are inappropriate for use in trend analyses. A weekly sampling frequency was considered the maximum frequency suitable for trend analysis. All samples at a site were assigned to calendar weeks (Sunday through Saturday) and if two or more samples were collected during the same week, only the sample collected closest in time to noon Wednesday was retained for trend analysis.

Reassignment of the Concentration Value for Selected Routine Nondetections to the Median Concentration of Low-Level Detections

As mentioned previously, the GCMS analytical method does not have specified “detection limits” for each pesticide analyte. That is, there is no direct assessment by NWQL of the pesticide concentration where detection is 50 percent (or some larger percentage) probable. Instead, “reporting limits” are determined based on the variability of measured concentrations from low-concentration laboratory spikes (Oblinger Childress and others, 1999). This “signal-to-noise” based approach to determining detection works well for many types of analytical methods but is not well suited to the GCMS method which requires pesticide identification (detection) prior to quantitation.

The maximum value of the long-term method detection level (maxLT-MDL) has been used as a conservative estimate of the detection limit for previous studies of pesticide trends (Sullivan and others, 2009; Vecchia and others, 2009). Detections at concentrations less than maxLT-MDL were “censored” at maxLT-MDL (reassigned to nondetections at the concentration of maxLT-MDL) and trends assessed. For the trend assessment in this report, a less conservative estimate of the detection limit was desired because many pesticides and sites selected for assessment had a large number of detections less than maxLT-MDL (low-level detections) and using some of these low-level detections would increase the number of pesticides and sites that meet the criteria for trend assessment.

The ability to detect pesticides at low concentrations is expected to be dependent on the detection “sensitivity” of the analytical method, the concentration of the pesticide in the sample, and the matrix of the sample (the chemical, physical, and biological characteristics of the water sample). Detection sensitivity can vary through time, perhaps in response to short-term factors such as instrument maintenance or changes in reagents or supplies, or to long-term factors such as changes in instrumentation. The most pressing concern for trend analysis is a directional change in detection sensitivity over the period of trend analysis, such as from less sensitive to more sensitive. Information on temporal changes in detection sensitivity were not available but long-term trends in detection sensitivity were assessed by two approaches: (1) examining the frequency of low-level pesticide detections in selected NAWQA groundwater samples through time and (2) examining the consistency of low-level pesticide detections in NAWQA groundwater and stream-water field duplicate QC samples though time (appendixes 2 and 3). Groundwater samples were used to assess the frequency of low-level pesticide detections though time because temporal changes in concentrations in groundwater are expected to be less than in stream water—therefore, trends in detection sensitivity might be more apparent in groundwater samples than in stream-water samples. The first approach, examining groundwater samples (appendix 2), did not show evidence of long-term trends in detection sensitivity for the pesticides assessed in this report. The second approach, examining field duplicate QC samples (appendix 3), did not show increased detection sensitivity through time for most of the pesticides in this report. However, tebuthiuron and carbaryl showed increased consistency of low-level detections and a decrease in the concentrations detected through time. This might indicate that improvements in instrumentation have resulted in increased detection sensitivity for tebuthiuron and carbaryl over time. However, tebuthiuron remained highly censored throughout the period of this study and carbaryl showed significant upward and downward trends, so the effect of possible improvements in detection sensitivity is unclear.

Both pesticide concentration and sample matrix are expected to affect detection capability. Pesticide concentrations less than but close to maxLT-MDL likely are detected almost as readily as concentrations at or just above maxLT-MDL, whereas concentrations two orders of magnitude less than maxLT-MDL might rarely be detected. As was true for analytical recovery (Martin and others, 2009, p. 10–12, figs. 2 and 4), detection limits likely are a function of sample matrix. Concentrations readily detected in one matrix might not be detected in a more problematic matrix.

The less conservative estimate of the detection limit used for trend assessment in this report is the median value of the low-level detections (qlow50), calculated separately for each pesticide and stream-water site combination. The site-specific estimate of the detection limit was calculated only for pesticide and stream-water site combinations with five or more low-level detections for the period of record. Where qlow50 was calculated, routine nondetections at maxLT-MDL and any low-level detection less than qlow50 were assumed to be censored at a concentration equal to qlow50 (the true concentration was assumed to be less than qlow50, but the actual concentration was not known). All detections with concentrations greater than or equal to qlow50 were left unchanged. For each pesticide-site combination with fewer than five low-level detections, qlow50 was set equal to maxLT-MDL and the same procedure described previously was used to prepare the data for trend assessment. The resulting pesticide concentration data set used for trend assessment for this report is summarized in appendix 4, site information is provided as a downloadable data set in appendix 5, and the concentration data used for trend analysis is provided as a downloadable data set in appendix 6.

The procedure used for censoring the concentration data is illustrated with two examples. Pendimethalin concentrations for site 16 (LBUCK) are shown in figure A1–1. The maxLT-MDL for pendimethalin (the same for all sites) is 0.011 µg/L. For this site, 15 low-level detections had concentrations less than 0.011 µg/L (fig. A1–1*A*). The conservative censoring method (fig. A1–1*B*) censors all 15 low-level detections at maxLT-MDL, the same level used to censor the routine nondetections. Only the detections greater than or equal to maxLT-MDL were left uncensored. Because more than five low-level detections were measured at this site, qlow50 was computed as the median of the 15 low-level detections, which was 0.007 µg/L. The data used for trend assessment (fig. A1–1*C*) have all routine nondetections and low-level detections less than qlow50 censored at the lower level (0.007 µg/L). All routine detections or low-level detections greater than or equal to 0.007 µg/L were left uncensored.

Carbaryl had by far the most low-level detections of any of the pesticides considered. This is illustrated in figure A1–2, which shows the carbaryl data for site 10 (CHATT). There were 91 low-level detections for this site, compared to only 18 routine detections above maxLT-MDL (0.03 µg/L) and 29 routine nondetections (fig. A1–2*A*). Censoring at qlow50 (0.009 µg/L for this site; fig. A1–2*C*) resulted in a much larger number of uncensored values being used in the trend analysis than censoring at maxLT-MDL (fig. A1–2*B*). The site-specific limits used for censoring routine nondetections and low-level detections for each pesticide (qlow50, as described previously) are given in table A1–1.

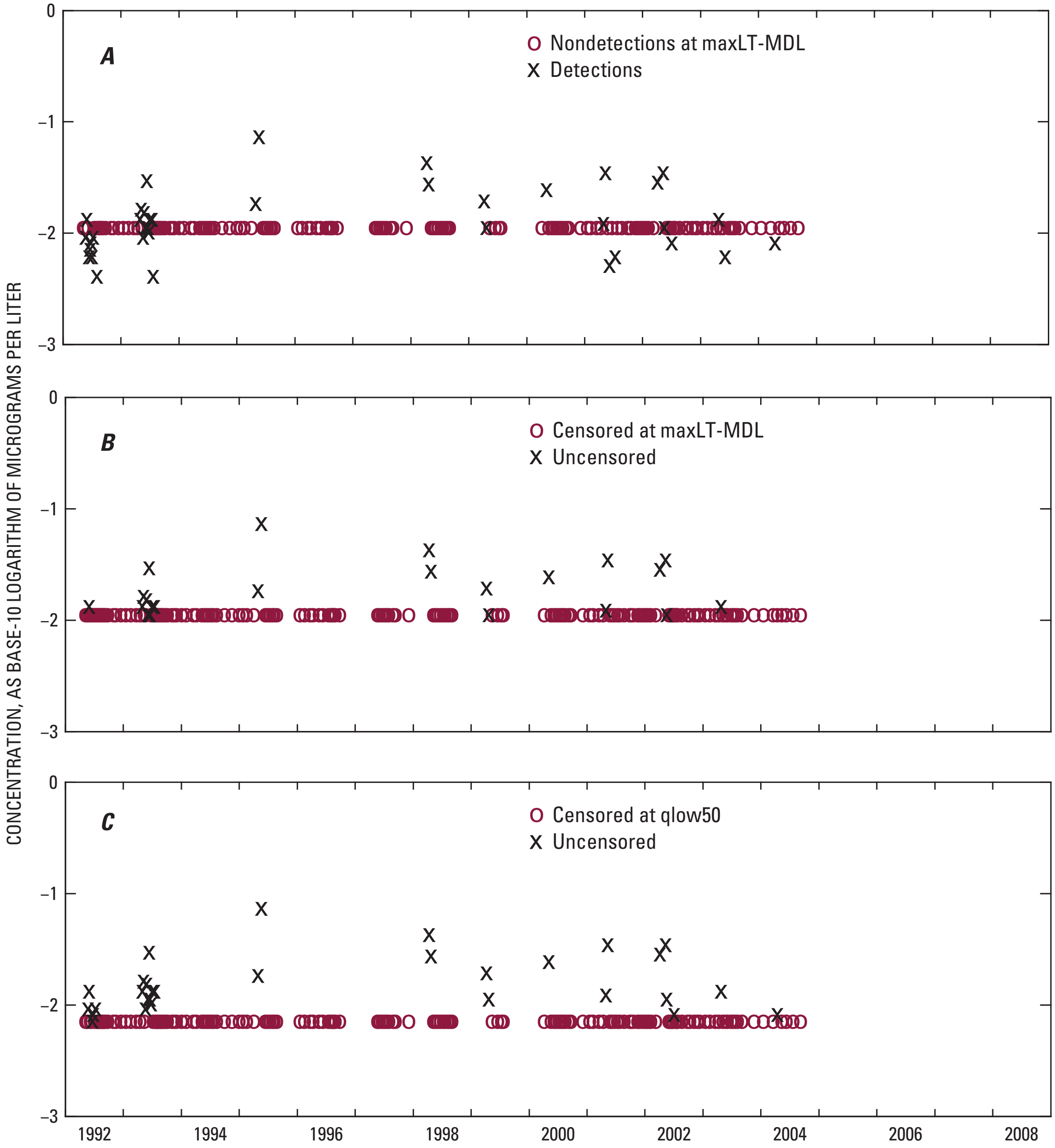


Figure A1–1. Pendimethalin concentration data for site 16 (LBUCK), 1992–2008. [(*A*) with routine nondetections censored at the maximum value of the long-term method detection level, maxLTMDL (0.011 µg/L); (*B*) with routine nondetections and low-level detections censored at maxLT-MDL; (*C*) with routine nondetections and low-level detections censored at the median value of the lowlevel detections, qlow50 (0.007 µg/L)]

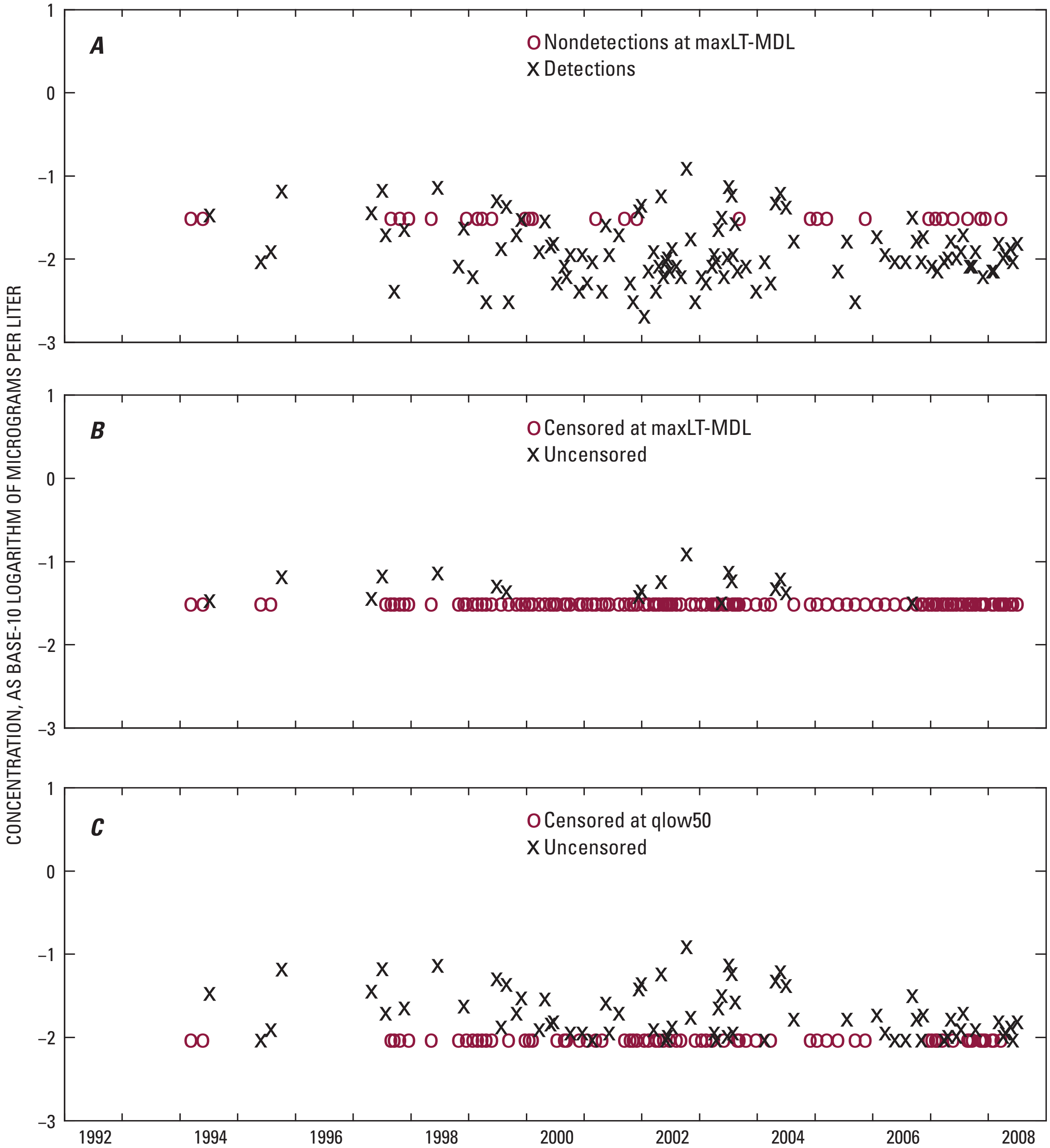


Figure A1–2. Carbaryl concentration data for site 10 (CHATT), 1992–2008. [(*A*) with routine nondetections censored at the maximum value of the long-term method detection level, maxLTMDL (0.03 µg/L); (*B*) with routine nondetections and low-level detections censored at maxLT-MDL; (*C*) with routine nondetections and low-level detections censored at the median value of the lowlevel detections, qlow50 (0.009 µg/L)]

Table A1–1. Censoring limits for each site-pesticide combination considered for trend analysis.

[qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination; maxLT-MDL, the maximum value of the long-term method detection level for water years 1994–2008; water year, the 1994 water year is the period from October 1, 1993 through September 30, 1994; DCPA, dimethyl tetrachloroterephthalate]

Site number (fig. 1)	Site short name	qlow50, in microgram per liter (maxLT-MDL given in parentheses below pesticide name)								
		Simazine (0.006)	Prometon (0.007)	Atrazine (0.004)	Deethylatrazine (0.007)	Metolachlor (0.006)	Trifluralin (0.005)	Pendimethalin (0.011)	Tebuthiuron (0.008)	Dacthal (DCPA) (0.002)
						Northeast				
1	ABERJ	0.0040	0.0060	0.0040	0.0040	0.0040	0.0010	0.0080	0.0055	0.0020
2	CHRLS	.0040	.0045	.0040	.0050	.0040	.0050	.0110	.0080	.0020
3	NRWLK	.0040	.0050	.0030	.0060	.0040	.0025	.0110	.0080	.0020
4	LISHA	.0060	.0040	.0040	.0070	.0050	.0050	.0110	.0080	.0020
5	BOUND	.0050	.0070	.0040	.0070	.0040	.0035	.0110	.0060	.0010
6	ACCOT	.0060	.0070	.0040	.0060	.0040	.0025	.0110	.0050	.0010
						South				
7	SWIFT	0.0060	0.0070	0.0040	0.0070	0.0040	0.0050	0.0110	0.0050	0.0020
8	GILLS	.0060	.0050	.0040	.0070	.0045	.0050	.0110	.0080	.0020
9	SOPEC	.0060	.0050	.0030	.0050	.0030	.0020	.0095	.0080	.0020
10	CHATT	.0060	.0050	.0040	.0050	.0030	.0050	.0110	.0080	.0020
11	CAHAB	.0060	.0050	.0040	.0070	.0050	.0020	.0110	.0040	.0020
12	FLTCH	.0060	.0070	.0040	.0070	.0060	.0030	.0110	.0080	.0020
13	WHITE	.0060	.0070	.0040	.0070	.0040	.0030	.0090	.0055	.0010
14	SALAD	.0050	.0070	.0040	.0070	.0030	.0050	.0110	.0080	.0020
						Midwest				
15	HOLES	0.0050	0.0070	0.0040	0.0070	0.0040	0.0030	0.0110	0.0080	0.0020
16	LBUCK	.0050	.0070	.0040	.0070	.0030	.0030	.0070	.0050	.0010
17	LINCO	.0060	.0070	.0040	.0070	.0040	.0050	.0110	.0080	.0020
18	CLINT	.0060	.0070	.0040	.0070	.0040	.0030	.0110	.0080	.0010
19	SHING	.0060	.0070	.0040	.0070	.0040	.0020	.0110	.0080	.0010
20	SALTC	.0060	.0070	.0040	.0070	.0040	.0020	.0110	.0080	.0020
21	DPLAI	.0060	.0070	.0040	.0070	.0060	.0040	.0110	.0080	.0020
						West				
22	LCOTT	0.0035	0.0060	0.0040	0.0055	0.0060	0.0020	0.0110	0.0080	0.0020
23	WARMC	.0050	.0040	.0040	.0070	.0060	.0050	.0110	.0030	.0020
24	SANTA	.0060	.0070	.0040	.0070	.0050	.0050	.0110	.0080	.0020
25	ARCAD	.0060	.0070	.0040	.0070	.0050	.0030	.0110	.0080	.0020
26	THORN	.0040	.0070	.0030	.0070	.0060	.0050	.0110	.0080	.0020
27	FANNO	.0060	.0060	.0040	.0060	.0040	.0030	.0110	.0050	.0020

Table A1–1. Censoring limits for each site-pesticide combination considered for trend analysis.—Continued

[qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination; maxLT-MDL, the maximum value of the long-term method detection level for water years 1994–2008; water year, the 1994 water year is the period from October 1, 1993 through September 30, 1994; DCPA, dimethyl tetrachloroterephthalate]

Site number (fig. 1)	Site short name	qlow50, in microgram per liter (maxLT-MDL given in parentheses below pesticide name)						
		Chlorpyrifos (0.003)	Malathion (0.014)	Diazinon (0.003)	Fipronil (0.01)	Fipronil sulfide (0.006)	Desulfinylfipronil (0.006)	Carbaryl (0.03)
				Northeast				
1	ABERJ	0.0030	0.0140	0.0030	0.0100	0.0060	0.0060	0.0090
2	CHRLS	.0030	.0140	.0030	.0065	.0050	.0045	.0080
3	NRWLK	.0030	.0140	.0020	.0100	.0060	.0060	.0105
4	LISHA	.0030	.0140	.0030	.0100	.0060	.0060	.0080
5	BOUND	.0030	.0100	.0030	.0070	.0060	.0050	.0130
6	ACCOT	.0030	.0095	.0030	.0090	.0060	.0040	.0110
				South				
7	SWIFT	0.0030	0.0140	0.0030	0.0080	0.0050	0.0050	0.0090
8	GILLS	.0030	.0080	.0030	.0070	.0060	.0050	.0080
9	SOPEC	.0030	.0090	.0030	.0070	.0040	.0050	.0090
10	CHATT	.0030	.0075	.0030	.0080	.0050	.0050	.0090
11	CAHAB	.0030	.0140	.0030	.0070	.0050	.0045	.0070
12	FLTCH	.0030	.0140	.0030	.0100	.0060	.0060	.0130
13	WHITE	.0030	.0085	.0030	.0080	.0030	.0050	.0120
14	SALAD	.0030	.0070	.0030	.0060	.0040	.0050	.0100
				Midwest				
15	HOLES	0.0030	0.0090	0.0030	0.0100	0.0060	0.0060	0.0070
16	LBUCK	.0030	.0095	.0030	.0100	.0060	.0060	.0110
17	LINCO	.0030	.0140	.0030	.0100	.0060	.0050	.0100
18	CLINT	.0030	.0140	.0030	.0060	.0060	.0060	.0080
19	SHING	.0030	.0140	.0030	.0070	.0050	.0040	.0120
20	SALTC	.0030	.0140	.0030	.0080	.0060	.0045	.0095
21	DPLAI	.0030	.0140	.0030	.0100	.0060	.0060	.0120
				West				
22	LCOTT	0.0030	0.0070	0.0030	0.0100	0.0060	0.0060	0.0085
23	WARMC	.0030	.0140	.0030	.0100	.0060	.0060	.0065
24	SANTA	.0030	.0140	.0030	.0060	.0050	.0050	.0090
25	ARCAD	.0030	.0100	.0030	.0100	.0050	.0060	.0165
26	THORN	.0030	.0140	.0030	.0050	.0060	.0040	.0120
27	FANNO	.0030	.0140	.0030	.0070	.0050	.0040	.0120

Appendix 2. Examination of Low-Level Pesticide Detections in Selected National Water-Quality Assessment Program Groundwater Samples through Time

This appendix describes the first of two approaches for assessing trends in detection sensitivity for the pesticides summarized in this report. In brief, the frequency and magnitude of low-level detections in groundwater samples from selected NAWQA wells were plotted as a function of time for water years 1994 to 2005. Trends in detection sensitivity were assessed by visually examining the timeseries to determine if monotonic trends in the frequency of low-level detections or in the magnitude of concentrations detected were apparent.

Hypothesis

Improvements to instrumentation might have resulted in increased detection sensitivity through time. Increased detection sensitivity is expected to cause an increase in the frequency of low-level detections and a decrease in the magnitude of low-level concentrations.

Approach

Pesticide concentrations in groundwater are expected to change slowly. An examination of resampled wells might show evidence of increased detection sensitivity through time. Only wells in groundwater networks that were used to summarize the national occurrence of pesticides (Gilliom and others, 2006, appendix 5b) were used for assessing detection sensitivity. Three periods were defined: 1993–1997, 1998–2001, and 2002–2006. Wells were used in the analysis if water samples were analyzed for pesticides in at least two of the three periods. If a well had multiple samples in a period, one sample was randomly selected to represent the period. “Low-level detections” were defined as pesticide detections at concentrations less than the maximum value of the long-term method detection level for water years 1994–2006 (maxLT-MDL; Martin, 2009, table 1). A 3-year window was used to smooth the detection statistics through time (for example, statistics plotted at 1994 include data for 1993, 1994, and 1995). Low-level detection frequency was calculated as the number of water samples having low-level detections divided by the total number of water samples and expressed as a percentage. Confidence limits for the frequency of low-level detections were calculated using the binomial method presented in Hahn and Meeker (1991, p. 103–108). The magnitudes of the low-level detections were plotted as boxplots (boxplots are explained in the first figure, fig. A2–1, of the appendix).

Results

The frequency and magnitude of low-level detections in groundwater samples from selected NAWQA wells are shown in figures A2–2 to A2–17. Most pesticides had very few low-level detections. Simazine, prometon, atrazine, deethylatrazine, and metolachlor generally had more than 10 low-level detections per 3-year time window.

Simazine (fig. A2–2) exhibited a general increase in the frequency of low-level detections for the period 1994 to 2005, but confidence limits indicated that the change in frequency was not statistically significant. The median concentrations for low-level simazine detections tended to increase through time—a finding contrary to the expectation of decreasing low-level concentrations because of increasing detection sensitivity. Atrazine (fig. A2–4) had a general increase in the frequency of low-level detections for the period 1994–1996 and a general decrease in the frequency for the period 1996–2005—a pattern inconsistent with the expectation of a monotonic trend of an increasing frequency of low-level detections through time. The median concentrations for low-level atrazine detections were relatively stable through time. The frequency of low-level detections for prometon, deethylatrazine, and metolachlor varied through time and the median concentrations for low-level detections were either stable through time or showed a general pattern of increasing concentrations (deethylatrazine, fig. A2–5).

Conclusion

An examination of low-level detections in resampled wells did not support the hypothesis that improvements to instrumentation have resulted in increased detection sensitivity through time.

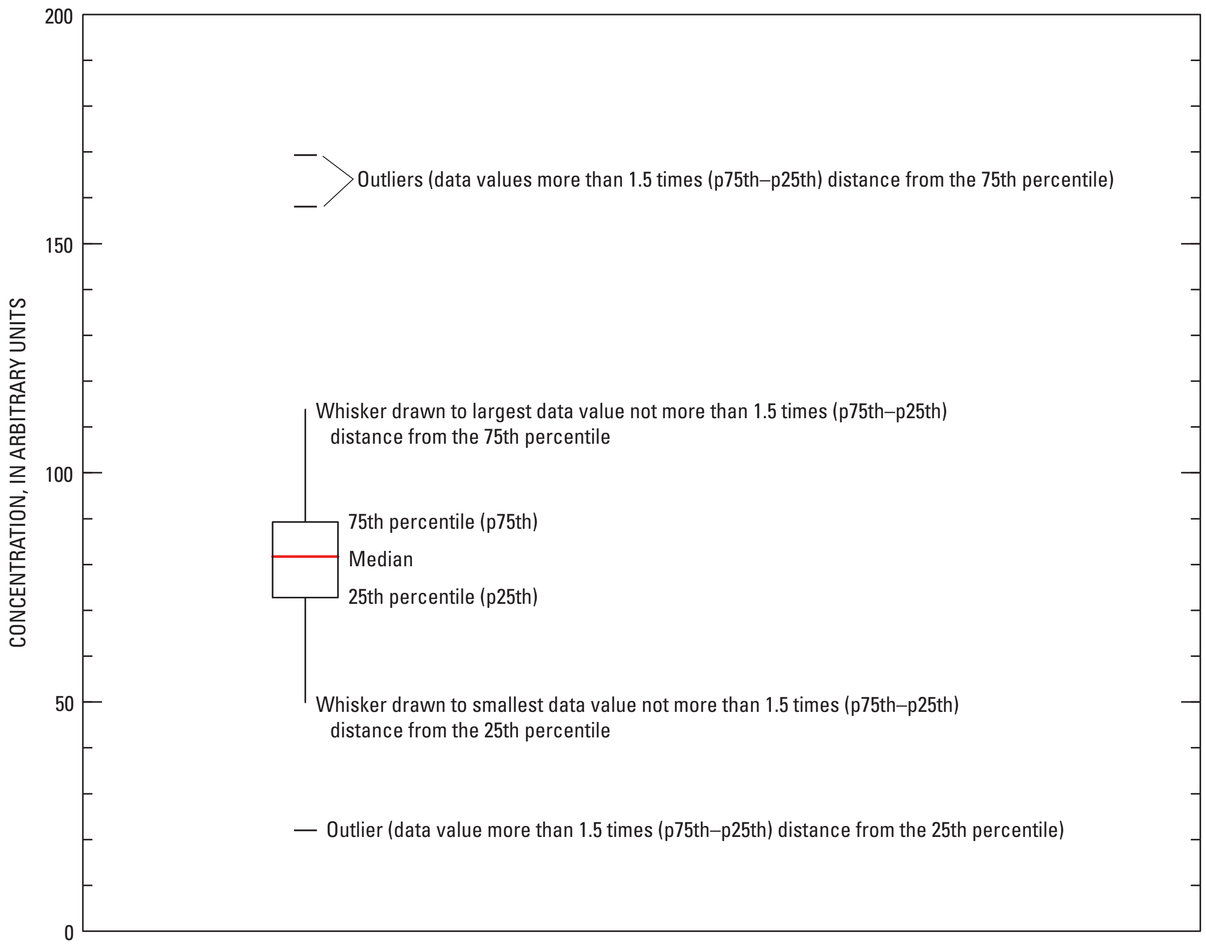


Figure A2–1. Explanation of a boxplot that is used to depict the distribution of concentrations.

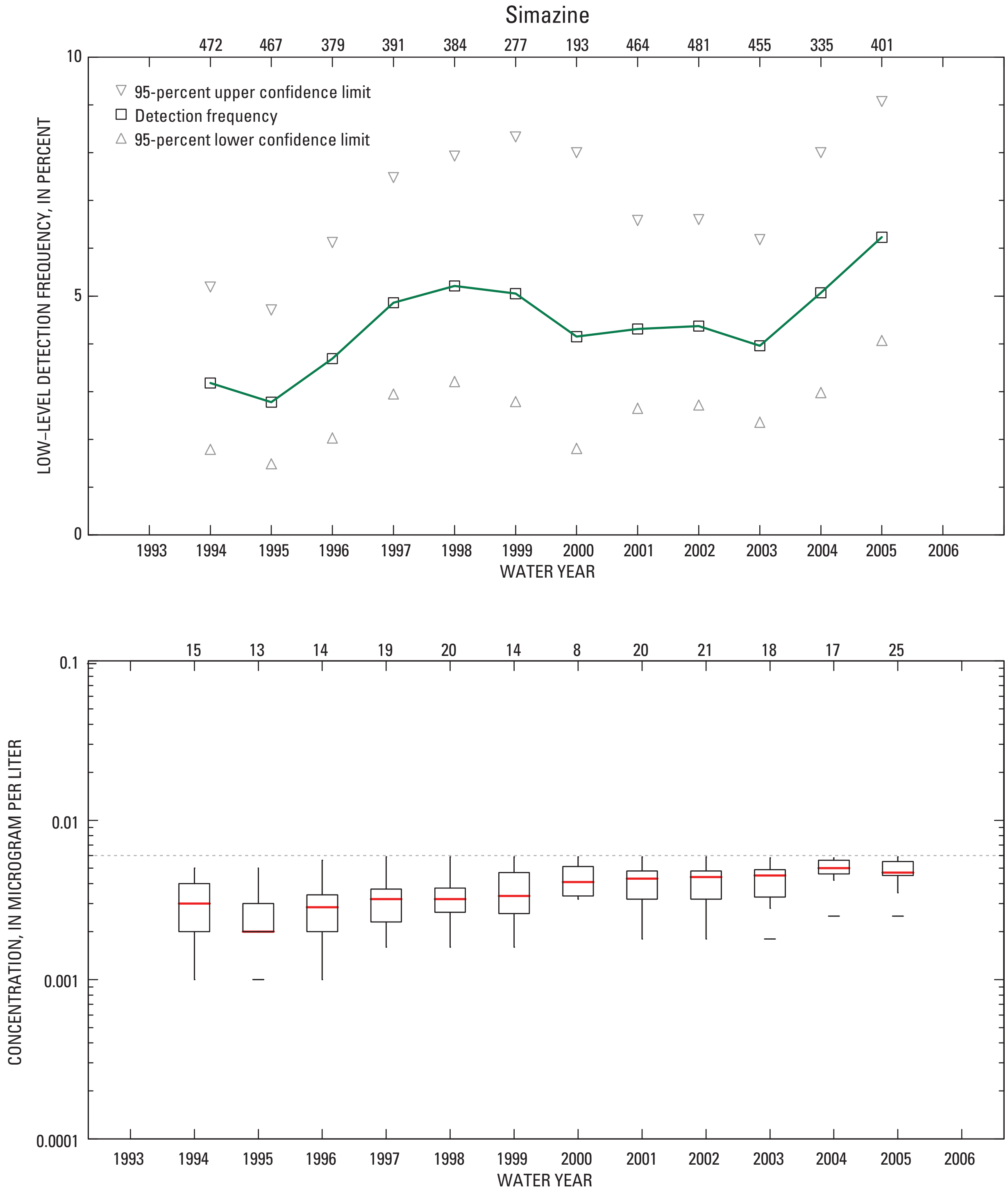


Figure A2–2. Detection frequency and concentration of simazine detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

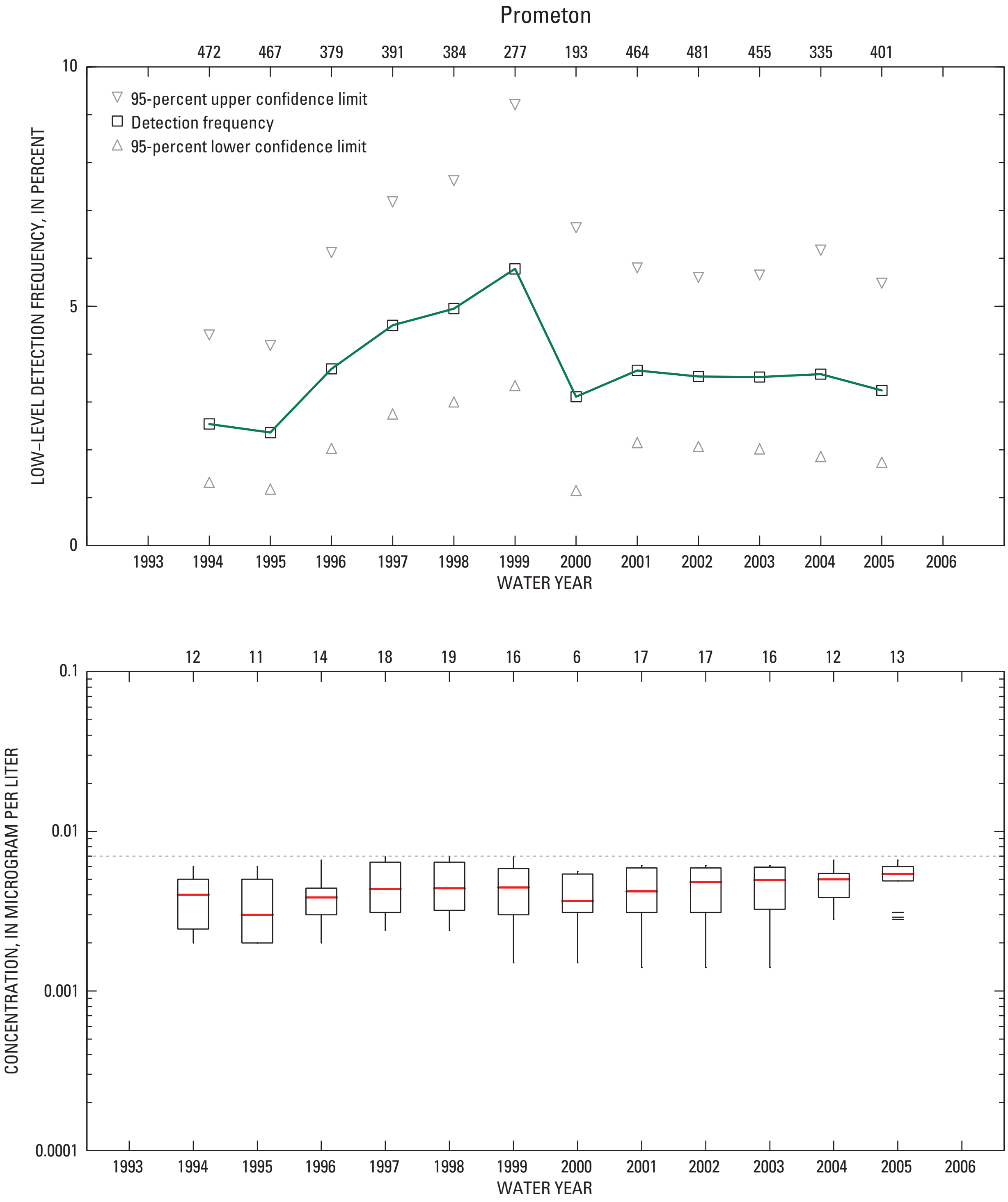


Figure A2–3. Detection frequency and concentration of prometon detected at concentrations less than the maximum value of the long-term method detection level for 1994–2006 (0.007 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water-Quality Assessment Program. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low-level detections is shown at the top of the second panel. Boxplots are explained in figure A2-1.

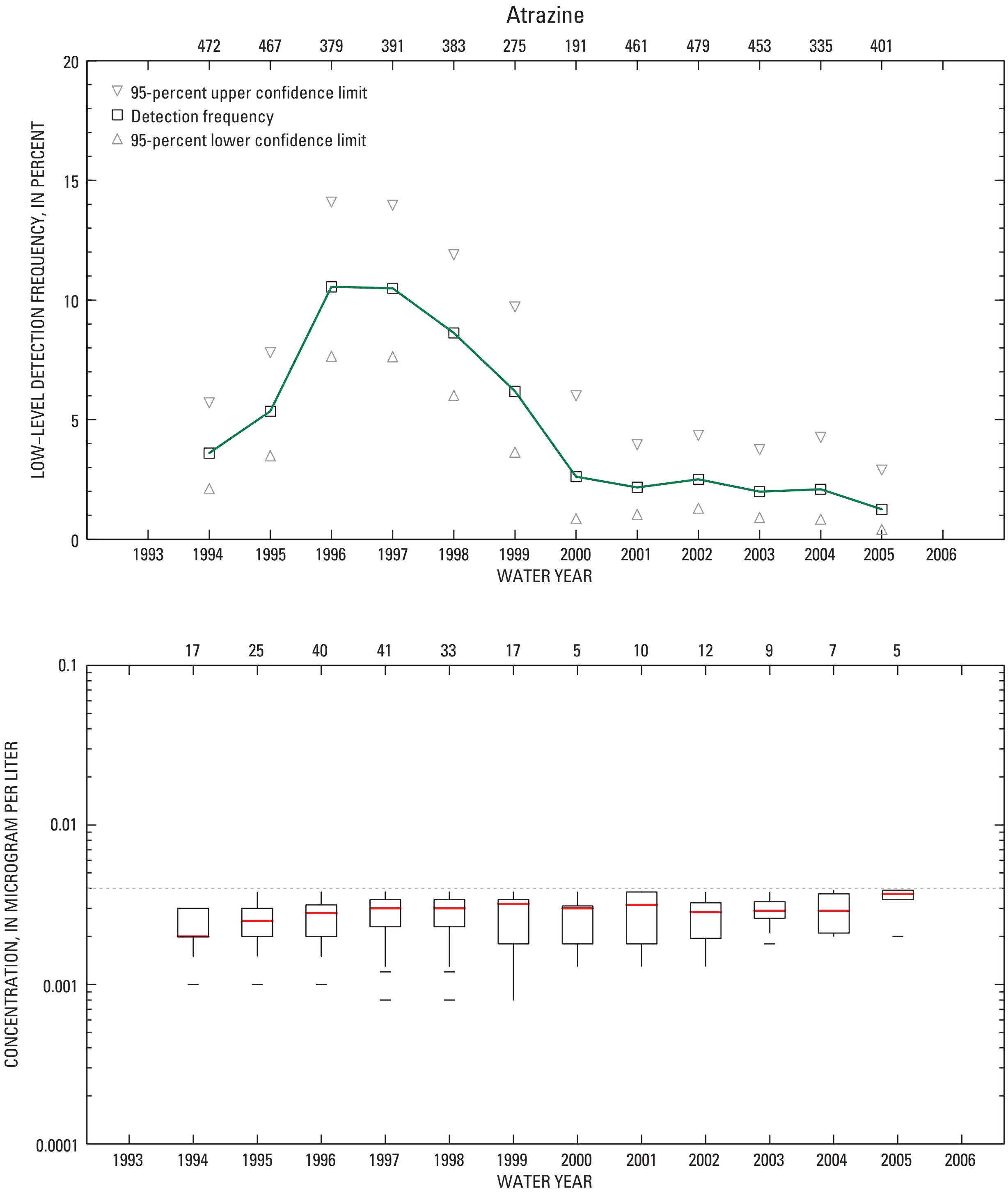


Figure A2–4. Detection frequency and concentration of atrazine detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.004 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

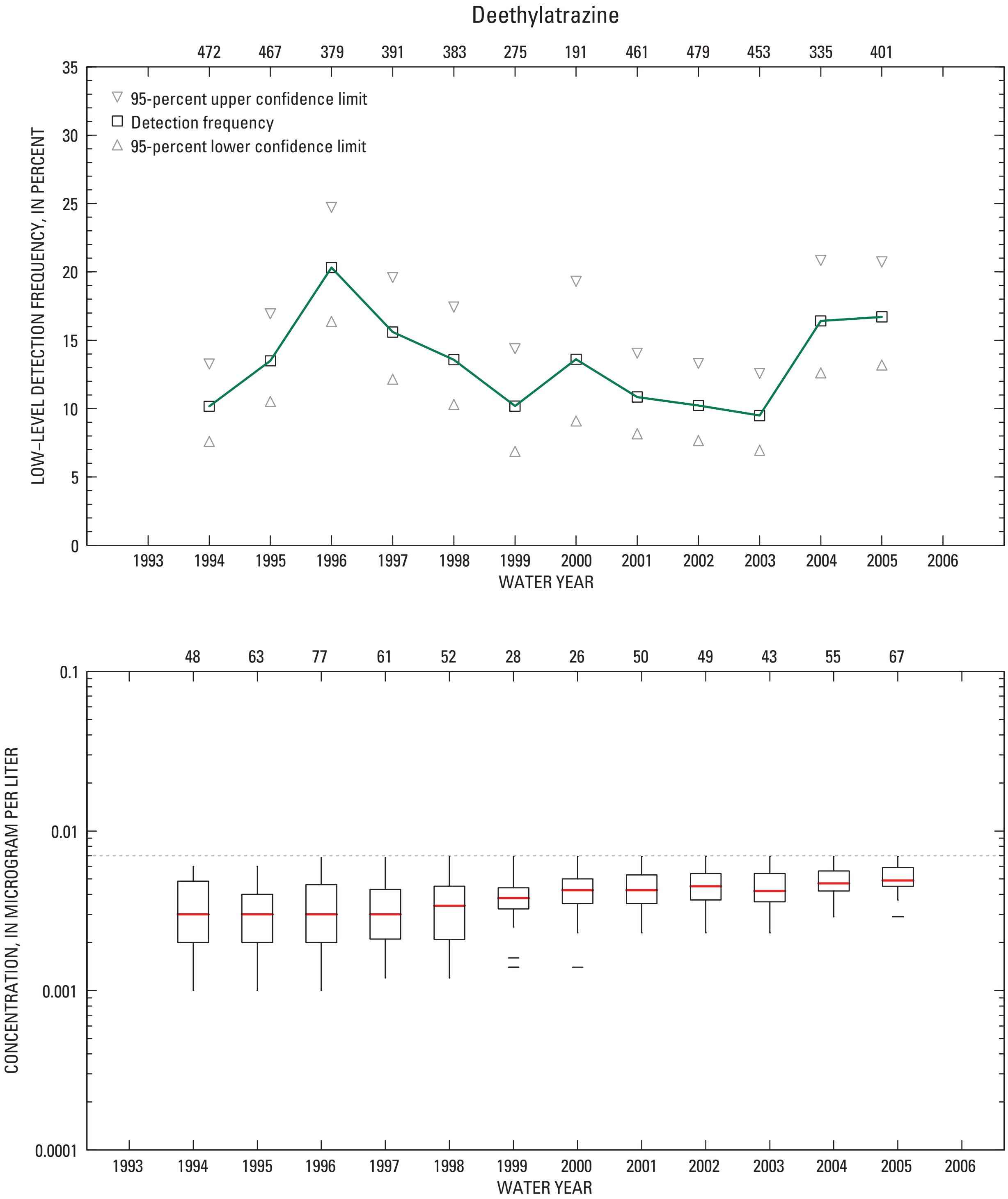


Figure A2–5. Detection frequency and concentration of deethylatrazine detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.007 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

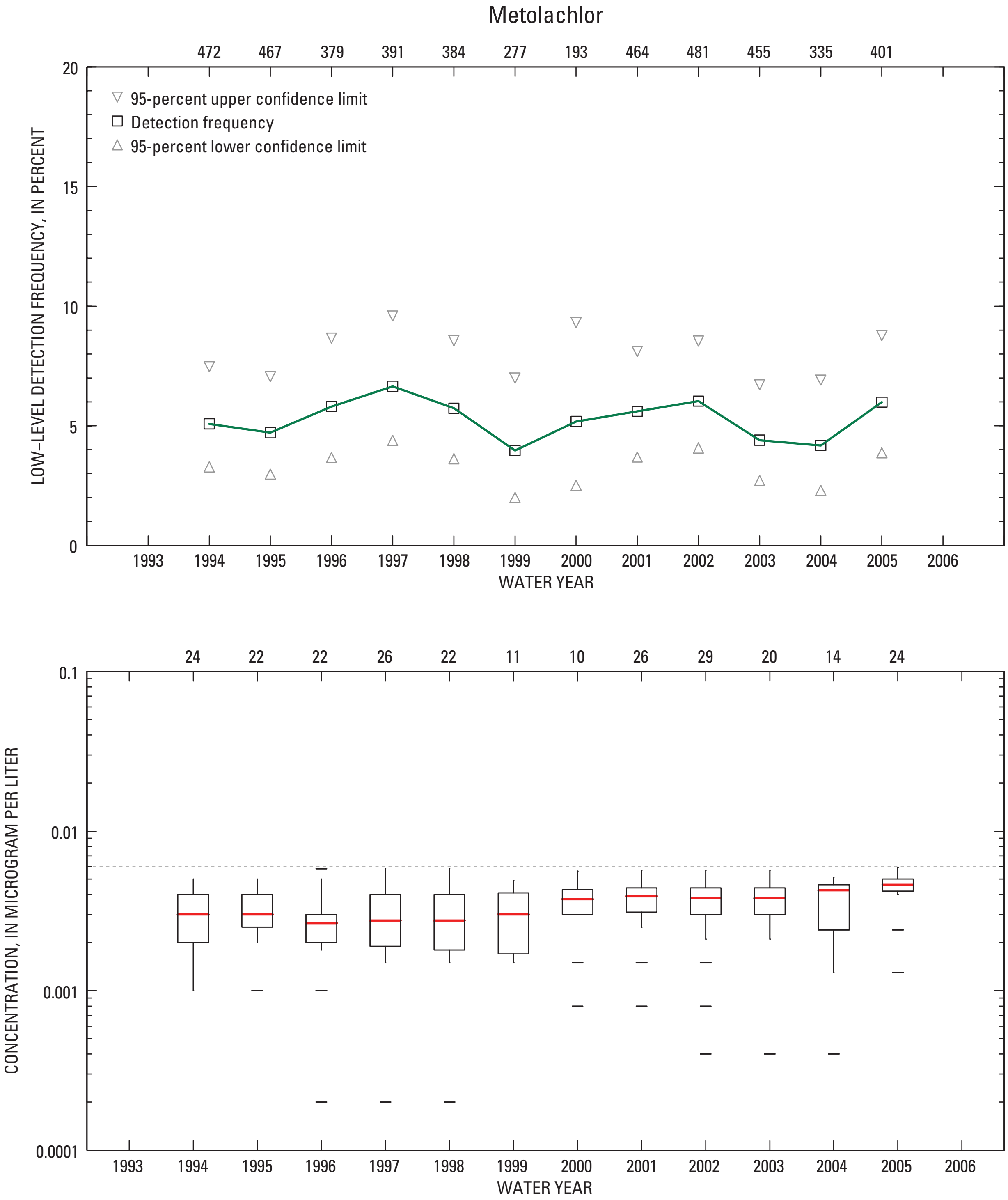


Figure A2–6. Detection frequency and concentration of metolachlor detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

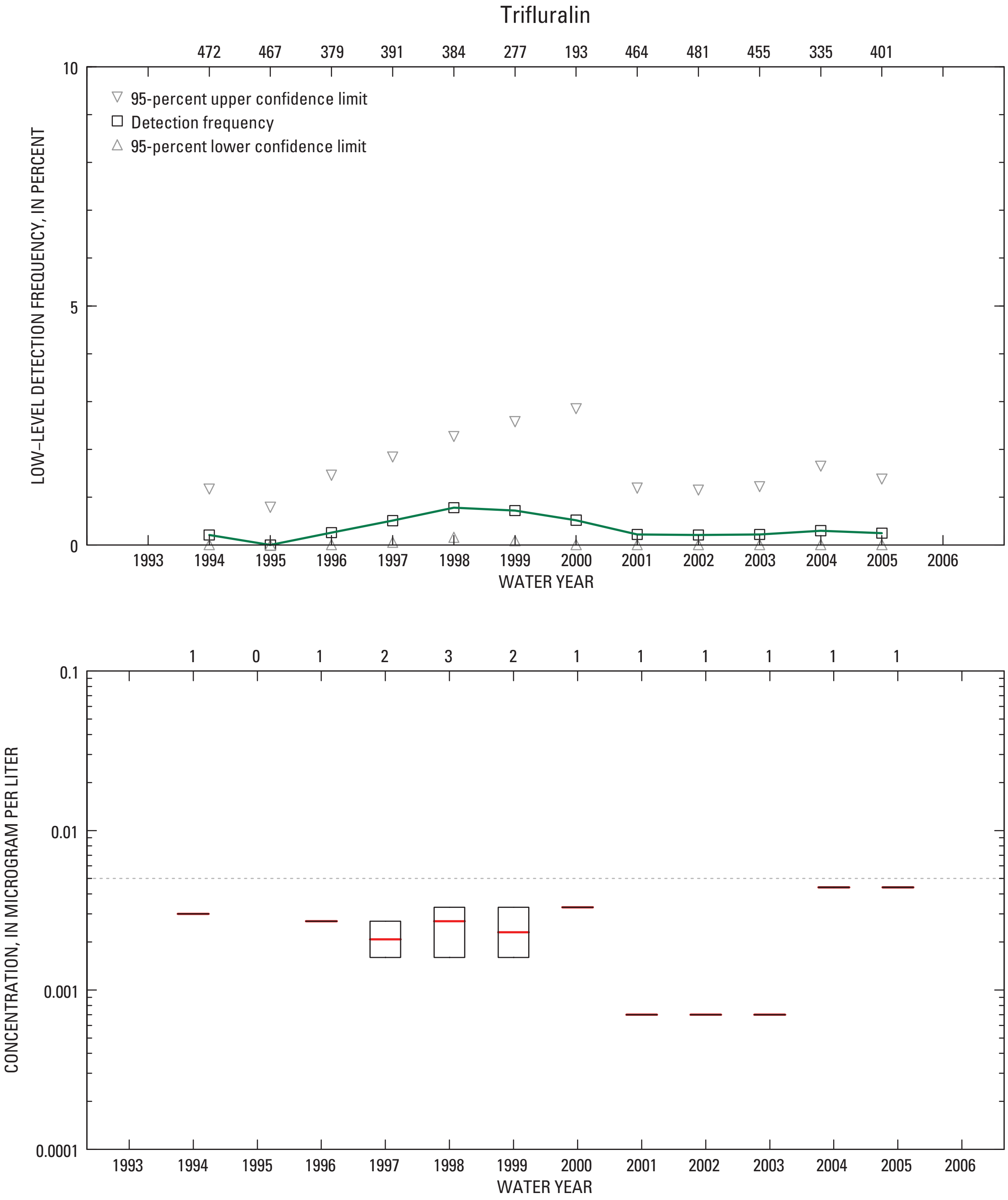


Figure A2–7. Detection frequency and concentration of trifluralin detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.005 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

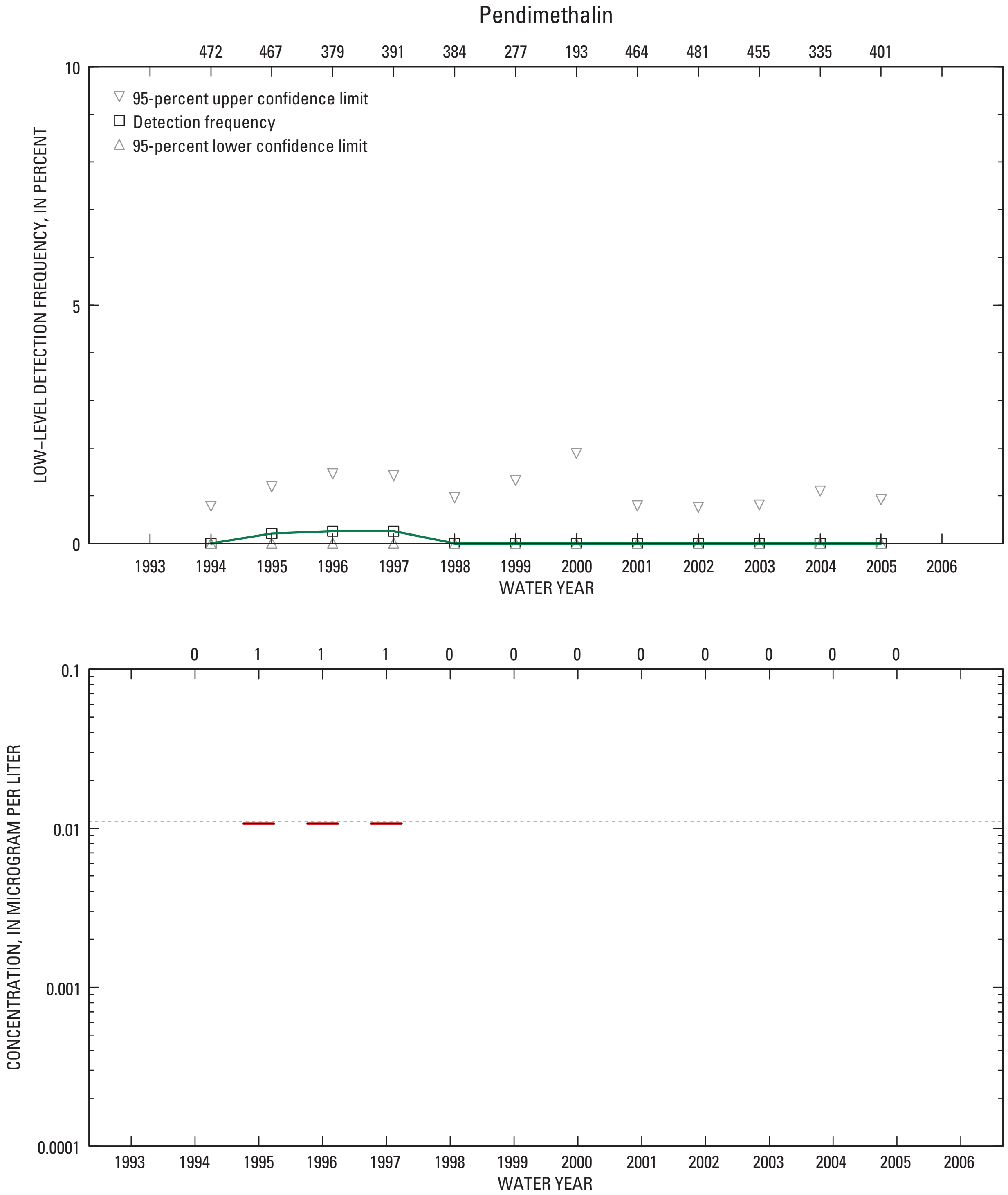


Figure A2–8. Detection frequency and concentration of pendimethalin detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.011 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

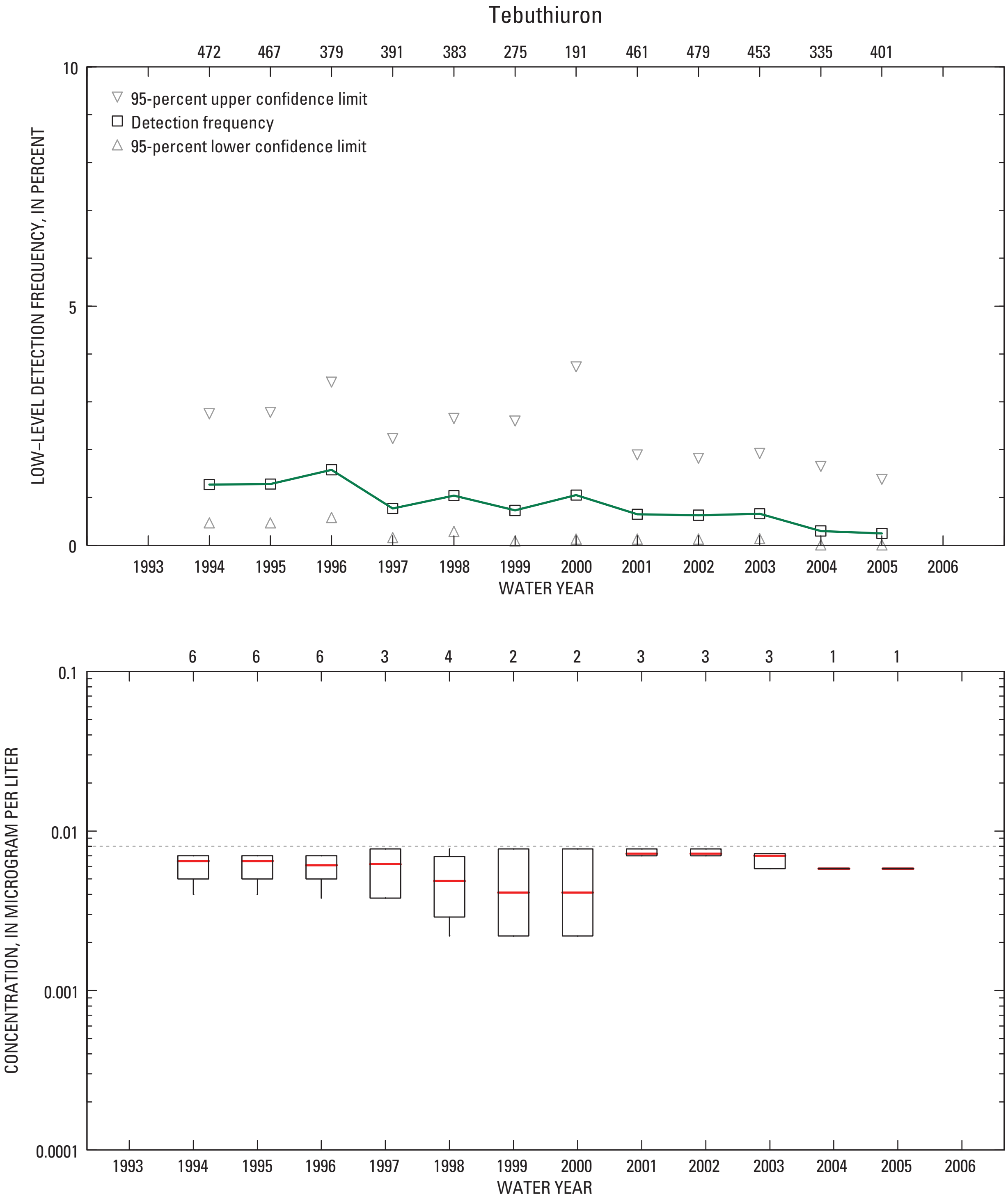


Figure A2–9. Detection frequency and concentration of tebuthiuron detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.008 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

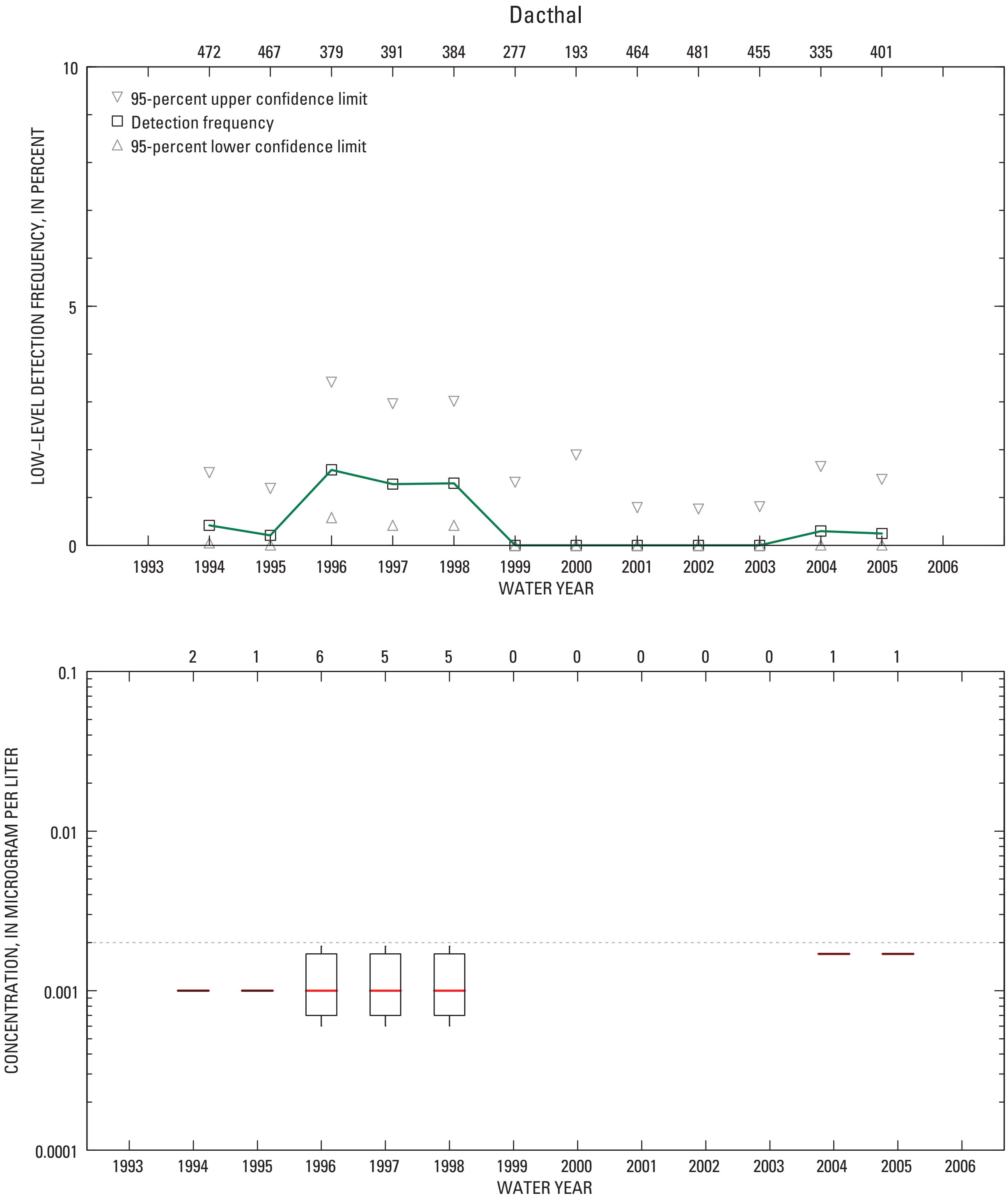


Figure A2–10. Detection frequency and concentration of Dacthal detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.002 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

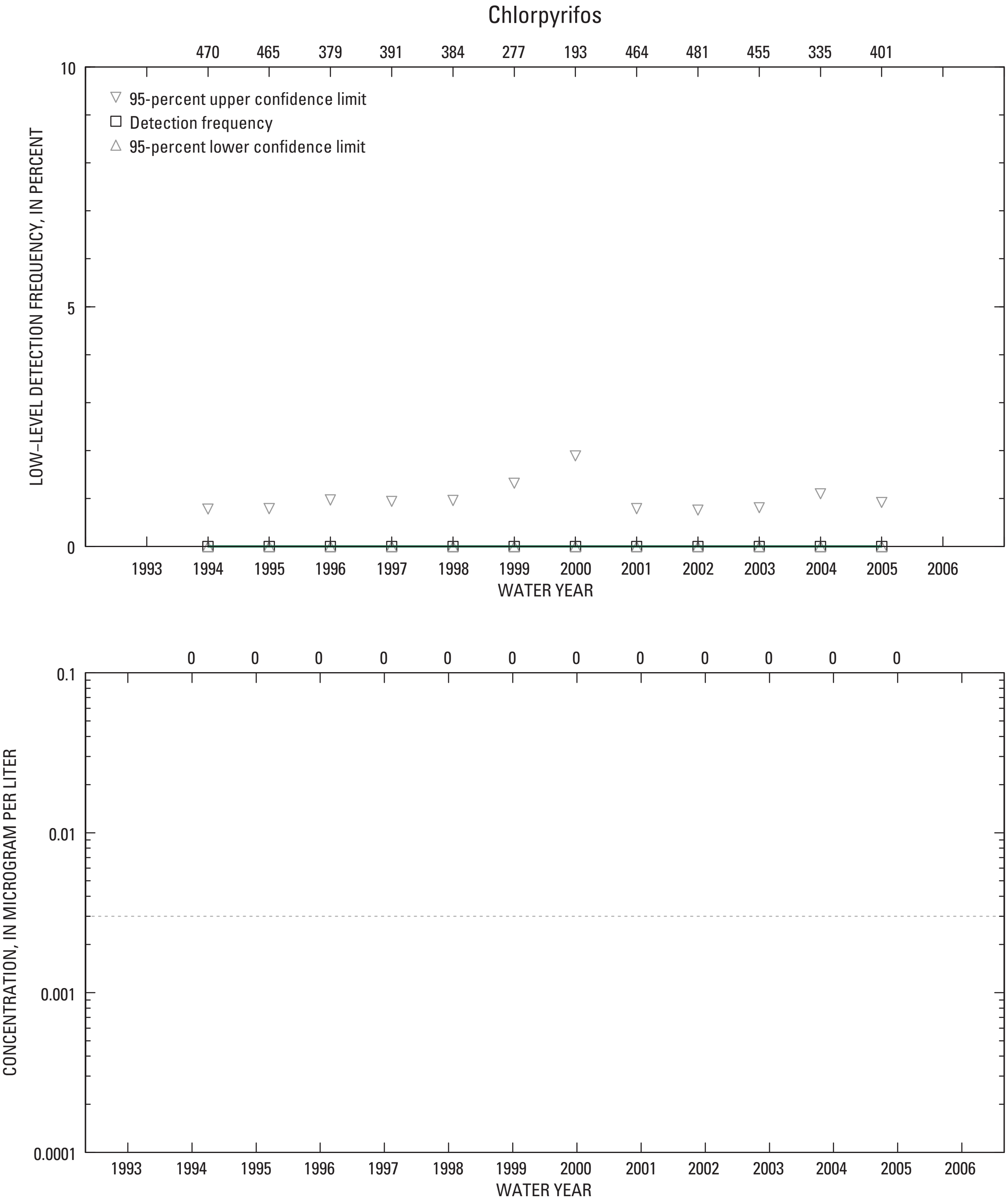


Figure A2–11. Detection frequency and concentration of chlorpyrifos detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.003 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater easurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

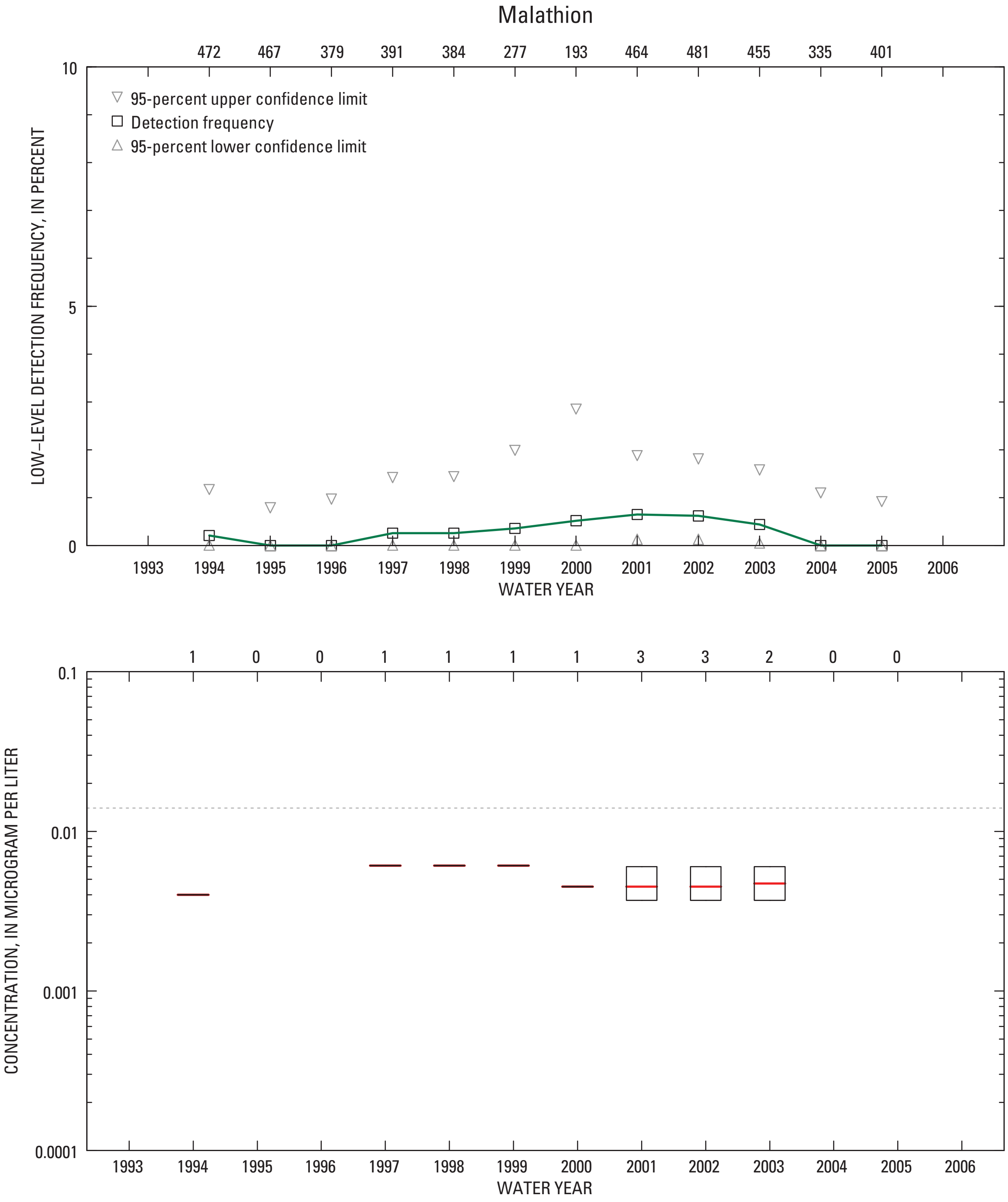


Figure A2–12. Detection frequency and concentration of malathion detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.014 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

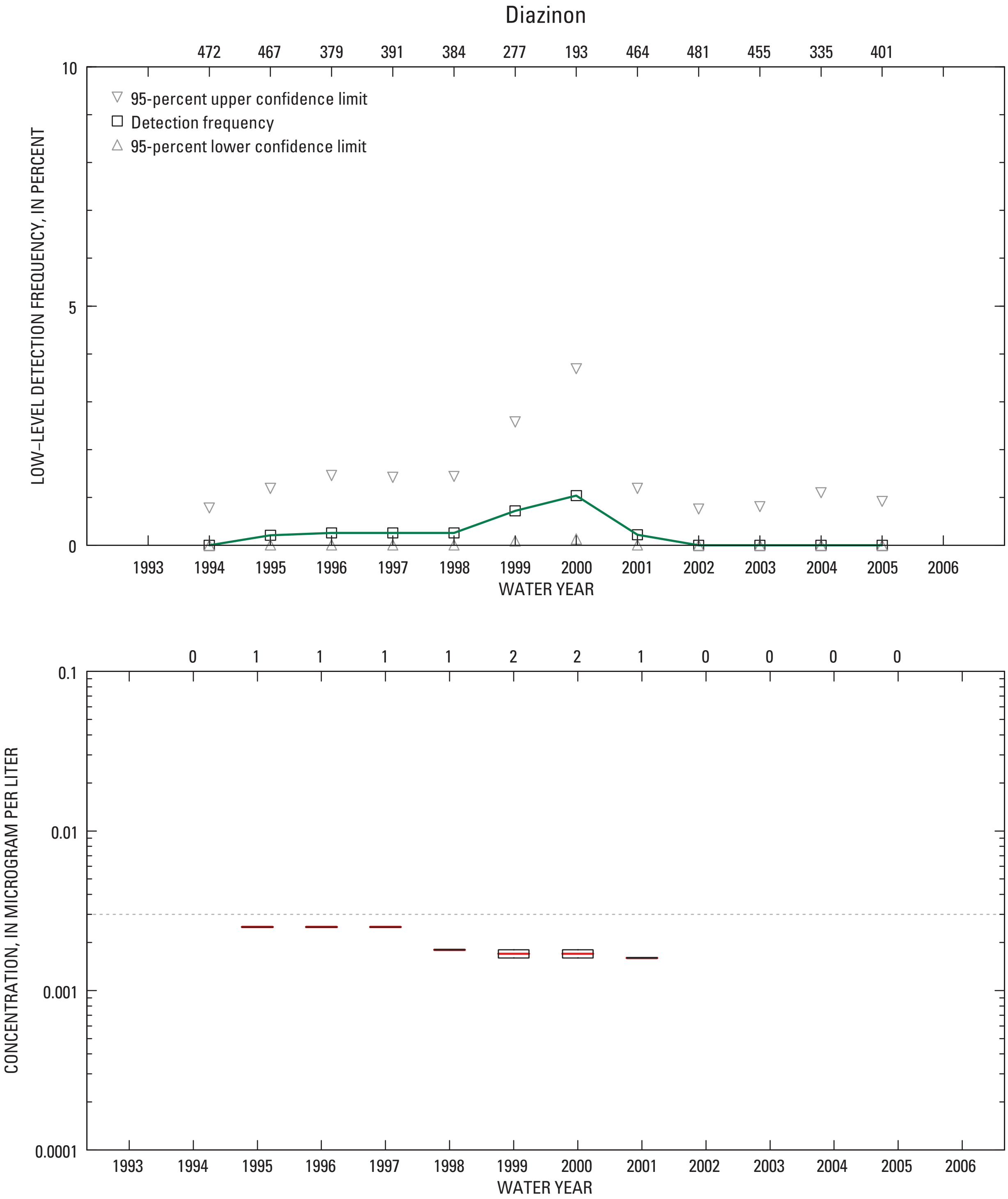


Figure A2–13. Detection frequency and concentration of diazinon detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.003 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

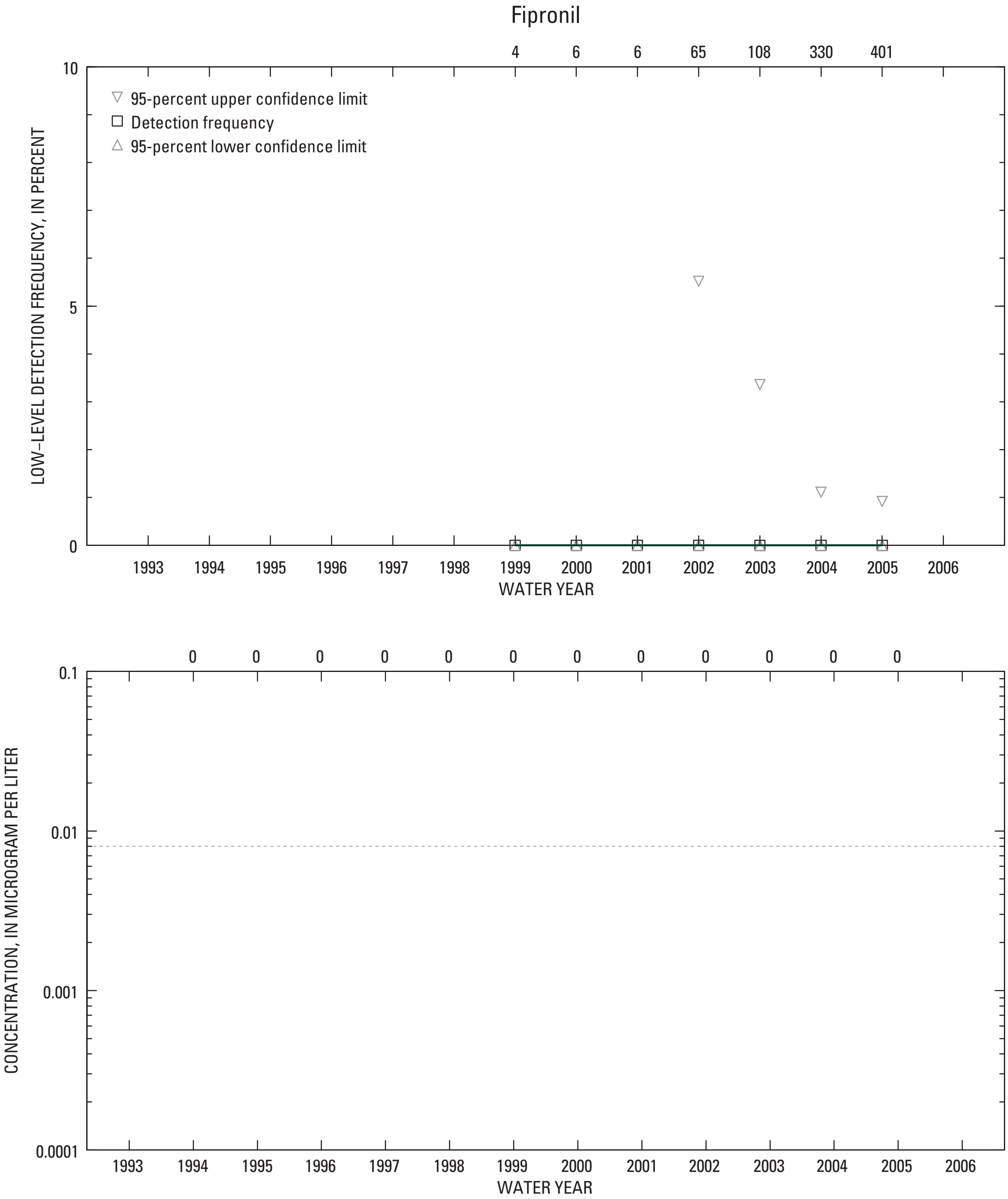


Figure A2–14. Detection frequency and concentration of fipronil detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.008 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

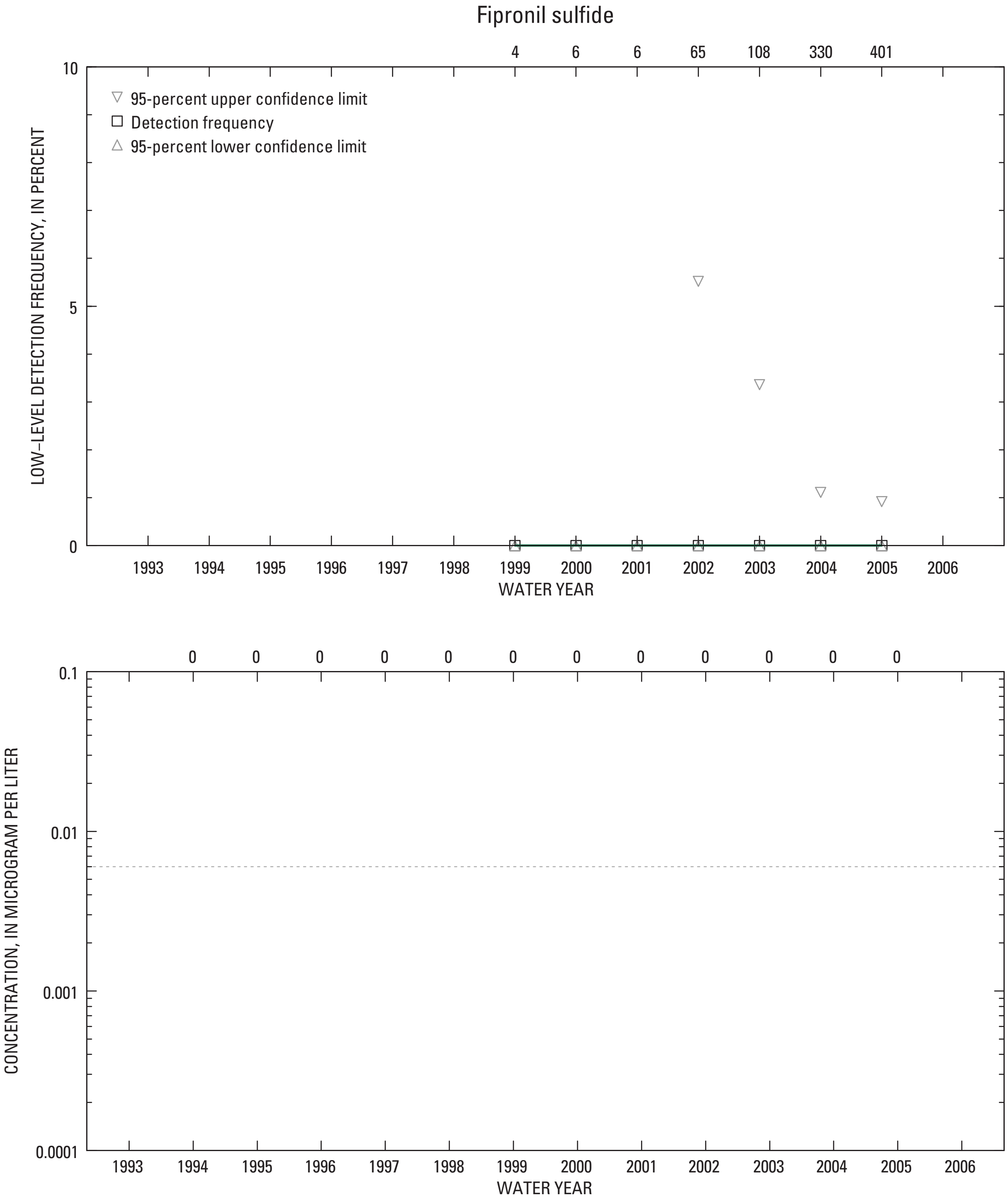


Figure A2–15. Detection frequency and concentration of fipronil sulfide detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

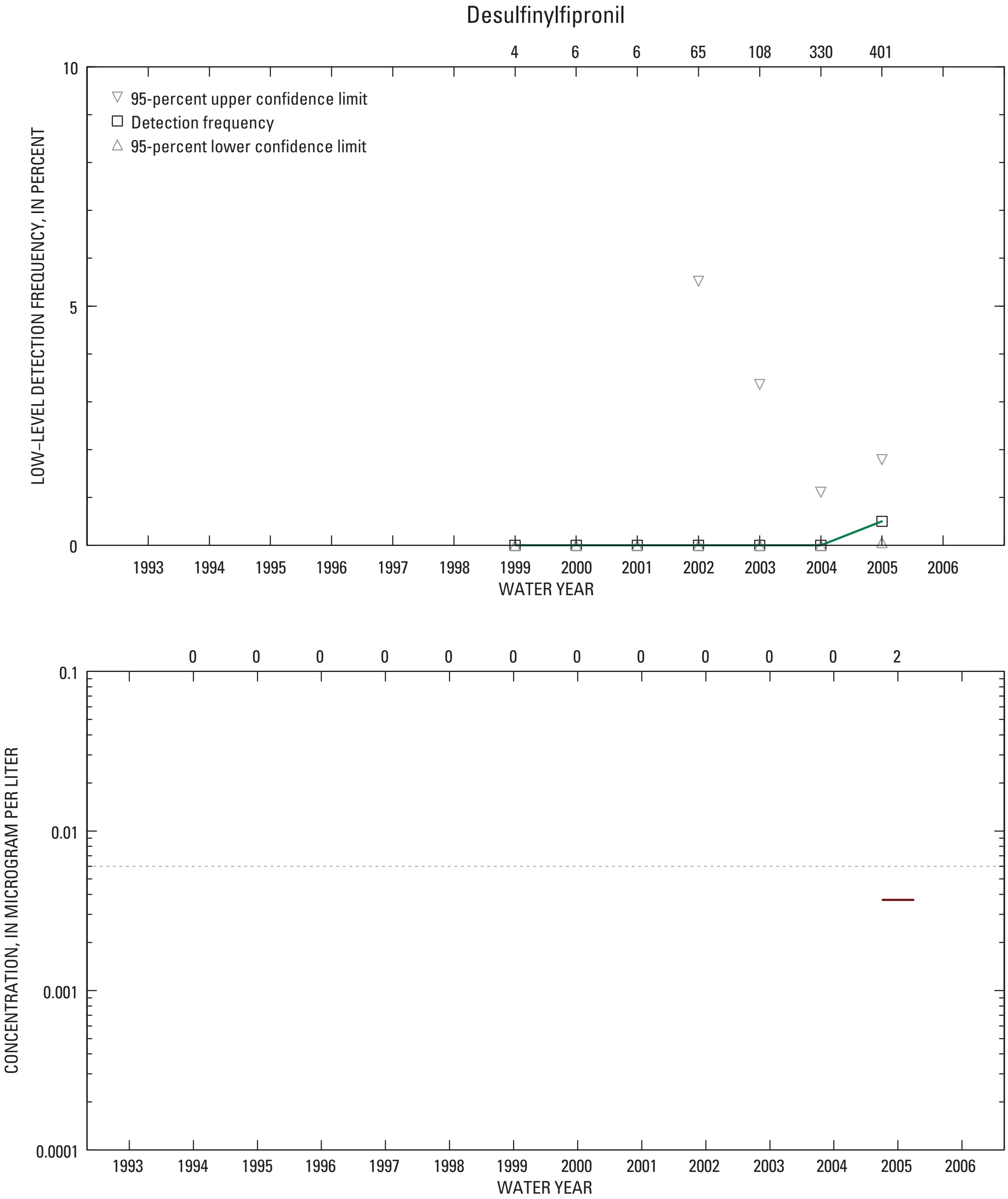


Figure A2–16. Detection frequency and concentration of desulfinylfipronil detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

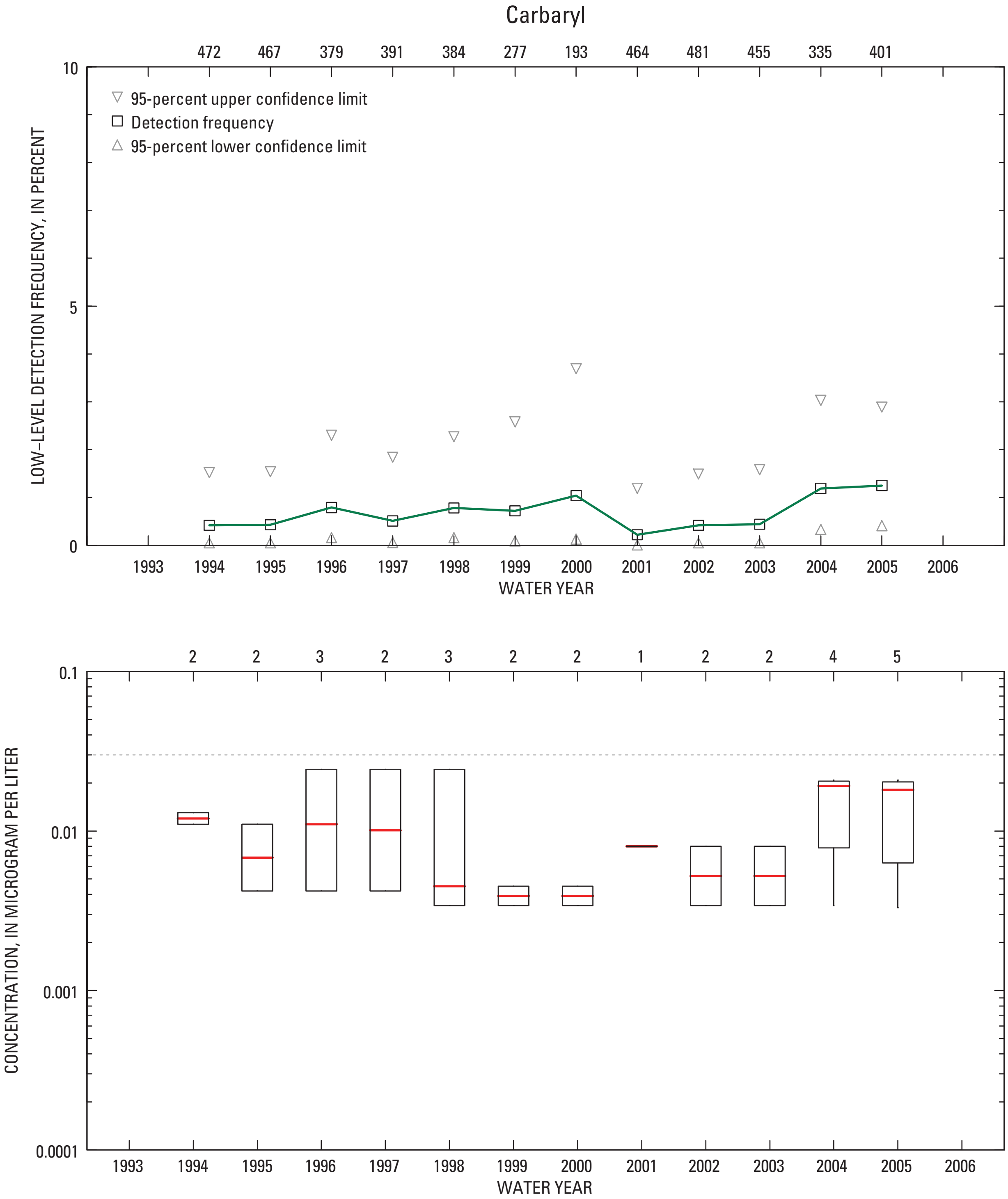


Figure A2–17. Detection frequency and concentration of carbaryl detected at concentrations less than the maximum value of the long–term method detection level for 1994–2006 (0.03 microgram per liter, and shown as a dashed line in the second panel) at selected wells sampled for the National Water–Quality Assessment Program. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of groundwater measurements is shown at the top of the first panel. The number of low–level detections is shown at the top of the second panel. Boxplots are explained in figure A2–1.

Appendix 3. Examination of the Consistency of Low-Level Pesticide Detections in Duplicate Water Samples through Time

This appendix describes the second of two approaches for assessing trends in detection sensitivity for the pesticides summarized in this report. The consistency and magnitude of low-level detections in field-collected, duplicate quality-control (QC) water samples were plotted as a function of time for water years 1994 to 2005. Trends in detection sensitivity were assessed by visually examining the timeseries to determine if monotonic trends in the consistency of low-level detections or in the magnitude of concentrations detected were apparent.

Hypothesis

Improvements to instrumentation could have resulted in increased detection sensitivity through time. Increased detection sensitivity is expected to cause an increase in the consistency of low-level detections in duplicate water samples and a decrease in the magnitude of low-level concentrations.

Approach

Field-collected, duplicate QC stream-water and groundwater samples are routinely collected by field crews of the National Water-Quality Assessment (NAWQA) Program to measure the variability of pesticide measurements (Koterba and others, 1995; Mueller and others, 1997; Martin, 2002). An examination of the consistency of low-level detections in duplicate water samples could show evidence of increased detection sensitivity through time.

NAWQA water-quality data were provided by NAWQA Data Warehouse data managers (Nathaniel L. Booth, U.S. Geological Survey, written commun., September 22, 2006). Duplicate samples were matched by sampling site identification number, date, and other codes stored with the data. Sites and dates with more than one possible match were reviewed to ensure the appropriateness of the match. “Low-level detections” were defined as pesticide detections at concentrations less than the maximum value of the long-term method detection level for water years 1994–2006 (maxLT-MDL; Martin, 2009, table 1). For each pesticide, only pairs of duplicates where the pesticide was detected at low levels in one or both of the duplicates were used in the analysis. Consistency of low-level detection was calculated as the number of duplicate pairs where the pesticide was detected in both duplicates divided by the number of duplicate pairs where the pesticide was detected in one or both of the duplicates and was expressed as a percentage. A 3-year window was used to smooth the consistency of detection statistics through time (for example, statistics plotted at 1994 include data for 1993, 1994, and 1995). Confidence limits for the consistency of low-level detections were calculated using the binomial method presented in Hahn and Meeker (1991, p. 103–108). The magnitudes of the low-level detections are plotted as boxplots (boxplots are explained in the first figure, fig. A3–1, of this appendix).

Results

The consistency and magnitude of low-level detections in duplicate water samples are shown in figures A3–2 to A3–17 of this appendix. Most pesticides had relatively stable low-level detection consistency for the period 1994–2005. The temporal pattern of detection consistency was highly variable for chlorpyrifos (fig. A3–11), diazinon (fig. A3–13), and fipronil sulfide (fig. A3–15), most likely because many of the years had a small number of duplicate pairs. Simazine (fig. A3–2), atrazine (fig. A3–4), metolachlor (fig. A3–6), trifluralin (fig. A3–7), tebuthiuron (fig. A3–9), and carbaryl (fig. A3–17) exhibited similar temporal patterns in detection consistency where consistency of low-level detections was lowest during 1994 or 1995 and was higher in later years. Confidence limits on the consistency of detection, however, indicated that the change in consistency was not statistically significant for most of these pesticides. On the basis of non-overlapping 95-percent confidence limits on the consistency of detection, detection consistency for tebuthiuron was statistically significantly higher in 2003 than in 1994 or 1995 and for carbaryl was statistically significantly higher in 2002, 2003, and 2004 than in 1994 or 1995.

The median concentrations for low-level detections were relatively stable or tended to increase through time—a finding contrary to the expectation of decreasing low-level concentrations because of increasing detection sensitivity. Concentrations of low-level detections for tebuthiuron and carbaryl tended to decrease through time—a finding consistent with the expectation of decreasing low-level concentrations because of increasing detection sensitivity.

Conclusion

An examination of low-level detections in field-collected, duplicate QC water samples did not support the hypothesis that improvements to instrumentation have resulted in increased detection sensitivity through time for most of the pesticides examined. For tebuthiuron and carbaryl, however, increased consistency of low-level detections and a decrease in the concentrations detected through time support the hypothesis that improvements to instrumentation have resulted in increased detection sensitivity through time.

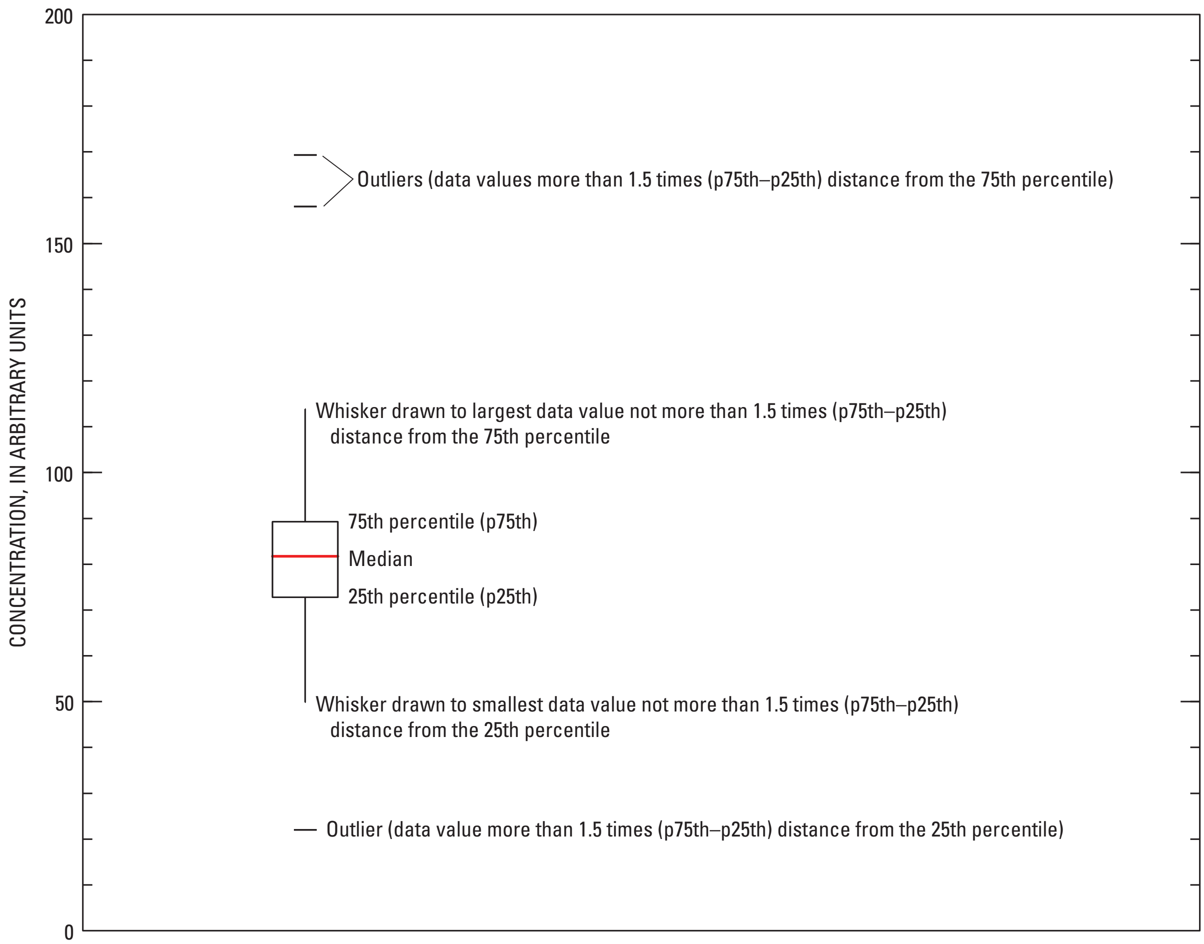


Figure A3–1. Explanation of a boxplot that is used to depict the distribution of concentrations.

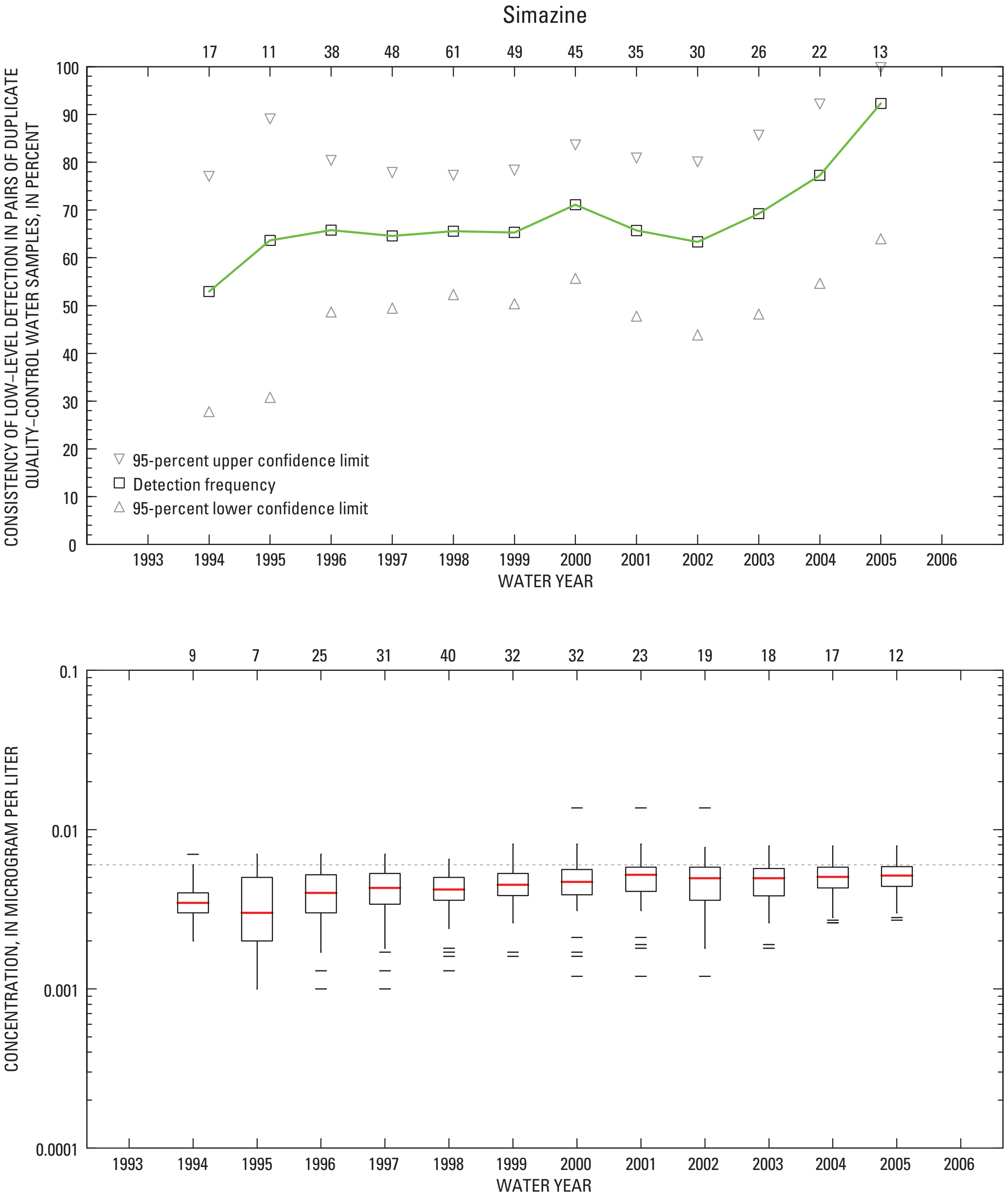


Figure A3–2. Consistency of detection and concentrations of simazine detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where simazine was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

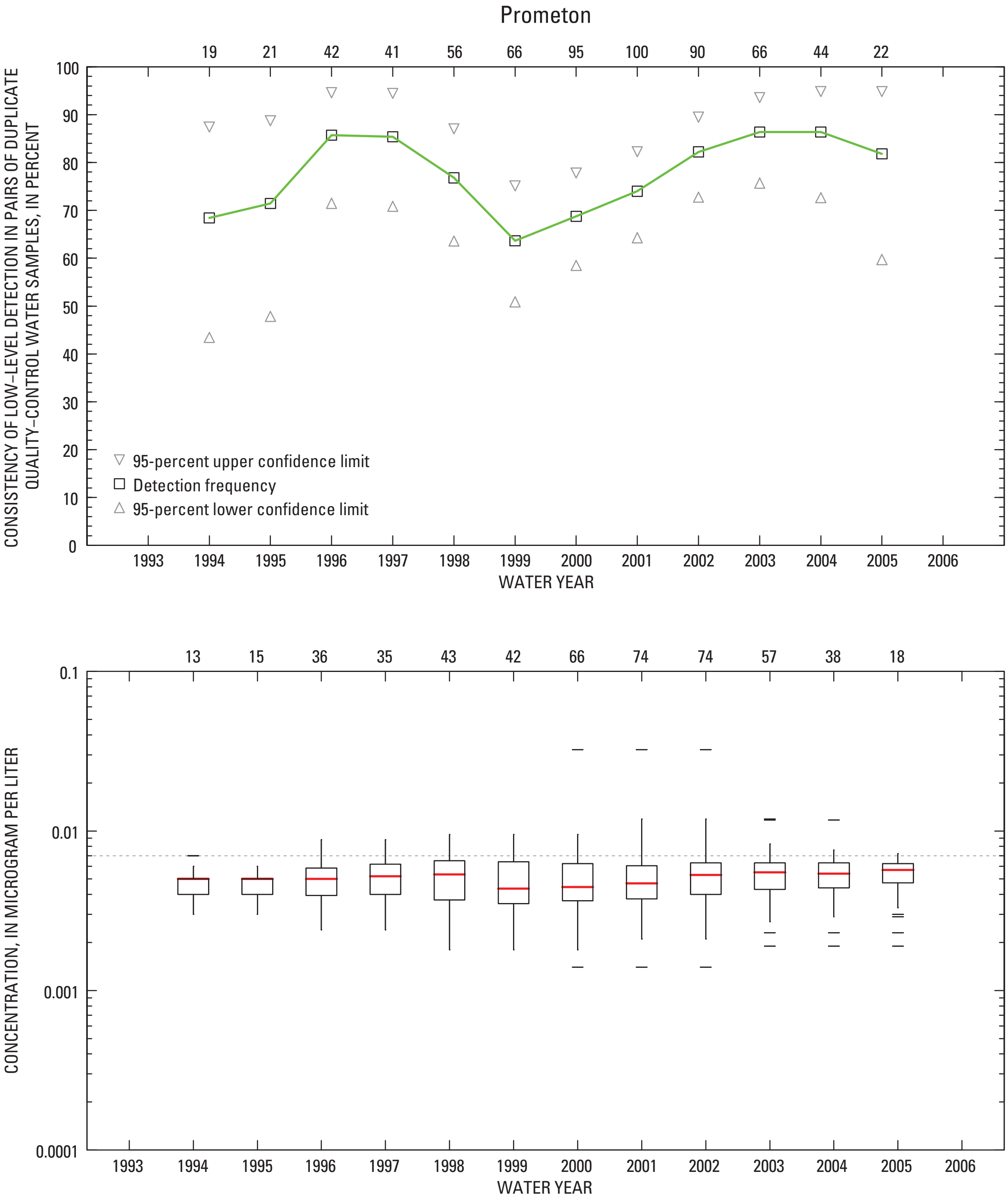


Figure A3–3. Consistency of detection and concentrations of prometon detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where prometon was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.007 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

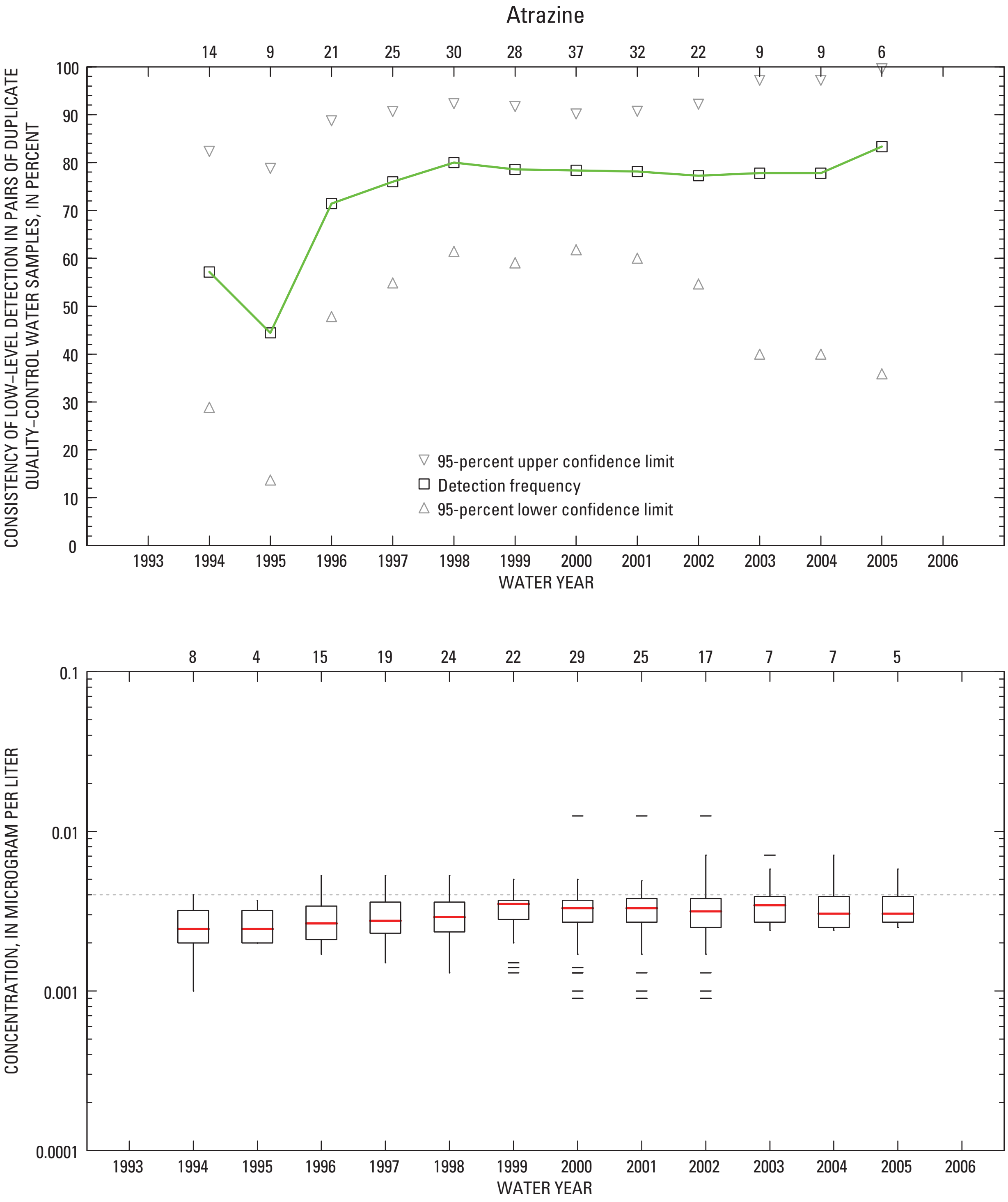


Figure A3–4. Consistency of detection and concentrations of atrazine detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where atrazine was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.004 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

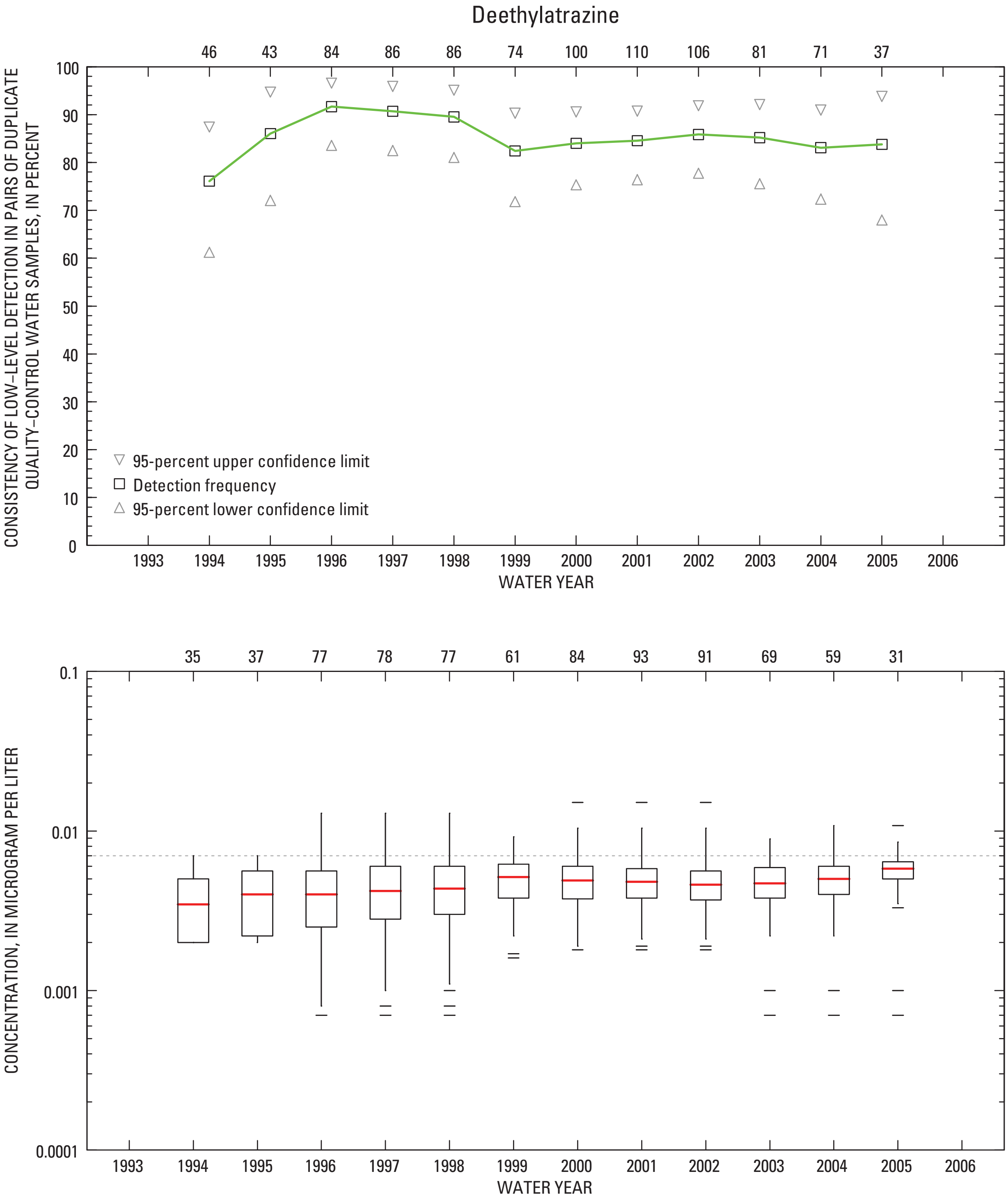


Figure A3–5. Consistency of detection and concentrations of deethylatrazine detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where deethylatrazine was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.007 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

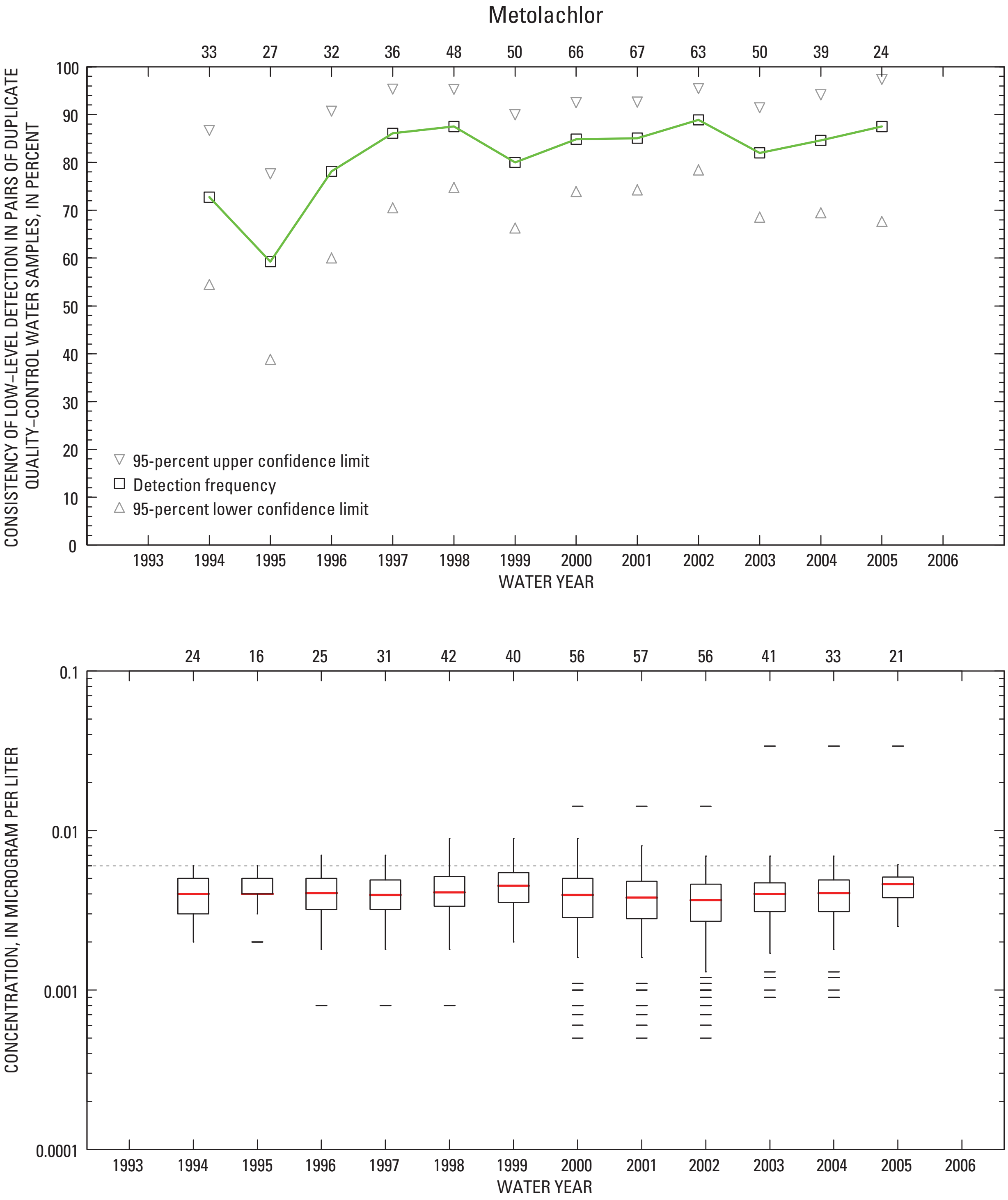


Figure A3–6. Consistency of detection and concentrations of metolachlor detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where metolachlor was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

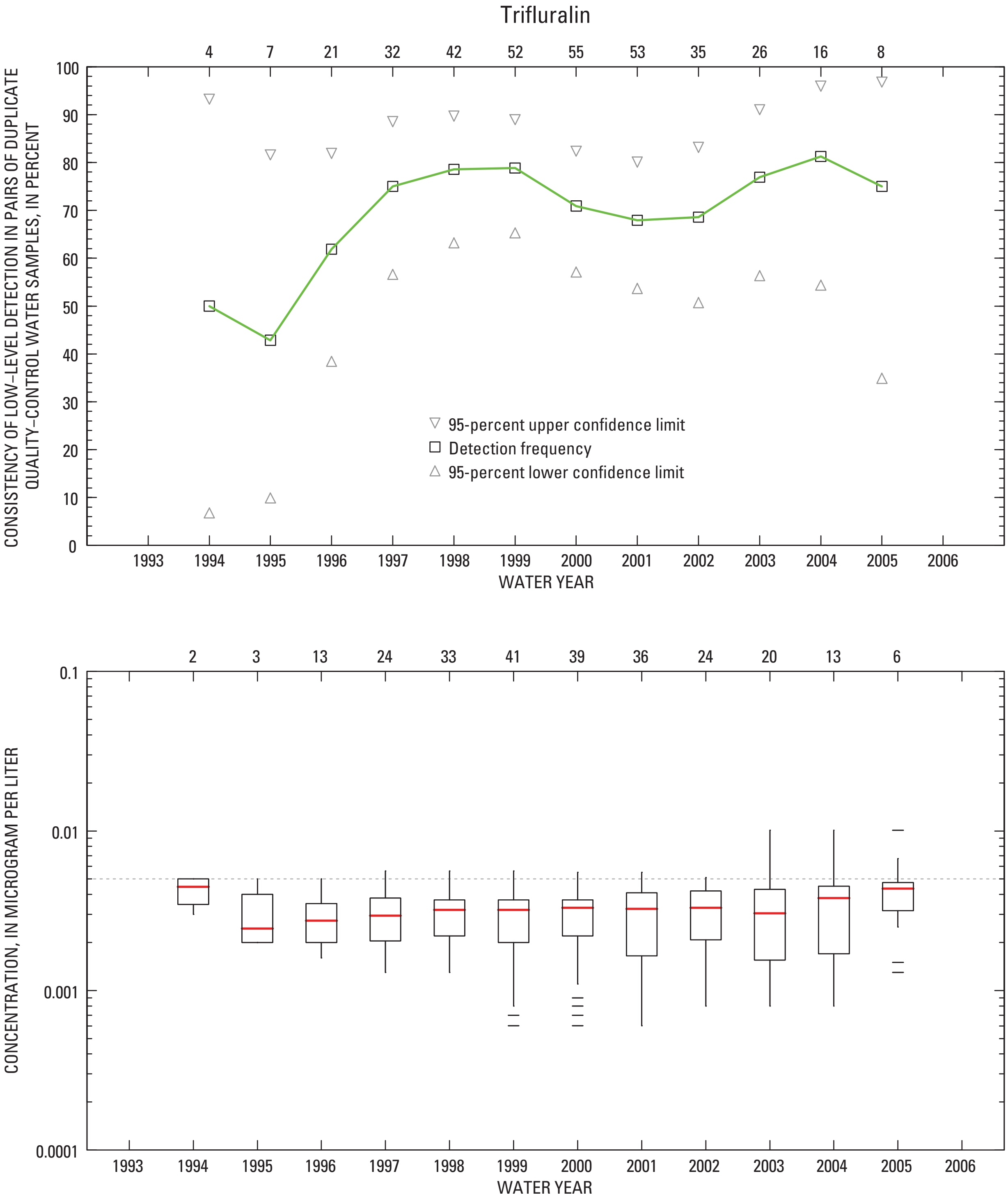


Figure A3–7. Consistency of detection and concentrations of trifluralin detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where trifluralin was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.005 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

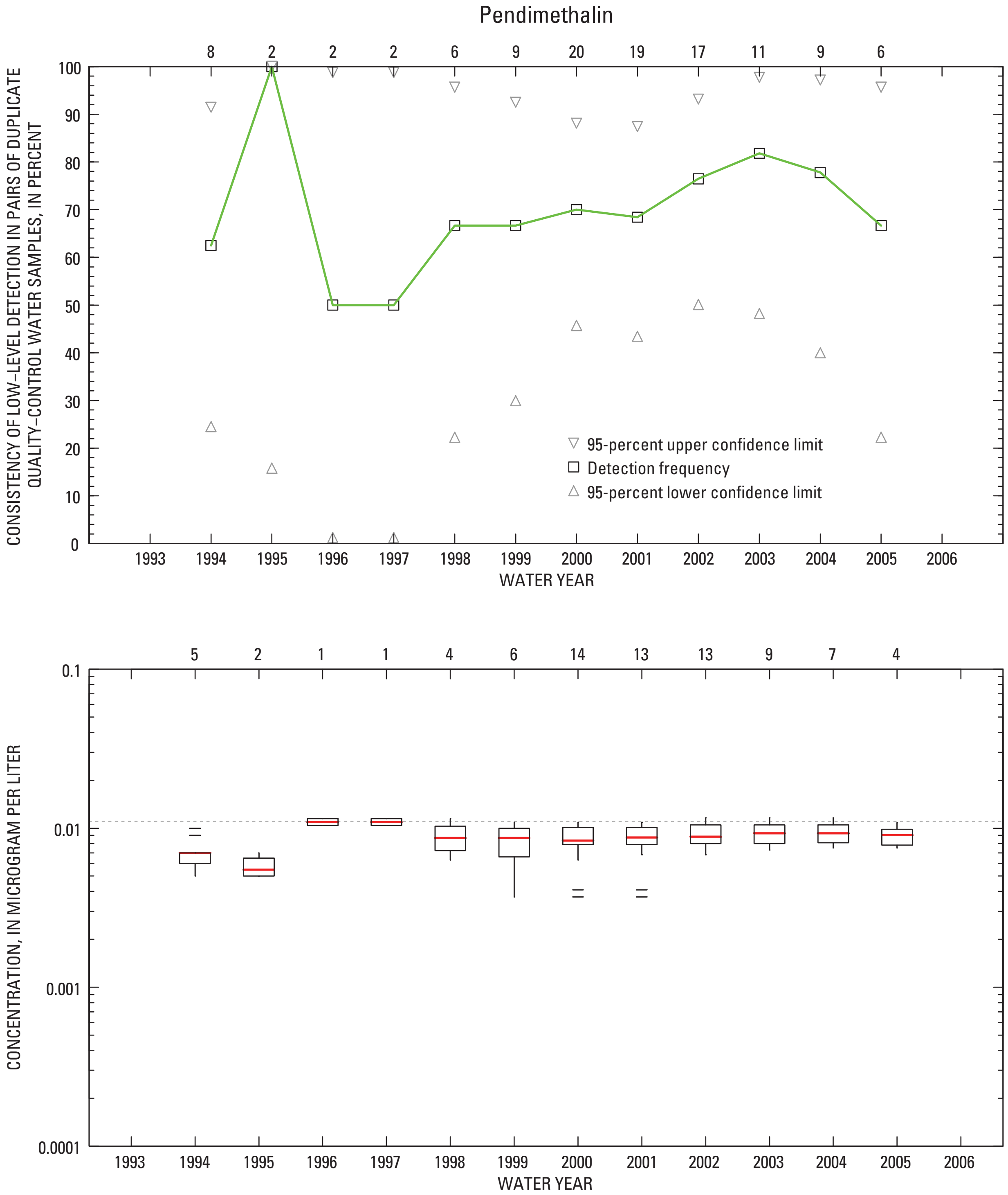


Figure A3–8. Consistency of detection and concentrations of pendimethalin detected in pairs of duplicate quality-control water samples. Only pairs of duplicates where pendimethalin was detected in at least one of the duplicates at a concentration less than the maximum value of the long-term method detection level for 1994–2006 (0.011 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

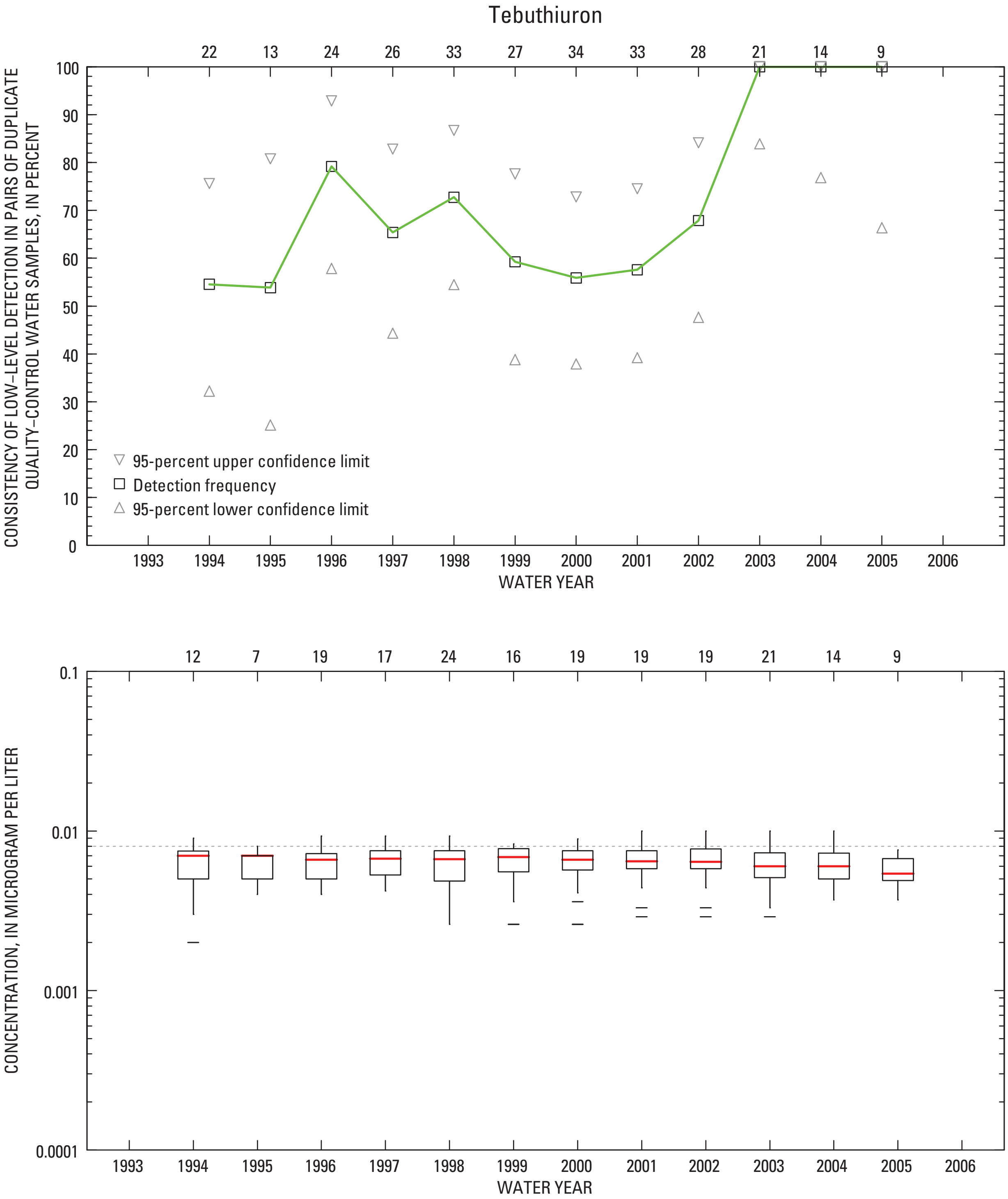


Figure A3–9. Consistency of detection and concentrations of tebuthiuron detected in pairs of duplicate quality-control water samples. Only pairs of duplicates where tebuthiuron was detected in at least one of the duplicates at a concentration less than the maximum value of the long-term method detection level for 1994–2006 (0.008 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

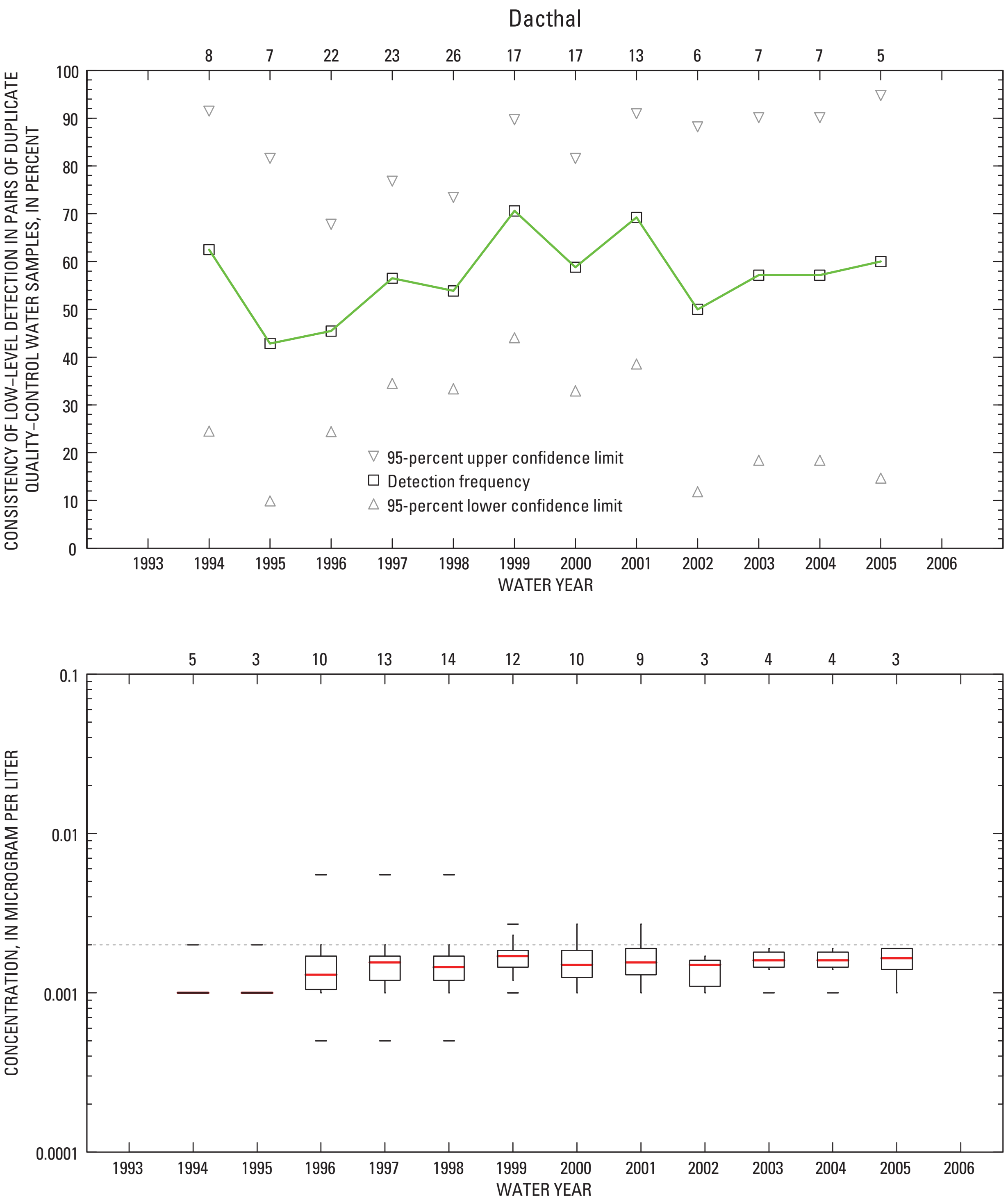


Figure A3–10. Consistency of detection and concentrations of Dacthal detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where Dacthal was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.002 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

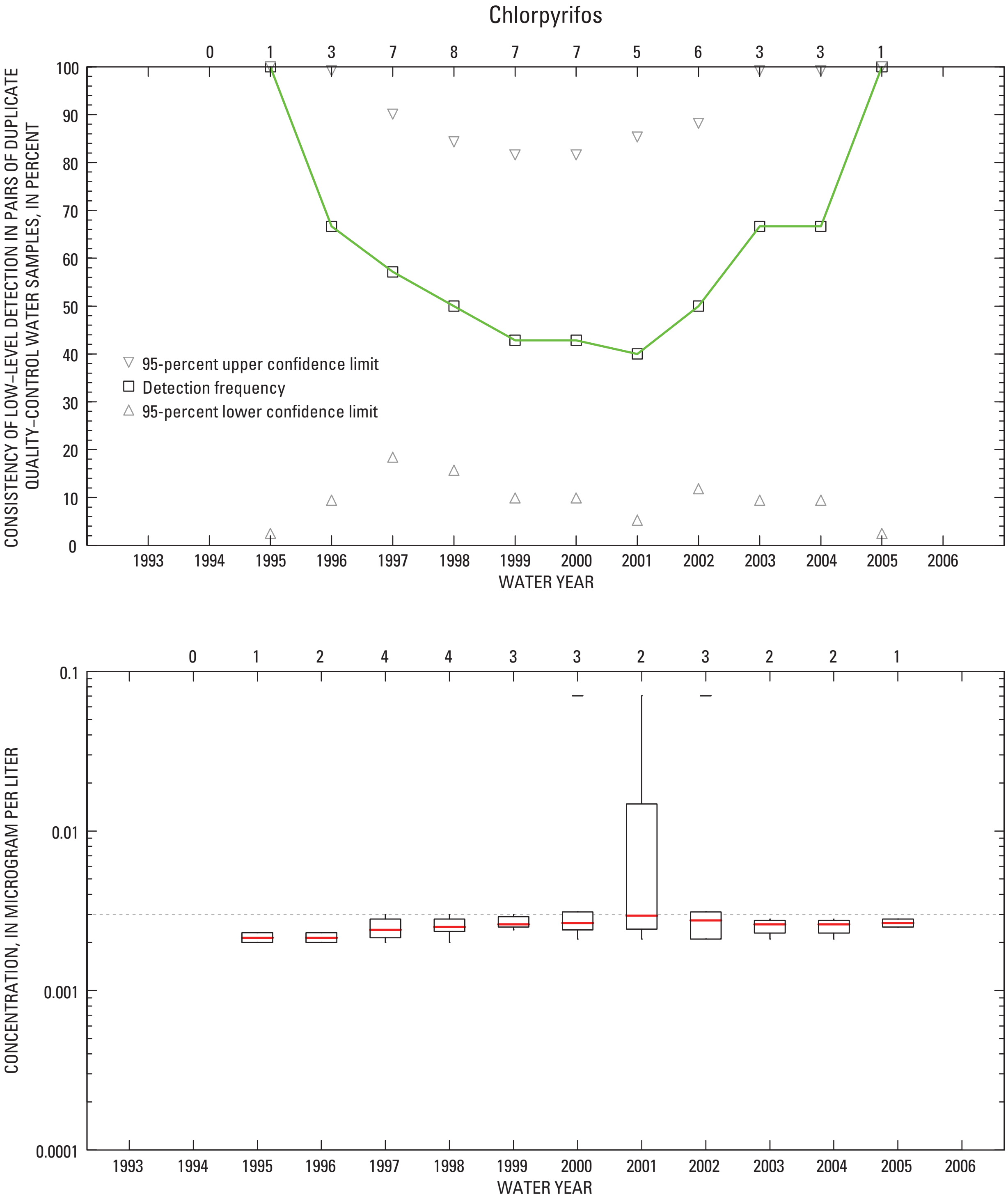


Figure A3–11. Consistency of detection and concentrations of chlorpyrifos detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where chlorpyrifos was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.003 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

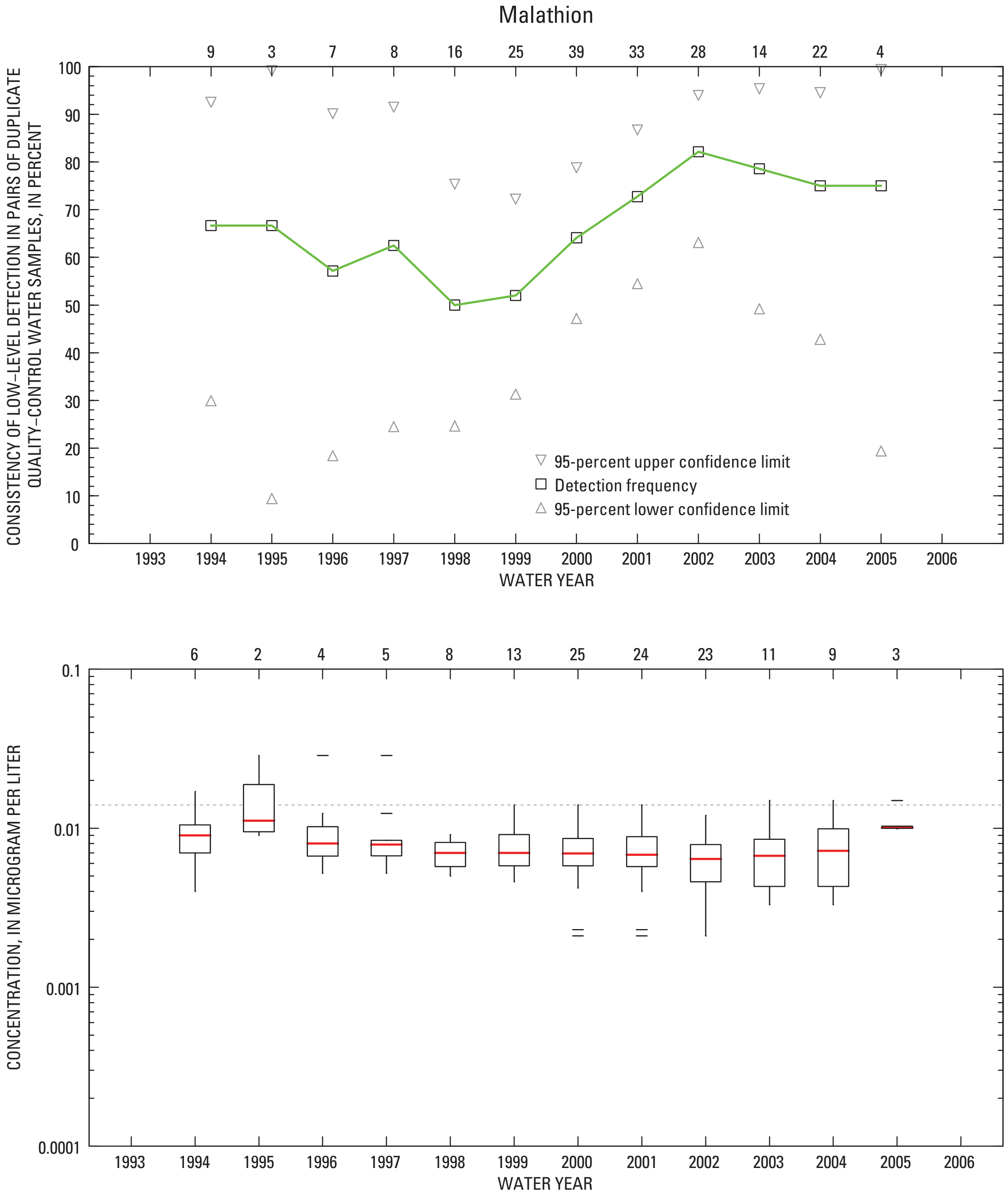


Figure A3–12. Consistency of detection and concentrations of malathion detected in pairs of duplicate quality-control water samples. Only pairs of duplicates where malathion was detected in at least one of the duplicates at a concentration less than the maximum value of the long-term method detection level for 1994–2006 (0.014 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

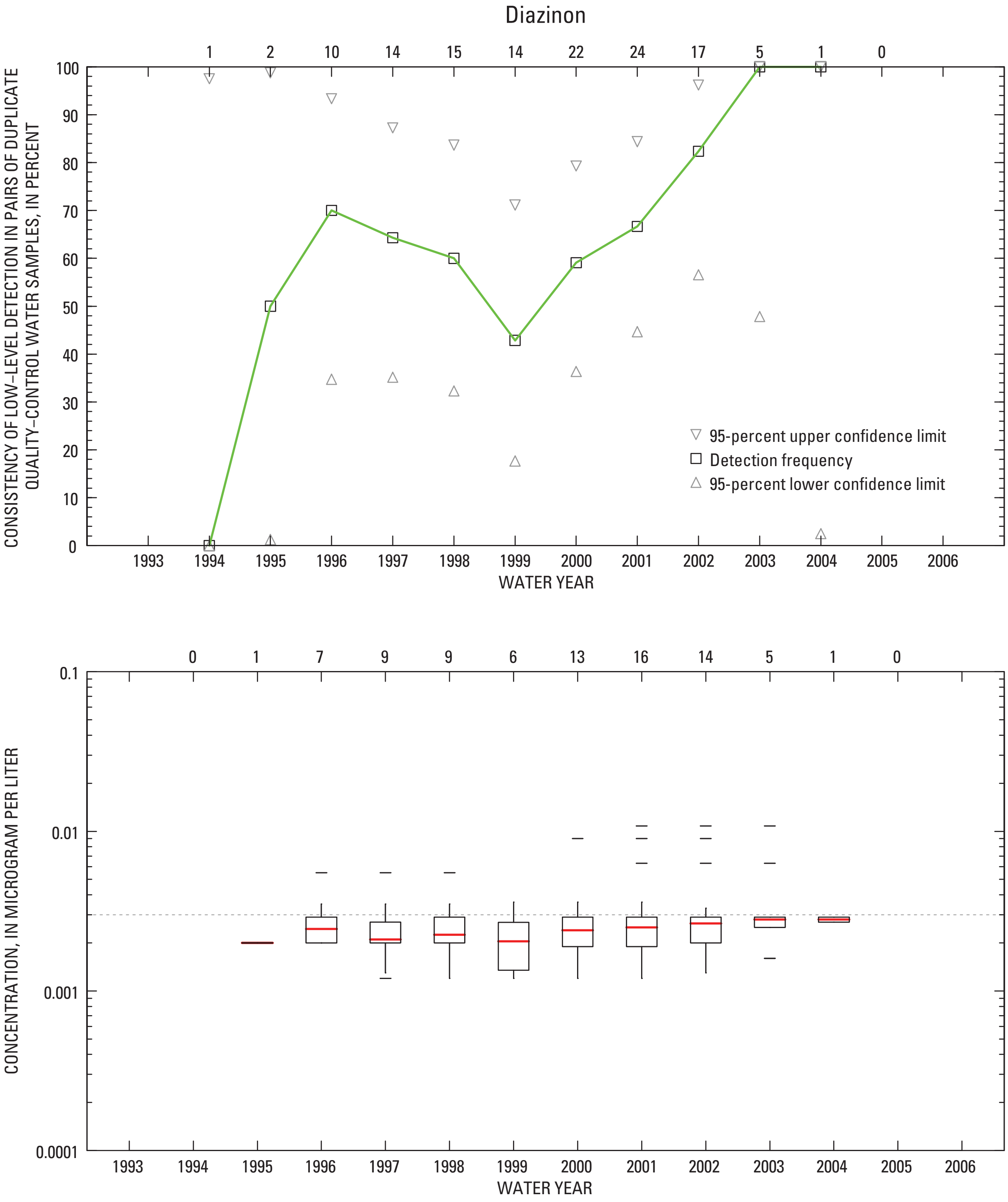


Figure A3–13. Consistency of detection and concentrations of diazinon detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where diazinon was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.003 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

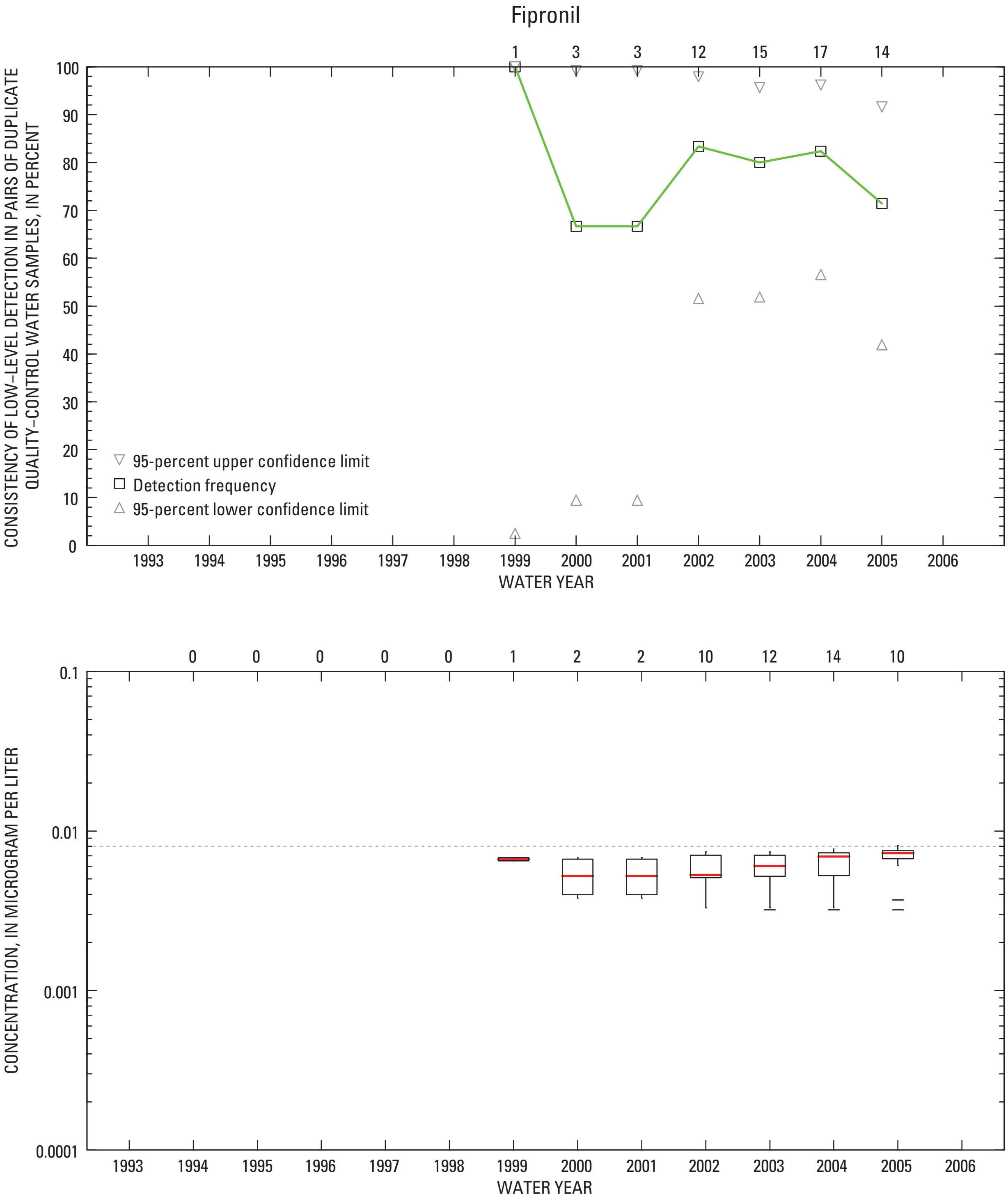


Figure A3–14. Consistency of detection and concentrations of fipronil detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where fipronil was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.008 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

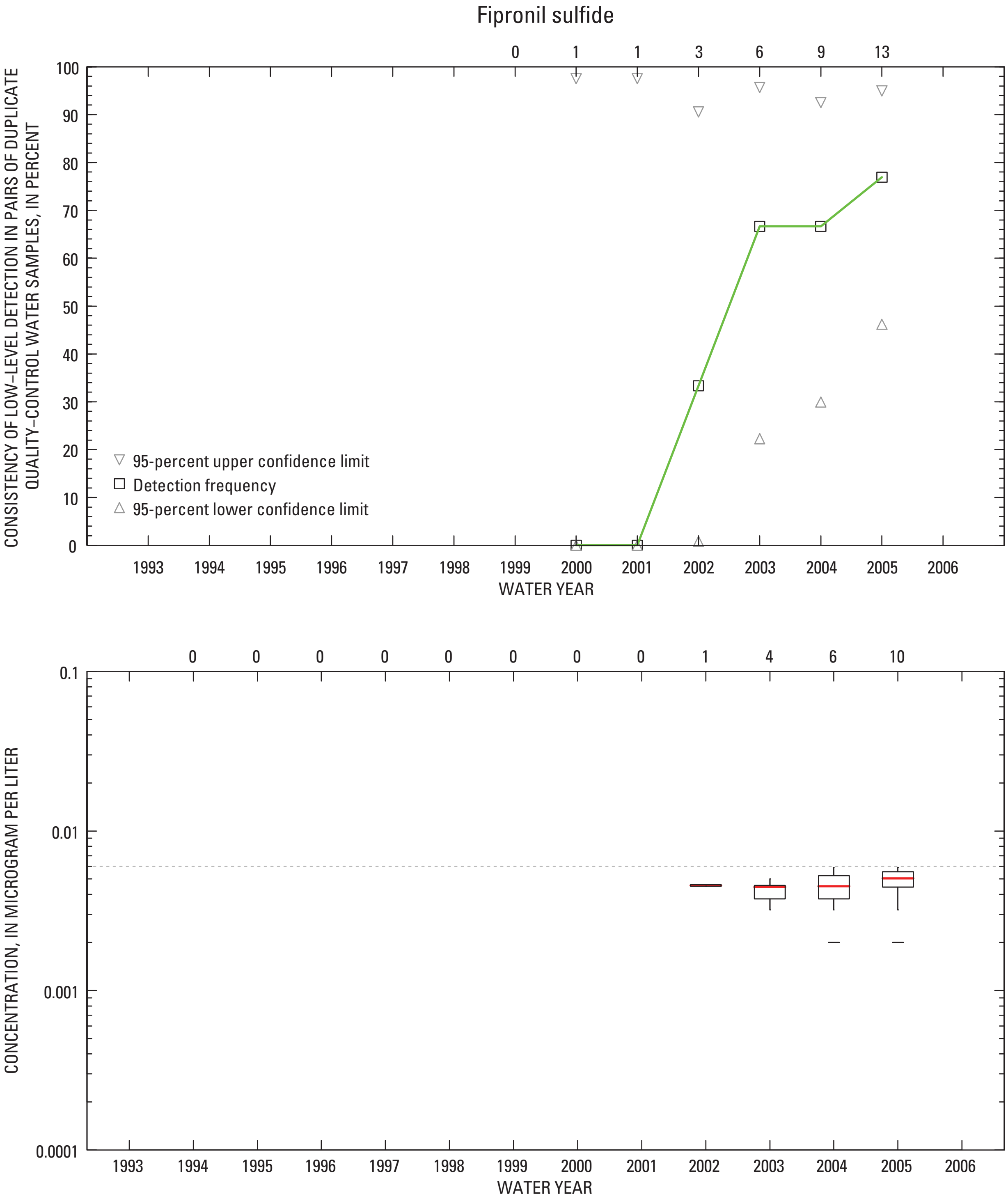


Figure A3–15. Consistency of detection and concentrations of fipronil sulfide detected in pairs of duplicate quality–control water samples. Only pairs of duplicates where fipronil sulfide was detected in at least one of the duplicates at a concentration less than the maximum value of the long–term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3–year time window was used for plotting values on the X–axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

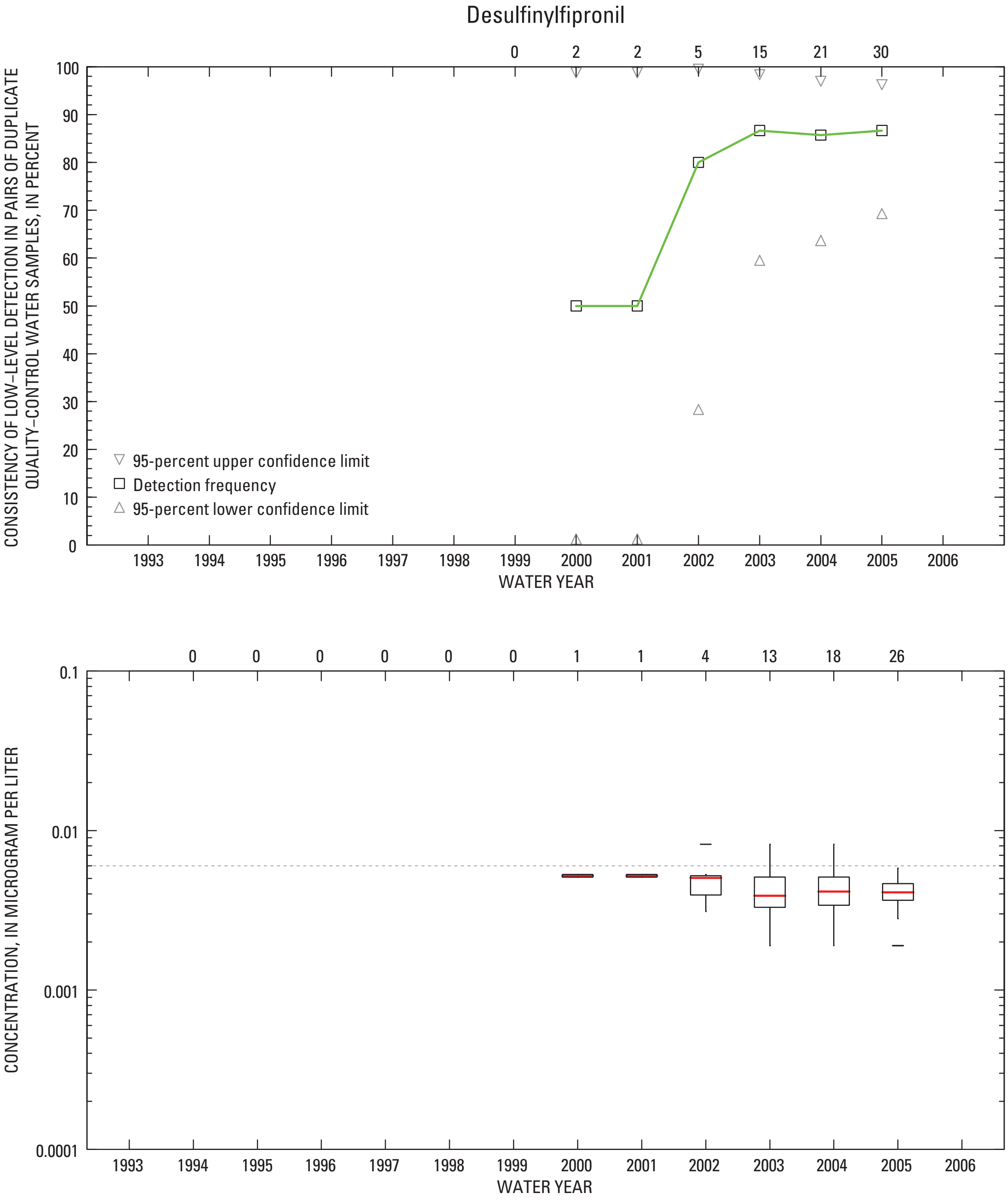


Figure A3–16. Consistency of detection and concentrations of desulfinylfipronil detected in pairs of duplicate quality-control water samples. Only pairs of duplicates where desulfinylfipronil was detected in at least one of the duplicates at a concentration less than the maximum value of the long-term method detection level for 1994–2006 (0.006 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

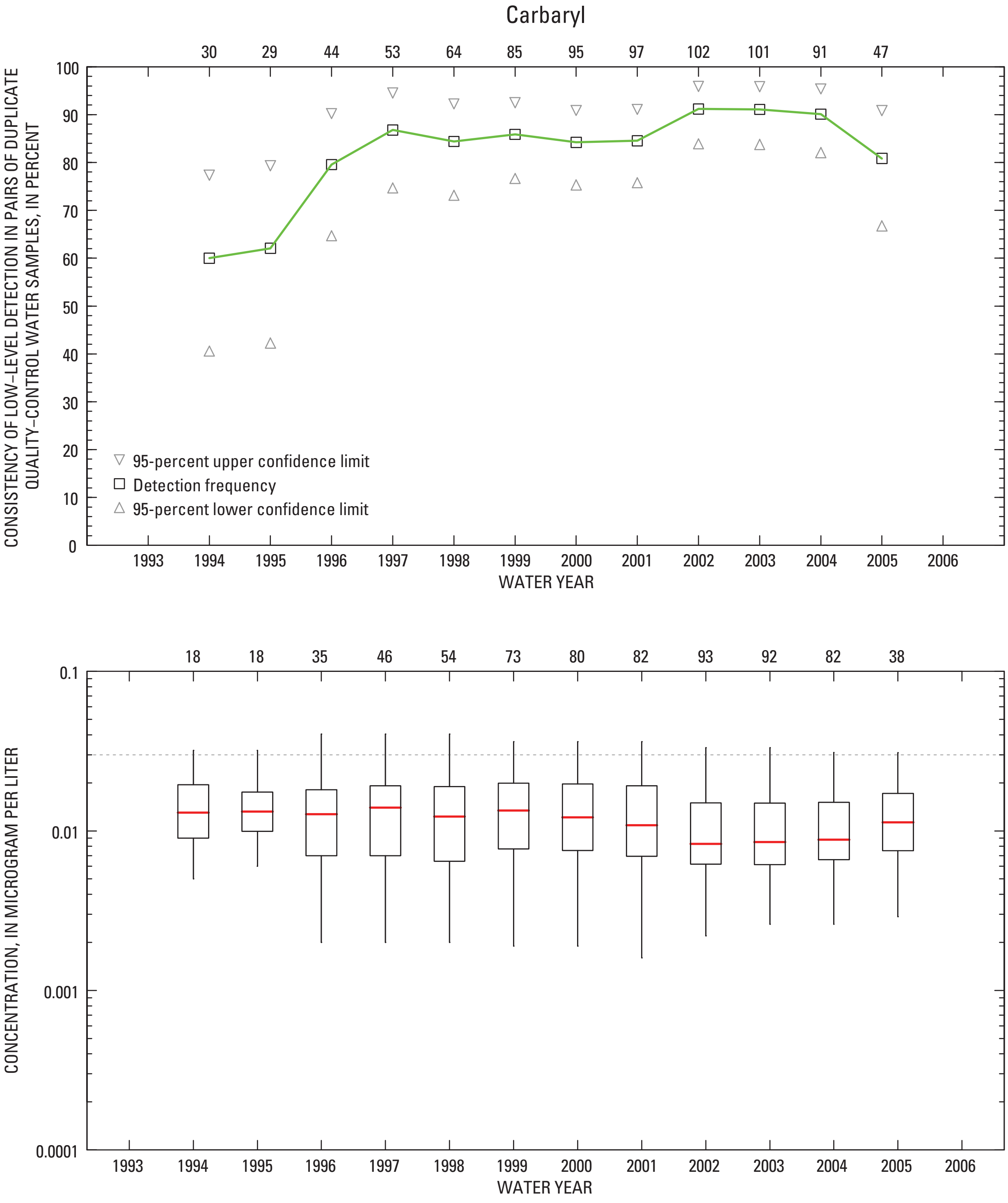


Figure A3–17. Consistency of detection and concentrations of carbaryl detected in pairs of duplicate quality-control water samples. Only pairs of duplicates where carbaryl was detected in at least one of the duplicates at a concentration less than the maximum value of the long-term method detection level for 1994–2006 (0.03 microgram per liter, and shown as a dashed line in the second panel) were used in this analysis. A 3-year time window was used for plotting values on the X-axis. For example, data plotted at 1994 include data for 1993, 1994, and 1995. The 1994 water year is the period October 1, 1993 through September 30, 1994. The number of pairs of duplicates is shown at the top of the first panel. The number of pairs of duplicates with consistent detection is shown at the top of the second panel. Boxplots are explained in figure A3–1.

Appendix 4. Summary of Data for Urban-Stream Pesticide Trend Analysis, 1992–2008

The data available for this study were examined extensively prior to analysis and underwent a number of preparation steps prior to trend analysis (appendix 1), including rounding concentrations to a consistent level of precision for the concentration range, adjustment of concentrations to compensate for temporal changes in bias of recovery of the gas chromatography/mass spectrometry (GCMS) analytical method, and identification and removal of samples collected too frequently for trend analysis. Detections at concentrations less than long-term method detection level (maxLT-MDL) were "censored" at maxLT-MDL (reassigned to nondetections at the concentration of maxLT-MDL). For a number of pesticides/sites, a less conservative estimate of the detection limit was calculated (qlow50, the median value of the low-level detections, calculated separately for each pesticide and streamwater site combination with five or more low-level detections for the period of record) because many pesticides and sites selected for assessment had a large number of detections less than maxLT-MDL (low-level detections) and using some of these low-level detections increased the number of pesticides and sites that meet the criteria for trend assessment. In addition, the years in which samples were collected varied considerably from site to site and this had some effect on reportable trends. The resulting data set is summarized in table A4–1, which shows the degree of censoring, maxLT-MDLs, qlow50s, and differences in seasonal and annual sampling.

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
04035 Simazine — Maximum long-term method detection level 0.006																						
1	ABERJ	01102500	72	7	2	46	17	0.0040	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	2	1	60	8	.0040	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	31	5	129	33	.0040	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	10	4	96	2	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	39	8	33	13	.0050	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	161	8	8	1	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	83	0	3	0	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	97	2	2	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	187	1	4	0	maxLT-MDL	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	136	1	2	0	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	118	0	1	0	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	56	0	0	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	154	0	0	0	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	78	3	24	7	.0050	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	65	7	20	12	.0050	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	162	0	18	13	.0050	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	24	9	36	4	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	73	9	7	1	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	8	11	101	4	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	54	17	25	3	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	30	5	17	1	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	8	2	81	6	.0035	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	38	3	24	7	.0050	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	83	0	0	0	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	75	14	22	0	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	28	12	69	16	.0040	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	114	2	8	2	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
04037 Prometon — Maximum long-term method detection level 0.007																						
1	ABERJ	01102500	72	39	2	15	16	0.0060	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	8	3	38	22	.0045	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	164	4	23	7	.0050	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	45	8	44	15	.0040	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	83	1	7	2	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	171	1	5	1	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	74	2	8	2	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
04037 Prometon — Maximum long-term method detection level 0.007—Continued																						
8	GILLS	02169570	101	84	2	4	11	0.0050	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	191	107	1	62	21	.0050	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	14	14
10	CHATT	02338000	139	93	1	29	16	.0050	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	24	1	67	27	.0050	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	43	1	10	2	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	139	3	12	0	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	112	0	0	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	99	0	3	2	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	193	0	0	0	maxLT-MDL	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	72	64	4	3	1	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	8	5	3	3	3
18	CLINT	04161820	90	79	2	6	3	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	116	3	5	0	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	83	7	7	2	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	50	1	1	1	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	79	3	8	7	.0060	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	14	0	29	29	.0040	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	69	3	10	1	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	105	4	2	0	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	102	3	16	4	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	94	13	13	6	.0060	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
39632 Atrazine — Maximum long-term method detection level 0.004																						
1	ABERJ	01102500	72	40	9	21	2	maxLT-MDL	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	46	3	21	1	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	129	3	60	6	.0030	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	48	1	61	2	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	86	1	4	2	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	134	5	36	3	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	69	2	15	0	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	99	1	1	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	178	2	7	5	.0030	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	135	1	2	1	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	118	1	0	0	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	54	2	0	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	154	0	0	0	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	112	0	0	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
39632 Atrazine — Maximum long-term method detection level 0.004—Continued																						
15	HOLES	393944084120700	104	104	0	0	0	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	193	0	0	0	maxLT-MDL	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	70	2	1	0	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	90	0	0	0	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	104	2	18	0	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	99	0	0	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	53	0	0	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	93	65	5	23	0	maxLT-MDL	12/23/1998	9/12/2007	8	2	9	12	13	11	10	5	9	2	9	3
23	WARMC	11060400	72	2	7	62	1	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	59	4	17	3	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	110	17	4	89	0	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	7	6	9	7
26	THORN	12128000	125	13	2	98	12	0.0030	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	125	110	1	11	3	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	5	12	11	10
04040 Deethylatrazine — Maximum long-term method detection level 0.007																						
1	ABERJ	01102500	72	9	0	51	12	0.0040	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	14	1	51	5	.0050	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	70	3	112	13	.0060	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	22	0	87	3	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	73	0	18	2	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	94	3	75	6	.0060	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	36	0	47	3	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	88	3	7	3	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	98	0	67	27	.0050	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	63	4	54	18	.0050	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	115	0	3	1	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	51	1	4	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	154	0	0	0	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	107	1	3	1	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	94	1	8	1	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	181	1	9	2	maxLT-MDL	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	63	3	7	0	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	82	1	4	3	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	75	2	43	4	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	95	2	1	1	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	51	0	2	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
04040 Deethylatrazine — Maximum long-term method detection level 0.007—Continued																						
22	LCOTT	10168000	93	54	2	31	6	0.0055	12/23/1998	9/12/2007	8	2	9	12	13	11	10	5	9	2	9	3
23	WARMC	11060400	72	2	0	68	2	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	37	4	41	1	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	109	2	1	105	1	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	7	6	8	7
26	THORN	12128000	125	0	0	123	2	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	125	58	2	58	7	.0060	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	5	12	11	10
39415 Metolachlor — Maximum long-term method detection level 0.006																						
1	ABERJ	01102500	72	11	0	38	23	0.0040	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	2	0	58	11	.0040	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	22	0	125	51	.0040	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	108	36	0	52	20	.0050	3/14/1994	7/15/2008	4	6	9	8	20	17	14	7	4	9	4	6
5	BOUND	01403900	93	56	0	17	20	.0040	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	120	0	18	40	.0040	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	32	1	38	15	.0040	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	23	2	58	18	.0045	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	191	7	2	174	8	.0030	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	14	14
10	CHATT	02338000	139	13	1	109	16	.0030	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	2	0	109	8	.0050	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	54	0	0	2	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	123	0	9	22	.0040	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	11	0	87	14	.0030	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	51	1	14	38	.0040	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	177	0	2	14	.0030	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	44	1	17	11	.0040	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	71	0	3	16	.0040	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	60	2	33	29	.0040	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	72	1	15	11	.0040	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	48	0	2	3	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	0	0	96	1	maxLT-MDL	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	2	0	66	4	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	12	1	63	7	.0050	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	110	70	4	18	18	.0050	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	8	7
26	THORN	12128000	125	0	0	125	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	52	0	45	29	.0040	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
82661 Trifluralin — Maximum long-term method detection level 0.005																						
1	ABERJ	01102500	72	4	0	56	12	0.0010	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	0	0	69	2	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	10	0	172	16	.0025	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	1	0	110	1	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	13	0	70	10	.0035	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	19	1	140	18	.0025	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	7	0	76	3	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	0	0	101	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	11	0	172	9	.0020	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	2	1	135	1	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	10	0	102	7	.0020	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	8	0	42	6	.0030	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	7	0	138	9	.0030	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	3	0	108	1	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	11	0	70	23	.0030	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	23	0	155	15	.0030	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	1	0	69	3	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	3	0	81	6	.0030	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	3	0	116	5	.0020	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	8	0	85	6	.0020	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	5	0	41	7	.0040	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	5	0	85	7	.0020	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	0	0	72	0	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	1	0	82	0	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	20	0	77	14	.0030	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	13	0	112	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	16	0	98	12	.0030	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
82683 Pendimethalin — Maximum long-term method detection level 0.011																						
1	ABERJ	01102500	71	4	2	60	5	0.0080	4/7/1999	9/1/2004	2	6	2	9	8	10	9	10	6	2	5	2
2	CHRLS	01104615	71	1	0	70	0	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	1	0	197	0	maxLT-MDL	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	3	1	106	2	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	13	1	75	4	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	50	7	117	4	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	9	0	76	1	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
82683 Pendimethalin — Maximum long-term method detection level 0.011—Continued																						
8	GILLS	02169570	101	4	0	97	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	43	4	137	8	0.0095	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	6	1	130	2	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	12	1	104	2	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	20	1	35	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	76	4	66	8	.0090	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	8	1	103	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	23	2	76	3	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	22	3	153	15	.0070	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	11	1	58	3	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	5	0	81	4	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	4	0	120	0	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	6	3	90	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	3	3	47	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	19	1	74	3	maxLT-MDL	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	0	2	68	2	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	2	0	80	1	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	31	4	72	4	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	0	0	124	1	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	6	2	117	1	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
82670 Tebuthiuron — Maximum long-term method detection level 0.008																						
1	ABERJ	01102500	64	4	1	49	10	0.0055	5/10/1999	9/1/2004	2	6	2	5	8	9	8	9	6	2	5	2
2	CHRLS	01104615	68	0	0	67	1	maxLT-MDL	6/1/1999	9/13/2007	3	7	3	6	6	10	8	8	6	3	5	3
3	NRWLK	01209710	198	1	1	196	0	maxLT-MDL	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	0	1	111	0	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	22	2	58	11	.0060	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	4	1	161	12	.0050	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	4	0	75	7	.0050	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	94	3	4	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	166	2	23	1	maxLT-MDL	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	95	7	35	2	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	8	2	96	13	.0040	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	19	0	33	4	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	34	3	103	14	.0055	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
82670 Tebuthiuron — Maximum long-term method detection level 0.008—Continued																						
14	SALAD	08178800	112	108	1	3	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	102	0	0	102	0	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	10	14	13	13	10	7	6	5	7
16	LBUCK	03353637	193	35	1	135	22	0.0050	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	60	5	8	0	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	1	0	86	3	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	44	7	69	4	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	2	2	95	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	25	10	18	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	93	46	6	37	4	maxLT-MDL	12/23/1998	9/12/2007	8	2	9	12	13	11	10	5	9	2	9	3
23	WARMC	11060400	72	14	0	51	7	.0030	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	6	4	72	1	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	110	25	3	81	1	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	7	6	9	7
26	THORN	12128000	125	2	0	123	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	75	3	43	5	.0050	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
82682 Dacthal — Maximum long-term method detection level 0.002																						
1	ABERJ	01102500	72	0	0	71	1	maxLT-MDL	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	4	0	66	1	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	11	0	183	4	maxLT-MDL	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	0	0	111	1	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	17	1	70	5	0.0010	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	19	1	152	6	.0010	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	1	0	85	0	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	100	2	0	98	0	maxLT-MDL	2/12/1996	9/25/2006	4	6	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	10	0	180	2	maxLT-MDL	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	5	0	132	2	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	0	0	119	0	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	2	0	52	2	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	12	0	135	7	.0010	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	7	1	100	4	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	0	0	103	1	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	36	0	146	11	.0010	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	3	0	69	1	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	3	0	82	5	.0010	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	17	0	102	5	.0010	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	6	1	92	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
82682 Dacthal — Maximum long-term method detection level 0.002—Continued																						
21	DPLAI	05532500	53	3	0	48	2	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	33	0	63	1	maxLT-MDL	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	25	0	44	3	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	48	0	32	3	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	65	2	40	4	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	7	0	118	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	12	0	112	2	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
38933 Chlorpyrifos — Maximum long-term method detection level 0.003																						
1	ABERJ	01102500	72	3	1	68	0	maxLT-MDL	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	0	0	71	0	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	3	0	195	0	maxLT-MDL	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	2	2	108	0	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	25	2	66	0	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	47	11	119	1	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	4	0	82	0	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	33	1	66	1	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	191	54	3	134	0	maxLT-MDL	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	14	14
10	CHATT	02338000	139	17	5	117	0	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	27	2	89	1	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	30	0	26	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	63	9	80	2	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	14	5	93	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	18	9	76	1	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	69	8	114	2	maxLT-MDL	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	0	0	73	0	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	8	1	81	0	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	1	1	122	0	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	9	5	85	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	1	3	49	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	1	2	94	0	maxLT-MDL	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	5	2	63	2	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	3	0	80	0	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	61	9	41	0	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	124	3	4	117	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	11	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	36	2	85	3	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
39532 Malathion — Maximum long-term method detection level 0.014																						
1	ABERJ	01102500	71	0	0	71	0	maxLT-MDL	4/7/1999	9/1/2004	2	5	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	0	0	70	1	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	3	0	192	3	maxLT-MDL	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	1	0	110	1	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	4	0	83	6	0.0100	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	16	2	154	6	.0095	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	0	0	85	1	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	26	0	60	15	.0080	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	192	9	0	175	8	.0090	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	15	14
10	CHATT	02338000	139	0	0	133	6	.0075	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	2	0	113	4	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	25	1	26	4	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	27	2	111	14	.0085	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	9	0	93	10	.0070	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	4	1	92	7	.0090	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	24	0	153	16	.0095	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	2	0	70	1	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	1	2	86	1	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	5	2	113	4	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	6	0	93	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	3	2	47	1	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	96	6	4	77	9	.0070	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	2
23	WARMC	11060400	72	3	1	66	2	maxLT-MDL	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	9	1	72	1	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	47	1	55	8	.0100	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	7	0	115	3	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	5	0	118	3	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
39572 Diazinon — Maximum long-term method detection level 0.003																						
1	ABERJ	01102500	72	55	5	12	0	maxLT-MDL	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	70	23	1	44	2	maxLT-MDL	5/4/1999	9/13/2007	3	7	3	6	8	10	8	8	6	3	5	3
3	NRWLK	01209710	198	48	1	143	6	0.0020	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	101	50	2	49	0	maxLT-MDL	3/14/1994	7/15/2008	4	6	9	8	17	14	12	8	4	9	4	6
5	BOUND	01403900	93	63	2	28	0	maxLT-MDL	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	144	2	32	0	maxLT-MDL	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	50	1	35	0	maxLT-MDL	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
39572 Diazinon — Maximum long-term method detection level 0.003—Continued																						
8	GILLS	02169570	101	65	1	35	0	maxLT-MDL	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	191	128	4	57	2	maxLT-MDL	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	14	14
10	CHATT	02338000	139	91	2	46	0	maxLT-MDL	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	60	2	57	0	maxLT-MDL	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	47	2	7	0	maxLT-MDL	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	134	2	18	0	maxLT-MDL	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	55	7	50	0	maxLT-MDL	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	90	0	11	3	maxLT-MDL	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	180	0	13	0	maxLT-MDL	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	45	2	26	0	maxLT-MDL	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	53	4	33	0	maxLT-MDL	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	66	8	50	0	maxLT-MDL	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	55	16	28	0	maxLT-MDL	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	49	41	4	4	0	maxLT-MDL	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	0	3	0	3
22	LCOTT	10168000	97	69	1	27	0	maxLT-MDL	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	71	40	2	27	2	maxLT-MDL	11/16/1998	8/13/2004	8	9	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	39	7	37	0	maxLT-MDL	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	107	1	3	0	maxLT-MDL	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	57	1	67	0	maxLT-MDL	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	88	4	33	1	maxLT-MDL	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10
62166 Fipronil — Maximum long-term method detection level 0.01																						
1	ABERJ	01102500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2	CHRLS	01104615	22	1	0	1	20	0.0065	10/18/2005	9/13/2007	1	1	1	2	3	4	3	3	2	1	0	1
3	NRWLK	01209710	7	0	0	4	3	maxLT-MDL	9/6/2005	8/21/2006	1	1	1	0	1	1	0	1	1	0	0	0
4	LISHA	01356190	57	0	0	56	1	maxLT-MDL	10/8/2002	7/15/2008	2	4	4	5	10	7	8	5	1	6	1	4
5	BOUND	01403900	19	5	0	2	12	.0070	10/3/2006	9/27/2007	1	0	1	1	2	3	3	3	2	2	1	0
6	ACCOT	01654000	52	31	0	12	9	.0090	10/30/2002	7/8/2008	5	1	5	4	9	7	7	2	5	1	5	1
7	SWIFT	02087580	61	42	0	3	16	.0080	10/17/2002	9/17/2007	3	7	6	6	4	6	3	6	3	5	5	7
8	GILLS	02169570	40	4	0	20	16	.0070	11/12/2002	9/25/2006	3	2	5	4	5	4	4	2	5	1	4	1
9	SOPEC	02335870	69	23	0	12	34	.0070	10/9/2002	7/2/2008	5	3	8	5	10	6	8	5	5	4	6	4
10	CHATT	02338000	69	32	0	11	26	.0080	10/8/2002	7/2/2008	6	4	9	6	7	5	8	4	5	4	7	4
11	CAHAB	0242354750	50	20	0	13	17	.0070	11/5/2002	9/20/2007	6	2	6	4	6	4	5	2	6	2	7	0
12	FLTCH	07031692	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
13	WHITE	08057200	59	40	0	5	14	.0080	10/7/2002	9/18/2007	3	5	3	8	6	6	5	6	3	6	3	5

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

			n						Period of record		Samples in each month											
Site number (fig. 1)	Site short name	USGS station number	Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections	qlow50	Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
62166 Fipronil — Maximum long-term method detection level 0.01—Continued																						
14	SALAD	08178800	61	5	0	39	17	0.0060	10/17/2002	7/7/2008	3	6	8	7	8	7	5	3	1	5	3	5
15	HOLES	393944084120700	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
16	LBUCK	03353637	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
17	LINCO	040869415	17	0	0	15	2	maxLT-MDL	11/13/2006	9/14/2007	1	0	0	1	3	3	3	3	2	0	1	0
18	CLINT	04161820	39	0	0	32	7	.0060	10/29/2002	9/19/2006	1	3	1	4	4	4	4	7	2	4	1	4
19	SHING	05288705	53	0	0	46	7	.0070	10/9/2002	7/9/2008	4	2	3	5	8	7	6	5	5	3	3	2
20	SALTC	05531500	51	24	1	9	17	.0080	10/9/2002	9/18/2007	2	4	1	6	7	7	6	8	2	4	1	3
21	DPLAI	05532500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
22	LCOTT	10168000	41	0	0	40	1	maxLT-MDL	11/22/2002	9/12/2007	5	0	5	3	6	4	5	2	5	1	5	0
23	WARMC	11060400	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
24	SANTA	11074000	61	9	0	25	27	.0060	10/17/2002	7/9/2008	6	8	6	7	5	8	2	5	1	6	2	5
25	ARCAD	11447360	62	58	2	0	2	maxLT-MDL	11/15/2002	7/8/2008	7	7	5	6	6	7	5	2	4	4	4	5
26	THORN	12128000	66	0	0	56	10	.0050	11/6/2002	9/19/2007	6	2	6	6	7	8	8	6	7	2	6	2
27	FANNO	14206950	61	7	0	32	22	.0070	10/22/2002	9/19/2007	4	7	4	6	5	7	4	5	3	6	4	6
62167 Fipronil sulfide — Maximum long-term method detection level 0.006																						
1	ABERJ	01102500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2	CHRLS	01104615	22	12	0	3	7	0.0050	10/18/2005	9/13/2007	1	1	1	2	3	4	3	3	2	1	0	1
3	NRWLK	01209710	7	4	0	3	0	maxLT-MDL	9/6/2005	8/21/2006	1	1	1	0	1	1	0	1	1	0	0	0
4	LISHA	01356190	57	1	0	56	0	maxLT-MDL	10/8/2002	7/15/2008	2	4	4	5	10	7	8	5	1	6	1	4
5	BOUND	01403900	19	16	0	0	3	maxLT-MDL	10/3/2006	9/27/2007	1	0	1	1	2	3	3	3	2	2	1	0
6	ACCOT	01654000	52	21	0	27	4	maxLT-MDL	10/30/2002	7/8/2008	5	1	5	4	9	7	7	2	5	1	5	1
7	SWIFT	02087580	61	42	0	9	10	.0050	10/17/2002	9/17/2007	3	7	6	6	4	6	3	6	3	5	5	7
8	GILLS	02169570	40	18	0	19	3	maxLT-MDL	11/12/2002	9/25/2006	3	2	5	4	5	4	4	2	5	1	4	1
9	SOPEC	02335870	69	38	0	24	7	.0040	10/9/2002	7/2/2008	5	3	8	5	10	6	8	5	5	4	6	4
10	CHATT	02338000	69	33	0	28	8	.0050	10/8/2002	7/2/2008	6	4	9	6	7	5	8	4	5	4	7	4
11	CAHAB	0242354750	50	27	0	18	5	.0050	11/5/2002	9/20/2007	6	2	6	4	6	4	5	2	6	2	7	0
12	FLTCH	07031692	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
13	WHITE	08057200	59	29	1	20	9	.0030	10/7/2002	9/18/2007	3	5	3	8	6	6	5	6	3	6	3	5
14	SALAD	08178800	61	16	0	38	7	.0040	10/17/2002	7/7/2008	3	6	8	7	8	7	5	3	1	5	3	5
15	HOLES	393944084120700	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
16	LBUCK	03353637	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
17	LINCO	040869415	17	1	0	14	2	maxLT-MDL	11/13/2006	9/14/2007	1	0	0	1	3	3	3	3	2	0	1	0
18	CLINT	04161820	39	1	0	38	0	maxLT-MDL	10/29/2002	9/19/2006	1	3	1	4	4	4	4	7	2	4	1	4
19	SHING	05288705	53	3	0	44	6	.0050	10/9/2002	7/9/2008	4	2	3	5	8	7	6	5	5	3	3	2
20	SALTC	05531500	51	24	0	23	4	maxLT-MDL	10/9/2002	9/18/2007	2	4	1	6	7	7	6	8	2	4	1	3

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.–Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2167 Fipronil sulfide — Maximum long-term method detection level 0.006—Continued																						
21	DPLAI	05532500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
22	LCOTT	10168000	41	1	0	40	0	maxLT-MDL	11/22/2002	9/12/2007	5	0	5	3	6	4	5	2	5	1	5	0
23	WARMC	11060400	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
24	SANTA	11074000	61	19	0	23	19	0.0050	10/17/2002	7/9/2008	6	8	6	7	5	8	2	5	1	6	2	5
25	ARCAD	11447360	62	43	0	8	11	.0050	11/15/2002	7/8/2008	7	7	5	6	6	7	5	2	4	4	4	5
26	THORN	12128000	66	4	0	62	0	maxLT-MDL	11/6/2002	9/19/2007	6	2	6	6	7	8	8	6	7	2	6	2
27	FANNO	14206950	61	20	0	34	7	.0050	10/22/2002	9/19/2007	4	7	4	6	5	7	4	5	3	6	4	6
62170 Desulfinylfipronil — Maximum long-term method detection level 0.006																						
1	ABERJ	01102500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2	CHRLS	01104615	22	13	0	3	6	0.0045	10/18/2005	9/13/2007	1	1	1	2	3	4	3	3	2	1	0	1
3	NRWLK	01209710	7	2	0	1	4	maxLT-MDL	9/6/2005	8/21/2006	1	1	1	0	1	1	0	1	1	0	0	0
4	LISHA	01356190	57	1	0	53	3	maxLT-MDL	10/8/2002	7/15/2008	2	4	4	5	10	7	8	5	1	6	1	4
5	BOUND	01403900	19	12	0	0	7	.0050	10/3/2006	9/27/2007	1	0	1	1	2	3	3	3	2	2	1	0
6	ACCOT	01654000	52	21	0	24	7	.0040	10/30/2002	7/8/2008	5	1	5	4	9	7	7	2	5	1	5	1
7	SWIFT	02087580	61	43	0	5	13	.0050	10/17/2002	9/17/2007	3	7	6	6	4	6	3	6	3	5	5	7
8	GILLS	02169570	40	12	0	18	10	.0050	11/12/2002	9/25/2006	3	2	5	4	5	4	4	2	5	1	4	1
9	SOPEC	02335870	69	31	0	22	16	.0050	10/9/2002	7/2/2008	5	3	8	5	10	6	8	5	5	4	6	4
10	CHATT	02338000	69	33	0	24	12	.0050	10/8/2002	7/2/2008	6	4	9	6	7	5	8	4	5	4	7	4
11	CAHAB	0242354750	50	22	1	17	10	.0045	11/5/2002	9/20/2007	6	2	6	4	6	4	5	2	6	2	7	0
12	FLTCH	07031692	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
13	WHITE	08057200	59	41	0	10	8	.0050	10/7/2002	9/18/2007	3	5	3	8	6	6	5	6	3	6	3	5
14	SALAD	08178800	61	13	0	25	23	.0050	10/17/2002	7/7/2008	3	6	8	7	8	7	5	3	1	5	3	5
15	HOLES	393944084120700	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
16	LBUCK	03353637	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
17	LINCO	040869415	17	1	0	11	5	.0050	11/13/2006	9/14/2007	1	0	0	1	3	3	3	3	2	0	1	0
18	CLINT	04161820	39	1	0	35	3	maxLT-MDL	10/29/2002	9/19/2006	1	3	1	4	4	4	4	7	2	4	1	4
19	SHING	05288705	53	4	0	35	14	.0040	10/9/2002	7/9/2008	4	2	3	5	8	7	6	5	5	3	3	2
20	SALTC	05531500	51	25	0	18	8	.0045	10/9/2002	9/18/2007	2	4	1	6	7	7	6	8	2	4	1	3
21	DPLAI	05532500	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
22	LCOTT	10168000	41	1	0	37	3	maxLT-MDL	11/22/2002	9/12/2007	5	0	5	3	6	4	5	2	5	1	5	0
23	WARMC	11060400	0	--	--	--	--	maxLT-MDL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
24	SANTA	11074000	61	31	0	15	15	.0050	10/17/2002	7/9/2008	6	8	6	7	5	8	2	5	1	6	2	5
25	ARCAD	11447360	62	56	0	2	4	maxLT-MDL	11/15/2002	7/8/2008	7	7	5	6	6	7	5	2	4	4	4	5
26	THORN	12128000	66	6	0	50	10	.0040	11/6/2002	9/19/2007	6	2	6	6	7	8	8	6	7	2	6	2
27	FANNO	14206950	61	14	0	30	17	.0040	10/22/2002	9/19/2007	4	7	4	6	5	7	4	5	3	6	4	6

Table A4-1. Summary of data for urban stream pesticide trend analysis, 1992–2008.—Continued

[Values censored at a higher level than the maximum long-term method detection level (maxLT-MDL) were removed from the analysis. For the data to be used in the for a particular trend analysis period the dates for which water samples were collected and analyzed for a particular site needed to be representative of the trend period and there needed to be at least 10 uncensored concentration values (detections at or above the censoring level) for a particular site-pesticide combination. USGS, U.S. Geological Survey; n, number of samples; qlow50, the median value of the low-level detections, calculated separately for each pesticide and stream-water site combination with five or more low-level detections for the period of record; number preceding pesticide name is USGS parameter code for pesticide; maxLT-MDL in place of a numeric value for qlow50 indicates that qlow50 was not calculated because of insufficient low-level detections]

Site number (fig. 1)	Site short name	USGS station number	n					qlow50	Period of record		Samples in each month											
			Total	Uncensored	Censored at a level higher than maxLT-MDL	Censored at maxLT-MDL	Low-level detections		Begin date	End Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
82680 Carbaryl — Maximum long-term method detection level 0.03																						
1	ABERJ	01102500	72	18	0	20	34	0.0090	4/7/1999	9/1/2004	2	6	2	9	9	10	9	10	6	2	5	2
2	CHRLS	01104615	71	6	0	36	29	.0080	5/4/1999	9/13/2007	3	7	3	6	8	10	8	9	6	3	5	3
3	NRWLK	01209710	198	16	1	125	56	.0105	3/17/1993	8/21/2006	10	7	16	21	27	26	25	24	17	8	10	7
4	LISHA	01356190	112	25	0	42	45	.0080	3/14/1994	7/15/2008	4	6	9	8	20	18	15	9	4	9	4	6
5	BOUND	01403900	93	26	0	33	34	.0130	4/23/1996	9/27/2007	5	3	6	12	13	13	9	9	9	5	6	3
6	ACCOT	01654000	178	55	1	34	88	.0110	3/16/1994	7/8/2008	9	3	12	21	27	26	24	16	16	7	11	6
7	SWIFT	02087580	86	6	0	19	61	.0090	10/12/2001	9/17/2007	7	10	8	8	6	7	4	7	4	6	8	11
8	GILLS	02169570	101	4	0	54	43	.0080	2/5/1996	9/25/2006	4	7	13	13	11	10	12	8	10	6	5	2
9	SOPEC	02335870	191	26	0	82	83	.0090	3/9/1993	7/2/2008	13	13	20	18	23	19	18	14	14	11	14	14
10	CHATT	02338000	139	18	1	29	91	.0090	3/7/1994	7/2/2008	10	8	15	11	16	11	16	9	10	10	13	10
11	CAHAB	0242354750	119	7	1	80	31	.0070	2/10/1999	9/20/2007	9	5	15	12	12	12	12	9	13	7	11	2
12	FLTCH	07031692	56	27	0	10	19	.0130	10/1/1996	9/8/2004	4	4	3	8	6	7	7	5	4	1	4	3
13	WHITE	08057200	154	32	1	48	73	.0120	2/7/1995	9/18/2007	8	11	13	18	18	19	17	16	6	11	7	10
14	SALAD	08178800	112	17	0	58	37	.0100	1/23/1997	7/7/2008	6	9	10	13	16	12	12	9	6	7	5	7
15	HOLES	393944084120700	104	17	0	52	35	.0070	3/24/1999	9/7/2004	6	5	6	11	15	13	13	10	7	6	5	7
16	LBUCK	03353637	193	22	0	105	66	.0110	5/5/1992	9/7/2004	10	6	8	17	27	31	33	24	15	5	9	8
17	LINCO	040869415	73	3	0	46	24	.0100	5/15/2001	9/14/2007	3	3	4	8	11	11	10	9	5	3	3	3
18	CLINT	04161820	90	7	1	45	37	.0080	4/4/1996	9/19/2006	3	7	4	10	12	10	11	11	5	7	4	6
19	SHING	05288705	124	10	0	82	32	.0120	4/22/1996	7/9/2008	7	5	10	13	17	16	16	13	11	6	5	5
20	SALTC	05531500	99	13	0	36	50	.0095	3/2/1999	9/18/2007	3	6	6	12	14	17	12	13	3	6	2	5
21	DPLAI	05532500	53	6	0	19	28	.0120	3/2/1999	8/18/2004	1	4	3	8	7	8	6	6	1	4	1	4
22	LCOTT	10168000	97	11	0	42	44	.0085	12/23/1998	9/12/2007	8	2	10	12	13	12	11	6	9	2	9	3
23	WARMC	11060400	72	1	0	63	8	.0065	11/16/1998	8/13/2004	8	10	8	6	3	6	4	7	4	6	3	7
24	SANTA	11074000	83	5	0	45	33	.0090	7/13/2000	7/9/2008	8	10	8	9	6	10	4	8	3	8	2	7
25	ARCAD	11447360	111	69	0	4	38	.0165	11/26/1996	7/8/2008	12	12	10	11	11	11	9	5	8	6	9	7
26	THORN	12128000	125	10	0	90	25	.0120	3/7/1996	9/19/2007	10	5	12	12	15	14	13	10	11	5	12	6
27	FANNO	14206950	126	37	1	27	61	.0120	3/1/1993	9/19/2007	8	10	9	13	15	13	9	10	6	12	11	10

Appendix 5. Download Data File of Urban Site Information (online only).

Online only urban stream-water site information for the sites used in this report is in appendix 5, a tab-delimited text file with metadata further describing the data.

http://pubs.usgs.gov/sir/2010/5139/downloads/appendix5.txt

Appendix 6. Download Data File of Pesticide Concentrations (online only).

The water-quality data used for trend analysis of pesticides in the 27 urban streams used in this report are in appendix 6, a tab-delimited text file with metadata further describing the data.

http://pubs.usgs.gov/sir/2010/5139/downloads/appendix6.txt

Publishing support provided by:
Rolla Publishing Service Center

For additional information concerning this publication, contact:
Director, USGS North Dakota Water Science Center
821 E. Interstate Ave.
Bismarck, ND 58503
(701) 250–7400

Or visit the North Dakota Water Science Center Web site at:
http://nd.water.usgs.gov

Ryberg and others—**Trends in Pesticide Concentrations in Urban Streams in the United States, 1992–2008**—Scientific Investigations Report 2010–5139