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Use of Set Blanks in Reporting Pesticide Results at the U.S. Geological Survey National Water Quality Laboratory, 2001–15

Scientific Investigations Report 2019–5055

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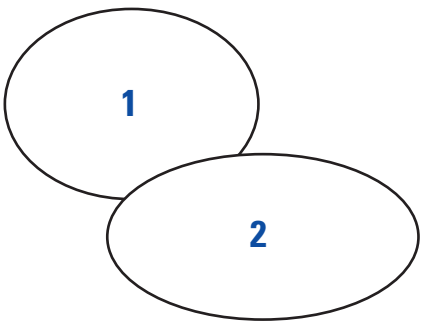

Cover. 1. A U.S. Geological Survey (USGS) chemist at the National Water Quality Laboratory prepares a sample for analysis of pesticides by gas chromatography with mass spectrometry; photograph by Mark Sandstrom, USGS.
2. An instrument at the U.S. Geological Survey (USGS) National Water Quality Laboratory used to determine pesticides in water samples by liquid chromatography with tandem mass spectrometry; photograph by Duane Wydoski, USGS.

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Supplemental Information

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

Abbreviations

ASTM	American Society for Testing and Materials
CAAT	2-chloro-4,6-diamino-s-triazine
DL	detection level
DLDQC	detection limit calculated by DQCALC software
EPA	U.S. Environmental Protection Agency
GCMS	gas chromatography/mass spectrometry
IRL	interim reporting level
LCMS	liquid chromatography/mass spectrometry
LIMS	Laboratory Information Management System
LRC	lowest reportable concentration
LRL	laboratory reporting level
LT–MDL	long-term method detection limit
MDL	method detection limit
MRL	minimum reporting level
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OBSP	Organic Blind Sample Project
QA	quality assurance
QC	quality control
QSB	Quality Systems Branch
RL	reporting level
RLDQC	reporting level established based on detection limit calculated by DQCALC software
RRL	raised reporting level
USGS	U.S. Geological Survey

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Executive Summary

Background.—Pesticide results from the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) are used for water-quality assessments by many agencies and organizations. The USGS is committed to providing data of the highest possible quality to the consumers of its data. A cooperator's inquiries about specific pesticide detections in water revealed potential laboratory contamination issues for some results. Consequently, the USGS conducted an extensive evaluation of potential low-level contamination related to processing or analysis of water-quality samples at NWQL for 21 pesticide compounds of interest to the cooperator. This is the most comprehensive study of NWQL pesticide quality-control (QC) results to date.

Purpose and scope.—The purpose of this study was to document protocols used by the NWQL to censor pesticide results and to determine the effects of laboratory contamination—as determined from detections in laboratory set blanks—on pesticide detections in groundwater and surface-water samples. More than 30,000 pesticide results from 113 selected batches of samples (2 percent or less of total batches) analyzed by the NWQL during the 15 years from 2001 to 2015 were reviewed. All laboratory results from the selected batches, including results from environmental (surface water and groundwater) and QC (set-blank, blind-blank, and blind-spike) samples, were evaluated. The study includes results for 21 pesticide compounds analyzed in groundwater and surface-water samples collected across the United States. Eleven pesticide compounds were analyzed by a gas chromatography/mass spectrometry method and 10 compounds by a liquid chromatography/mass spectrometry method.

Objectives and methods.—The objectives of this study were to (1) determine the characteristics of laboratory contamination over time, (2) compare distributions of pesticide results in set blanks with distributions in environmental samples, (3) evaluate the potential for false-positive and false-negative reporting of results, and (4) evaluate the effects of reevaluating historical pesticide results using 2017 compound identification protocols on detections of pesticides in groundwater and surface-water samples. The 113 instrument batches selected for this study contained detections of one or more of the 21 pesticide compounds in set blanks or were among those batches with the highest pesticide detection frequencies in set blanks. As a result, the dataset for this study was targeted toward pesticides and batches with laboratory contamination. The objectives were addressed by statistically comparing environmental and set-blank results; computing moving averages of set-blank detection frequencies to identify periods of episodic contamination; and using summary statistics, tabular summaries, and graphical approaches, such as time-series plots and cumulative distribution functions.

Results.—Objective 1: Laboratory contamination, as determined by pesticide detections in set blanks, was found in 13 percent of set-blank results from the 113 targeted batches included in this study (as compared to 6 percent of set-blank results from all 7,620 batches analyzed during the study period). It is estimated that 92 percent of the laboratory contamination during the study period was episodic, meaning that it occurred during discrete periods of time. All 21 of the targeted pesticide compounds had periods of episodic contamination, with most episodes ranging in duration from about 1 to 8 months. The remaining 8 percent of laboratory contamination was random or from a known source (deterministic).

Objective 2: For some compounds, graphs of cumulative distribution functions of the entire distributions of set-blank and environmental samples overlap, suggesting that there is no difference in the distributions of the two types of samples. However, time-series graphs show that detections in set blanks often occur at different times (sometimes separated by years) than detections in environmental samples, indicating clear differences in those distributions, and indicating the importance of evaluating the timing of detections in all sample types.

For most compounds detected in set-blank and environmental samples, detection frequencies were significantly greater in set blanks than in groundwater or surface-water samples ($p<0.05$). There are several explanations for this finding, including that the 113 batches of samples chosen for this study targeted batches with detections in set blanks or that detections in set-blank samples were historically determined

with less stringent identification criteria than for environmental samples (groundwater and surface-water samples).

Objective 3: The false-positive and false-negative rates from blind samples submitted during the study period by the USGS Quality Systems Branch generally were less than 1 and 5 percent, respectively, for the 21 pesticides. The only compound with a false-positive rate greater than 1 percent was flumetsulam (2.6 percent), indicating that there is a higher likelihood of flumetsulam being reported as a detection when it is not present in an environmental sample compared with the reporting of other compounds.

Objective 4: Altogether, for data in targeted batches, NWQL would have reported 0.1 percent of results from groundwater samples and 1.4 percent of results from surface-water samples differently if 2017 identification protocols were applied to historical pesticide results. In most of these cases, detections observed in historical results would change to nondetections. The small percentages of changes that would occur if historical data were reevaluated indicate that historical protocols used by the NWQL to identify detections in environmental samples were robust and produced results that are predominantly consistent with current [2017] practices.

Conclusions.—The NWQL produces high-quality pesticide results at environmentally relevant concentrations. NWQL identification protocols and censoring practices are largely effective at minimizing the reporting of false-positive and false-negative results. Laboratory contamination, when it occurred, tended to occur in episodes; thus, evaluating the timing and magnitude of detections in set blanks relative to detections in environmental samples was determined to be an important consideration for analysis of environmental results. Because NWQL censoring practices do not address all types and occurrences of laboratory contamination, options for additional censoring practices are provided for data users with more specific or stringent data-quality objectives. The methods used to analyze the 21 compounds for this report can similarly be applied to all 173 pesticide compounds that were analyzed by the NWQL during the same time period. This study also has helped to identify potential improvements in reporting USGS data, such as conducting more frequent review of set-blank datasets.

Introduction

Each year, the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) analyzes several thousand water-quality samples for pesticide compounds, using analytical methods that are developed, quality assured, and documented at the laboratory; these methods are validated and accredited independently (by non-USGS agencies). Pesticide results from the NWQL, reported in the USGS National Water Information System (NWIS) database (https://waterdata.usgs.gov/), are used extensively in water-quality studies conducted by the USGS and by numerous additional agencies, organizations, and stakeholders at local, state, regional, and national scales. The National Academies of Sciences, Engineering, and Medicine (2018) recently remarked that the USGS "has a long-established reputation for collecting and delivering high-quality, unbiased scientific information related to the Nation's water resources." The USGS is committed to providing data of known and highest possible quality to its stakeholders, cooperators, and the public.

In 2015, a cooperator approached the USGS with questions regarding the detections of some pesticide compounds in groundwater, which they considered to be unlikely based on the physical properties of the pesticides and pesticide usage patterns. The cooperator requested extensive quality control (QC) and environmental data from the NWQL to further evaluate the occurrence of 21 pesticides in samples collected throughout the United States from 2001 to 2015. Although the cooperator was primarily interested in groundwater data, the USGS determined that the issue should be expanded to include surface-water data. This report documents protocols used by the NWQL to report pesticide results and assesses the effects of laboratory contamination, as determined by detections in set blanks, on pesticide detections in groundwater and surface-water samples for commonly used analytical methods.

During the past 15 years, NWQL analytical methods used to measure pesticide compounds in water samples have evolved and improved. With these improvements, analytical **detection levels**[1] (DLs) and **reporting levels** (RLs) have changed, and NWQL protocols for identifying and reporting detections of pesticide compounds in water samples have been refined. Although the general criteria for identifying pesticide detections have not changed during this study period (Zaugg and others, 1995; Werner and others, 1996; Furlong and others, 2001; Sandstrom and others, 2001), protocols used by the NWQL to identify pesticide detections at the end of the study period in 2015, described in NWQL standard operating procedure (SOP) ORGF0500.2 (U.S. Geological Survey, written commun., November 21, 2017), have more specific instructions about qualitative identification and confirmation of the presence of the pesticide in the sample and how results are reported relative to detections in associated set blanks compared with the protocols used at the beginning of the study period in 2001. To determine if the application of 2015 NWQL protocols for qualitative identification of pesticides, as updated in 2017, would affect historical pesticide results, the USGS extensively reevaluated a subset of pesticide results from the NWQL from 2001 to 2015 as part of this study.

Because some of the data described in this report have not been previously published by the USGS, they are now published in Riskin and others (2019), which includes results for samples from both before (**original results**) and after (**reevaluated results**) the NWQL 2017 protocols for

[1]Terms listed in the glossary at the back of this report are in bold type where first used in the text. Press the Alt key followed by the left arrow key to return to the original page in the document after following the hyperlink.

identification and reporting of detections were applied. Results are provided for **environmental samples**, a variety of field-related QC samples, and a variety of laboratory-related QC samples, including **set blanks** (previously unpublished). Set-blank results play a critical role in qualifying detections in environmental samples and determining the potential presence of laboratory contamination. Comparing these original and reevaluated results enables users to better understand how pesticide data are reported and how reporting has evolved during the study period.

The purpose of this report is to document pesticide data **censoring** protocols used by the NWQL and to determine the effects of potential low-level contamination related to storage, processing, or analysis at the laboratory (referred to as "laboratory contamination" in this report)—as determined from detections in laboratory set-blank samples—on pesticide detections in groundwater and surface-water samples. Laboratory contamination is distinguished from field contamination that is related to field processes such as sample collection, storage, or transport. The study includes environmental and QC results for 21 pesticide compounds (table 1) analyzed by the NWQL during the 15-year period from 2001 to 2015. Of the 21 pesticide compounds, 11 were analyzed by gas chromatography/mass spectrometry (GCMS) methods (NWQL pesticide schedules 2001, 2003, 2032, and 2033) and 10 by a liquid chromatography/mass spectrometry (LCMS) method (NWQL pesticide schedule 2060). More than 30,000 pesticide results from 113 selected batches were reviewed (table 2), making this the most comprehensive USGS NWQL pesticide QC study to date. The four primary objectives of this study are as follows:

- *Objective 1.*—Determine the characteristics of laboratory contamination (occurrence, timing, concentrations) over time.
- *Objective 2.*—Statistically compare the distributions of pesticide results (detections and nondetections) in set-blank samples with distributions in groundwater and surface-water samples.
- *Objective 3.*—Evaluate the potential for **false-positive** and **false-negative** reporting of pesticide results in environmental samples.
- *Objective 4.*—Determine the effects of reevaluating historical pesticide results using 2017 identification protocols for identification of detections of pesticides in groundwater and surface-water samples.

Table 1. List of 21 pesticide compounds investigated to evaluate the use of set blanks in reporting pesticide results at the U.S. Geological Survey National Water Quality Laboratory from 2001 to 2015.

[GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; CAS, Chemical Abstract Service registry number; CAAT, 2-chloro-4,6-diamino-s-triazine]

Parameter code	Analyte	CAS	Analytical schedule[1]
	GCMS compounds		
34653	*p,p'*-DDE	72-55-9	2001
39381	Dieldrin	60-57-1	2001, 2003, 2032, 2033
39415	Metolachlor	51218-45-2	2001, 2003, 2032, 2033
39572	Diazinon	333-41-5	2001, 2003, 2032, 2033
49295	1-Naphthol	90-15-3	2003, 2032, 2033
61600	Oxyfluorfen	42874-03-3	2033
61606	Tefluthrin	79538-32-2	2033
82661	Trifluralin	1582-09-8	2001, 2003, 2032, 2033
82671	Molinate	2212-67-1	2001, 2032, 2033
82673	Benfluralin	1861-40-1	2001, 2003, 2032, 2033
82682	Dacthal	1861-32-1	2001, 2003, 2032, 2033
	LCMS compounds		
04033	Diphenamid	957-51-7	2060
04039	CAAT[2]	3397-62-4	2060
49297	Fenuron	101-42-8	2060
49310	Carbaryl	63-25-2	2060
50337	Sulfometuron-methyl	74222-97-2	2060
50356	Imazaquin	81335-37-7	2060
50407	Imazethapyr	81335-77-5	2060
50471	Propiconazole	60207-90-1	2060
61694	Flumetsulam	98967-40-9	2060
61697	Metsulfuron-methyl	74223-64-6	2060

[1]Periods of time that analytical schedules were operational:

Schedule 2001: December 7, 1994, to present (ongoing, as of June 30, 2018)
Schedule 2003: July 22, 2002, to present (ongoing as low-demand method, as of June 30, 2018)
Schedule 2032: March 4, 2005, to February 12, 2016
Schedule 2033: March 4, 2005, to present (ongoing, as of June 30, 2018)
Schedule 2060: May 14, 2001, to present (ongoing as low-demand method, as of June 30, 2018

[2]CAAT was discontinued on December 31, 2006.

Table 2. Description of environmental and quality-control data compiled by the U.S. Geological Survey National Water Quality Laboratory to evaluate the use of set blanks in reporting pesticide results from 2001 to 2015.

[Numbers of records shown inside parentheses indicate the number of records in the respective table in Riskin and others (2019), for the 11 gas chromatography/mass spectrometry (GCMS) or 10 liquid chromatography/mass spectrometry (LCMS) compounds included in this study. QC, quality control; QSB, USGS Quality Systems Branch; OBBP, Organic Blind Blank Project; OBSP, Organic Blind Sample Project]

Contents of data table	Name of table in Riskin and others (2019)	Number of records in table	Sample types	Type of water source	Instrument batches and analysis dates	Compounds included	Number of results by sample type
Environmental and quality-control results for 113 selected instrument batches (called "environmental and QC data tables" in the report)							
GCMS[1] results from selected batches	USGS_GCMS_Pesticides_Environmental.csv	16,429	Environmental and QC samples[2]	All water sample types[3]	70 batches from May 2001 to June 2015	11 selected for this study[4]	Set blank: 1,663 Groundwater: 4,553 Surface water: 7,199 Other[2,3]: 3,014
LCMS[5] results from selected batches	USGS_LCMS_Pesticides_Environmental.csv	14,620	Environmental and QC samples[2]	All water sample types[3]	43 batches from October 2001 to July 2015	10 selected for this study[6]	Set blank: 1,673 Groundwater: 4,118 Surface water: 5,528 Other[2,3]: 3,301
Set-blank results for all 7,620 instrument batches in the study period (called "set-blank tables" in the report)							
GCMS set blank results	USGS_GCMS_Pesticides_Set-BlankResults.csv	385,707 (51,159)	Set blanks	Laboratory reagent-grade water	All available batches from May 2001 to May 2016	104 in selected NWQL pesticide schedules[7]	All are set blanks
LCMS set blank results	USGS_LCMS_Pesticides_Set-BlankResults.csv	114,566 (17,954)	Set blanks	Laboratory reagent-grade water	All available batches from May 2001 to Aug 2015	69 in selected NWQL pesticide schedule[8]	All are set blanks
All available blind-blank results from NWQL and QSB (called "blind-blank tables" in the report)							
GCMS blind-blank results	USGS_GCMS_Pesticides_BB.csv	30,680 (4,036)	Blind blanks from OBBP and unspiked blind spikes from OBSP	Laboratory reagent-grade water	All available blind blanks from April 2004 to June 2012	96 in NWQL pesticide schedules 2001 and 2033	Blind blanks: 416 Unspiked blind spikes: 30,264
LCMS blind-blank results	USGS_LCMS_Pesticides_BB.csv	4,670 (719)	Blind blanks from OBBP and unspiked blind spikes from OBSP	Laboratory reagent-grade water	All available blind blanks from Jan 2004 to May 2012	64 in NWQL pesticide schedule 2060	Blind blanks: 1,053 Unspiked blind spikes: 3,617
All available blind-spike results from QSB (called "blind-spike tables" in the report)							
GCMS blind-spike results	USGS_GCMS_Pesticides_BS.csv	8,346	Blind spikes from QSB	Laboratory-prepared spikes	All available blind spikes from January 2001 to January 2016	11 selected for this study[4]	All are blind spikes
LCMS blind-spike results	USGS_LCMS_Pesticides_BS.csv	4,086	Blind spikes from QSB	Laboratory-prepared spikes	All available blind blanks from May 2001 to April 2014	10 selected for this study[6]	All are blind spikes

[1]NWQL pesticide schedules 2001, 2003, 2032, and 2033.

[2]QC samples include field blanks, field spikes, laboratory blanks (including set blanks), laboratory spikes, and samples from the USGS Quality Systems Branch.

[3]Groundwater, surface water, wet deposition, treated water, and various types of blank and spiked water.

[4]The 11 compounds analyzed by GCMS methods are *p,p'*-DDE, dieldrin, metolachlor, diazinon, 1-naphthol, oxyfluorfen, tefluthrin, trifluralin, molinate, benfluralin, and dacthal.

[5]NWQL pesticide schedule 2060.

[6]The 10 compounds analyzed by LCMS methods are diphenamid, 2-chloro-4,6-diamino-s-triazine (CAAT), fenuron, carbaryl, sulfometuron-methyl, imazaquin, imazethapyr, propiconazole, flumetsulam, and metsulfuron-methyl.

[7]GCMS schedules 2001, 2003, 2032, and 2033 include a total of 104 individual compounds.

[8]LCMS schedule 2060 includes a total of 69 individual compounds.

Reporting of Pesticide Results at the NWQL

General steps for production of NWQL pesticide results involve sample collection, laboratory analysis, data analysis, and publication of environmental sample results in the USGS NWIS water database (https://waterdata.usgs.gov/). To help ensure the quality of the published data, multiple review steps are performed by analysts at the NWQL, by field personnel or project reviewers at USGS water science centers (WSCs) where the samples were collected, and if necessary, by technical reviewers to troubleshoot questionable results (fig. 1). Review steps for the preliminary result (fig. 1, green rectangle) are undertaken, preferably as quickly as possible, so that obvious errors can be fixed in NWIS. Not all review steps in the last two parts (fig. 1, red and orange rectangles) are done routinely for all pesticide results produced by the NWQL; review of long-term QC data is typically done for water-quality data that are part of USGS national programs or long-term WSC projects. Revisions to data that were originally published in NWIS are either changed in NWIS through a data reload (if the change corrects analytical or reporting errors by the NWQL) or are published in a data release (if the change involves reinterpretation of data, with original data in NWIS not changed) in accordance with USGS Fundamental Science Practices.

Results from the determination of pesticides in environmental samples are reported (1) with a concentration if the compound is determined to be present in the sample based on qualitative identification criteria or (2) with a reporting level value and remark code "<" if the compound is not detected or the detection is censored for any reason. DLs and RLs are dynamic and are periodically reassessed by the NWQL to reflect recent conditions at the laboratory. The NWQL used primarily two types of RL conventions to report pesticide results in the laboratory schedules covered in this report (fig. 2). The first was the **laboratory reporting level** (LRL) convention (Childress and others, 1999), with the LRL typically set at twice the **long-term method detection limit** (LT–MDL). The second, applied to selected compounds analyzed with LCMS methods for specified periods, was the **minimum reporting level** (MRL) convention, where the MRL is defined as the smallest measured concentration of a constituent that may be reliably measured by using a given analytical method (Childress and others, 1999). A third RL convention, the **interim reporting level** (IRL), was only used during periods when the pesticide schedule specified the application of the LRL convention but the DLs for some or all method analytes had not yet been established or verified using the LT–MDL procedure. A detailed history of RLs and reporting procedures used by the NWQL from 2001 through 2015 is presented in appendix 1. Beginning in 2001, the RL type and RL value have been populated in NWIS (U.S. Geological Survey, 2017a) as sample-associated metadata and are available for the public to retrieve along with the associated data.

The LT–MDL is determined so that detections with concentrations at the LT–MDL, in theory, have no more than a 1-percent probability of being false-positive detections (Childress and others, 1999). The LRL, which is designed to minimize the risks of both false-positive and false-negative detections, corresponds to the concentration threshold at which a nondetection reported as <LRL, in theory, has no more than 1-percent probability of being a false negative (Childress and others, 1999; U.S. Geological Survey, 2010, attachment C). The LT–MDLs are established by using spiked reagent-water matrices (and occasionally adjusted based on set-blank or blind-blank results), and the NWQL typically has set the LRL at two times the LT–MDL by assuming 100-percent analyte **recovery** (recovery is the primary indicator of the analytical bias of a measurement; recovery of 100 percent indicates no bias) for most pesticides in these methods (U.S. Geological Survey, 2010, attachment C).

Because the analytical methods for pesticides used by the NWQL are information-rich mass spectrometry methods, detections may be reported below both the RL or the DL with appropriate qualifiers (Childress and others, 1999). One benefit of reporting values at these low concentrations is to help characterize the presence of environmental contaminants, including pesticide residues, in water resources that might be bioactive or have water-quality benchmarks at trace (part-per-trillion or lower) levels. However, concentrations reported below the DL have a greater risk of being a false positive (the compound is reported as present when not truly present); detailed information is in the "Objective 3: False-Positive and False-Negative Results" section of this report. Results for compounds determined by these information-rich methods can be reported as low as the **lowest reportable concentration**, which the NWQL often has set at 1 to 10 percent of the DL for the analyte (fig. 2), although historic practices with regard to this lower limit have not been documented.

Reporting results for compounds analyzed by mass spectrometry methods is inherently a two-part process: identification of the compound followed by quantification (Zaugg and others, 1995; Werner and others, 1996; Furlong and others, 2001; Sandstrom and others, 2001). Identification of a pesticide during chemical analysis is based on qualitative identification criteria for chromatographic retention time and the presence and ratios of characteristic mass spectrometry fragment ions. If the compound meets qualitative identification criteria, the concentration is determined and reported in the quantitation part of the process, which is the assignment of the numerical concentration value. When the compound does not meet qualitative identification, the result is reported as <RL unless conditions warrant use of a **raised reporting level** (RRL), which is greater than the RL in place at the time of the analysis (fig. 2).

For most of the period covered by this report (May 1, 2001, through September 30, 2010), results that met qualitative identification criteria with a concentration less than the reporting level were reported with an NWIS remark code of "E" for estimated concentration (fig. 1.1*A*; Childress and

Responsible party	Steps to collect, analyze, review, and publish water-quality data	Status of analytical result at each step
Data collector†,‡	**Collect, process, and send the environmental sample to the NWQL using protocols in the NFM:** Collect and process associated field quality-control (QC) samples as specified in the sampling plan Send sample to the NWQL using shipping protocols specified in the NFM Begin sample tracking and data management according to protocols of the project	Not applicable
NWQL	**Receive and log in sample:** Check that the temperature of the cooler, the container types, and holding times match requirements Verify that information on bottle labels and sample shipping form are consistent Send sample to the appropriate staging area **Prepare sample for analysis within a set (group) of samples:** Prepare set reagent blank and spike samples and other requested QC samples Prepare sample for analysis according to method requirements	
NWQL	**Analyze sample on instrument:** Follow procedures specified in method for instrument cleaning, tuning, and maintenance Perform initial calibration Perform continuing calibration verification and other performance assessments during sample analysis	Raw result
NWQL	**Initial review of result by primary instrument analyst:** Review instrument standard and laboratory QC sample results and apply censoring or qualification to sample result as appropriate Reanalyze sample if significant failure of set or instrument batch QC samples **Secondary review of result by an independent instrument analyst:** Primary instrument analyst responds to or modifies sample results based on secondary review **Upload preliminary result to LIMS:** Primary instrument analyst corrects discrepancies identified by automated data review at upload to LIMS	Preliminary result; not publicly available
NWQL	**Upload preliminary result to NWIS for review by data analyst and WSC**	Interim result, published in NWIS with code to indicate "presumed satisfactory" (unless result does not pass this preliminary review step or code is changed to prevent publication while result is "in review")
DA, WSC†,‡	**Review the preliminary result:** Check completeness and accuracy of sample and result, including ancillary data such as assignment of database codes Perform basic check of laboratory result, such as examination of outliers or inconsistencies with field results Examine laboratory QC sample results (blank, spike) associated with the environmental result Examine field QC results (blank, spike, and replicate) associated with the environmental result Evaluate result in context of project- or program-specific knowledge Request rerun, verification, or reload from NWQL, if necessary	
DA, NWQL	**If necessary, troubleshoot problems or issues identified during review by DA and WSC**	
DA, WSC†,‡	**If result is deemed satisfactory based on review by WSC DA, code to indicate "reviewed and accepted"**	Final result published in NWIS, coded "reviewed and accepted"
DA, WSC†,‡	**If result is deemed unsatisfactory based on review by WSC DA, code to indicate "reviewed and rejected"**	Result not published
DA, NP, LP, ‡WSC	**Review collective results over time in context of long-term QC data [this step may involve reinterpretation of the laboratory analytical result]:** Evaluate long-term laboratory reagent spike and field spike results and adjust for recovery corrections, as necessary Evaluate long-term laboratory blank results to determine potential contamination from laboratory-derived contamination Evaluate long-term blind-blank and blind-spike results from QSB Evaluate field blank results to determine potential bias from nonlaboratory-derived contamination Evaluate field replicate results to quantify variability	If published (NWIS) results are revised based on evaluations of long-term QC data, revised results are published in USGS data release; results in NWIS generally are not changed
NWQL	**Identify errors, if any, related to laboratory analysis or reporting after results are published in NWIS**	NWQL changes results in NWIS by a data reload

others, 1999; U.S. Geological Survey, 2015). For these results, even though detections are considered to be certain (not estimated) because qualitative identification criteria applied at the time of analysis were met, final quantitative results that are near or even below the lowest **calibration standard** have some uncertainty in the numerical value of the result (Childress and others, 1999). At low concentrations, detections with an "E" remark code are no less certain than detections without an "E" remark code. In addition to its application to concentrations <LRL or <IRL, some other possible reasons for "E" remark code use include reported concentrations that are greater than the highest calibration standard, flag raised by some type of associated QC sample, or lower than expected recovery of one or more surrogate compounds in the sample. Some compounds are always reported with an "E" remark code because either the bias or variability (or both) is outside the acceptable range defined for the method (Childress and others, 1999).

Beginning October 1, 2010, use of the "E" remark code for results <RL was replaced with use of more descriptive NWIS result-level value-qualifier codes (fig. 1.1; U.S. Geological Survey, 2010). Beginning January 1, 2012, additional coding was routinely implemented for cases where the concentration might be influenced by detections in corresponding set blanks, with inclusion of an "E" remark code and a "v" result-level value-qualifier code with the concentration (app. 1; U.S. Geological Survey, 2011).

When the RL type is an MRL, reporting conventions differ from the preceding description of the LRL and IRL types. Before October 1, 2000, detections of compounds with RL type MRL were not censored if the determined concentration was below the MRL (fig. 1.1*B*). On October 1, 2000, the NWQL began censoring results below the MRL unless the chemist included the "E" remark code with the result and used the Laboratory Information Management System (LIMS) to implement this change. If the result included the "E" remark code, a quantified result below the MRL could be reported. For example, reporting under this condition was the case for all LCMS **analytical schedule** 2060 compounds that had the MRL RL type code at the start of the method in May 2001 through August 2002 (see additional discussion regarding MRL reporting for schedule 2060 compounds in the "Results and Discussion by Study Objective" section of this report). Beginning December 1, 2009, any quantified values below the MRL for compounds reported using the NWIS MRL report level type code were automatically censored regardless of the presence of an "E" remark code. Thus, any results that were detections according to instrument software but that were less than the MRL concentration were reported to the NWIS database as <MRL (U.S. Geological Survey, 2015).

Figure 1 (facing page). The steps used to collect, analyze, review, and publish water-quality data collected by the U.S. Geological Survey (USGS) and analyzed by the National Water Quality Laboratory (NWQL), including responsibilities and status of analytical result. These steps generally are completed in the order indicated by the arrows. All projects and water science centers (WSCs) carry out the steps shown in the first five rectangles (up to and including the blue rectangle) but not all projects and WSCs necessarily carry out the steps in the last two rectangles (red and orange). Steps designated with † are not discussed in this report; steps designated with ‡ indicate that some projects, such as the National Water Quality Assessment Project or the California Water Science Center Groundwater Ambient Monitoring Assessment Project, perform additional steps not shown in this diagram. NFM, National Field Manual (U.S. Geological Survey, variously dated); QC, quality control; NWIS, National Water Information System; QSB, Quality Systems Branch; DA, data analyst; NP, national program; LP, large project.

Censoring of Results by the NWQL

Censoring is a tool used to prevent the reporting of false-positive detections, where the analyte is reported present when not in the environment. The NWQL censors analytical results under several circumstances. When the primary instrument analyst determines that an apparent detection of a compound from the instrument cannot be distinguished from laboratory contamination (the result cannot be confidently considered a detection), the analyst will report the result as a nondetection. (A nondetection is more accurately viewed as the analyte not being classified as present in the sample above a specified threshold concentration, which typically is the reporting level, or a raised reporting level in the case of an **interference** or for other reasons, as it is possible that the compound was detected yet not reported because of censoring). This section describes protocols that the NWQL has historically used and that were used in 2017 for censoring environmental sample data based on laboratory contamination.

Set Blanks and Sample Sets

For the pesticide methods discussed in this report, the type of laboratory QC sample used by the NWQL to assess laboratory contamination is the set blank. The set blank consists of a reagent matrix (**reagent-grade water** for these methods) that is known to be free of the analytes of interest. One set blank is prepared along with a laboratory reagent spike (set spike) and up to eight environmental samples, which constitutes the complete set of samples that are extracted and further prepared for subsequent instrument analysis (table 3). For these analytical methods, a set is defined based on sample preparation (not sample analysis) because the assumption for doing set-based censoring is that contamination arises during the sample preparation step and not from something related to the batch.

Results that meet qualitative identification criteria and have RL codes of LRL or IRL may be reported as low as the LRC value
Results that do not meet qualitative identification criteria are reported as less than (<) RL (default) or < RRL if conditions warrant the RRL
Reporting of results that meet qualitative identification criteria and have an RL code of MRL is described in appendix 1

EXPLANATION

LRC **Lowest reportable concentration**—Applies to compounds analyzed using mass spectrometry methods and has typically been established as either 1 percent (results through September 30, 2009) or 10 percent (results beginning October 1, 2009) of the detection level (DL)

DL **Detection level**—Designated as method detection limit (MDL) or long-term method detection limit (LT–MDL)

RL **Reporting level**—Designated as laboratory reporting level (LRL), interim reporting level (IRL), or minimum reporting level (MRL)

RRL **Raised reporting level**—An RL that is greater than the default RL; the most common reasons for applying a RRL are the presence of an interfering compound, analyte presence in associated set blank, or insufficient sample volume

Figure 2. Reporting conventions used by the National Water Quality Laboratory for pesticides analyzed by mass spectrometry methods. Terms in **bold** typeface are defined in the glossary.

Table 3. Typical composition and order of environmental and quality-control samples in an instrument batch, which includes at least two sample preparation sets.

[The term "preparation set" used in this table is synonymous with "sample set" used in this report. A detailed sequence of samples for liquid chromatography/mass spectrometry analysis is listed in Furlong and others (2001, table 12). CCV, continuing calibration verification standard; QC, quality control]

Vial	Daily CCV sequence	Description of QC sample type
	Preparation set 1	
1 (or more)	CCV (or multiple calibration standard samples)	CCV checks whether the instrument still meets calibration criteria (at one concentration) since the instrument was last calibrated using multiple calibration standards. Use of multiple calibration standards at batch start is more common than just CCV use.
2	Instrument detection level standard	Used to verify that analytes can be qualitatively identified and quantified within criteria at a concentration equal to or less than the report level prior to injecting prepared samples in the batch.
3	Performance Evaluation Blank (instrument blank)	A solvent-only blank that monitors instrument (injection) carryover. Only detector response (peak area) is reviewed as concentration is not available.
4	Preparation set method spike (set 1 spike)	Used to monitor laboratory recovery of method analytes from spiked reagent water. A given set spike recovery is evaluated relative to recovery criteria compiled using many set spikes and is considered relative to performance information (such as surrogate recoveries) for other samples in the given set. Set spike recovery is used to monitor continuous and overall method performance over time.
5	Preparation set method blank (set 1 blank)	Used to establish analyte contamination derived from laboratory sample preparation and analysis. Set 1 blank is used, as needed, to censor samples prepared in set 1.
6–13	Environmental samples (typically eight)	
14	CCV	
	Preparation set 2	
15	Preparation set method spike (set 2 spike)	Same as the set 1 spike.
16	Preparation set method blank (set 2 blank)	Same as the set 1 blank.
17–24	Environmental samples (typically eight)	
25–[as needed]	Additional set quality-control and environmental samples from other preparation sets that are bracketed with CCVs, if also analyzed in the batch	
Second to last vial	CCV	This QC sample does the same as described above for set 1.
End vial	Instrument detection level standard	This QC sample does the same as described above for set 1.

Two or more sets of prepared samples (QC and environmental) typically are grouped together to form the instrument **batch** (or sequence) for analysis that also includes instrument QC standards (calibration, continuing calibration verification, and instrument DL standards) and other instrument QC samples (table 3). An **instrument blank** is a type of blank sample (where for these methods, the vial contains only solvent) analyzed as a part of the instrument batch but that is not specifically prepared (extracted) with a given set of associated environmental samples. A pesticide detection in the instrument blank is an indication of the potential for contamination during the GCMS or LCMS instrument analysis step. For these methods, instrument blanks were used by the primary analyst during initial data review only and are not reported to LIMS nor are they available to data users.

During analysis of pesticide compounds by GCMS or LCMS, reporting a pesticide as a detection in a set blank can be attributed to the pesticide's introduction during sample preparation-related steps, to carryover during the GCMS or LCMS instrumental analysis, to the observation of the quantitation ion at the correct retention time where there are insufficient or no responses for qualification ions (this condition does not meet normal qualitative identification criteria), or to the incorrect identification of a coeluting compound (an interference) as a pesticide. For all these example cases, the set blank is contaminated by a compound, although not necessarily by the pesticide being detected; all instances of such circumstances are referred to as blank contamination. Contamination can result from the use of improperly cleaned equipment or supplies or through contact with equipment or the atmosphere from other samples with high concentrations of the compound (other types of carryover). Peripherally related to sources of contamination, but potentially important in the conversation about contamination, some amount of variability among instruments is intrinsic to the measurement process.

Detections based on insufficient qualitative information or incorrect identification of the compound due to interference can be reported in mass spectrometry methods when qualitative identification criteria are not stringent enough or are not applied consistently by different analysts. This is especially important when the signal of the qualifier ion is very low by comparison to the response of the primary ion used for quantitation and is difficult to distinguish from the background signal (noise) of the chromatogram. Evaluation of a sufficient number of laboratory set-blank samples and adherence to quality assurance standards are important for verification of qualitative identification criteria procedures that are based on retention time and characteristic ion ratios; verification also is used to ensure that these procedures are appropriate and are applied correctly (Lehotay and others, 2015; Mol and others, 2015).

Set Censoring

The primary-instrument analysts at the NWQL use information about detections in set blanks in a process called set-by-set censoring (called "**set censoring**" in this report) to further evaluate detections (beyond identification of the compound) in environmental samples in the same set. The decision by the primary instrument analyst to apply set censoring is reviewed by an independent (secondary) instrument analyst at the NWQL (fig. 1).

Set censoring of original results for compounds analyzed with GCMS methods (that is, "GCMS compounds") was based on a detection in the set blank of either the same set (set censoring) or a different set blank in the same instrument batch (batch censoring). Batch censoring was rarely applied to environmental GCMS data throughout the study period, primarily because contamination is most likely to occur during sample extraction and other preparation steps rather than from the injection on the GCMS instrument. None of the original LCMS results in the 43 batches that were reviewed had evidence of batch censoring; rather, unique to the LCMS method, detections of compounds were censored by analysts based on detections in bracketing instrument (solvent only) blanks.

Where sets are censored, the frequency of detection of some analytes in the set blank might be greater than the frequency of detection observed for field-related blank and environmental results in the set (that were set censored) because the set blank is the only type of sample for which analyte detections are not censored; in other words, field-related blanks, similar to results for all other sample types in the set except for set blanks, are subject to the same censoring rules as those applied to environmental samples. Potential contamination from equipment cleaning and sample collection, processing, shipping, and laboratory analysis is determined from field blanks, which are exposed to the same sampling equipment and conditions associated with the collection of an environmental sample. A field-related blank refers to either a field blank, a source-solution blank (a sample of blank water taken directly from its source container without exposure to sampling equipment or conditions), or an equipment blank (a sample of blank water used to demonstrate that the collection and processing equipment is not introducing contamination). Field-blank results may be used by the data analyst to help identify potential sources of nonlaboratory contamination (Martin and others, 1999; Medalie and Martin, 2016), but are not used by the NWQL as the basis for censoring samples. Data users typically are not aware when a field-blank result was a detection that was reported as a nondetection because it was subject to set censoring, unless the concentration was more than three times the concentration in the set blank and a "v" value-qualifier code was used.

For GCMS compounds, protocols for set censoring of detections in environmental samples based on detections in the set blank associated with the environmental samples have changed over time. For samples collected through December 31, 2011, detections in environmental and field QC samples were censored if the concentration was less than a detected concentration in the set blank. For samples collected on or after January 1, 2012, censoring of environmental and field QC samples has depended on the RL and the

Table 4. Data-reporting conventions for compounds analyzed using gas chromatography/mass spectrometry methods for pesticide results at the National Water Quality Laboratory.

[These conventions are for compounds analyzed when there is a detection in the associated set blank and are applied by the U.S. Geological Survey National Water Quality Laboratory as of January 1, 2012. Data in this table are reproduced from U.S. Geological Survey (2011). C_s, concentration of sample; C_b, concentration of set blank; RL, analyte reporting level concentration; NWIS, National Water Information System; >, greater than; ×, times; ≤, less than or equal to; <, less than; E, estimated; v, analyte detected in laboratory blank]

C_s in relation to C_b and RL	Remark code	Sample result reported to NWIS	Result-level value qualifier code
$C_s > 10 \times C_b$	None	C_s	None
$3 \times C_b \leq C_s \leq 10 \times C_b$	E	C_s	v
$C_s < 3 \times C_b$ and $C_s \leq$ RL	<	RL	None
$C_s < 3 \times C_b$ and $C_s >$ RL	<	C_s	v

concentration in the environmental sample relative to that in the set blank (table 4; U.S. Geological Survey, 2011). For compounds analyzed using the pesticide schedule 2060 LCMS method, the threshold used to censor environmental samples was less than or equal to 10 times the concentration of the set blank (NWQL SOP ORGF0338.3, U.S. Geological Survey, written commun., December 20, 2011).

MRL Censoring

The NWQL used MRL as the RL type for all pesticide schedules (except 2033) until the advent of the LRL reporting convention (tables 1.1 to 1.5). The NWQL has used MRLs in different ways over time as a mechanism to systematically censor data, especially for analytes that exhibited performance limitations. Before October 1, 2000, the MRL was not used as a censoring threshold below which no result was reported (fig. 1.1). Between October 1, 2000, and November 30, 2009, detected results could be reported below the MRL concentration only if the result included an "E" remark code by the analyst. Beginning December 1, 2009, any detections that were less than the MRL concentration were censored and reported as <MRL.

Review of Results in Context of Long-Term QC Data

Data review for pesticide results does not necessarily end with publication in NWIS. The NWQL is a fee-for-service laboratory, and as such, is obligated to provide results to customers in a timely manner. An additional layer of data review entails retroactive examination of information from long-term QC data that are not fully available when results are published. Long-term QC data include laboratory and field spikes, field replicates, field-related blanks, set blanks, and blind blanks and blind spikes from the independent USGS Quality Systems Branch (QSB, fig. 1). Spike, replicate, and blank samples collected in the field (field QC samples) are typically evaluated by the WSC data analyst during WSC review in the context of the association of these samples with individual environmental results prior to publication of the environmental results in NWIS (fig. 1, "Review the preliminary result" step). After publication in NWIS, data analysts from national programs, large projects, or WSCs of the USGS might compile and review long-term and multistation field QC sample results to assess bias and variability of national water-quality datasets that are in the same collective inference space (QC samples that represent the same conditions, in terms of potential bias and variability, under which environmental samples were collected); in general, water-quality samples collected and analyzed by the USGS using standard and published protocols can be assumed to be in the same inference space (Mueller and others, 2015).

Reviews of long-term QC data are typically undertaken by a USGS national program, which has resources and perspective for a comprehensive evaluation, rather than by an individual WSC. Because USGS policy generally prohibits revising water-quality results that have been published in NWIS, any changes to results based on review of long-term QC data are published separately in an appropriate outlet (app. 4; U.S. Geological Survey, 2017b). The rationale is that results produced by the NWQL are noninterpretive data, whereas new findings that are reached based on interpretation of laboratory and field quality-control results collected over time are interpretive data.

In addition to use for review of individual results by the data analyst and national programs, collective long-term QC data periodically are reviewed by the NWQL or a national program to identify and troubleshoot problems or issues related to data quality (fig. 1, bottom row). One type of NWQL review uses information about detections in set blanks to establish MRLs (app. 1). The primary reason that the NWQL uses the MRL reporting convention, rather than the LRL, is chronic detections in set blanks (chronic detections are defined as having a detection frequency of 10 percent or more; U.S. Geological Survey, 2005), although other methods or instrument performance issues also can be triggers. Although a protocol for establishing or setting a censoring MRL for pesticides is not published, the protocol is similar to that used for some blank-limited analytes in the NWQL method for steroid hormones (Foreman and others, 2012). Decisions to use either the MRL or LRL reporting convention and to set the value for the RL are made at annual quality-assurance data-review meetings involving analysts from different departments within the NWQL and, historically, from the USGS QSB LT–MDL project. Multiple years-worth of QC data are typically considered at these annual data-review meetings.

Another type of periodic NWQL review of long-term QC data is assessment of blind-blank samples (mostly from the Organic Blind Blank Project [OBBP]) and blind-spike samples (from the Organic Blind Sample Project [OBSP]) submitted to the NWQL by the USGS QSB. The QSB implemented these projects to provide independent quality assurance of organic analyses at the NWQL through the submission of QC samples (blind-blank and blind-spike samples) that are treated the same as environmental samples and are designed to capture the same sources of variability as environmental samples. These QSB projects provide an independent tool to investigate detections in set blanks at the NWQL. Blind-blank samples were submitted to some of the pesticide schedules by the NWQL Quality Assurance Unit in 2004 and then by QSB from 2007 to 2012 (all collectively grouped under the OBBP for this report). Blind-spike samples, fortified with an unknown (to the NWQL) subset of the schedule analytes, were submitted by the OBSP during the entire study period.

Every unexpected result for blind blanks and blind spikes triggers an investigation and corrective action if needed. The NWQL investigation into unexpected OBSP results involves the search for correlations with detections in set blanks that could independently confirm false-positive or false-negative (for blind spikes) results and the search for possible explanations for detections in blind blanks. Explaining detections in blind blank samples and of nonspiked analytes in OBSP blind-spike samples (referred to elsewhere as unspiked blind spikes) entails a review of possible **random contamination** missed by set censoring for unspiked analytes and the emergence of **episodic contamination** for the method that is inadequately identified because of few detections in set blanks. It also requires a review of possible non-NWQL-derived contamination arising from the OBSP spike mixture used to prepare blind-spike samples when there are detections of nonspiked analytes. Unspiked blind-spike samples are blind spikes for which an incomplete set of analytes were included in the spike mixture. Analytes not included in the spike mixture, if found in the blind-spike sample, provide evidence for contamination of the spike during sample processing and analysis and represent a false-positive result.

The contribution of blind-blank and blind-spike results towards understanding the distribution of random laboratory contamination may be limited because detections in these types of samples, which are treated as environmental samples, might be censored depending on the relative concentration in the associated set blank, similar to field-related blanks or environmental samples or on whether MRL censoring was in effect (fig. 1.1). On the other hand, blind-sample results that are not censored are useful for assessing when random contamination affects environmental samples. Pesticide results from the OBBP and the OBSP are used, in general and for this study, to help define the potential for false-positive and false-negative (OBSP samples) reporting of environmental results.

Types of Laboratory Contamination and the Relation to QC Censoring

The source and timing of laboratory contamination are important considerations for censoring results. Set censoring immediately addresses **deterministic contamination** from the laboratory, which assumes that all contamination observed in the set blank sample occurred during processing (extraction through analysis) and affects all associated environmental samples in that particular set. An example of deterministic laboratory contamination is when equipment such as a contaminated syringe is used during processing for a set and contaminates all samples in that set, but the same contaminated syringe is not used and does not contaminate samples in the previous or subsequent sets. Set censoring also addresses **semideterministic contamination**, where some but not all samples in the set could be contaminated depending on the source and level of contamination. Hereinafter, the term "deterministic laboratory contamination" is used to mean either deterministic or semideterministic laboratory contamination.

Set censoring cannot address **random laboratory contamination**, such as from airborne dust particles that land on some samples, for example, unless the source of random contamination happens to affect the set blank to the same degree. **Episodic laboratory contamination** is related to the timing of laboratory contamination as determined by detections in set blanks that occur in clusters or episodes in time. It is defined specifically in this report as times when detection frequencies in set blanks are above 10 percent for a variable-sample moving average window (the calculation is described in "Objective 1: Determine the Characteristics of Laboratory Contamination Over Time" of the "Methods" section of this report). To summarize, set censoring is used primarily to address deterministic contamination (detections in set blanks are seen and censoring of detections at similar concentrations for other samples in the set takes place almost immediately), and collective information from many set blanks over time is used retrospectively (fig. 1, red rectangle) to identify and address random and episodic contamination.

Methods

This section describes the composition and processing steps of the four distinct types of datasets (table 2) used as the basis of analysis in this study (Riskin and others, 2019), as well as statistical and graphical approaches used in this study.

Environmental and Quality-Control Results for Selected Instrument Batches

The environmental and QC data (Riskin and others, 2019) include all laboratory results from the selected instrument batches, including environmental, field QC, set blank, and QSB blind-blank and blind-spike results. NWQL analysts retrieved these environmental and QC data in 2016 and 2017 from the NWQL internal LIMS database. The five pesticide schedules included in this study were the most commonly requested schedules for pesticides in filtered water for the study period. The four GCMS pesticide schedules listed in table 5 have the same preparation steps and are analyzed using the same method; the only difference among these schedules is the different subsets of pesticide compounds included in each schedule and the different dates that each schedule was available (table 1).

Table 5. Instrument batches selected for this study of 21 compounds analyzed by the National Water Quality Laboratory with gas and liquid chromatography/mass spectrometry methods from 2001 to 2015.

[GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry]

Year	All batches analyzed at the National Water Quality Laboratory		Targeted batches included in this report	
	GCMS, schedules 2001, 2003, 2032, 2033	LCMS, schedule 2060	GCMS, schedules 2001, 2003, 2032, 2033	LCMS, schedule 2060
2001	318	130	13	1
2002	515	244	4	3
2003	518	128	7	2
2004	627	159	1	5
2005	503	205	14	7
2006	450	171	8	4
2007	361	155	2	3
2008	496	137	6	4
2009	346	103	2	3
2010	385	134	8	4
2011	457	96	2	2
2012	350	121	1	2
2013	162	45	0	1
2014	160	43	1	1
2015	97	14	1	1
Total	5,745	1,885	70	43
Percent			1	2

Selection of Instrument Batches for Retrieval of Pesticide Data

For the investigation in this study, 70 batches of GCMS compounds from NWQL pesticide schedules 2001, 2003, 2032, and 2033 (Zaugg and others, 1995; Sandstrom and others, 2001) analyzed between January 2001 and June 2015 and 43 batches of LCMS compounds from pesticide schedule 2060 (Werner and others, 1996; Furlong and others, 2001) analyzed between November 2001 and July 2015 were selected (table 5). In April and June 2016, the NWQL reviewed for accuracy (both identification and quantitation) 241 set-blank results from 126 batches of samples analyzed between January 2001 and January 2016 representing 41 compounds. The review was prompted in part by finding that the laboratory QC database contained results with concentrations in set blanks for several compounds above 1 microgram per liter (µg/L), which were possibly the result of transcription errors. Because detections in set blanks at these concentrations tended to be episodic, the initial review of GCMS compounds in these set blanks by the NWQL did not reflect the temporal distribution of all samples analyzed. This initial review also identified some set-blank results that would change on the basis of 2017 identification protocols for identifying pesticide detections that differed from protocols in place at the time the samples were originally analyzed. The 70 batches of GCMS compounds examined in this study were selected to be analyzed to assess how these changes might affect results for environmental samples and intentionally contained detections in set blanks of one or more of the 11 target GCMS pesticides, resulting in a dataset with a purposeful bias.

While the detailed review of GCMS batches was taking place, the batch-selection strategy for a parallel review of samples from LCMS schedule 2060 was determined. To select batches from LCMS schedule 2060 to review, the NWQL weighted the number of instrument batches proportionately to the number of samples analyzed each year from 2001 to 2015. Within this annual sampling stratification, batches were targeted that included one or more field blanks, blind-blank and blind-spike samples from the QSB, and set-blank concentrations of one-third or more of the RL. Batches were reviewed for 10 of the LCMS method compounds that had some of the highest detection frequencies in set blanks.

Types of Results Reported

Two types of environmental and QC data are used in this report: “original” and “reevaluated” (Riskin and others, 2019). Results from the LIMS system are referred to in this report as “original” and are appended with “_OR.” Original results consist of data that were reviewed by the NWQL and stored in the LIMS. Original results include samples for which the NWQL applied censoring based on detections in set blanks or, in some cases, **batch blanks** (GCMS only) or bracketing instrument

blanks (LCMS only) to address potential laboratory contamination. Records were removed from the dataset if they were for surrogate compounds or if the sample was logged but the result was unavailable (for example, if the bottle was broken).

Reevaluated results are original results that were reevaluated using the 2017 protocols for identification of pesticide detections and are appended with "_RE." Most reevaluated results are the same as original results. A detailed description of the types of changes that may have been implemented to original results during the data reevaluation is provided in the "Data Reevaluation" section of this report. If not specified as a reevaluated result, results in this report refer to original results.

Ancillary Data Fields

To help data users who are interested in directly comparing environmental and field QC sample results (field QC results include field replicates, field spikes, field-related blanks, source-solution blanks, and equipment blanks) with their associated set blank, the set-blank result from the analytical set associated with each sample is provided as a separate ancillary field with the environmental and QC data (Riskin and others, 2019). The environmental and QC data include an indicator (cens_ind) with information about NWQL censoring that was applied to the result (Riskin and others, 2019). Indicator and comment fields allow the data user to understand how and why data were adjusted by the NWQL.

Data Reload

In February 2005, the NWQL issued Technical Memorandum 2005.03 (U.S. Geological Survey, 2005) that describes a chronology of performance issues related to analytical recovery for some compounds in analytical schedule 2060 and steps being taken to address these issues. In March 2007, the NWQL issued Rapi-Note 07–005 (fig. 2.1) to describe retroactive correction of data in NWIS (referred to in this report as the "data reload") that were affected by the issues in Technical Memorandum 2005.03. Rapi-Note 07–005 lists actions for 34 compounds in schedule 2060, including 6 of the 10 LCMS compounds included in this study. For most of the 34 affected compounds, actions in Rapi-Note 07–005 were limited to the population of remark, data qualifier, or comment fields in NWIS with coding to reflect qualification of data, and changes in the type of reporting level (from MRL to IRL). Four of the 10 LCMS compounds included in this study had these limited actions.

Two of the 10 LCMS compounds included in this study, 2-chloro-4,6-diamino-s-triazine (CAAT) and fenuron, had more extensive actions in Rapi-Note 07–005 because the type of reporting level was changed to MRL and detections below the Rapi-Note MRL level were expected to be censored to the specified MRL level. With Rapi-Note 07–005, the NWQL issued instructions to USGS WSCs that are responsible for carrying out the data reload in NWIS. Many, though not all, WSCs enacted the changes specified in Rapi-Note 07–005, leading to some results in NWIS for CAAT and fenuron for dates associated with the data reload (August 1, 2002, through March 31, 2006) not reflecting changes specified in Rapi-Note 07–005. However, data in Riskin and others (2019) for original and reevaluated results were changed to reflect information according to the data reload instructions; where results differ from results retrieved from LIMS, an indicator phrase "Rapi-Note 07-005" was added as a comment to the appropriate data.

Data Reevaluation

Every pesticide result for the 21 selected compounds in the selected instrument batches (31,049 records in "USGS_GCMS_Pesticides_Environmental.csv" and "USGS_LCMS_Pesticides_Environmental.csv" in Riskin and others [2019]; table 2) was reevaluated according to the 2017 identification protocols to determine whether the application of the protocols would affect historical pesticide results. For GCMS data, identification protocols used in 2017 were governed by standard operating procedure NWQL SOP ORGF0500.2 (U.S. Geological Survey, written commun., November 21, 2017). For LCMS data, identification protocols have not changed since 2007 (ORGF0338.3; U.S. Geological Survey, written commun., December 20, 2011) because use of analyte schedule 2060 began to decrease in about 2010. Consequently, the LCMS reevaluation in 2017 was done on the basis of the 2007 protocols. Identification protocols for GCMS and LCMS methods have changed between 2001 and 2015 with the assimilation of new information by the NWQL. In addition to the numerical value and the remark associated with the result, other data descriptors, such as the type and value of the RL, also were reexamined during the data reevaluation.

General qualitative identification criteria used at the NWQL from 2001 through 2015 required that the retention time and abundance of three selected ions match that of a standard analyzed at the same time (Zaugg and other, 1995; Werner and others, 1996; Sandstrom and others, 2001; Furlong and others, 2001). Although these general criteria did not change, compared with protocols in place at the time of analysis for data covered by this report, the 2017 identification protocols have more specific information about identification, including strict analyte identification criteria (meeting expected retention time and ion ratio criteria) and consistent ways to report results when interferences are present (NWQL SOP ORGF0500.2, U.S. Geological Survey, written commun., November 21, 2017). Before implementation of the 2017 identification protocols, more lenient criteria for identifying detections in set blanks that did not meet absolute qualitative identification criteria were sometimes used for some compounds when there were episodes of frequent detections in blank samples; this strategy was intended to minimize the potential for false-positive results in environmental samples.

Other types of changes applied to results during the data reevaluation came from examination of interferents, review

of the original designation as a detection or nondetection, and implementation of MRL censoring that had been missed with publication of the original result. An interferent is characterized by an instrument response in the set blank or in an environmental sample that does not conform to the protocol for identifying the analyte as being qualitatively detected.

As described in the "Set Censoring" section of this report, the procedure for set censoring has evolved over time. For GCMS environmental data reevaluated using 2017 identification protocols, set censoring was based only on a detection in the set blank of the set; original results that were censored based on a detection in a batch blank are not censored as reevaluated results. For LCMS compounds with original results that were censored based on detections in bracketing instrument (solvent only) blanks, information about these bracketing instrument blanks is not available to data users to assess the use of this type of censoring in the data reevaluation undertaken for this study; this information was only available to the analysts reevaluating the data.

Most changes to results from the reevaluation were not made in the LIMS or to data published in NWIS because the reevaluation was done for fewer than 2 percent of batches and changing data in LIMS or NWIS would result in inconsistent data.

Limitations of the Design of the Study

The 113 instrument batches that were reviewed for this study were selected based on having high detection frequencies or high concentrations in set blanks for at least one of the 21 pesticide compounds of interest. This resulted in a modified stratified random approach because the entire group of 11 or 10 pesticides (in GCMS or LCMS methods) was reviewed in each batch, not just those compounds detected in a given set blank. Although more than 30,000 individual records were reviewed for this report, the 113 batches reviewed represent about 1 or 2 percent (for GCMS and LCMS methods, respectively) of the total number of batches (7,630) analyzed by the NWQL during the study period (table 5) and therefore may not be representative of all batches.

The 21 pesticide compounds in this study represent 12 percent of the 173 compounds on the GCMS and LCMS analytical schedules. Detections of other pesticide compounds on these analytical schedules in water might also be influenced by laboratory contamination or by the inconsistent application of qualitative identification criteria, particularly when environmental concentrations are near or below the RL or DL. Set-blank data for these other 152 compounds are provided in Riskin and others (2019); more details are provided in the "Set-Blank Results for All Instrument Batches" section of this report.

Another study design-related limitation is that sample results for analytical schedule 2001 between December 7, 1994, and May 16, 2001, were not reviewed because some of the required ancillary data used to conduct the review were not available in the NWQL database before implementation of a new LIMS (StarLIMS) in 2001. The other schedules included in this report became operational in or after 2001 (table 1).

The NWQL also analyzes pesticide compounds using schedules that were not included in this study. Pesticide results from filtered-water pesticide schedules 2002 and 2050 were not included in this study either because the original chromatographic results were not readily retrievable to conduct a comprehensive review or because of less frequent use. Pesticide results from schedules 2010 and 2051 were not included in this study because these are complementary methods to schedules 2001 and 2050, respectively, where surrogate addition and solid-phase extraction sample preparation steps were performed in the field instead of at the NWQL.

Set-Blank Results for All Instrument Batches

Set-blank data ("USGS_GCMS_Pesticides_SetBlankResults.csv" and "USGS_LCMS_Pesticides_SetBlankResults.csv" in Riskin and others [2019]) are provided for all 7,630 instrument batches during the study period and for all 173 pesticide compounds (104 GCMS and 69 LCMS compounds, table 2) in the analytical schedules covered by this study. These set-blank data, published in Riskin and others (2019), were previously unavailable and provide a complete dataset to data users, which is important for a comprehensive evaluation of potential sources of laboratory contamination. Data users can use these set-blank data to evaluate laboratory contamination for these 173 compounds, not just the 21 included in this study, following the methods described in the "Methods" section of this report and in appendix 3. NWQL QC data, including set blank data, are not currently [2019] available in NWIS but are available by request (labhelp@usgs.gov).

This complete set-blank dataset across all 7,630 instrument batches also was used to determine the characteristics of laboratory contamination for the 21 pesticide compounds included in this study (Objective 1); that is, whether the observed laboratory contamination was deterministic, episodic, or random.

Laboratory results in the set-blank tables show results as reevaluated in accordance with the 2017 identification protocols (described in the "Data Reevaluation" section of this report), if different than the LIMS results. As much as 1 percent of all results of set blanks during the study period were in batches selected for this investigation and have the possibility of being identified as "reevaluated" (Riskin and others, 2019).

Because the batch selection process targeted batches with detections in set blanks, it likely led to selection of more sets with set censoring than there are in the general population of batches for compounds with detections in the set blanks. As a result, batches of samples that were not selected for review might have more detections in environmental samples at concentrations within ranges of detections of their corresponding set blanks than the batches included in this study. However, the batch review process included all

compounds in the batch, not just the compounds detected in the set blank, which helps to mitigate any bias from targeting batches for review and to increase the representativeness of selected batches for most compounds.

Blind-Blank and Blind-Spike Results From the NWQL and QSB

Blind-blank results from this study (Riskin and others, 2019) are a combination of data from two QSB projects: blind-blank samples from the OBBP and unspiked analytes in blind-spike samples from the OBSP. These QSB projects and use in 2004 of blind-blank samples by the NWQL for QC of environmental data are described in detail in the "Review of Results in Context of Long-Term Quality-Control Data" section of this report. In total, 416 GCMS and 1,053 LCMS blind-blank OBBP samples, 30,264 unspiked blind spikes from analytical schedules 2001 and 2033, and 3,617 unspiked blind spikes from analytical schedule 2060 were used in this study (table 2). All available results from blind blanks and unspiked blind spikes in the respective GCMS and LCMS schedules are included in the analysis; results are not limited to the 113 batches selected for this study. OBSP blind-spike sample results are used by the QSB and NWQL to assess method performance; blind-spike results from the OBSP for the 21 compounds investigated in this study are listed in Riskin and others (2019).

Blind-blank and blind-spike samples from the QSB are submitted to the NWQL disguised as regular environmental samples so that they are treated no differently than other samples. For this report, the QSB provided authors with codes that enabled identification of QSB samples and specification of whether the **blind sample** was a blank or spike. Data used for this study and presented in Riskin and others (2019) reflect QSB samples in their true, not blind (disguised), state. Codes in the "BlankType" field in the environmental and QC data tables of Riskin and others (2019) identify different types of blanks (shorthand references used in this report to types of tables in the Riskin and others (2019) are cross-referenced in table 2). The data-release metadata in Riskin and others (2019) identifies QSB blind-blank samples using code "160" and QSB blind-spike samples using code "170." For spike samples, OBSP also provided a summary of false-positive and false-negative occurrence. The subset of blind-blank and blind-spike results that were in selected batches evaluated for this study are included in the environmental and QC data tables. In addition, all results for these types of samples are provided in separate tables in Riskin and others (2019).

Statistical and Graphical Approaches for Data Analysis

Statistical and graphical approaches of data analysis are organized in this section by study objectives (table 6). The level of significance (α) for all statistical tests, unless otherwise indicated, is 0.05.

Objective 1: Determine the Characteristics of Laboratory Contamination Over Time

Detections in set blanks across all 7,630 batches (not just the 113 selected batches), by compound and year, were used to characterize the overall extent of laboratory contamination during the study period (table 6, reference A). In addition, the complete set-blank dataset was used to distinguish time periods affected by episodic or random contamination.

Set censoring is the indicator for deterministic laboratory contamination at the NWQL (table 6, reference B; see also "Types of Laboratory Contamination and the Relation to QC Censoring" section of this report). Many detections in environmental samples that coincide with detections in the associated set blank could signify pervasive deterministic laboratory contamination. Deterministic contamination is assessed by counting occurrences of set censoring in records in the environmental and QC data from the 113 batches selected for this study.

The distinction between random and episodic contamination was made based on the temporal pattern of detection frequencies of set blanks (table 6, reference C). All set blanks in the study period were used for this analysis, not just those in batches reviewed for this study. Because of potential differences in contamination sources and pathways among instruments or analytical schedules, this distinction was made separately for compounds in three of the four GCMS analytical schedules (schedules 2001, 2003, and 2033). The fourth GCMS analytical schedule (2032) had only occasional random contamination (no episodic contamination), as indicated by very few detections in set blanks (9 detections in 758 results spread across five compounds).

The statistical method to distinguish between random and episodic contamination is based on a 21-sample moving average of detections in set blanks (Fram and Belitz, 2011). The method used by Fram and Belitz (2011) was modified to account for large differences in the time range for 21 consecutive samples (ranging from 3 to 290 days) in the dataset of set blanks from this study, with longer time ranges generally seen beginning in about 2012 when an alternative new pesticide method (schedule 2437) became available and began to be widely used.

Instead of the fixed 21-sample moving average used by Fram and Belitz (2011), a variable-sample (between 11 and 21 samples) moving average was used. When the time between set-blank samples was large, fewer than 21 samples were used to calculate the average to reduce the length of time the average represents. The first step was to determine the difference in the number of days represented by 10 samples before and after each given sample (this is the calculation for the 21-sample moving average). Next, the largest and smallest 21-sample differences in the numbers of days for the

Table 6. Statistical and graphical approaches used to address the objectives of the study to evaluate the use of set blanks in reporting pesticide results at the U.S. Geological Survey National Water Quality Laboratory from 2001 to 2015.

[Original results were used to address study objectives 1 through 3, and original and reevaluated results were used to address study objective 4. NA, not applicable; —, none]

Study objective	Hypothesis	Reference in report	Approach	Statistical test	Table no.[1]	Graphical approach
1. Determine the characteristics of laboratory contamination (occurrence, timing, concentrations) over time	NA[2]	A	Characterize the overall extent of laboratory contamination as the number and frequency of detections in set blanks	—	7	—
		B	Characterize the extent of deterministic contamination by counting the occurrences of set censoring	—	8	—
		C	Define dates of episodic contamination where the detection frequency in set-blank samples is greater than 10 percent for at least seven consecutive samples using the moving average approach Define dates of random contamination where the detection frequency in set-blank samples is not greater than 10 percent for at least seven consecutive samples using the moving average approach; random contamination occurs on dates not defined by episodic contamination	Moving average of detection frequencies in set blanks (scaled between 11 and 21 samples to adjust for variable time between samples) to identify periods of time with random or episodic laboratory contamination	9, 10	Moving averages of detection frequencies of set-blank samples by schedule
		D	Characterize the temporal pattern of episodic and random contamination by visually inspecting all set-blank samples between 2001 and 2015	—	—	Patterns of detections of set-blank results in time-series plots
2. Statistically compare the distributions of pesticide results (detections and nondetections) in set-blank samples with distributions in groundwater and surface-water samples	No difference in distributions of results between set blanks and environmental samples	E	Statistically compare summary statistics and detection frequencies	Summary statistics and Fisher's exact test of independence of proportions of detections	11	Time-series plots, boxplots, and cumulative distribution function plots
		F	Statistically compare distributions of detected results	Calculate 99th percentile of concentration and 95% upper confidence limit for the 99th percentile Calculate the highest percentile that produces a nondetection to estimate the percent of groundwater and surface-water samples not affected by contamination	12	

Table 6. Statistical and graphical approaches used to address the objectives of the study to evaluate the use of set blanks in reporting pesticide results at the U.S. Geological Survey National Water Quality Laboratory from 2001 to 2015.—Continued

[Original results were used to address study objectives 1 through 3, and original and reevaluated results were used to address study objective 4. NA, not applicable; —, none]

Study objective	Hypothesis	Reference in report	Approach	Statistical test	Table no.[1]	Graphical approach
3. Evaluate the potential for false-positive and false-negative reporting of pesticide results in environmental samples	NA[3]	G	Determine the number of false-positive results from Quality Systems Branch Organic Blind Blank Project (OBBP) blind-blank samples and Organic Blind Sample Project (OBSP) unspiked blind-spike samples; and the number of false-negative from OBSP blind-spike samples	Count and percentage	13	—
		H	Determine the number of false-positive results above the LT–MDL	Count and percentage	13	
4. Determine the effects of re-evaluating historical pesticide results using 2017 protocols for identification of detections of pesticides in groundwater and surface-water samples.	The 2017 reevaluation had no effect on (1) the detection frequency of set blanks or environmental samples or on (2) the relative distributions of detections in set blanks and environmental samples	I	Determine the number of results that would change from detections to nondetections (and from nondetections to detections) when data were reevaluated	Count	14, 15	Comparison of detections in time-series plots and boxplots between original and reevaluated results
		J	Compare detection frequencies of original and reevaluated results	Fisher's exact test of independence of proportions for detection frequencies	16	
		K	Compare distributions of detected results of environmental results with set blanks using reevaluated results. Contrast these comparisons with those using original results	Summary statistics of detected results and Fisher's exact test of independence of proportions for detection frequencies	17, contrasted with 11	
		L	List periods most affected by changes in detections in groundwater and surface-water samples resulting from the data reevaluation of 2017	—	18	

[1]Table that lists the given test result or comparison.

[2]This study objective is met by observation rather than a statistical test.

[3]This study objective is met by description rather than a statistical test.

entire dataset was determined. This minimum and maximum difference in days was inversely scaled (using "rescale" in R statistical evaluation software) to an odd number between 11 and 21 to get the variable number of samples used to calculate the moving average. An odd number for the scaling variable ensures the same number of values before and after the given sample to calculate the moving average. The minimum rescaled number was selected to be 11 to make sure there were sufficient numbers of samples to calculate the moving average. If the time span between the 1st and 21st samples was near the minimum difference in days for the dataset, the number of samples that was included in the moving average was 21. Increasing time differences resulted in decreases in the number of set blanks included in the moving average.

The next step, using the variable moving average window, was to calculate the detection frequency of sequential set blanks within the given window. An instance of episodic laboratory contamination (called an "episode" in this report) was indicated if the detection frequency was greater than 10 percent for at least seven samples in a row. Having detections in at least seven consecutive blank samples was chosen as the definition for an episode because seven represents approximately three batches of samples (calculated by multiplying the average of 2.4 sets per batch in this dataset by three for the number of batches and rounding the result to seven). The extent of an episode was widened to include samples with detections (even if the detection frequency was less than 10 percent) that were within the moving average window of samples within the episode. Episodes were buffered by 10 days before and after the date range. If the time between two episodes was less than 60 days, then the two episodes were consolidated into one.

Episodes define periods of episodic laboratory contamination. Random laboratory contamination is contamination that occurs outside of episodes. Episodes are expressed as date ranges of apparent laboratory contamination and, along with the maximum and 95th percentile concentrations of set blanks during the episode, help with data interpretation by enabling the comparison of the timing of detections in set blanks to the timing of detections in environmental samples.

One limitation to this method of defining episodic and random laboratory contamination is that this determination of episodes using the moving average of detections in set blanks cannot be applied in real-time; it is typically done after several years of QC data have been collected. The method is considered part of the "review collective results over time in context of long-term QC data" step (red rectangle of fig. 1). A second limitation to this method of defining episodes based on detections in set blanks is that the NWQL method for the identification of detections in set blanks did not remain constant through the study period (see "Data Reevaluation" section).

Time-series plots showing detections in set blanks were used to qualitatively assess the presence and degree of randomness of the timing of laboratory contamination (table 6, reference D). Detections in all set blanks for the study period were distinguished on time-series plots from detections in set blanks in batches selected for this study. Clusters of detections in set blanks indicated the occurrence of a nonrandom process contributing to contamination. Sporadic or isolated detections without a pattern indicated a random process contributing to contamination.

Objective 2: Compare Distributions of Results From Set Blanks and Environmental Samples

Distributions of results from set blanks and environmental samples were characterized and compared in several ways. If distributions are similar, then data users might have less confidence that detected environmental results reflect real occurrences of the analyte in the environment and are not the result of laboratory-derived contamination. Comparisons between groundwater and set blanks and between surface-water and set blanks were done separately because certain audiences might have a specific interest in just one of these types of sample media.

Summary statistics were calculated for detected concentrations of set blanks and environmental samples (table 6, reference E). Detection frequencies between set blanks and environmental samples were compared using Fisher's exact test of independence of proportions (fisher.test in R code; Agresti, 2002), using the null hypothesis that there is no difference in detection frequencies. The Fisher's exact test of independence of proportions, a contingency table test, is conservative but is more accurate than the chi-squared (χ^2) or likelihood-ratio tests when the expected numbers are small (McDonald, 2014).

Distributions that include nondetections also were evaluated by comparing summary statistics between set blanks and environmental results (table 6, reference F). High sample percentiles are the type of summary statistic that are useful for making comparisons between highly censored datasets (Helsel and Hirsch, 2002). The 99th percentile of concentration, not calculated for sample sizes less than 101, was calculated by ranking results so that all detections ranked higher than nondetections (Martin and others, 1999). The one-sided, 95-percent upper confidence limits for the 99th percentile concentrations of set blanks and environmental samples were calculated (Hahn and Meeker, 1991) to provide information on the uncertainty in the estimated frequency and magnitude of contamination (for set blanks) or uncertainty in the estimated percentiles of concentrations of environmental samples. The 99th percentile concentrations in set blanks indicated magnitudes of contamination that occur in no more than 1 percent of samples. The highest percentile that produces a nondetection in set blanks also was calculated (Hahn and Meeker, 1991) to estimate the percentage of environmental samples not affected by contamination (Martin and others, 1999).

Time-series plots and cumulative distribution function plots of detections confirm and supplement statistical results that address objective 2, by showing detected results in the context of a comparison between set blanks and environmental

samples. Cumulative distribution function plots are useful for comparing the full distributions because, even though only detections are plotted, the positions of the plotted data points are derived from all results, including nondetections (Cunnane, 1978). For compounds with an unequal number of results for different sample types plotted on cumulative distribution function plots, data plotting positions based on the percent exceedance of concentrations will be different even if medians and distributions of detected results are not statistically different.

Objective 3: Evaluate the Potential for False-Positive and False-Negative Reporting

The potential for false-positive and false-negative reporting of pesticide results in environmental samples will be determined by computing the percentages of false-positive and false-negative results from blind samples independently submitted to the NWQL by QSB. False positive- and false-negative results, based on the OBBP and OBSP blind blanks and blind spikes (Riskin and others, 2019), were generated from all available QSB results from 2001 through 2015 for the 11 GCMS compounds and the 10 LCMS compounds (table 6, reference G), not just results from the 113 selected batches. Detections in blind blanks and blind spikes (where nondetections are expected because the analyte was not spiked) provide an assessment of the potential for false positives for each compound. If the false-positive rate based on these blank-type blind samples is more than 1 percent, then depending on the data-quality objective of the individual data user (U.S. Environmental Protection Agency, 2006), additional censoring of environmental and field QC results to ensure that no more than 1 percent are false positives might be warranted depending on the data-quality objectives of the project (app. 3).

Nondetected results for OBSP blind-spike samples where a known amount of the compound has been added to each sample were used to assess the false-negative rate for each compound. Considerations for applying additional censoring using false-positive or false-negative rates to meet data-quality objectives are provided in appendix 3. A supplemental investigation assessed only the subset of false positives from the QSB blind blank-type samples with concentration greater than the LT–MDL (table 6, reference H) to compare with the no more than 1-percent false-positive rate predicted by using the LT–MDL procedure and because other water-quality laboratories sometimes do not report results at the low concentrations (below the DL or the RL) provided by the NWQL.

Objective 4: Determine the Effects of the Data Reevaluation

To determine the effects of the data reevaluation, results were analyzed in several ways. Numbers of results that would change from detections to nondetections and from nondetections to detections were listed for each compound for set blanks, QSB blind blanks, groundwater samples, and surface-water samples (table 6, reference I). These changes are not true false positives or false negatives because the truth of the presence of a detection in an environmental sample is unknowable (as opposed to set blanks and QSB blind blanks, where the reagent-blank water used is of high purity and is designed to have no detectable concentration of pesticides). Percentages of detections in set blanks, groundwater samples, and surface-water samples for original and reevaluated results were compared statistically by using the Fisher's exact test of independence of proportions (fisher.test in R code [Agresti, 2002]; table 6, reference J) and were juxtaposed with original results (table 6, reference K). Effects of the data reevaluation were summarized for data users by providing specific dates that captured the largest number of changes in environmental samples (table 6, reference L). The results from the data reevaluation are presented in Riskin and others (2019) but are not reflected in data in NWIS or LIMS.

Results and Discussion by Study Objectives

Objective 1: Types of Laboratory Contamination at the NWQL

Laboratory contamination for the 21 compounds of interest, determined as detections in set blanks, was 13 percent for the 113 targeted batches of samples included in this study and was 6 percent across all 7,630 batches of samples (in selected and unselected batches) during the study period (table 7). That detections in set blanks were more than two times greater in targeted batches than in all batches reflects the purposeful selection of batches with detections in set blanks (discussed in the "Selection of Instrument Batches for Retrieval of Pesticide Data" section of this report).

Characterizing laboratory contamination at the NWQL as episodic, random, and deterministic enables data users to examine the censoring strategies used for assessing each type and their effectiveness at addressing contamination. For the 21 compounds included in this study, detections associated with episodic and random laboratory contamination accounted for 92 and 8 percent, respectively, of all detections in set blanks during the study period (table 7). Deterministic laboratory contamination, addressed by set censoring, applied to less than 1 percent of results from environmental samples (table 8).

About 0.75 percent of results for GCMS and LCMS compounds were set censored (table 8). Three quarters of the results for GCMS compounds that were set censored were for surface-water samples (table 8). The division of set censoring between groundwater and surface-water samples was split evenly for LCMS compounds.

Table 7. Detection frequencies of 21 selected pesticides and classification of detections in set-blank results analyzed using gas or

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Data in column presents information based on the 113 batches selected for this study. Numbers of set blanks per year vary by compound because some of these compounds
—, no samples; NA, not available; CAAT, 2-chloro-4,6-diamino-s-triazine]

Parameter code	Analyte	Metric (number or percent)	Year							
			2001	2002	2003	2004	2005	2006	2007	2008
			GCMS compounds							
34653	*p,p′*-DDE	Number of set blanks	318	504	347	351	171	152	96	123
		Number of detections	187	300	117	130	11	1	2	3
		Detection frequency	59	60	34	37	6.4	0.7	2.1	2.4
39381	Dieldrin	Number of set blanks	318	515	518	627	503	450	361	496
		Number of detections	0	1	1	2	13	7	0	23
		Detection frequency	0	0.2	0.2	0.3	2.6	1.6	0	4.6
39415	Metolachlor	Number of set blanks	318	515	518	626	503	448	361	491
		Number of detections	0	0	1	0	22	8	3	10
		Detection frequency	0	0	0.2	0	4.4	1.8	0.8	2.0
39572	Diazinon	Number of set blanks	318	515	517	627	503	450	361	496
		Number of detections	0	6	16	2	1	0	0	0
		Detection frequency	0	1.2	3.1	0.3	0.2	0	0	0
49295	1-Naphthol	Number of set blanks	—	11	171	271	332	298	265	373
		Number of detections	—	0	0	2	3	0	2	2
		Detection frequency	—	0	0	0.7	0.9	0	0.8	0.5
61600	Oxyfluorfen	Number of set blanks	—	—	—	—	201	298	265	373
		Number of detections	—	—	—	—	7	3	0	12
		Detection frequency	—	—	—	—	3.5	1.0	0	3.2
61606	Tefluthrin	Number of set blanks	—	—	—	—	201	298	265	370
		Number of detections	—	—	—	—	9	11	4	32
		Detection frequency	—	—	—	—	4.5	3.7	1.5	8.6
82661	Trifluralin	Number of set blanks	318	515	518	627	503	448	361	486
		Number of detections	14	14	19	26	94	109	78	112
		Detection frequency	4.4	2.7	3.7	4.1	19	24	22	23
82671	Molinate	Number of set blanks	318	504	347	351	383	448	361	491
		Number of detections	1	0	0	0	1	3	26	18
		Detection frequency	0.3	0	0	0	0.3	0.7	7.2	3.7
82673	Benfluralin	Number of set blanks	318	515	518	627	503	448	361	486
		Number of detections	24	10	30	16	85	119	104	126
		Detection frequency	7.5	1.9	5.8	2.6	17	27	29	26
82682	Dacthal	Number of set blanks	318	515	518	627	503	450	361	491
		Number of detections	0	0	0	1	67	68	70	68
		Detection frequency	0	0	0	0.2	13.3	15.1	19.4	13.8
	Total for GCMS compounds	Number of set blanks	2,544	4,109	3,972	4,734	4,306	4,188	3,418	4,676
		Number of detections	226	331	184	179	313	329	289	406
		Detection frequency	8.9	8.1	4.6	3.8	7.3	7.9	8.5	8.7

liquid chromatography/mass spectrometry methods at the National Water Quality Laboratory from 2001 to 2016.

unshaded columns include information about all set-blank samples from 2001 to 2016 (beyond the study period of 2001 to 2015). In contrast, data in the shaded are not measured in all the schedules included in this report. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry;

Year								Total	Set-blank detections associated with episodic contamination[1]	Set-blank detections associated with random contamination[2]	Set-blank detections in 113 selected batches included in this study
2009	2010	2011	2012	2013	2014	2015	2016				
GCMS compounds											
93	79	106	77	72	60	33	16	2,598	NA	NA	89
1	5	7	4	31	53	20	11	883	872	11	54
1.1	6.3	6.6	5.2	43	88	61	69	34	99	1	61
346	385	457	350	162	160	97	72	5,817	NA	NA	186
25	35	18	7	14	15	9	0	170	150	20	14
7.2	9.1	3.9	2.0	8.6	9.4	9.3	0	3	88	12	7.5
346	385	457	350	162	160	97	72	5,809	NA	NA	186
11	12	3	2	3	1	3	1	80	65	15	25
3.2	3.1	0.7	0.6	1.9	0.6	3.1	1.4	1	81	19	13
346	385	457	350	162	160	97	72	5,816	NA	NA	186
0	0	0	0	0	0	0	0	25	6	19	16
0	0	0	0	0	0	0	0	0	24	76	8.6
252	306	350	273	90	100	64	56	3,212	NA	NA	97
8	4	4	0	1	0	0	0	26	5	21	3
3.2	1.3	1.1	0	1.1	0	0	0	1	19	81	3.1
253	306	351	273	90	100	64	56	2,630	NA	NA	94
8	2	2	1	0	0	0	0	35	24	11	10
3.2	0.7	0.6	0.4	0	0	0	0	1	69	31	11
253	306	351	273	90	100	64	56	2,627	NA	NA	94
29	35	6	1	2	2	3	0	134	118	16	24
11	11	1.7	0.4	2.2	2.0	4.7	0	5	88	12	26
346	385	456	350	162	160	97	72	5,804	NA	NA	185
59	21	7	2	0	1	1	1	558	499	59	60
17	5.5	1.5	0.6	0	0.6	1.0	1.4	10	89	11	32
345	385	456	350	162	160	97	72	5,230	NA	NA	183
2	0	0	0	0	0	0	0	51	47	4	3
0.6	0	0	0	0	0	0	0	1	92	8	1.6
346	385	456	350	162	160	97	72	5,804	NA	NA	186
58	32	9	0	0	7	1	0	621	573	48	56
17	8.3	2.0	0	0	4.4	1.0	0	11	92	8	30
346	385	457	350	162	160	97	72	5,812	NA	NA	186
30	23	6	3	3	3	3	2	347	326	21	41
8.7	6.0	1.3	0.9	1.9	1.9	3.1	2.8	6	94	6	22
3,272	3,692	4,354	3,346	1,476	1,480	904	688	51,159	NA	NA	1,672
231	169	62	20	54	82	40	15	2,930	2,685	245	306
7.1	4.6	1.4	0.6	3.7	5.5	4.4	2.2	6	92	8	18

Table 7. Detection frequencies of 21 selected pesticides and classification of detections in set-blank results analyzed using gas or

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Data in column presents information based on the 113 batches selected for this study. Numbers of set blanks per year vary by compound because some of these compounds no samples; NA, not available; CAAT, 2-chloro-4,6-diamino-s-triazine]

Parameter code	Analyte	Metric (number or percent)	Year							
			2001	2002	2003	2004	2005	2006	2007	2008
			LCMS compounds							
04033	Diphenamid	Number of set blanks	141	238	129	162	203	176	144	136
		Number of detections	2	25	5	5	0	0	0	0
		Detection frequency	1.4	11	3.9	3.1	0	0	0	0
04039	CAAT	Number of set blanks	141	238	125	162	203	155	—	—
		Number of detections	22	11	28	4	0	0	—	—
		Detection frequency	16	4.6	22	2.5	0	0	—	—
49297	Fenuron	Number of set blanks	141	238	129	162	203	176	151	136
		Number of detections	85	122	46	109	144	26	0	0
		Detection frequency	60	51	36	67	71	15	0	0
49310	Carbaryl	Number of set blanks	141	238	129	162	199	174	145	129
		Number of detections	7	2	13	16	5	0	0	0
		Detection frequency	5.0	0.8	10	10	2.5	0	0	0
50337	Sulfometuron Methyl	Number of set blanks	141	238	129	162	203	176	144	136
		Number of detections	16	10	13	21	75	1	0	0
		Detection frequency	11	4.2	10	13	37	0.6	0	0
50356	Imazaquin	Number of set blanks	141	238	129	162	203	176	144	136
		Number of detections	8	6	14	3	6	0	0	0
		Detection frequency	5.7	2.5	10.9	1.9	3.0	0.0	0	0
50407	Imazethapyr	Number of set blanks	141	234	129	162	203	176	151	136
		Number of detections	1	16	2	3	4	4	2	1
		Detection frequency	0.7	6.8	1.6	1.9	2.0	2.3	1.3	0.7
50471	Propiconazole	Number of set blanks	141	238	129	162	203	175	151	136
		Number of detections	72	39	6	2	0	0	0	0
		Detection frequency	51	16	4.7	1.2	0	0	0	0
61694	Flumetsulam	Number of set blanks	141	238	129	158	203	176	151	133
		Number of detections	1	0	1	9	26	9	0	0
		Detection frequency	0	0	0.8	5.7	12.8	5.1	0	0
61697	Metsulfuron Methyl	Number of set blanks	138	238	125	162	198	176	144	127
		Number of detections	7	1	0	13	35	1	0	0
		Detection frequency	5.1	0.4	0	8.0	18	0.6	0	0
	Total for LCMS compounds	Number of set blanks	1,407	2,376	1,282	1,616	2,021	1,736	1,325	1,205
		Number of detections	221	232	128	185	295	41	2	1
		Detection frequency	15.7	9.8	10.0	11	15	2.4	0.2	0.1
	Total for GCMS and LCMS compounds	Number of set blanks	3,951	6,485	5,254	6,350	6,327	5,924	4,743	5,881
		Number of detections	447	563	312	364	608	370	291	407
		Detection frequency	11	8.7	5.9	5.7	9.6	6.2	6.1	6.9

[1]Detection frequency in this column refers to the percentage of set-blank detections associated with episodic contamination.

[2]Detection frequency in this column refers to the percentage of set-blank detections associated with random contamination.

liquid chromatography/mass spectrometry methods at the National Water Quality Laboratory from 2001 to 2016.—Continued

unshaded columns include information about all set-blank samples from 2001 to 2016 (beyond the study period of 2001 to 2015). In contrast, data in the shaded are not measured in all the schedules included in this report. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; —,

Year								Total	Set-blank detections associated with episodic contamination[1]	Set-blank detections associated with random contamination[2]	Set-blank detections in 113 selected batches included in this study
2009	2010	2011	2012	2013	2014	2015	2016				
LCMS compounds											
101	140	94	118	45	42	14	NA	1,883	NA	NA	176
0	0	0	0	0	0	0	NA	37	33	4	8
0	0	0	0	0	0	0	NA	2	89	11	5
—	—	—	—	—	—	—	NA	1,024	NA	NA	82
—	—	—	—	—	—	—	NA	65	64	1	4
—	—	—	—	—	—	—	NA	6	98	2	5
101	140	94	118	45	42	14	NA	1,890	NA	NA	183
0	0	0	0	0	0	0	NA	532	532	0	48
0	0	0	0	0	0	0	NA	28	100	0	26
101	140	94	118	45	42	14	NA	1,871	NA	NA	171
0	0	0	0	0	0	0	NA	43	34	9	6
0	0	0	0	0	0	0	NA	2	79	21	4
101	140	94	118	45	42	14	NA	1,883	NA	NA	176
0	0	0	0	0	0	0	NA	136	129	7	11
0	0	0	0	0	0	0	NA	7	95	5	6
101	140	94	118	45	42	14	NA	1,883	NA	NA	176
0	0	0	0	2	0	0	NA	39	29	10	10
0	0	0	0	4.4	0	0	NA	2	74	26	6
101	140	94	118	45	42	14	NA	1,886	NA	NA	183
0	0	0	0	0	0	0	NA	33	24	9	1
0	0	0	0	0	0	0	NA	2	73	27	1
101	140	94	118	45	42	14	NA	1,889	NA	NA	183
0	0	0	0	0	0	0	NA	119	107	12	8
0	0	0	0	0	0	0	NA	6	90	10	4
101	140	94	118	45	42	14	NA	1,883	NA	NA	183
0	0	0	0	0	0	0	NA	46	42	4	18
0	0	0	0	0	0	0	NA	2	91	9	10
101	140	94	118	45	42	14	NA	1,862	NA	NA	171
0	0	0	0	0	0	0	NA	57	48	9	4
0	0	0	0	0	0	0	NA	3	84	16	2
909	1,260	846	1,062	405	378	126	NA	17,954	NA	NA	1,684
0	0	0	0	2	0	0	NA	1,107	1,042	65	118
0.0	0.0	0.0	0.0	0.5	0.0	0.0	NA	6	94	6	7
4,181	4,952	5,200	4,408	1,881	1,858	1,030	688	69,113	NA	NA	3,356
231	169	62	20	56	82	40	15	4,037	3,727	310	424
5.5	3.4	1.2	0.5	3.0	4.4	3.9	2.2	6	92	8	13

Table 8. Groundwater and surface-water results in selected batches affected by set and minimum reporting level censoring at the National Water Quality Laboratory from 2001 to 2015.

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period. MRL, minimum reporting level; GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; NA, not applicable]

Type of censoring	GCMS compounds			LCMS compounds		
	Groundwater results	Surface-water results	Total	Groundwater results	Surface-water results	Total
Total number of results	4,553	7,199	11,752	4,118	5,528	9,646
Set censored:						
Number	20	68	88	37	35	72
Percent	0.44	0.94	0.75	0.90	0.63	0.75
MRL censored:						
Number	NA	NA	NA	18	51	69
Percent	NA	NA	NA	0.44	0.92	0.72
Both set and MRL censored:						
Number	NA	NA	NA	56	19	75
Percent	NA	NA	NA	1.36	0.34	0.78
Total censored:						
Number	20	68	88	111	105	216
Percent	0.44	0.94	0.75	2.70	1.90	2.24

Detections in set blanks were clustered in time for most compounds in this study, providing evidence of episodic laboratory contamination at the NWQL (figs. 3 and 4, in back of report; tables 9 and 10). In figures 3 and 4, detections in all set blanks from 2001 through 2015 are shown as gray circles; detections of set blanks in batches reviewed for this study are shown as red triangles; the absence of light gray circles means that detections were not observed in the set blanks. Episodes typically lasted 1 to 8 months (tables 9 and 10). Detections in set blanks that do not occur in clusters are evidence of random laboratory contamination. The 10 LCMS compounds in this study show fewer isolated detections in set blanks, and therefore less random laboratory contamination, than GCMS compounds.

Time-series plots illustrate the temporal distribution and magnitude of detections in set blanks relative to environmental samples, whereas moving-average plots show the application of criteria developed for this study to define dates of periods of episodic laboratory contamination (fig. 5, in back of report). Episodic laboratory contamination is indicated for periods of time when vertical lines extend above the applied detection frequency threshold of 10 percent (horizontal red line) in the plots of moving averages (the tabular depiction of episodes is found in tables 9 and 10). Detections in set blanks for dates in between episodes indicate random laboratory contamination.

Episodic Laboratory Contamination for GCMS Compounds

About 92 percent of the detections in set blanks during the study period for the 11 GCMS compounds occurred during periods of episodic contamination (table 7), as calculated by the moving average of detection frequencies in set blanks. Periods of episodic laboratory contamination were observed for each of the 11 GCMS compounds, with most episodes ranging in duration from about 1 to 6 months (figs. 5*A–K,* in back of report; table 9). Although there is no difference among GCMS analytical schedules in preparation or analysis for a given method, some differences in the timing and frequencies of detection of set blanks by analytical schedule were found (fig. 5, in back of report; table 9) that could provide a useful framework for characterization of results. Episodic laboratory contamination accounted for more than two-thirds of all laboratory contamination for 9 of the 11 GCMS compounds included in this study and for about 20 percent of laboratory contamination for diazinon and 1-naphthol (table 7); however, there were fewer detections in set-blank samples for diazinon and 1-naphthol compared to the other GCMS compounds.

A large number of detections of *p,p′*-DDE in set blanks (figs. 3*A* and 4*A,* in back of report) were observed before March 4, 2004. A possible scenario for those detections at

that time was contamination from reused bottle caps used exclusively during the processing of set blanks and set spikes. After the practice of reusing bottle caps was terminated, the number of detections for *p,p′*-DDE decreased. Cap reuse might have contributed to some set-blank detections for other analytes (benfluralin, trifluralin) during this period, but this suspected contamination source was believed to primarily affect *p,p′*-DDE. This episodic contamination did not affect environmental samples because the contaminated bottle caps were not used for environmental samples. The only two detections of *p,p′*-DDE in groundwater samples from selected batches before March 4, 2004, were at higher concentrations (the y-axis scale in fig. 3*A*, in back of report, is logarithmic) than had been seen to that point in set blanks. Detections of *p,p′*-DDE in surface-water samples also mostly occurred in the early 2000s and at concentrations generally higher than most concentrations in set blanks.

Scattered and isolated instances of detections in set blanks for dieldrin and metolachlor show more evidence of random laboratory contamination than is seen for many of the other GCMS compounds (figs. 3*B–C,* in back of report). Low-level diazinon detections in set blanks and environmental samples from 2001 through 2003 might have originated from trace diazinon impurity in one or more lots of diazinon-d_{10} surrogate standard that was added to every sample or from something else that acted as an interferent. This contamination did not affect groundwater samples in reviewed batches; there were no detections of diazinon in groundwater.

Metolachlor in groundwater samples is used here to illustrate a possible censoring strategy using information about episodic contamination. When considered during the entire study period (ignoring dates), concentrations of metolachlor in set blanks and in groundwater samples are similar except that the upper tails in the cumulative distribution function plots extend to higher concentrations in groundwater samples than in set blanks (figs. 3*C* and 6*C,* in back of report). A refined approach would be to match dates of detections of metolachlor in groundwater samples with dates of episodic contamination (fig. 5*C*, in back of report; table 9). Where dates overlap, a censoring level can be set based on concentrations of detections in set blanks and on data-quality objectives (app. 3). For example, metolachlor in groundwater samples before June 2005 occurred in the absence of evidence of laboratory contamination. Episodic laboratory contamination for metolachlor samples that were analyzed using schedule 2033 occurred between mid-June 2005 and mid-June 2006 (table 9). Although nine other periods of episodic contamination were observed for metolachlor for analytical schedules 2001, 2003, and 2033, none lasted more than 3 months (table 9). Other GCMS and LCMS compounds can be evaluated using this same approach.

Episodic laboratory contamination of molinate (schedule 2033) occurred during the discrete periods between October and December 2006 and between May 2007 and January 2008 (fig. 3*I,* in back of report; table 9) when 43 set blanks had detections ranging from 0.013 to 0.035 µg/L per liter (Riskin and others, 2019), at least four times above the LRL of 0.003 microgram per liter (table 1.4).

Episodic Laboratory Contamination of LCMS Compounds and Retroactive Minimum Reporting Level Censoring for Two Compounds

The 10 LCMS compounds analyzed in this study each had some periods of episodic laboratory contamination from 2001 through the beginning of 2006, with most episodes ranging in duration from about 2 to 8 months (figs. 3*L–U* and 5*L–U*, in back of report; table 10). Episodic laboratory contamination accounted overall for about 94 percent of detections in set blanks for the 10 LCMS compounds over the course of the study and ranged from 73 percent for imazethapyr to 100 percent for fenuron (table 7).

All compounds in schedule 2060 were assigned the MRL report level type when analysis with the LCMS method started on May 14, 2001. Before December 1, 2009, the reporting convention was that detected results less than the MRL value were reported with an "E" remark for these mass spectrometry methods. The MRL report-level type continued for variable lengths of time (figs. 3*L–U* and 5*L–U* (in back of report), orange horizontal lines; table 1.5). Detections in set blanks (figs. 3*L–U* and 5*L–U*, in back of report) indicate that the episodes of laboratory contamination occurred primarily during periods of time when the report level type was an MRL and that the MRL values were greater than nearly all detected concentrations in set blanks. The presence of very few detected environmental results less than the MRL value during these periods of time when the report level type was an MRL indicates that set censoring seems to have prevented the reporting of false-positive detections in environmental results.

For CAAT and fenuron, MRL values and censoring rules were changed retroactively as a result of the data reload (described in the "Data Reload" section of this report), which censored environmental sample detections possibly arising from laboratory contamination during all but the earliest analysis period (detections in the May 2001 through July 2002 period were not addressed by the reload; figs. 3*M–N*, in back of report, green dashed line). Fenuron has the largest number of detections in set blanks; all set-blank detections occurred before 2007 and were less than the MRL value (figs. 5*N* and 6*N*, in back of report).

Table 9. Dates with episodic contamination for set-blank results from all instrument batches analyzed at the National Water Quality Laboratory using gas chromatography/mass spectrometry from 2001 to 2015.

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. Data in gray typeface represent results from dates without episodic contamination. No data are included for analytical schedule 2032 compounds because there was no episodic contamination for compounds in schedule 2032. See table 1 for dates that each schedule was operational; dates that reporting level types and concentrations were in effect are listed in tables 1.1, 1.2, and 1.4. µg/L, microgram per liter; f, fewer than 20 detections; NA, not applicable]

Parameter code	Analyte	Analytical schedule 2001									
		Number of set blanks	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes,[1] in days	Set blanks within episodes			Reporting level during episode (IRL or LRL),[3] in µg/L
			Start	End				Number of detections	Maximum concentration, in µg/L	95th percentile[2] concentration, in µg/L	
34653	*p,p'*-DDE	2,490	5/19/2001	10/4/2004	1,234	41	NA	693	0.0073	0.003	0.0025
			4/23/2005	7/28/2005	96	3	201	10	0.0010	f	0.0030
			7/22/2007	9/10/2007	50	2	724	2	0.0020	f	0.0030
			4/12/2010	7/10/2010	89	3	945	4	0.0011	f	0.0020
			7/24/2011	12/10/2011	139	5	379	6	0.0017	f	0.0020
			9/9/2012	11/13/2015	1,160	39	274	111	0.0060	0.0038	0.0048/0.0064
39381	Dieldrin	2,490	5/29/2001	10/29/2009	NA	NA	NA	NA	NA	NA	NA
			10/30/2009	2/1/2010	94	3	3,076	3	0.0010	f	0.0090
			3/9/2014	7/12/2014	125	4	1,497	5	0.0053	f	0.0080
			7/13/2014	11/13/2015	NA	NA	489	NA	NA	NA	NA
39415	Metolachlor	2,487	5/29/2001	3/28/2008	NA	NA	NA	NA	NA	NA	NA
			3/29/2008	6/18/2008	81	3	2,496	2	0.0020	f	0.0100
			6/19/2008	11/13/2015	NA	NA	2,704	NA	NA	NA	NA
39572	Diazinon	2,489	5/29/2001	11/7/2002	NA	NA	NA	NA	NA	NA	NA
			11/8/2002	7/28/2003	262	9	528	22	0.0038	0.0035	0.0050
			7/29/2003	11/13/2015	NA	NA	4,491	NA	NA	NA	NA
82661	Trifluralin	2,488	5/29/2001	6/11/2001	NA	NA	NA	NA	NA	NA	NA
			6/12/2001	9/23/2001	103	3	14	12	0.0010	f	0.0090
			4/2/2002	5/3/2002	31	1	191	4	0.0025	f	0.0090
			8/19/2002	9/19/2002	31	1	108	4	0.0047	f	0.0090
			4/6/2003	7/4/2003	89	3	199	17	0.0040	f	0.0090
			12/9/2003	2/5/2004	58	2	158	3	0.0041	f	0.0090
			8/30/2004	10/15/2004	46	2	207	6	0.0040	f	0.0090
			6/12/2005	7/28/2005	46	2	240	3	0.0020	f	0.0090
			10/26/2007	5/3/2008	190	6	820	6	0.0020	f	0.0060
			7/13/2008	8/31/2008	49	2	71	2	0.0020	f	0.0060
			9/1/2008	11/13/2015	NA	NA	2,630	NA	NA	NA	NA

Table 9. Dates with episodic contamination for set-blank results from all instrument batches analyzed at the National Water Quality Laboratory using gas chromatography/mass spectrometry from 2001 to 2015.—Continued

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. Data in gray typeface represent results from dates without episodic contamination. No data are included for analytical schedule 2032 compounds because there was no episodic contamination for compounds in schedule 2032. See table 1 for dates that each schedule was operational; dates that reporting level types and concentrations were in effect are listed in tables 1.1, 1.2, and 1.4. µg/L, microgram per liter; f, fewer than 20 detections; NA, not applicable]

Parameter code	Analyte	Analytical schedule 2001—Continued									
		Number of set blanks	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes,[1] in days	Set blanks within episodes			Reporting level during episode (IRL or LRL),[3] in µg/L
			Start	End				Number of detections	Maximum concentration, in µg/L	95th percentile[2] concentration, in µg/L	
82671	Molinate	2,488	5/29/2001	11/13/2015	NA	NA	NA	NA	NA	NA	NA
82673	Benfluralin	2,488	5/29/2001	6/11/2001	NA	NA	NA	NA	NA	NA	NA
			6/12/2001	10/11/2001	121	4	14	18	0.0019	f	0.0100
			8/24/2002	9/19/2002	26	1	317	4	0.0051	f	0.0100
			4/6/2003	7/6/2003	91	3	199	24	0.0045	0.0042	0.0100
			8/30/2004	10/15/2004	46	2	421	5	0.0050	f	0.0100
			10/8/2007	4/26/2008	201	7	1,088	8	0.0020	f	0.0040
			7/13/2008	10/6/2008	85	3	78	5	0.0020	f	0.004/0.014
			5/7/2010	10/8/2010	154	5	578	6	0.0022	f	0.0140
			4/2/2011	7/28/2011	117	4	176	5	0.0029	f	0.0140
			3/9/2014	10/12/2014	217	7	955	7	0.0033	f	0.0140
			10/13/2014	11/13/2015	NA	NA	397	NA	NA	NA	NA
82682	Dacthal	2,488	5/29/2001	12/16/2013	NA	NA	NA	NA	NA	NA	NA
			12/17/2013	6/7/2014	172	6	4,585	3	0.0028	f	0.0076
			6/8/2014	11/13/2015	NA	NA	524	NA	NA	NA	NA

[1]Also includes time before first or after last episode.

[2]The 95th percentile of the set-blank concentration within episodes is provided only if there are at least 20 detected results in the period.

[3]Two or more values in this column indicate that the IRL or LRL changed during the given period. See tables 1.1, 1.2, and 1.4 for specific time periods associated with each IRL and LRL.

Table 9. Dates with episodic contamination for set-blank results from all instrument batches analyzed at the National Water Quality Laboratory using gas chromatography/mass spectrometry from 2001 to 2015.—Continued

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. Data in gray typeface represent results from dates without episodic contamination. No data are included for analytical schedule 2032 compounds because there was no episodic contamination for compounds in schedule 2032. See table 1 for dates that each schedule was operational; dates that reporting level types and concentrations were in effect are listed in tables 1.1, 1.2, and 1.4. µg/L, microgram per liter; f, fewer than 20 detections; NA, not applicable]

Parameter code	Analyte	Analytical schedule 2003									
		Number of set blanks	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes,[1] in days	Set blanks within episodes			Reporting level during episode (IRL or LRL),[3] in µg/L
			Start	End				Number of detections	Maximum concentration, in µg/L	95th percentile[2] concentration, in µg/L	
39381	Dieldrin	2,490	10/28/2002	8/20/2004	NA	NA	NA	NA	NA	NA	NA
			8/21/2004	10/1/2004	41	1	663	2	0.0026	f	0.009
			4/2/2005	5/18/2005	46	2	183	4	0.0017	f	0.009
39415	Metolachlor	2,487	10/28/2002	4/15/2005	NA	NA	NA	NA	NA	NA	NA
			4/16/2005	5/18/2005	32	1	901	2	0.0057	f	0.006
39572	Diazinon	2,489	10/28/2002	5/18/2005	NA	NA	NA	NA	NA	NA	NA
49295	1-Naphthol	NA	10/28/2002	5/18/2005	NA	NA	NA	NA	NA	NA	NA
82661	Trifluralin	2,488	10/28/2002	7/10/2004	NA	NA	NA	NA	NA	NA	NA
			7/11/2004	8/29/2004	49	2	622	4	0.0032	f	0.009
			2/8/2005	5/18/2005	99	3	163	8	0.0048	f	0.009
82673	Benfluralin	2,488	10/28/2002	2/7/2005	NA	NA	NA	NA	NA	NA	NA
			2/8/2005	5/18/2005	99	3	834	8	0.0057	f	0.0100
82682	Dacthal	2,488	10/28/2002	4/14/2005	NA	NA	NA	NA	NA	NA	NA
			4/15/2005	5/18/2005	33	1	900	3	0.0023	f	0.003

[1]Also includes time before first or after last episode.

[2]The 95th percentile of the set-blank concentration within episodes is provided only if there are at least 20 detected results in the period.

[3]Two or more values in this column indicate that the IRL or LRL changed during the given period. See tables 1.1, 1.2, and 1.4 for specific time periods associated with each IRL and LRL.

Table 9. Dates with episodic contamination for set-blank results from all instrument batches analyzed at the National Water Quality Laboratory using gas chromatography/mass spectrometry from 2001 to 2015.—Continued

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. Data in gray typeface represent results from dates without episodic contamination. No data are included for analytical schedule 2032 compounds because there was no episodic contamination for compounds in schedule 2032. See table 1 for dates that each schedule was operational; dates that reporting level types and concentrations were in effect are listed in tables 1.1, 1.2, and 1.4. µg/L, microgram per liter; f, fewer than 20 detections; NA, not applicable]

Parameter code	Analyte	Analytical schedule 2033									
		Number of set blanks	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes,[1] in days	Set blanks within episodes			Reporting level during episode (IRL or LRL),[3] in µg/L
			Start	End				Number of detections	Maximum concentration, in µg/L	95th percentile[2] concentration, in µg/L	
39381	Dieldrin	2,588	6/10/2005	9/11/2005	NA	NA	NA	NA	NA	NA	NA
			9/12/2005	10/13/2005	31	1	94	2	0.004	f	0.0090
			1/20/2006	3/31/2006	70	2	99	5	0.005	f	0.0090
			2/9/2008	7/6/2008	148	5	680	22	0.005	0.004	0.0090
			3/9/2009	6/20/2010	468	16	246	56	0.006	0.005	0.0090
			3/5/2011	4/18/2011	44	1	258	3	0.0076	f	0.0080
			8/9/2011	10/14/2011	66	2	113	12	0.0039	f	0.0080
			2/21/2012	4/15/2012	54	2	130	3	0.0061	f	0.0080
			9/3/2012	10/6/2012	33	1	141	3	0.0014	f	0.0080
			5/18/2013	12/12/2013	208	7	224	13	0.0046	f	0.0080
			4/5/2014	10/20/2014	198	7	114	10	0.003	f	0.0080
			5/16/2015	8/27/2015	103	3	208	8	0.0069	f	0.0080
			8/28/2015	4/6/2016	NA	NA	223	NA	NA	NA	NA
39415	Metolachlor	2,585	6/10/2005	6/13/2005	NA	NA	NA	NA	NA	NA	NA
			6/14/2005	6/16/2006	367	12	4	25	0.0072	f	0.0060
			7/31/2007	8/30/2007	30	1	410	3	0.009	f	0.0100
			5/11/2008	7/4/2008	54	2	255	7	0.006	f	0.0100
			5/29/2009	7/11/2009	43	1	329	10	0.0104	f	0.0140
			11/30/2009	1/23/2010	54	2	142	3	0.008	f	0.0140
			5/28/2010	7/29/2010	62	2	125	5	0.0121	f	0.0140
			6/15/2013	7/29/2013	44	1	1,052	2	0.005	f	0.0120
			5/19/2015	7/27/2015	69	2	659	2	0.0072	f	0.0120
			7/28/2015	4/6/2016	NA	NA	254	NA	NA	NA	NA
39572	Diazinon	2,588	6/10/2005	4/6/2016	NA	NA	NA	NA	NA	NA	NA
49295	1-Naphthol	2,586	6/10/2005	7/3/2009	NA	NA	NA	NA	NA	NA	NA
			7/4/2009	8/15/2009	42	1	1,485	5	0.0026	f	0.0400
			8/16/2009	4/6/2016	NA	NA	2,426	NA	NA	NA	NA
61600	Oxyfluorfen	2,588	5/31/2005	7/3/2005	33	1	NA	4	0.0069	f	0.0073
			3/20/2008	4/20/2008	31	1	991	2	0.0058	f	0.0060
			8/9/2008	3/27/2009	230	8	111	14	0.0069	f	0.0060
			2/21/2011	3/31/2011	38	1	696	2	0.0052	f	0.0060
			4/1/2011	4/6/2016	NA	NA	1,833	NA	NA	NA	NA

Table 9. Dates with episodic contamination for set-blank results from all instrument batches analyzed at the National Water Quality Laboratory using gas chromatography/mass spectrometry from 2001 to 2015.—Continued

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. Data in gray typeface represent results from dates without episodic contamination. No data are included for analytical schedule 2032 compounds because there was no episodic contamination for compounds in schedule 2032. See table 1 for dates that each schedule was operational; dates that reporting level types and concentrations were in effect are listed in tables 1.1, 1.2, and 1.4. µg/L, microgram per liter; f, fewer than 20 detections; NA, not applicable]

Parameter code	Analyte	Analytical schedule 2033—Continued									
		Number of set blanks	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes,[1] in days	Set blanks within episodes			Reporting level during episode (IRL or LRL),[3] in µg/L
			Start	End				Number of detections	Maximum concentration, in µg/L	95th percentile[2] concentration, in µg/L	
61606	Tefluthrin	2,585	6/10/2005	9/12/2005	NA	NA	NA	NA	NA	NA	NA
			9/13/2005	10/19/2005	36	1	95	6	0.0029	f	0.0077
			4/21/2006	6/23/2006	63	2	184	7	0.0045	f	0.0033
			5/15/2007	6/18/2007	34	1	326	3	0.0036	f	0.0033
			9/22/2007	9/12/2008	356	12	96	31	0.006	0.0055	0.0033
			1/18/2009	3/2/2009	43	1	128	2	0.005	f	0.0033
			5/11/2009	8/22/2010	468	16	70	61	0.0062	0.006	0.0100
			2/21/2011	5/26/2011	94	3	183	4	0.0052	f	0.0100
			12/23/2012	2/18/2013	57	2	577	2	0.0017	f	0.0140
			2/19/2013	4/6/2016	NA	NA	1,143	NA	NA	NA	NA
82661	Trifluralin	2,579	5/31/2005	11/2/2009	1,616	54	NA	420	0.01	0.007	0.009/0.006/0.012/0.018
			4/25/2010	8/8/2010	105	4	174	11	0.006	f	0.0180
			2/7/2011	3/31/2011	52	2	183	3	0.006	f	0.0180
			4/1/2011	4/6/2016	NA	NA	1,833	NA	NA	NA	NA
82671	Molinate	2,583	6/10/2005	10/21/2006	NA	NA	NA	NA	NA	NA	NA
			10/22/2006	12/9/2006	48	2	499	3	0.003	NA	0.0030
			5/15/2007	1/12/2008	242	8	157	43	0.035	0.0347	0.0030
			1/13/2008	4/6/2016	NA	NA	3,007	NA	NA	NA	NA
82673	Benfluralin	2,579	5/31/2005	11/2/2009	1,616	54	NA	453	0.0180	0.0074	0.01/0.004/0.014
			1/12/2010	8/22/2010	222	7	1,687	20	0.0186	0.0107	0.0140
			2/7/2011	3/31/2011	52	2	169	3	0.0075	NA	0.0140
			6/19/2011	7/17/2011	28	1	80	2	0.0034	NA	0.0140
			7/18/2011	4/6/2016	NA	NA	1,725	NA	NA	NA	NA
82682	Dacthal	2,585	5/31/2005	9/13/2008	1,201	40	NA	250	0.004	0.003	0.0030
			12/13/2008	11/2/2009	324	11	91	35	0.004	0.003	0.006/0.0076
			1/12/2010	8/27/2010	227	8	71	17	0.0042	NA	0.0076
			10/19/2013	1/6/2014	79	3	1,149	2	0.0016	NA	0.0076
			1/7/2014	4/6/2016	NA	NA	821	NA	NA	NA	NA

[1]Also includes time before first or after last episode.

[2]The 95th percentile of the set-blank concentration within episodes is provided only if there are at least 20 detected results in the period.

[3]Two or more values in this column indicate that the IRL or LRL changed during the given period. See tables 1.1, 1.2, and 1.4 for specific time periods associated with each IRL and LRL.

Table 10. Dates with episodic contamination for set-blank results from all instrument batches for compounds analyzed in analytical schedule 2060 using liquid chromatography/mass spectrometry at the National Water Quality Laboratory from 2001 to 2015.

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. See table 1 for dates that schedule 2060 was operational and table 1.5 for dates that reporting level types and concentrations were in effect. Text in gray typeface represents data for dates without episodic contamination. µg/L, microgram per liter; CAAT, 2-chloro-4,6-diamino-s-triazine; NA, not applicable; f, fewer than 20 detections]

Parameter code	Analyte (number of set blanks)	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes[1], in days	Set blanks within episodes			Reporting level during episode[3]	
							Number of detections	Maximum	95th percentile[2]	Type	Concentration, in µg/L
		Start	End					Concentration, in µg/L			
		6/8/2001	3/17/2002	NA	NA	NA	NA	NA	NA	NA	NA
		3/18/2002	8/29/2002	164	5	283	25	0.0125	0.00073	MRL	0.0264
04033	Diphenamid (1,083)	9/14/2003	12/26/2003	103	3	381	4	0.0007	f	MRL	0.0264
		9/10/2004	10/30/2004	50	2	259	4	0.0017	f	IRL/LRL	0.0264/0.01
		10/31/2004	2/25/2015	NA	NA	3,770	NA	NA	NA	NA	NA
		5/30/2001	10/13/2001	136	5	NA	18	0.0011	f	MRL	0.01
		5/18/2002	6/23/2002	36	1	217	4	0.0020	f	MRL	0.01
04039	CAAT (883)	10/22/2002	7/7/2003	258	9	121	25	0.0024	0.00182	MRL	0.01
		9/14/2003	3/26/2004	194	6	69	13	0.0024	f	MRL	0.01
		3/27/2004	5/1/2006	NA	NA	766	NA	NA	NA	NA	NA
49297	Fenuron (1,083)	5/30/2001	5/29/2006	1,825	61	NA	518	0.0105	0.0023	MRL/IRL/LRL	0.0316/0.019/0.018
		5/30/2006	2/25/2015	NA	NA	3,194	NA	NA	NA	NA	NA
		6/8/2001	6/10/2001	NA	NA	NA	NA	NA	NA	NA	NA
		6/11/2001	8/9/2001	59	2	3	6	0.0018	f	MRL	0.0286
		12/8/2002	3/24/2003	106	4	486	6	0.0012	f	MRL	0.0284
49310	Carbaryl (1,079)	8/29/2003	12/5/2003	98	3	158	5	0.0012	f	MRL	0.0284
		5/14/2004	10/1/2004	140	5	161	13	0.0068	f	MRL/IRL	0.0284/0.0284
		1/29/2005	4/8/2005	69	2	120	4	0.0009	f	LRL	0.018
		4/9/2005	2/25/2015	NA	NA	3,610	NA	NA	NA	NA	NA
		5/30/2001	8/20/2001	82	3	NA	13	0.0033	f	MRL	0.0088
		4/28/2002	6/29/2002	62	2	251	7	0.0011	f	MRL	0.0088
		12/30/2002	4/26/2003	117	4	184	5	0.0015	f	MRL	0.0088
50337	Sulfometuron-methyl (1,083)	8/15/2003	9/11/2004	393	13	111	23	0.0045	0.0036	MRL/IRL	0.0088
		11/20/2004	11/25/2005	370	12	70	78	0.0137	0.0127	LRL	0.038
		11/26/2005	2/25/2015	NA	NA	3,379	NA	NA	NA	NA	NA

Table 10. Dates with episodic contamination for set-blank results from all instrument batches for compounds analyzed in analytical schedule 2060 using liquid chromatography/mass spectrometry at the National Water Quality Laboratory from 2001 to 2015.—Continued

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Dates are based on sample preparation date. See table 1 for dates that schedule 2060 was operational and table 1.5 for dates that reporting level types and concentrations were in effect. Text in gray typeface represents data for dates without episodic contamination. µg/L, microgram per liter; CAAT, 2-chloro-4,6-diamino-s-triazine; NA, not applicable; f, fewer than 20 detections]

Parameter code	Analyte (number of set blanks)	Episode or study period		Length of episode (days)	Length of episode (months)	Time between episodes[1], in days	Set blanks within episodes			Reporting level during episode[3]	
		Start	End				Number of detections	Maximum Concentration, in µg/L	95th percentile[2] Concentration, in µg/L	Type	Concentration, in µg/L
50356	Imazaquin (1,083)	6/8/2001	9/22/2001	NA	NA	NA	NA	NA	NA	NA	NA
		9/23/2001	3/1/2002	159	5	107	7	0.0011	f	MRL	0.016
		5/26/2003	3/26/2004	305	10	451	16	0.0014	f	MRL	0.016
		10/16/2005	1/6/2006	82	3	569	6	0.0054	f	LRL	0.036
		1/7/2006	2/25/2015	NA	NA	3,337	NA	NA	NA	NA	NA
50407	Imazethapyr (1,079)	6/8/2001	1/5/2002	NA	NA	NA	NA	NA	NA	NA	NA
		1/6/2002	4/4/2002	88	3	212	10	0.0015	f	MRL	0.017
		11/25/2002	2/20/2003	87	3	235	4	0.0002	f	MRL	0.017
		10/10/2005	3/17/2006	158	5	963	7	0.0011	f	LRL	0.038
		3/18/2006	2/25/2015	NA	NA	3,267	NA	NA	NA	NA	NA
50471	Propiconazole (1,083)	6/8/2001	6/14/2001	NA	NA	NA	NA	NA	NA	NA	NA
		6/15/2001	5/31/2002	350	12	7	102	0.0215	0.0060	MRL	0.0210
		6/1/2002	2/25/2015	NA	NA	4,653	NA	NA	NA	NA	NA
61694	Flumetsulam (1,079)	6/8/2001	7/17/2004	NA	NA	NA	NA	NA	NA	NA	NA
		7/18/2004	11/13/2004	118	4	1,136	7	0.0100	f	IRL/LRL	0.011/0.04
		9/12/2005	5/4/2006	234	8	303	35	0.2030	0.0500	IRL/LRL	0.011/0.04
		5/5/2006	2/25/2015	NA	NA	3,219	NA	NA	NA	NA	NA
61697	Metsulfuron-methyl (1,071)	6/8/2001	7/26/2001	NA	NA	NA	NA	NA	NA	NA	NA
		7/27/2001	9/30/2001	65	2	49	4	0.0320	f	MRL	0.025
		7/13/2004	10/1/2004	80	3	1,017	11	0.0051	f	IRL/LRL	0.025
		3/11/2005	11/17/2005	251	8	161	33	0.0081	0.0079	MRL	0.025
		11/18/2005	2/25/2015	NA	NA	3,387	NA	NA	NA	NA	NA

[1]Also includes time before first or after last episode.

[2]The 95th percentile of the set blank concentration within episodes is provided only if there are at least 20 detected results in the period.

[3]Two or more values in this column for the same date range indicate that the MRL, IRL, or LRL changed during the given period. See table 1.5 for specific periods associated with each MRL, IRL, and LRL.

Objective 2: Comparing Distributions of Set Blanks and Environmental Results

For the 21 compounds overall, detection frequencies were 13 percent for set blanks, 1 percent for groundwater results, and 10 percent for surface-water results; the overall detection frequency in surface-water samples was driven by detections of metolachlor, diazinon, and trifluralin (table 11). Although the original intention was to include the comparison of distributions of set blanks with field blanks, the small number of detected field-blank results from the selected batches—seven detections for three GCMS compounds and six detections for four LCMS compounds (Riskin and others, 2019)—precludes the ability to perform meaningful data analysis of field blanks similar to that done for set blanks. All analytical results for field blanks in reviewed batches are included with the environmental and QC data in Riskin and others (2019; filter results for BlankType =100G or 100S for groundwater or surface-water field blanks, respectively).

GCMS Compounds in Groundwater and Surface-Water Samples

For GCMS compounds, detection frequencies were 18 percent for set blanks, 1 percent for groundwater results, and 15 percent for surface-water results; this latter percentage is largely driven by the 69-percent detection frequency for metolachlor in surface-water samples (table 11). Three GCMS compounds—*p,p′*-DDE, dieldrin, and metolachlor—were detected two or more times in groundwater samples (table 11). Concentrations of dieldrin in set blanks were much lower than concentrations in groundwater samples (figs. 3*B* and 6*B,* in back of report; table 11). The two detections of *p,p′*-DDE in groundwater samples were at higher concentrations than detections in set blanks during the same 4-month period (fig. 3*A,* in back of report).

For all GCMS compounds detected in both set blanks and groundwater samples (except metolachlor, which is discussed in the "Episodic Laboratory Contamination for GCMS Compounds" section of this report), detection frequencies were significantly greater for set blanks than for groundwater (table 11). This finding was expected for several reasons: the dataset used in this study intentionally targeted the selection of batches with detections in set blanks; set censoring decreases the number of detections in environmental samples but not in set blanks; and the data reevaluation process revealed that the NWQL at times identified detections in set blanks more leniently than in environmental samples before use of SOP ORGF0500.2 (U.S. Geological Survey, written commun., November 21, 2017), in particular for compounds such as *p,p′*-DDE, trifluralin, benfluralin, and dacthal where there were frequent detections in set blanks (explained in the "Data Reevaluation" section of this report). This latter condition also explains the significantly greater detection frequencies in set blanks compared to surface-water samples for the four listed compounds.

The comparison of surface-water samples and set blanks shows that all GCMS compounds with detections except 1-naphthol have statistically significant differences in percentages of detections (table 11). Unlike the comparison with groundwater samples, four compounds (metolachlor, diazinon, 1-naphthol, and molinate) have a greater detection frequency in surface water than in set blanks. Time-series plots (figs. 4*A–K*, in back of report) and cumulative distribution function plots (figs. 7*A–K*, in back of report), using logarithmic scales, illustrate that the highest concentrations are generally for surface-water samples rather than for set blanks. Although the distributions of detected results of dieldrin in set blanks and surface-water samples appear similar between about 2005 and 2010 (fig. 4*B*, in back of report), the many surface-water samples with high concentrations before 2005 influence the overall statistical outcome of higher concentrations in surface-water samples than set blanks (table 11).

For set blanks, the 99th percentile of concentration is a detection for all GCMS compounds with at least 100 samples (the minimum number of samples for which the 99th percentile was calculated; table 12). Among groundwater samples, the 99th percentile concentration is a detection for three compounds (*p,p′*-DDE, dieldrin, and metolachlor). For the latter two compounds, the 99th percentile detected concentrations in groundwater samples is more than an order of magnitude higher than the 99th percentile detected concentrations in set blanks. All GCMS compounds have higher percentiles of groundwater samples than set blanks that result in nondetections. Except for benfluralin, the 99th percentile of concentration and the 95-percent upper confidence limit for the 99th percentile is greater for surface-water samples than for set blanks (table 12). Benfluralin has a significantly greater percent of detected results for set blanks than surface-water samples (30 versus 1 percent) and a slightly lower 99th percentile concentration in surface-water samples compared to set blanks. Eight GCMS compounds (except for metolachlor, diazinon, and molinate) have higher percentiles of surface-water samples than set blanks that result in nondetections.

LCMS Compounds in Groundwater and Surface-Water Samples

For LCMS compounds, detection frequencies were 7 percent for set blanks, 1 percent for groundwater results, and 4 percent for surface-water results (table 11). As with GCMS compounds, the LCMS compounds experienced one or more periods of episodic contamination in the 2001 through 2006 period, with few or no set blank detections in later years (figs. 3*L–U* and 4*L–U*, in back of report; tables 7 and 11). For CAAT and fenuron, the NWQL retroactively censored most results (through a data reload to NWIS) for environmental samples collected from August 2002 through March 2006 by applying MRL censoring to address the majority period of

Table 11. Comparison of distributions of detections between set blanks and groundwater and surface-water results for selected compounds analyzed by gas or liquid chromatography/mass spectrometry methods using original results for the subset of batches reviewed for this study.

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period. Results significant at α=0.05 are in bold typeface. Data in columns with shading were compared using the Fisher exact test. µg/L, microgram per liter; XX, not applicable; —, insufficient data for analysis; CAAT, 2-chloro-4,6-diamino-s-triazine; <. less than]

Parameter code	Analyte	Set-blank results						Groundwater results							Surface-water results						
		Number of results	Detected results					Number of results	Detected results					Fisher exact test,[1] *p*-value	Number of results	Detected results					Fisher exact test,[1] *p*-value
			Number of results with detections	Detection frequency, in percent	Concentration, in µg/L				Number of results with detections	Detection frequency, in percent	Concentration, in µg/L					Number of results with detections	Detection frequency, in percent	Concentration, in µg/L			
					Minimum	Median	Maximum				Minimum	Median	Maximum					Minimum	Median	Maximum	
GCMS compounds																					
34653	*p,p'*-DDE	89	54	61	0.0002	0.0016	0.0032	178	2	1	0.0037	0.0042	0.0046	**<0.001**	478	20	4	0.0003	0.0054	0.4760	**<0.001**
39381	Dieldrin	186	14	8	0.0010	0.0032	0.0069	526	8	2	0.0070	0.0771	3.7200	**<0.001**	837	24	3	0.0005	0.0073	0.6300	**0.005**
39415	Metolachlor	186	25	13	0.0010	0.0070	0.0150	525	47	9	0.0009	0.0115	4.5200	0.090	837	580	69	0.0008	0.0228	15.3000	**<0.001**
39572	Diazinon	186	16	9	0.0029	0.0043	0.0063	526	0	0	—	—	—	—	837	219	26	0.0015	0.0102	0.6970	**<0.001**
49295	1-Naphthol	97	3	3	0.0030	0.0060	0.0063	348	0	0	—	—	—	—	359	14	4	0.0040	0.0160	0.0456	1
61600	Oxyfluorfen	94	10	11	0.0050	0.0060	0.0070	232	0	0	—	—	—	—	287	2	1	0.0140	0.0227	0.0314	**<0.001**
61606	Tefluthrin	94	24	26	0.0019	0.0030	0.0069	231	0	0	—	—	—	—	288	0	0	—	—	—	—
82661	Trifluralin	185	60	32	0.0008	0.0050	0.0100	526	1	0.2	0.0040	0.0040	0.0040	**<0.001**	837	102	12	0.0004	0.0090	0.5660	**<0.001**
82671	Molinate	183	3	2	0.0050	0.0160	0.0200	411	0	0	—	—	—	—	765	61	8	0.0023	0.0149	16.0000	**0.001**
82673	Benfluralin	186	56	30	0.0018	0.0060	0.0110	525	1	0.2	0.0060	0.0060	0.0060	**<0.001**	837	10	1	0.0028	0.0075	0.5640	**<0.001**
82682	Dacthal	186	41	22	0.0007	0.0020	0.0042	525	1	0.2	0.0020	0.0020	0.0020	**<0.001**	837	50	6	0.0005	0.0027	0.7260	**<0.001**
	Total for GCMS results	1,672	306	18	XX	XX	XX	4,553	60	1.3	XX	XX	XX	XX	7,199	1,082	15	XX	XX	XX	XX
LCMS compounds																					
04033	Diphenamid	176	8	5	0.0001	0.0003	0.0125	422	2	0.5	0.0006	0.0053	0.0100	**0.001**	579	9	2	0.0030	0.0060	0.0190	**0.036**
04039	CAAT	82	4	5	0.0008	0.0010	0.0016	220	16	7	0.0030	0.0031	0.8900	0.606	339	15	4	0.0063	0.0330	0.0850	0.773
49297	Fenuron	183	48	26	0.0003	0.0009	0.0105	451	0	0	—	—	—	—	589	1	0.2	0.0250	0.0250	0.0250	**<0.001**
49310	Carbaryl	171	6	4	0.0007	0.0057	0.0068	419	0	0	—	—	—	—	531	39	7	0.0030	0.0140	0.3730	0.104
50337	Sulfometuron-methyl	176	11	6	0.0006	0.0036	0.0140	422	9	2	0.0010	0.0100	0.1010	**0.021**	579	36	6	0.0030	0.0245	0.4240	1
50356	Imazaquin	176	10	6	0.0003	0.0040	0.0080	422	5	1	0.0030	0.0190	0.0510	**0.003**	579	41	7	0.0034	0.0180	18	0.609
50407	Imazethapyr	183	1	1	0.0050	0.0050	0.0050	451	4	1	0.0040	0.0050	0.4250	1	589	21	4	0.0040	0.0210	0.2100	**0.038**
50471	Propiconazole	183	8	4	0.0007	0.0009	0.0011	451	0	0	—	—	—	—	589	27	5	0.0080	0.0410	1.9600	1
61694	Flumetsulam	183	18	10	0.0052	0.0100	0.2030	451	3	1	0.0054	0.0070	0.1220	**<0.001**	589	6	1	0.0042	0.0320	0.4070	**<0.001**
61697	Metsulfuron-methyl	171	4	2	0.0022	0.0059	0.0078	409	1	0.2	0.0106	0.0106	0.0106	**0.028**	565	6	1	0.0630	0.6450	16	0.253
	Total for LCMS results	1,684	118	7	XX	XX	XX	4,118	40	1.0	XX	XX	XX	XX	5,528	201	3.6	XX	XX	XX	XX
	Total for all GCMS and LCMS results	3,356	424	13	XX	XX	XX	8,671	100	1.2	XX	XX	XX	XX	12,727	1,283	10.1	XX	XX	XX	XX

[1]Test to compare detection frequencies between set blanks and groundwater or surface-water samples.

Table 12. Number of detections, detection frequencies, and summary statistics, with uncertainty, for set blanks, groundwater samples, and surface-water samples analyzed using gas or liquid chromatography/mass spectrometry methods for the subset of batches reviewed for this study.

[Data are from the Laboratory Information Management System of the National Water Quality Laboratory and are published in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period. µg/L, microgram per liter; UCL, upper confidence limit; GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; —, insufficient data for analysis; CAAT, 2-chloro-4,6-diamino-s-triazine; ND, nondetection; >, greater than]

Parameter code	Analyte	Set-blank results						Groundwater results						Surface-water results					
		Number of results	Number of results with detections	Detection frequency (percent)	99th percentile of concentration, in µg/L	95 percent UCL for the 99th percentile, in µg/L	Highest percentile resulting in a nondetection	Number of results	Number of results with detections	Detection frequency (percent)	99th percentile of concentration, in µg/L	95 percent UCL for the 99th percentile, in µg/L	Highest percentile resulting in a nondetection	Number of results	Number of results with detections	Detection frequency (percent)	99th percentile of concentration, in µg/L	95 percent UCL for the 99th percentile, in µg/L	Highest percentile resulting in a nondetection
GCMS compounds																			
34653	*p,p'*-DDE	89	54	61	—	—	30	178	2	1	0.0037	0.0046	96	478	20	4	0.0168	0.0194	93
39381	Dieldrin	186	14	8	0.0063	0.0069	88	526	8	2	0.0669	0.1400	97	837	24	3	0.0100	0.0109	95
39415	Metolachlor	186	25	13	0.0150	0.0150	81	525	47	9	0.2020	0.4860	89	837	580	69	2.5700	3.7200	29
39572	Diazinon	186	16	9	0.0052	0.0063	87	526	0	0	ND	ND	>99	837	219	26	0.1140	0.2220	72
49295	1-Naphthol	97	3	3	—	—	92	348	0	0	ND	ND	>99	359	14	4	0.0210	0.0280	94
61600	Oxyfluorfen	94	10	11	—	—	82	232	0	0	ND	ND	>99	287	2	1	ND	0.0314	99
61606	Tefluthrin	94	24	26	—	—	66	231	0	0	ND	ND	>99	288	0	0	ND	ND	>99
82661	Trifluralin	185	60	32	0.0080	0.0100	61	526	1	0	ND	ND	>99	837	102	12	0.0658	0.0700	86
82671	Molinate	183	3	2	0.0160	0.0200	95	411	0	0	ND	ND	>99	765	61	8	0.9000	3.4100	91
82673	Benfluralin	186	56	30	0.0080	0.0100	63	525	1	0	ND	ND	>99	837	10	1	0.0060	0.0080	98
82682	Dacthal	186	41	22	0.0040	0.0040	72	525	1	0	ND	ND	>99	837	50	6	0.0056	0.0121	93
LCMS compounds																			
04033	Diphenamid	176	8	5	0.0012	0.0125	91	422	2	0	ND	0.0006	99	579	9	2	0.0042	0.0121	98
04039	CAAT	82	4	5	—	—	91	220	23	10	0.2210	0.8900	85	339	49	14	0.0570	0.0660	85
49297	Fenuron	183	48	26	0.0062	0.0105	67	451	1	0	ND	ND	>99	589	1	0	ND	ND	>99
49310	Carbaryl	171	6	4	0.0068	0.0068	93	419	0	0	ND	ND	>99	531	39	7	0.1610	0.2120	91
50337	Sulfometuron-methyl	176	11	6	0.0130	0.0140	89	422	9	2	0.0180	0.0810	96	579	36	6	0.0840	0.1020	88
50356	Imazaquin	176	10	6	0.0070	0.0080	90	422	5	1	0.0070	0.0220	97	579	41	7	0.2230	0.8350	92
50407	Imazethapyr	183	1	1	ND	0.0050	99	451	4	1	ND	0.0060	99	589	21	4	0.0580	0.1440	96
50471	Propiconazole	183	8	4	0.0011	0.0011	92	451	0	0	ND	ND	>99	589	27	5	0.1650	0.5440	95
61694	Flumetsulam	183	18	10	0.0150	0.2030	85	451	3	1	ND	0.0070	99	589	6	1	0.0042	0.0420	97
61697	Metsulfuron-methyl	171	4	2	0.0074	0.0078	94	409	1	0	ND	ND	>99	565	6	1	0.063	0.7200	97

this laboratory contamination for these compounds (apps. 1 and 2). For the other eight LCMS compounds in this study (plus all other compounds in the method), estimated results (indicated with the "E" remark code) below the MRL were reported for the period from May 2001 (method start) through April 2004 when the MRL report level type was used. For imazaquin, imazethapyr, flumetsulam, and metsulfuron methyl (plus 28 other compounds in the method), the data reload also retroactively censored any detections less than 0.003 µg/L for samples collected from August 2002 through March 2006 and changed the reporting level type from MRL to IRL for most or all this timeframe (table 1.5; app. 2).

The example for metolachlor in the "GCMS Compounds in Groundwater and Surface-Water Samples" section of this report, which considers dates of episodic contamination for potential censoring of environmental data, similarly might be applied to these LCMS compounds during periods of episodic contamination. Few detections in set blanks occurred during later non-MRL periods (figs. 3*L–U* and 4*L–U*, in back of report), and when they did (in carbaryl, sulfometuron-methyl, imazaquin, imazethapyr, and flumetsulam), concentrations of any detections in set blanks that were close in time to detections in environmental samples were much lower than those in environmental samples.

Detection frequencies were significantly greater in set blanks than in groundwater samples for diphenamid, sulfometuron-methyl, imazaquin, flumetsulam, and metsulfuron-methyl, although the small number of detections for both sample types for some analytes is a comparison limitation (table 11). There is some overlap in concentrations of detections between groundwater samples and set blanks when considering the entire study period (figs. 6*L*, *P*, *Q*, *T*, and *U*, in back of report; tables 12 and 13). However, it is also important to evaluate these results in a temporal context to determine when detections were observed in set blanks relative to environmental samples. For example, detections in groundwater samples either occurred during completely different periods than detections in set blanks (diphenamid [fig. 3*L*, in back of report], sulfometuron-methyl [fig. 3*P,* in back of report], or imazaquin [fig. 3*Q,* in back of report]), or if detections in both types of samples occurred during overlapping periods, higher concentrations (generally at least an order of magnitude higher) occurred in groundwater samples than those in set blanks (CAAT; fig. 3*M,* in back of report).

Detection frequencies were significantly greater in set blanks than in surface-water samples for diphenamid, fenuron, and flumetsulam; and were significantly greater in surface-water samples than set blanks for imazethapyr (table 11). In contrast with groundwater results, many concentrations in surface-water samples were much greater than concentrations in set blanks for many but not all compounds (fig. 7, in back of report; table 12). The two compounds with the most overlap in concentrations between surface-water samples and set blanks, diphenamid (fig. 7*L,* in back of report) and flumetsulam (fig. 7*T,* in back of report), did not show overlap during the same periods of time (figs. 4*L* and *T,* in back of report), suggesting, as for groundwater samples, the importance of considering the relative timing of detections of environmental samples and set blanks.

Objective 3: False-Positive and False-Negative Results

Blind-blank and unspiked blind-spike samples from QSB are analyzed by NWQL in the same way as environmental samples and are similarly subject to set censoring. Detections in blind-blank and unspiked blind-spike samples provide estimates of the false-positive risk. None of the GCMS compounds and one of the LCMS compounds (flumetsulam, 2.6 percent) had a false-positive rate greater than 1 percent (table 13) as determined from blind-blank samples and unspiked blind-spike samples from the QSB. The implication for compounds with a false-positive rate greater than 1 percent is that there might be an increased risk of false-positive results in environmental samples, especially for periods that overlap episodes of detections in set blanks. If only results greater than the LT–MDL are considered, then flumetsulam (1.1 percent) remains the only compound with a false-positive rate greater than 1 percent.

The potential for false-positive results increases as concentrations decrease below the LT–MDL. This is the result of increased potential of low concentrations of the pesticide being present in the laboratory equipment or reduced ability to distinguish the pesticide signal from interferences (called interferents) and background noise. Rough estimates of the theoretical risk of false positives below the LT–MDL can be made by multiplying the standard deviation obtained from the LT–MDL (or MDL) determination by the Student's *t*-value at the α level of interest (Childress and others, 1999). The assumptions for making these estimates are that the distribution of measurements at the LT–MDL is representative of the distribution of blank measurements and that the distribution of blank measurements is centered at a concentration of zero (both conditions are limiting assumptions of the MDL/LT–MDL procedure).

For example, the LT–MDL (theoretically established as the concentration with no more than a 1-percent probability of being a false-positive; app. 1) for *p,p′*-DDE was 0.0013 µg/L from October 2000 through September 2003 (table 1.1). The LT–MDL is typically calculated using 24 determinations of low concentration spike samples (n=24). At the concentration of 0.0013 µg/L, the Student's *t*-value for the false-positive risk of 1 percent (α=0.01) for 23 degrees of freedom (n–1) is 2.5. Using these parameters and the calculation described in the previous paragraph, the standard deviation is 0.0013÷2.5=0.00052 µg/L. At the false-positive risk of 25 percent (α=0.25), the Student's *t*-value is 0.6853; the estimated concentration at which *p,p′*-DDE has a false-positive risk of 25 percent is 0.00052 µg/L×0.6853=0.00036 µg/L, which is 27 percent of the LT–MDL. Because there were many detections of *p,p′*-DDE in set blanks during this period,

Table 13. False-positive and false-negative results for 21 compounds analyzed using gas or liquid chromatography/mass spectrometry methods at the National Water Quality Laboratory from 2001 to 2015.

[The samples in this study were analyzed using blind-blank and blind-spike samples from the Quality Systems Branch (QSB) and are published in Riskin and others (2019). Data in this table are based on all results from 2001 through 2015, not just results from selected batches used for the study in this report. False positives (FPs) are determined from blind-blank samples from the QSB Blind Blank Program that operated in 2004 and from 2007 through 2012 and spiked samples that do not contain the given compound from the QSB Organic Blind Sample Project (OBSP) that operated during the entire study period. False negatives (FNs) are determined from spiked samples from the OBSP. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; LT–MDL, long-term method detection limit; NA, not applicable; CAAT, 2-chloro-4,6-diamino-s-triazine; NS, no samples; d, compound discontinued on schedule]

Analyte	Method of analysis	Year															Total	Number of results	Percentage FP or FN	Percentage FP above LT-MDL
		2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015				
										False positive										
p,p'-DDE	GCMS	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	2	407	0.5	0.0
Dieldrin	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	958	0.0	0.0
Metolachlor	GCMS	0	0	2	2	0	0	1	0	2	0	1	0	0	0	0	8	898	0.9	0.0
Diazinon	GCMS	0	0	1	2	0	0	1	2	0	0	0	0	0	0	0	6	891	0.7	0.7
1-Naphthol	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	478	0.2	0.0
Oxyfluorfen	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	476	0.0	0.0
Tefluthrin	GCMS	0	0	0	0	0	0	0	0	0	1	1	0	0	0	0	2	482	0.4	0.4
Trifluralin	GCMS	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	2	939	0.2	0.0
Molinate	GCMS	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	879	0.1	0.1
Benfluralin	GCMS	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	2	1,013	0.2	0.0
Dacthal	GCMS	0	0	0	2	0	0	0	0	0	1	0	0	0	0	0	3	733	0.4	0.0
Diphenamid	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	353	0.0	NA
CAAT	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	167	0.0	0.0
Fenuron	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	333	0.0	0.0
Carbaryl	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	273	0.0	0.0
Sulfometuron-methyl	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	291	0.0	0.0
Imazaquin	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	NS	0	282	0.0	0.0
Imazethapyr	LCMS	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	2	342	0.6	0.0
Propiconazole	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	311	0.0	0.0
Flumetsulam	LCMS	4	0	1	1	1	1	0	0	0	0	0	0	1	0	NS	9	350	2.6	1.1
Metsulfuron-methyl	LCMS	0	0	0	1	0	0	0	0	0	0	0	0	0	0	NS	1	333	0.3	0.0

Table 13. False-positive and false-negative results for 21 compounds analyzed using gas or liquid chromatography/mass spectrometry methods at the National Water Quality Laboratory from 2001 to 2015.—Continued

[The samples in this study were analyzed using blind-blank and blind-spike samples from the Quality Systems Branch (QSB) and are published in Riskin and others (2019). Data in this table are based on all results from 2001 through 2015, not just results from selected batches used for the study in this report. False positives (FPs) are determined from blind-blank samples from the QSB Blind Blank Program that operated in 2004 and from 2007 through 2012 and spiked samples that do not contain the given compound from the QSB Organic Blind Sample Project (OBSP) that operated during the entire study period. False negatives (FNs) are determined from spiked samples from the OBSP. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; LT–MDL, long-term method detection limit; NA, not applicable; CAAT, 2-chloro-4,6-diamino-s-triazine; NS, no samples; d, compound discontinued on schedule]

Analyte	Method of analysis	Year															Total	Number of results	Percentage FP or FN	Percentage FP above LT-MDL
		2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015				
										False negative										
p,p'-DDE	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	285	0.0	NA
Dieldrin	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	454	0.0	NA
Metolachlor	GCMS	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	514	0.2	NA
Diazinon	GCMS	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	518	0.2	NA
1-Naphthol	GCMS	0	0	0	0	2	4	0	0	0	0	0	0	0	0	0	6	224	2.7	NA
Oxyfluorfen	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	149	0.0	NA
Tefluthrin	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	143	0.0	NA
Trifluralin	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	473	0.0	NA
Molinate	GCMS	0	0	0	0	1	1	0	0	0	0	0	2	0	1	0	5	462	1.1	NA
Benfluralin	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	389	0.0	NA
Dacthal	GCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	480	0.0	NA
Diphenamid	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	161	0.0	NA
CAAT	LCMS	0	5	9	6	0	0	d	d	d	d	d	d	d	d	d	20	57	35	NA
Fenuron	LCMS	0	2	8	0	0	2	0	0	0	0	0	0	0	0	0	12	181	6.6	NA
Carbaryl	LCMS	0	0	1	0	0	2	0	0	0	0	0	0	0	0	0	3	241	1.2	NA
Sulfometuron-methyl	LCMS	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	189	0.5	NA
Imazaquin	LCMS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	NS	0	232	0.0	NA
Imazethapyr	LCMS	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	175	0.6	NA
Propiconazole	LCMS	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	203	0.5	NA
Flumetsulam	LCMS	1	0	0	0	0	1	1	0	1	0	0	0	0	0	NS	4	164	2.4	NA
Metsulfuron-methyl	LCMS	1	3	3	4	3	0	0	0	0	1	0	0	0	0	NS	15	181	8.3	NA

the assumption of a blank distribution centered on zero likely results in further underestimation of this false-positive risk.

Estimates of the theoretical false-positive risk for detections below the LT–MDL as described in the previous paragraph might not reflect the actual false-positive risk of pesticide results from the information-rich NWQL pesticide methods. Information-rich methods require multiple lines of rigorous criteria, such as retention times, presence of qualifying ions, and acceptable quantification-to-qualifying ratios, that need to be met to identify detections. The theoretical false-positive risk is based on the LT–MDL calculation, where the signal is based only on measurement variability from replicate spike sample measurements using the quantification ion (although the compound must meet identification criteria). The actual false-positive risk is more robust than the theoretical risk because several criteria beyond this variability alone need to be met to call a result a detection. Consequently, the NWQL has greater confidence in reported detections than the theoretically calculated risk of false-positives, even for detections below the LT–MDL. Although these methods provide enhanced qualitative identification capabilities, detections with concentrations less than the LT–MDL still have a risk of being the result of low-level laboratory contamination. The closest approximation of the actual false-positive risk associated with environmental samples is that identified by detections in blind-blank and unspiked blind-spike samples from QSB (table 13) because these samples, like environmental samples, are reported after set-censoring.

Molinate and 1-naphthol were the only GCMS compounds with false-negative rates greater than 1 percent as determined by blind-spike samples from the QSB (table 13). All 1-naphthol false-negative results occurred from November 2005 through May 2006 during a period of low recoveries and were likely related to a method recovery issue specific to schedule 2032 (Suranne Stineman-Lederer, U.S. Geological Survey, written commun., September 5, 2017). Five LCMS compounds had a false-negative rate greater than 1 percent, including CAAT (35 percent), which had fewer QSB blind-spike samples than the other 20 compounds for the determination of the false-negative rate (table 13). This finding indicates that the detection frequency of CAAT in environmental samples during 2001–6 (and especially during 2002–5) may be underreported. Data users who are concerned about the possibility of pesticide results that miss the identification of detections for these compounds should note that all false negatives for CAAT and most for fenuron and metsulfuron-methyl occurred during periods of lower recovery performance in reagent-water spikes (U.S. Geological Survey, 2005). For example, 14 of the 15 false-negative occurrences for metsulfuron-methyl (table 13) occurred before 2006 during low recovery periods. The extended period of low recoveries for CAAT resulted in its removal from the method in 2007 (U.S. Geological Survey, 2007).

The false-negative rate is less than 1 percent for 14 of the 21 compounds in this study (table 13). OBSP typically spikes compounds at concentrations two to five times higher than the RL (U.S. Geological Survey, 2018). Rates of nondetections in spiked OBSP samples that are greater than 1 percent indicate that the RL is set too low to provide a false-negative risk of no more than 1 percent (assuming data are not censored at the RL) and is especially relevant for periods of low compound recovery. In addition to compound recovery performance, false-negative occurrence is dependent on the concentration in the sample relative to the RL and the type of reporting convention used. Under the MRL convention that censors all results below the MRL concentration, the occurrence of false negatives will be much higher when the true concentration in the environmental sample is at or just above the MRL (U.S. Geological Survey, 2010, attachment C).

Objective 4: Effects of the Data Reevaluation

Fewer than 2 percent of set blank, groundwater, and surface-water results from targeted batches would change detection status—either from a detection to a nondetection or from a nondetection to a detection—as a result of the data reevaluation (table 14). Most changes in detection status would be from detections to nondetections, primarily because the 2017 identification protocols for identification of detections did not identify the analyte (table 14). There would be only two changes in detection status for the LCMS results.

The data reevaluation process did not have a substantive effect on the results in targeted batches for environmental samples, indicating that historical protocols used by the NWQL to identify detections produced results that are predominantly consistent with the 2017 protocols. Altogether, for data in targeted batches, NWQL would have reported 8 of 8,671 (0.1 percent) of results from groundwater samples and 193 of 12,727 (1.5 percent) of results from surface-water samples differently (from a detection to a nondetection or vice versa) if 2017 identification protocols were applied to historical pesticide results. Most (192 of 193) of the changes to surface-water results were associated with GCMS compounds, with diazinon accounting for nearly half of those changes. Fewer results would change from a nondetection to a detection because of the reevaluation: 2 results (0.02 percent) from groundwater samples and 13 results (0.1 percent) for surface-water samples.

The data reevaluation process would have a greater effect on the results for set-blank samples than for environmental samples. For GCMS compounds, 147 of 1,672 set-blank results (8.8 percent) would change from detections to nondetections, with the greatest number of changes for trifluralin and benfluralin. None of the LCMS set-blank results would change because of the reevaluation (table 15). Because the reevaluation produced a larger proportion of set-blank than environmental results that would change from detections to nondetections, the statistical comparison of detection frequencies between original and reevaluated results for set blanks produced more significant differences (five compounds) than did the comparisons for groundwater and surface-water samples (zero and one compound [diazinon], respectively; table 16).

Table 14. Summary of how and why pesticide set-blank and environment results from selected batches would be reported differently by the National Water Quality Laboratory if the data reevaluation and minimum reporting level censoring were applied.

[The numbers of comments of various types in the environmental and quality control (QC) data are from Riskin and others (2019). Terms in bold are defined in the glossary of this report. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; —, no records; LIMS, Laboratory Information Management System; MRL, minimum reporting level; RL, reporting level]

Comment in the environmental and QC data tables	Number and percent of records with the given comment													
	Results for GCMS compounds						Results for LCMS compounds						Total for all sample types and all GCMS and LCMS compounds	
	Set blanks		Groundwater		Surface-water		Set blanks		Groundwater		Surface-water			
	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent
No change in detection status of result from the data reevaluation														
No change from the original remark or value	1,524	91.15	4,545	99.82	6,991	97.11	1,638	97.27	3,890	94.46	5,136	92.91	23,724	95.84
Value of original result changed based on a revised laboratory **integration** but result remained either a detection or nondetection	—	—	—	—	9	0.13	—	—	1	0.02	1	0.02	11	0.04
Value of original detected result changed because it did not match value from the analytical instrument software but result remained a detection	—	—	1	0.02	7	0.10	—	—	—	—	—	—	8	0.03
The originally retrieved LIMS result was changed from a detection to a nondetection to reflect MRL censoring described in Rapi-Note 07-005[a] The result_OR value in this table shows the changed (nondetected) value, not the originally retrieved LIMS result.	—	—	—	—	—	—	—	—	8	0.19	34	0.62	42	0.17
The RL type, RL value, and censored result value were changed to reflect Rapi-Note 07-005; there was no change in detection status of the result	—	—	—	—	—	—	46	2.73	177	4.30	350	6.33	573	2.31
The RL type and RL value were changed to reflect Rapi-Note 07-005; however, the concentration is above the RL and remains a detection	—	—	—	—	—	—	—	—	2	0.05	2	0.04	4	0.02
The result was set censored because of a detection in the set or batch blank; in addition, the RL type, RL value, and censored result value were changed to reflect Rapi-Note 07-005	—	—	—	—	—	—	—	—	39	0.95	4	0.07	43	0.17
Total number of results with no change in detection status from the data reevaluation	1,524	91.15	4,546	99.85	7,007	97.33	1,684	100.00	4,117	99.98	5,527	99.98	24,405	98.59
Change from a detection to a nondetection from the data reevaluation														
2017 protocols for identification of detections[b] do not identify the analyte	34[c]	2.03	4[d]	0.09	117[c]	1.63	—	—	—	—	—	—	155	0.63
2017 protocols for identification of detections do not identify the analyte because **qualification criteria** were not met	113[c]	6.76	1[d]	0.02	62[c]	0.86	—	—	1	0.02	—	—	177	0.72
Result changed from a detection to a nondetection because the need to set censor the result was missed in the original evaluation	—	—	—	—	1	0.01	—	—	—	—	—	—	1	0.00
Total number of results that would change from a detection to a nondetection from the data reevaluation	147	8.79	5	0.11	180	2.50	0	0.00	1	0.02	0	0.00	333	1.35

Table 14. Summary of how and why pesticide set-blank and environment results from selected batches would be reported differently by the National Water Quality Laboratory if the data reevaluation and minimum reporting level censoring were applied.—Continued

[The numbers of comments of various types in the environmental and quality control (QC) data are from Riskin and others (2019). Terms in bold are defined in the glossary of this report. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; —, no records; LIMS, Laboratory Information Management System; MRL, minimum reporting level; RL, reporting level]

Comment in the environmental and QC data tables	Number and percent of records with the given comment													
	Results for GCMS compounds						Results for LCMS compounds						Total for all sample types and all GCMS and LCMS compounds	
	Set blanks		Groundwater		Surface-water		Set blanks		Groundwater		Surface-water			
	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent	Number	Percent
Change from a nondetection to a detection from the data reevaluation														
Original result was censored (reported as a nondetection) based on a detection in a set blank from the same instrument batch but not the same set	—	—	1	0.02	4	0.06	—	—	—	—	—	—	5	0.02
Original result was censored (reported as a nondetection) based on a detection in the set blank; however, the original detection in the set blank was changed to a nondetection in the reevaluation, eliminating the need for set censoring	—	—	—	—	1	0.01	—	—	—	—	—	—	1	0.00
Original nondetection was changed to a detection (a greater than ">" result) because the result was above the high **calibration standard**	—	—	—	—	—	—	—	—	—	—	1	0.02	1	0.00
Result changed from a nondetection to a detection because the detection was missed in the original evaluation	1	0.06	1	0.02	7	0.10	—	—	—	—	—	—	9	0.04
Total number of results that would change from a nondetection to a detection from the data reevaluation	1	0.06	2	0.04	12	0.17	0	0.00	0	0.00	1	0.02	16	0.06
Total number of results that would change from the data reevaluation	148	8.85	7	0.15	192	2.67	0	0.00	1	0.02	1	0.02	349	1.41
Total of all results, changed and unchanged, from the data reevaluation	1,672	100	4,553	100	7,199	100	1,684	100	4,118	100	5,528	100	24,754	100.00

[a]The original result (Result_OR field) in the environmental and QC data table reflects the change to a nondetection. Thus, there is no change in detection status from the 2017 reevaluation.

[b]The National Water Quality Laboratory standard operating procedure (SOP) for GCMS compounds is ORGF0500.2 (U.S. Geological Survey, written commun., November 21, 2017). The SOP for LCMS compounds is ORGF0338.3 (U.S. Geological Survey, written commun., December 20, 2011).

[c]A total of 32 results with either of these two comments occurred in analytical schedule 2001; 2, in schedule 2003; and 113, in schedule 2033.

[d]One result with either of these two comments occurred in analytical schedule 2001, and four, in schedule 2033.

[e]In total, 140 results with either of these two comments occurred in analytical schedule 2001; 11, in schedule 2003; and 28, in schedule 2033.

Table 15. Number of water-quality results from selected batches analyzed by gas or liquid chromatography/mass spectrometry methods that would change from detections to nondetections and from nondetections to detections after reevaluation by the National Water Quality Laboratory in 2017.

[Data are based on data in the Laboratory Information Management System of the National Water Quality Laboratory and in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period from 2001 to 2015. ND, nondetection; GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; CAAT, 2-chloro-4,6-diamino-s-triazine]

Parameter code	Analyte	Set blanks				Quality Systems Branch blind blanks			Groundwater results				Surface-water results			
		Number of results	Detection to ND		ND to detection, number	Number of results	Detection to ND, number	ND to detection, number	Number of results	Detection to ND		ND to detection, number	Number of results	Detection to ND		ND to detection, number
			Number	Percent						Number	Percent			Number	Percent	
							GCMS compounds									
34653	*p,p'*-DDE	89	7	7.9	0	0	0	0	178	1	0.6	0	478	7	1.5	0
39381	Dieldrin	186	3	1.6	0	6	0	0	526	0	0.0	0	837	7	0.8	1
39415	Metolachlor	186	14	7.5	0	6	0	1	525	1	0.2	0	837	28	3.3	1
39572	Diazinon	186	16	8.6	0	6	0	0	526	0	0.0	1	837	81	9.7	1
49295	1-Naphthol	97	0	0.0	0	6	0	0	348	0	0.0	0	359	0	0.0	1
61600	Oxyfluorfen	94	3	3.2	0	6	0	0	232	0	0.0	0	287	0	0.0	0
61606	Tefluthrin	94	19	20	0	6	0	0	231	0	0.0	0	288	0	0.0	0
82661	Trifluralin	185	36	19	0	6	0	0	526	1	0.2	1	837	21	2.5	2
82671	Molinate	183	2	1.1	0	6	0	0	411	0	0.0	0	765	14	1.8	0
82673	Benfluralin	186	33	18	1	6	0	0	525	1	0.2	0	837	1	0.1	0
82682	Dacthal	186	14	7.5	0	6	0	0	525	1	0.2	0	837	11	1.3	6
	Total for GCMS results	1,672	147	8.8	1	60	0	1	4,553	5	0.1	2	7,199	170	2.4	12
							LCMS compounds									
04033	Diphenamid	176	0	0	0	7	0	0	422	0	0.0	0	579	0	0.0	0
04039	CAAT	82	0	0	0	1	0	0	220	0	0.0	0	339	0	0.0	0
49297	Fenuron	183	0	0	0	7	0	0	451	0	0.0	0	589	0	0.0	0
49310	Carbaryl	171	0	0	0	7	0	0	419	0	0.0	0	531	0	0.0	0
50337	Sulfometuron-methyl	176	0	0	0	7	0	0	422	0	0.0	0	579	0	0.0	0
50356	Imazaquin	176	0	0	0	7	0	0	422	0	0.0	0	579	0	0.0	1
50407	Imazethapyr	183	0	0	0	7	0	0	451	0	0.0	0	589	0	0.0	0
50471	Propiconazole	183	0	0	0	7	0	0	451	0	0.0	0	589	0	0.0	0
61694	Flumetsulam	183	0	0	0	7	0	0	451	1	0.2	0	589	0	0.0	0
61697	Metsulfuron-methyl	171	0	0	0	7	0	0	409	0	0.0	0	565	0	0.0	0
	Total for LCMS results	1,684	0	0	0	64	0	0	4,118	1	0.0	0	5,528	0	0.0	1
	Total for all GCMS and LCMS results	3,356	147	4	1	124	0	1	8,671	6	0.1	2	12,727	170	1.3	13

Table 16. Comparison of detection frequencies between original and reevaluated results for set blanks for groundwater and surface-water samples analyzed by gas or liquid chromatography/mass spectrometry methods by the National Water Quality Laboratory from 2001 to 2015.

[Data are based on data in the Laboratory Information Management System of the National Water Quality Laboratory and in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period. Data in columns with shading were compared using the Fisher exact test. Results significant at α=0.05 are in bolded typeface. GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; CAAT, 2-chloro-4,6-diamino-s-triazine; <, less than; NA, not applicable]

Parameter code	Analyte	Set-blank results						Groundwater results						Surface-water results					
			Original results		Reevaluated results				Original results		Reevaluated results				Original results		Reevaluated results		
		Number of results	Number of results with detections	Detection frequency (percent)	Number of results with detections	Detection frequency (percent)	Fisher exact test[1]	Number of results	Number of results with detections	Detection frequency (percent)	Number of results with detections	Detection frequency (percent)	Fisher exact test[1]	Number of results	Number of results with detections	Detection frequency (percent)	Number of results with detections	Detection frequency (percent)	Fisher exact test[1]
GCMS compounds																			
34653	*p,p'*-DDE	89	54	61	47	53	0.364	178	2	1	1	1	1	478	20	4	13	3	0.288
39381	Dieldrin	186	14	8	11	6	0.680	526	8	2	8	2	1	837	24	3	18	2	0.435
39415	Metolachlor	186	25	13	11	6	**0.022**	525	47	9	46	9	1	837	580	69	553	66	0.174
39572	Diazinon	186	16	9	0	0	**<0.001**	526	0	0	1	0.2	1	837	219	26	139	17	**<0.001**
49295	1-Naphthol	97	3	3	3	3	1	348	0	0	0	0	NA	359	14	4	15	4	1
61600	Oxyfluorfen	94	10	11	7	7	0.612	232	0	0	0	0	NA	287	2	1	2	1	1
61606	Tefluthrin	94	24	26	5	5	**<0.001**	231	0	0	0	0	NA	288	0	0	0	0	NA
82661	Trifluralin	185	60	32	24	13	**<0.001**	526	1	0.2	1	0.2	1	837	102	12	83	10	0.160
82671	Molinate	183	3	2	1	1	0.623	411	0	0	0	0	NA	765	61	8	47	6	0.194
82673	Benfluralin	186	56	30	24	13	**<0.001**	525	1	0.2	0	0	1	837	10	1	9	1	1
82682	Dacthal	186	41	22	27	15	0.081	525	1	0.2	0	0	1	837	50	6	45	5	0.673
LCMS compounds																			
04033	Diphenamid	176	8	5	8	8	1	422	2	0	2	0	NA	579	9	2	9	2	1
04039	CAAT	82	4	5	4	3	1	220	16	7	16	7	1	339	15	4	15	4	1
49297	Fenuron	183	48	26	48	48	1	451	0	0	0	0	NA	589	1	0	1	0	NA
49310	Carbaryl	171	6	4	6	6	1	419	0	0	0	0	NA	531	39	7	39	7	1
50337	Sulfometuron-methyl	176	11	6	11	11	1	422	9	2	9	2	1	579	36	6	36	6	1
50356	Imazaquin	176	10	6	10	10	1	422	5	1	5	1	1	579	41	7	42	7	1
50407	Imazethapyr	183	1	1	1	1	1	451	4	1	4	1	1	589	21	4	21	4	1
50471	Propiconazole	183	8	4	8	8	1	451	0	0	0	0	NA	589	27	5	27	5	1
61694	Flumetsulam	183	18	10	18	18	1	451	3	1	2	0	1	589	6	1	6	1	1
61697	Metsulfuron-methyl	171	4	2	4	4	1	409	1	0	1	0	NA	565	6	1	6	1	1

[1]Test to compare detection frequencies between original results and reevaluated results.

For GCMS compounds like tefluthrin, trifluralin, and benfluralin where up to 20 percent of set-blank results would change from detections to nondetections with the data reevaluation (table 15), there is a theoretical effect on the identification of episodes of laboratory contamination because episodes are determined by moving average detection frequencies in set blanks (more information can be found in "Objective 1: Determine the Characteristics of Laboratory Contamination Over Time" of the "Methods" section of this report). However, only 1 percent of the available GCMS batches analyzed by the NWQL from 2001 to 2015 was included in this study (table 5). If the other 99 percent of GCMS batches that were not reviewed have similar percentages of changes from detections to nondetections in set blanks as the 1 percent that were reviewed (table 5), then there are likely to be fewer periods of episodic contamination than are shown in table 9. Another consideration is that percentages of set-blank results changing from detections to nondetections in unreviewed batches are likely to be less than percentages in reviewed batches because reviewed batches are targeted as having detections in set blanks.

As a result, the identification of periods of episodic contamination in table 9, based on data in LIMS, is a conservative estimate (high-end estimate) of the amount of episodic contamination at the NWQL during the study period for the 21 compounds. Because there are no changes in set-blank results for LCMS compounds, changes in the identification of episodes of laboratory contamination due to the reevaluation of data can be expected to be minimal or nonexistent (table 10).

An additional assessment of the reevaluation compares concentration summaries of detections and detection frequencies in set blanks, groundwater samples, and surface-water samples based on reevaluated data (table 17) with those based on original data (table 11). Considering environmental samples, the reevaluation had the largest effect on diazinon results from surface-water samples (tables 11 and 17). Nearly 10 percent of detections of diazinon in surface-water samples would change to nondetections (table 15) because qualitative identification criteria were not met in the reevaluation (discussed in the "Episodic Laboratory Contamination of GCMS Compounds" section of this report). Most changes in diazinon results to nondetections for set blanks and surface-water samples would occur between 2001 and 2003, with a few instances in 2005. Ranges in concentrations of detections in diazinon and other environmental samples that changed to nondetections in the data reevaluation and the dates most affected by these changes are provided to help data users review detected results in light of the data reevaluation (table 18). Only one LCMS result (for flumetsulam) would change from a detection to a nondetection.

The reevaluation procedure brought to light a historical difference in identification protocols between set blanks and environmental samples for some compounds. For example, for tefluthrin, trifluralin, benfluralin, and dacthal, the NWQL chemist doing the reevaluation noted that most of the changes to nondetections for set blanks occurred because only the quantification ion was present; qualifier ions were not observed (Riskin and others, 2019, GCMS set-blank table). According to 2017 identification protocols, a lack of qualifier ions results in a nondetection in all results, including set blanks. In the mid-2000s, detections were sometimes reported in set blanks even with the lack of qualifier ions because analysts were trying to prevent false positives in environmental samples and were not using qualitative identification rules for set blanks as strict as those in the 2017 identification protocols; thus, detections in blanks would trigger set censoring of environmental results, at least below the concentration in the set blank. This occurred at a time when there were more frequent detections (at least of quantification ion response) in set-blank samples from some part of the analytical procedure. However, some detections still occurred in set blanks for these compounds after reevaluation, which indicates the presence of some laboratory contamination according to the stricter qualitative identification rules of the 2017 identification protocols that were consistently applied to results from set blanks and environmental samples in the reevaluation.

A detailed look into the timing and concentration ranges of data in this study that were affected by the data reevaluation shows that the effects were not widespread in time for environmental samples (table 18). The GCMS compounds in environmental samples most affected by the data reevaluation were collected within a few months to up to about 2 years from the start of the study period. Although some changes to set-blank results would occur during the same period as changes to results from environmental samples, changes to most set-blank results from the data reevaluation would occur during 2005 or 2006 for dieldrin, metolachlor, trifluralin, benfluralin, and dacthal.

Table 17. Comparison of distributions of detections between set blanks and groundwater and surface-water results for selected compounds analyzed by gas or liquid chromatography/mass spectrometry methods using data reevaluated in 2017 for the subset of batches reviewed for this study.

[Data are based on data in the Laboratory Information Management System of the National Water Quality Laboratory and in Riskin and others (2019). Because of biased selection of analytical batches for this study, information in this table may not be representative of all data during the study period. Results significant at α=0.05 are in bold typeface. Data in columns with shading were compared using the Fisher exact test. µg/L, microgram per liter; XX, not applicable; —, insufficient data for analysis; CAAT, 2-chloro-4,6-diamino-s-triazine; <, less than]

Parameter code	Analyte	Set-blank results						Groundwater results							Surface-water results						
			Detected results						Detected results							Detected results					
		Number of results	Number of results with detections	Detection frequency, in percent	Concentration, in µg/L			Number of results	Number of results with detections	Detection frequency, in percent	Concentration, in µg/L			Fisher exact test,[1] *p*-value	Number of results	Number of results with detections	Detection frequency, in percent	Concentration, in µg/L			Fisher exact test,[1] *p*-value
					Minimum	Median	Maximum				Minimum	Median	Maximum					Minimum	Median	Maximum	
GCMS compounds																					
34653	*p,p'*-DDE	89	47	53	0.0002	0.0018	0.0032	178	1	1	0.0038	0.0038	0.0038	**<0.001**	478	13	3	0.0032	0.0143	0.4760	**<0.001**
39381	Dieldrin	186	11	6	0.0019	0.0040	0.0069	526	8	2	0.0070	0.0771	3.7200	**0.003**	837	18	2	0.0005	0.0098	0.6300	**0.012**
39415	Metolachlor	186	11	6	0.0010	0.0070	0.0104	525	46	9	0.0009	0.0123	4.5200	0.272	837	553	66	0.0008	0.0240	15.3000	**<0.001**
39572	Diazinon	186	0	0	--	--	--	526	1	0.2	0.0150	0.0150	0.0150	--	837	139	17	0.0022	0.0137	0.6970	--
49295	1-Naphthol	97	3	3	0.0029	0.0060	0.0063	348	0	0	--	--	--	--	359	15	4	0.0040	0.0160	0.1200	0.775
61600	Oxyfluorfen	94	7	7	0.0050	0.0060	0.0070	232	0	0	--	--	--	--	287	2	1	0.0140	0.0227	0.0314	**<0.001**
61606	Tefluthrin	94	5	5	0.0019	0.0030	0.0060	231	0	0	--	--	--	--	288	0	0	--	--	--	--
82661	Trifluralin	185	24	13	0.0017	0.0050	0.0100	526	1	0.2	0.0053	0.0053	0.0053	**<0.001**	837	83	10	0.0009	0.0105	0.5660	**0.232**
82671	Molinate	183	1	1	0.0050	0.0050	0.0050	411	0	0	--	--	--	--	765	47	6	0.0041	0.0184	15.7000	**<0.001**
82673	Benfluralin	186	24	13	0.0026	0.0060	0.0110	525	0	0	--	--	--	--	837	9	1	0.0028	0.0080	0.5640	**<0.001**
82682	Dacthal	186	27	15	0.0007	0.0020	0.0042	525	0	0	--	--	--	--	837	45	5	0.0005	0.0030	0.7260	**<0.001**
	Total for GCMS results	1,672	160	10	XX	XX	XX	4,553	57	1.3	XX	XX	XX	XX	7,199	924	12.8	XX	XX	XX	XX
LCMS compounds																					
04033	Diphenamid	176	8	5	0.0001	0.0003	0.0125	422	2	0.5	0.0006	0.0053	0.0100	**0.001**	579	9	2	0.0030	0.0060	0.0190	**0.036**
04039	CAAT	82	4	5	0.0008	0.0010	0.0016	220	16	7	0.0030	0.0031	0.8900	1	339	15	4	0.0063	0.0330	0.0850	0.773
49297	Fenuron	183	48	26	0.0003	0.0009	0.0105	451	0	0	--	--	--	--	589	1	0.2	0.0250	0.0250	0.0250	**<0.001**
49310	Carbaryl	171	6	4	0.0007	0.0057	0.0068	419	0	0	--	--	--	--	531	39	7	0.0030	0.0140	0.3730	0.104
50337	Sulfometuron-methyl	176	11	6	0.0006	0.0036	0.0140	422	9	2	0.0010	0.0100	0.1010	**0.021**	579	36	6	0.0030	0.0245	0.4240	1
50356	Imazaquin	176	10	6	0.0003	0.0040	0.0080	422	5	1	0.0030	0.0190	0.0510	**0.003**	579	42	7	0.0040	0.0320	18	0.610
50407	Imazethapyr	183	1	1	0.0050	0.0050	0.0050	451	4	1	0.0040	0.0050	0.4250	1	589	21	4	0.0040	0.0210	0.2100	**0.038**
50471	Propiconazole	183	8	4	0.0007	0.0009	0.0011	451	0	0	--	--	--	--	589	27	5	0.0080	0.0410	1.9600	1
61694	Flumetsulam	183	18	10	0.0052	0.0100	0.2030	451	2	0.4	0.0054	0.0637	0.1220	**<0.001**	589	6	1	0.0042	0.0320	0.4070	**<0.001**
61697	Metsulfuron-methyl	171	4	2	0.0022	0.0059	0.0078	409	1	0.2	0.0106	0.0106	0.0106	**0.028**	565	6	1	0.0630	0.6450	16	0.253
	Total for LCMS results	1,684	118	7	XX	XX	XX	4,118	39	0.9	XX	XX	XX	XX	5,528	202	3.7	XX	XX	XX	XX
	Total for all GCMS and LCMS results	3,356	278	8	XX	XX	XX	8671	96	1	XX	XX	XX	XX	12,727	1,126	9	XX	XX	XX	XX

[1]Test to compare detection frequencies between set blanks and groundwater or surface-water samples.

Table 18. Periods most affected by changes in detections of selected pesticide compounds in groundwater and surface-water samples from the data reevaluation at the National Water Quality Laboratory in 2017.

[A description of the data reevaluation is in the "Data Reevaluation" section of this report. This table is based on data in the Laboratory Information Management System of the National Water Quality Laboratory and in the data release associated with this report (Riskin and others, 2019). Because of biased selection of analytical batches for the study in this report, information in this table may not be representative of all data during the study period from 2001 to 2015. µg/L, microgram per liter; GCMS, gas chromatography/mass spectrometry; LCMS, liquid chromatography/mass spectrometry; NA, not applicable because there were no changes in detections in the given type of sample; CAAT, 2-chloro-4,6-diamino-s-triazine]

Parameter code	Analyte	Period affected	Changes from detections to nondetections		
			Number of changes in groundwater or surface-water results that occurred during the time period affected	Number of changes in set blanks that occurred during the time period affected or the specified period	Range of concentrations in groundwater or surface-water results associated with changes from the reevaluation, in µg/L
GCMS compounds					
34653	*p*,*p*′-DDE	June 2001–November 2001	7 of 8 changes	5 of 7 changes	0.0003–0.0046
39381	Dieldrin	October 2001–October 2003	6 of 7 changes	0 of 3 changes	0.0024–0.0113
39415	Metolachlor	May 2001–May 2002	19 of 29 changes	0; 12 of 14 changes between July 2005 and February 2006	0.0024–0.0144
39572	Diazinon	October 2001–September 2003	66 of 81 changes	15 of 16 changes	0.0015–0.0646
49295	1-Naphthol	NA	NA	NA	NA
61600	Oxyfluorfen	NA	NA	3 of 3 changes between June 2005 and August 2005	NA
61606	Tefluthrin	NA	NA	16 of 19 changes between June 2005 and February 2006	NA
82661	Trifluralin	June 2001–April 2002	16 of 22 changes	4; 27 of the remaining 32 changes between June 2005 and February 2006	0.0004–0.0125
82671	Molinate	May 2001–August 2001	10 of 14 changes	0; 2 of 2 changes in August 2007	0.0025–0.0107
82673	Benfluralin	June 2005	2 of 2 changes	5; 19 of remaining 28 changes between July 2005 through March 2006	0.006
82682	Dacthal	June 2001–May 2002; June 2005	10 of 11 changes	3; 9 of remaining 11 changes between July 2005 through April 2006	0.0006–0.0031
LCMS compounds					
04033	Diphenamid	March 2002–June 2004	NA	0 changes	NA
04039	CAAT	March 2002–June 2002	NA	0 changes	NA
49297	Fenuron	NA	NA	0 changes	NA
49310	Carbaryl	December 2002	NA	0 changes	NA
50337	Sulfometuron-methyl	March 2002	NA	0 changes	NA
50356	Imazaquin	March 2002–June 2004	NA	0 changes	NA
50407	Imazethapyr	March 2002–June 2002	NA	0 changes	NA
50471	Propiconazole	June 2002	NA	0 changes	NA
61694	Flumetsulam	November 2001	1 of 1 change	0 changes	0.007
61697	Metsulfuron-methyl	NA	NA	0 changes	NA

Key Findings and Implications

The results from this study demonstrate that the NWQL produces high-quality pesticide results. The identification protocols and censoring practices of the NWQL were demonstrated to be largely effective at minimizing the reporting of false-positive results while also providing results at environmentally relevant concentrations with a low percentage of false-negative results. However, despite rigid QC measures and selective qualitative identification procedures, NWQL censoring practices do not address all occurrences of episodic and random laboratory contamination. Options for additional censoring practices are provided in appendix 3 for data users with specific or stringent data-quality objectives, such as reducing the false-positive or false-negative risk to less than 1 percent or addressing episodic contamination, when present.

This study has helped to identify areas in which the reporting of USGS pesticide data from the NWQL can be improved. This study also has led to a list of potential follow-on actions, one of which is to investigate the creation of an automated protocol within either NWIS or LIMS that would automatically flag multiple or consecutive detections at similar low concentrations within a given preparation set. Other examples of potential future activities include revising NWQL SOPs to include more specific information to prevent set blanks from being identified differently than environmental samples, making NWQL censoring based on interferences more consistent, and reviewing large set-blank datasets more frequently than recent practice.

The key findings of the study, by objective, are summarized in the following sections.

Objective 1. Determine the Characteristics of Laboratory Contamination Over Time

- Laboratory contamination, as determined by detections in set blanks, was found in 13 percent of set-blank results from the 113 targeted batches included in this study during the study period (2001–15). By contrast, laboratory contamination occurred in 6 percent of set-blank results from all 7,630 batches (table 7). The implication of this finding is that the batches of samples selected for this study met the intention of the selection process, which was to target batches with detections of one or more of the 21 pesticide compounds in set blanks. However, determining the representativeness of targeted batches for all batches was outside the scope of this study.

- All 21 pesticide compounds had periods of episodic laboratory contamination, which accounted for about 92 percent of laboratory contamination for these compounds in all batches during the study period (table 7). Episodic laboratory contamination was intermittent in nature, with most episodes lasting from about 1 to 8 months (tables 9 and 10). The implication of this finding is that evaluating the timing and magnitude of detections in set blanks relative to detections in environmental samples is critical to consider in the analysis of environmental results (see discussions in the "Objective 1" and "Objective 2" sections of "Results and Discussion").

- Episodic laboratory contamination was identified for CAAT and fenuron from August 2002 through either 2004 or 2006 (table 10). NWQL previously addressed this contamination for these compounds (and other compounds not included in this study) by MRL censoring with a retroactive data reload (app. 2). The implication of this finding is that higher MRLs retroactively applied by the NWQL (fig. 2.1) conservatively censored environmental results for CAAT and fenuron from August 1, 2002, through June 30, 2006.

- Deterministic laboratory contamination, which is addressed by set censoring, occurred in fewer than 1 percent of environmental samples (table 8). The implication of this finding is that deterministic laboratory contamination is uncommon, and that although set censoring is effective at addressing laboratory contamination when detections in set blanks occur in the same sets as detections in environmental samples, the set censoring procedure may not address occurrences of episodic laboratory contamination at the NWQL if there is no detection in the set blank.

- All 21 pesticide compounds, except for fenuron, had some random laboratory contamination, which accounted for about 8 percent of all laboratory contamination for these compounds in all batches (table 7). Because NWQL censoring protocols do not always address random laboratory contamination, data users may choose to employ additional censoring depending on their data-quality objectives (app. 3).

- Some QC issues, such as the extent of episodic and random contamination, typically cannot be identified until after several years of QC data have been collected and environmental results are reported (red rectangle of fig. 1). The implication of this finding is that there may be lapses in addressing episodic and random laboratory contamination because it may not be possible to identify the extent of the contamination until years after environmental results are published. Such QC issues are typically identified through detailed QC assessments conducted by national programs, large projects such as the Groundwater Ambient Monitoring Assessment project in the USGS California WSC, or in some cases, by data analysts in WSCs.

Objective 2. Compare Distributions of Results From Set Blanks and Environmental Samples

- Comprehensively comparing distributions of results between set blanks and environmental samples requires the use of multiple tools, including various statistical tests and graphical approaches. None of these tools, by themselves, provide a complete comparison of results between set blanks and environmental samples, but time-series plots were shown to be a key element in data interpretation. The implication of this finding is that not examining set blank and environmental results from multiple perspectives may lead to misleading conclusions. For example, one tool (such as cumulative distribution plots) may suggest that there is no difference in the distributions between results for set blanks and environmental samples, which would indicate that detections in these samples could occur randomly and that detections in environmental samples could be indicative of laboratory contamination. Applying a different tool to the same dataset may suggest little or no overlap in the timing of detections between set blanks and environmental samples, which would indicate less likelihood of laboratory contamination.

- Detected concentrations in groundwater and surface-water samples for reviewed batches generally are higher than detected concentrations in set blanks (figs. 3 and 4, in back of report; table 11). The implication of this finding is that concentrations in environmental samples that are greater than concentrations in set blanks are less likely to be influenced by laboratory contamination than lower concentrations, particularly if the detections in environmental samples and set blanks are offset in time.

- For most compounds detected in set blanks and environmental samples, detection frequencies were significantly greater (p<0.05) in set blanks than in groundwater or surface-water samples. Collectively for the 21 pesticide compounds, the detection frequency in set blanks was 13 percent, compared to 1 percent for all groundwater results and 10 percent for surface-water results; the overall detection frequency in surface-water samples was driven by detections of metolachlor, diazinon, and trifluralin (table 11). The implication of this finding is that the 113 batches of samples chosen for this study successfully targeted batches with detections in set blanks. This finding also reflects that detections in set-blank samples were historically determined with less stringent identification criteria than criteria used for environmental samples.

Objective 3. Evaluate the Potential for False-Positive and False-Negative Reporting

- Few false-positive results were reported, especially after 2009. The false-positive rates from blind samples independently submitted to the NWQL from 2001 to 2015 by the QSB were less than 1 percent for 20 of the 21 pesticides included in this study; the exception was flumetsulam, which had a 2.6 percent false-positive rate (table 13). This same finding was observed regardless of whether the false-positive rates were computed using all detected concentrations in blind samples or only concentrations above the LT–MDL (table 13). The implication of this finding is that the identification protocols and censoring practices used by the NWQL are largely effective at minimizing the reporting of false-positive results near the reporting level concentration where most blind samples were spiked. Based on blind-sample results, the NWQL correctly identified detections of 20 of the 21 pesticide compounds in environmental samples more than 99 percent of the time from 2001 to 2015, even when considering concentrations less than the LT–MDL.

- Few false-negative results were observed, especially after 2006. Two-thirds of the 21 pesticides had false-negative rates less than 1 percent based on blind-spike samples independently submitted to the NWQL from 2001 to 2015 (table 13). False-negative rates greater than 1 percent were typically associated with low recovery periods and, for several LCMS compounds, were associated with periods of retroactive MRL censoring (app. 2) where some results changed from detections to nondetections. The implication of this finding is that, based on blind-sample results for seven pesticides with false-negative rates greater than 1 percent, there is an increased risk that concentrations of these pesticides in environmental samples were not detected (or were censored) at or just above the reporting level in use during analysis and, thus, are not reported or may be underreported (table 13).

Objective 4. Determine the Effects of the Data Reevaluation

- The data reevaluation process would not have a substantive effect on the results for environmental samples. Altogether, based on data in targeted batches, NWQL would have reported 0.1 percent of results from groundwater samples and 1.4 percent of results from surface-water samples differently (from a detection to a nondetection or vice versa) if 2017 identification protocols were applied to historical pesticide results. Most of these changes would be from

a detection to a nondetection (table 15). The results from the data reevaluation are presented in Riskin and others (2019) but are not reflected in data in NWIS or LIMS. The implications of this finding are that historical protocols used by the NWQL to identify detections in environmental samples were robust, these protocols produced results that are predominantly consistent with 2017 identification protocols, and historical pesticide results are of high quality.

- The data reevaluation process had the largest effect on diazinon results from surface-water samples. Nearly 10 percent of detections of diazinon in surface-water samples from targeted batches, many of which were analyzed between 2001 and 2003, would change to nondetections (tables 15 and 18) because qualitative identification criteria were not met in the reevaluation. Low-level diazinon detections in surface-water samples (and set blanks) could have originated from either a trace-level diazinon impurity in surrogate standards added to samples or from an interferent. Blind-blank samples from QSB identified one false-positive result for diazinon from 2001 to 2003 (table 13). The implication of this finding is that there may be an increased false-positive risk of low concentrations of diazinon in surface-water samples in all analytical batches between October 2001 and September 2003. To reduce the false-positive risk, data analysts might choose to employ a censoring strategy identified in appendix 3.

- The data reevaluation process revealed that, before implementation of the 2017 identification protocols, detections in set blanks were sometimes reported using more lenient identification criteria than for environmental samples with the intention of minimizing the potential for false-positive results in environmental samples. Consequently, 8.8 percent of set-blank results for GCMS compounds in targeted batches would change from detections to nondetections in the data reevaluation. The data reevaluation produced no changes to set-blank results for LCMS compounds (table 15). An implication of this finding is that, for some GCMS compounds, the determination of periods of episodic laboratory contamination at the NWQL may be a conservative (high-end) estimate because such episodes are determined using detections in set blanks. Because detections in set blanks can result in set censoring of detections in environmental samples and because some detections in set blanks would not be identified using 2017 identification protocols, there is also the possibility that some detections of GCMS compounds in environmental samples were unnecessarily set censored, producing a false-negative result.

- Changes to numbers of detected results in set blanks and environmental samples from the data reevaluation are not likely to occur uniformly throughout the study period. Rather, these changes would occur during discrete periods, mostly from 2001 to 2003 for environmental samples and before spring 2006 for set blanks (table 18). The implication of this finding is that reported detections in groundwater and surface-water samples after 2003 would be largely unaffected by the data reevaluation, further indicating that the historical and 2017 identification protocols of the NWQL produce predominantly similar results. For data analysts conducting analyses that may require stricter rules for consistency than other types of analyses (such as trends analyses), table 18 identifies periods and concentration ranges most affected by changes from detections to nondetections from the data reevaluation.

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EXPLANATION

Reporting level

Long-term method detection limit (LT-MDL)

Minimum reporting level

Detection from liquid chromatography/mass spectrometry methods (figs. 3*L* through 3*U* and 4*L* through 4*U*)

From data reload—See Rapi-Note 2007.05 (app. 2)

Detection in set blank

In 113 reviewed batches

All batches (includes 113 batches reviewed)

Detection in environmental result

Detection in field-blank result

Detection in blind-blank result

Date of reviewed instrument batch included in this report

***A. p,p′*-DDE**

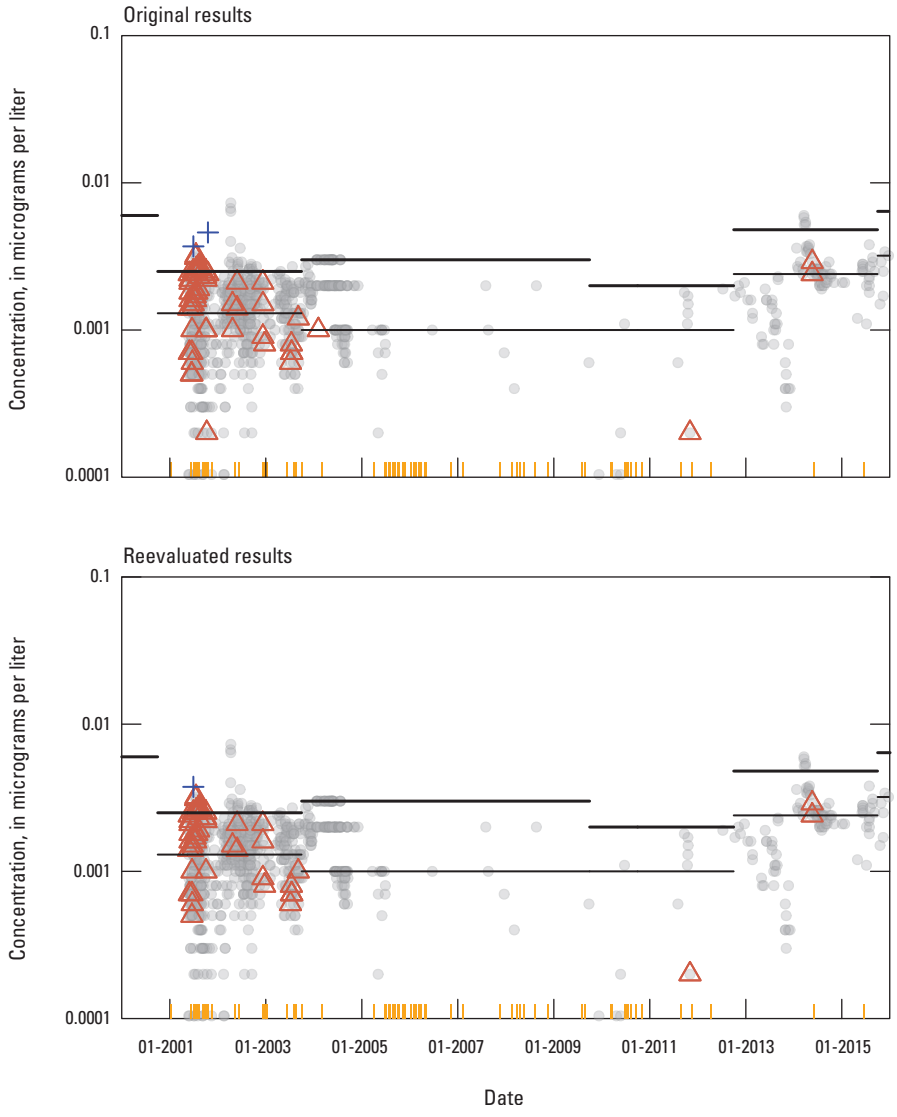
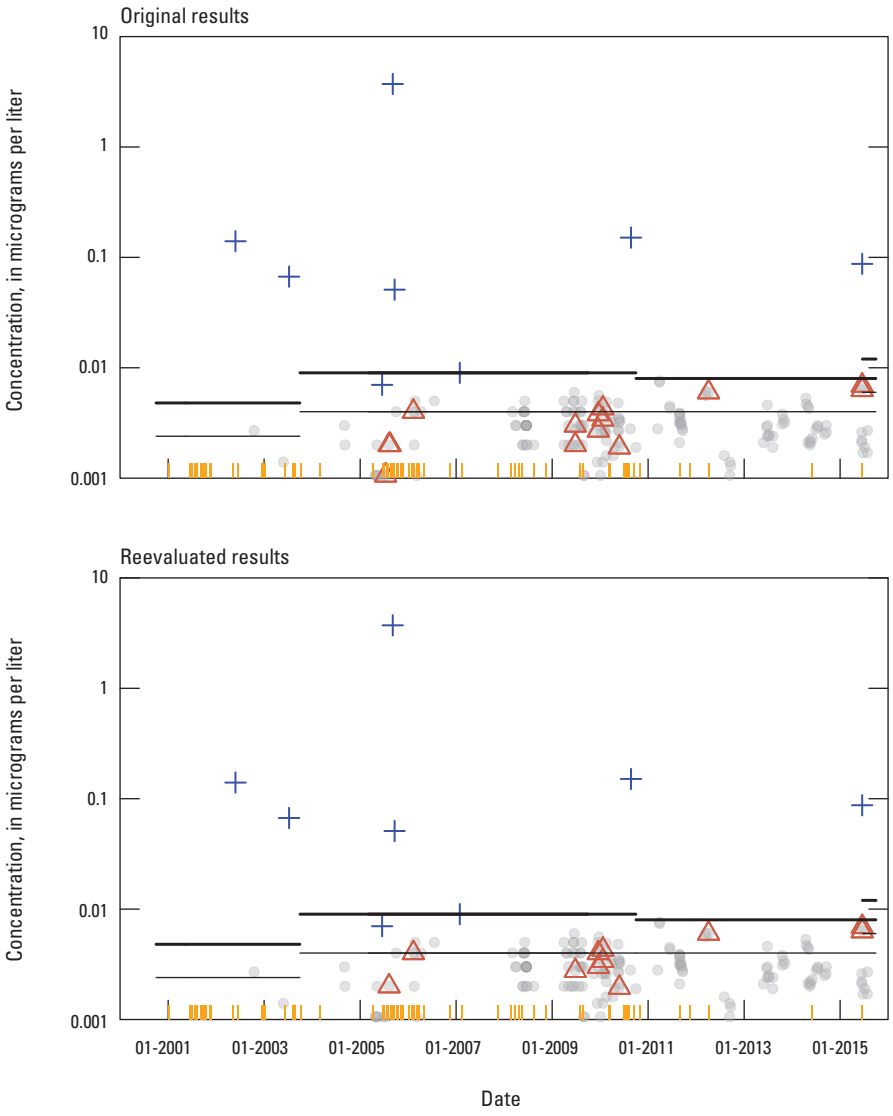


Figure 3. Concentrations of detections in groundwater samples and blanks (set, field, and blind samples from the U.S. Geological Survey Quality Systems Branch) for selected gas or liquid chromatography/mass spectrometry compounds for original and reevaluated results from a subset of instrument batches and from all set blanks analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p,p′*–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl.

***B.* Dieldrin**



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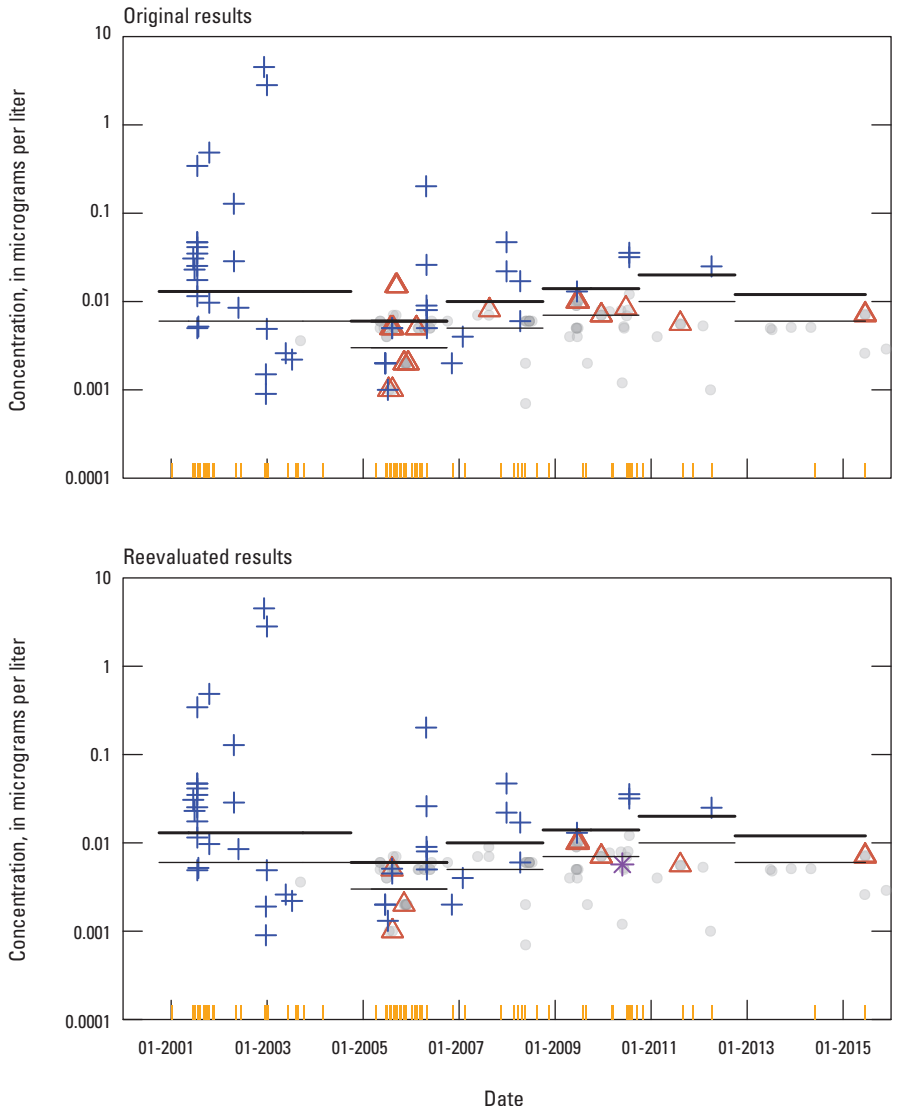
C. Metolachlor



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***D.* Diazinon**

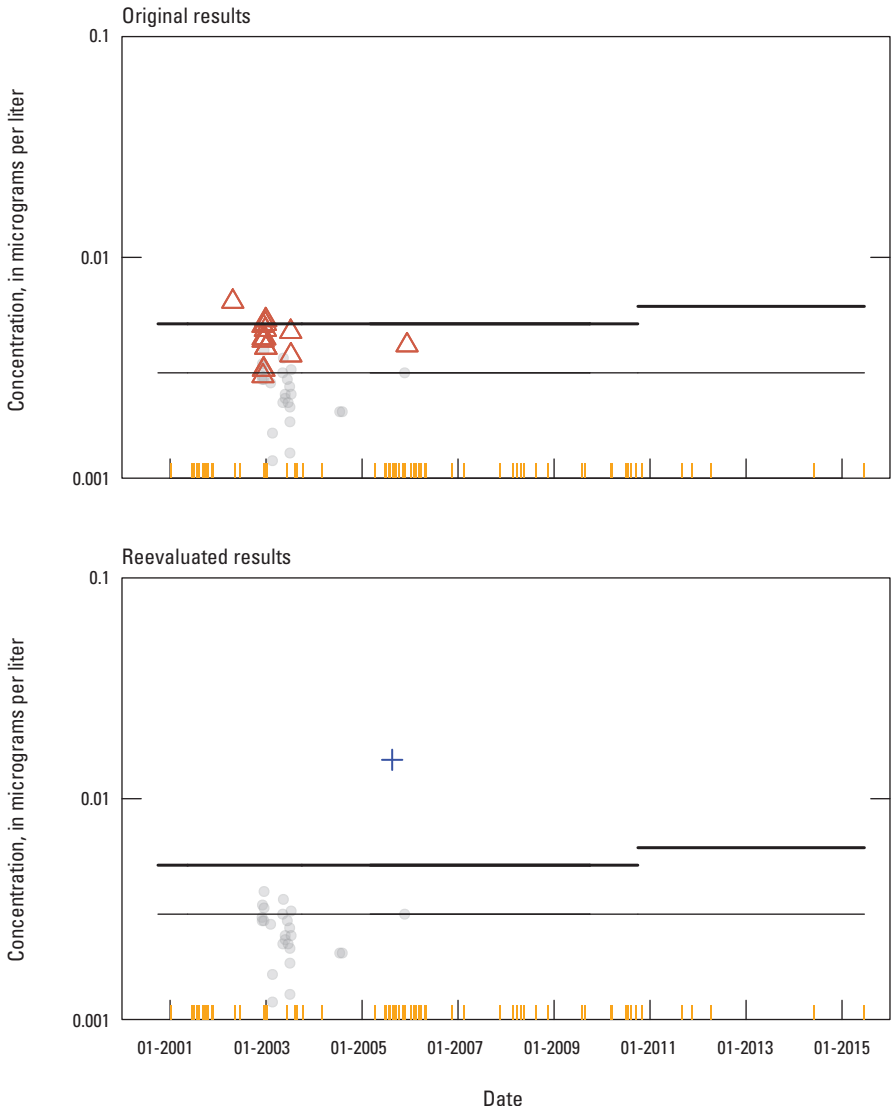


Figure 3. Concentrations of detections in groundwater samples and blanks (set, field, and blind samples from the U.S. Geological Survey Quality Systems Branch) for selected gas or liquid chromatography/mass spectrometry compounds for original and reevaluated results from a subset of instrument batches and from all set blanks analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p,p*′–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl.—Continued

E. 1-Naphthol

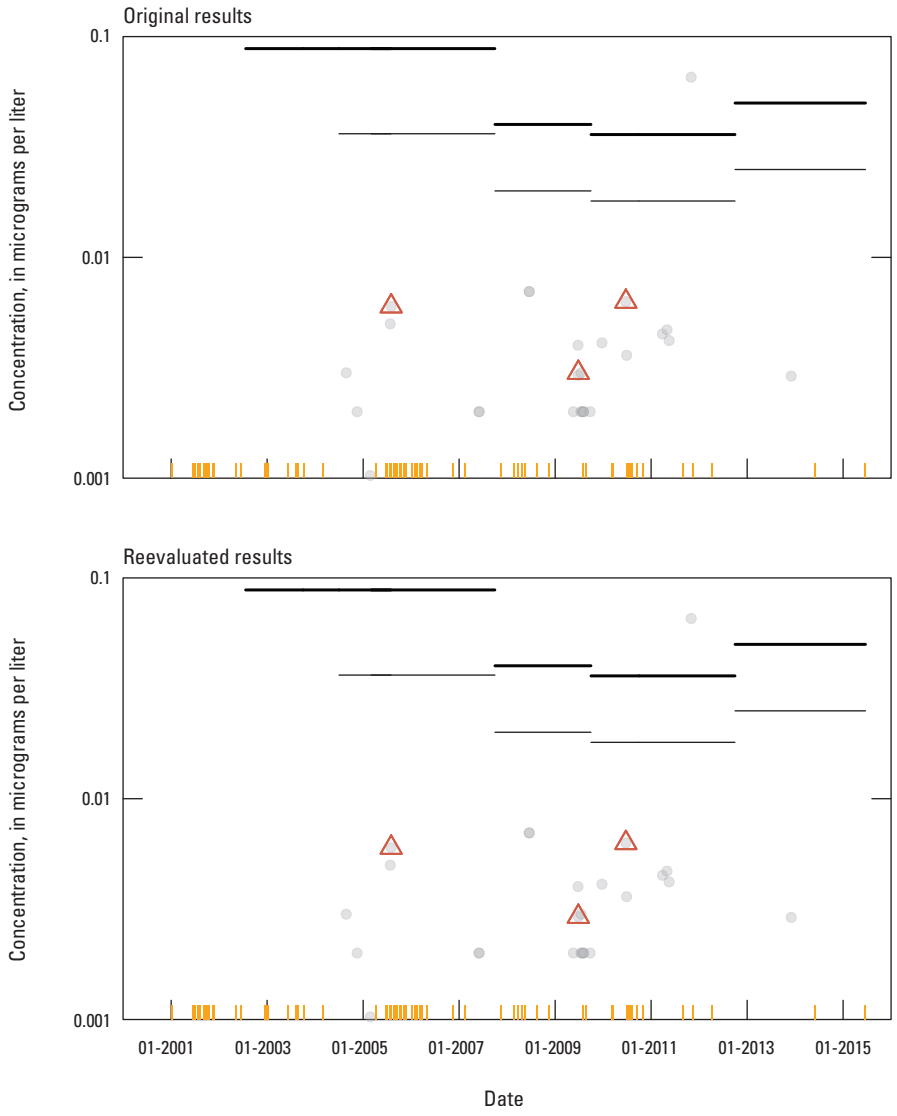
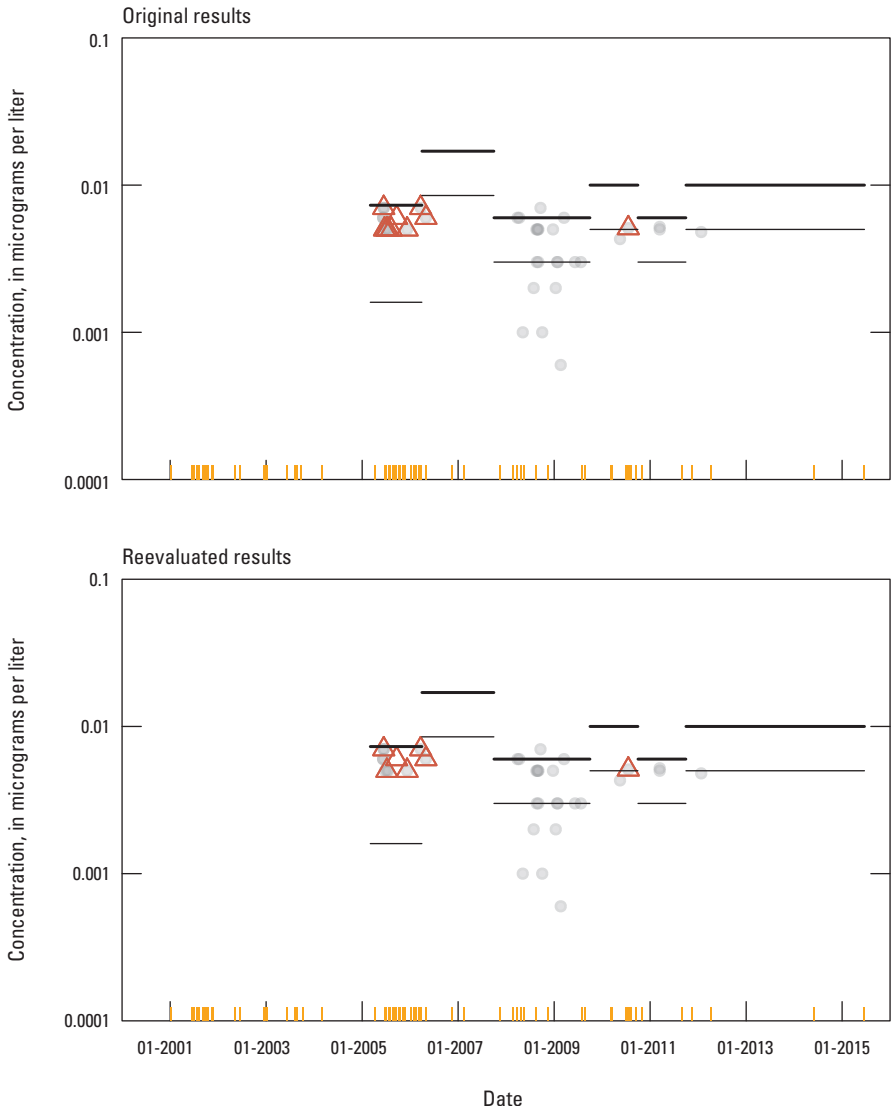


Figure 3. Concentrations of detections in groundwater samples and blanks (set, field, and blind samples from the U.S. Geological Survey Quality Systems Branch) for selected gas or liquid chromatography/mass spectrometry compounds for original and reevaluated results from a subset of instrument batches and from all set blanks analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p*,*p*′–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl.—Continued

***F.* Oxyfluorfen**



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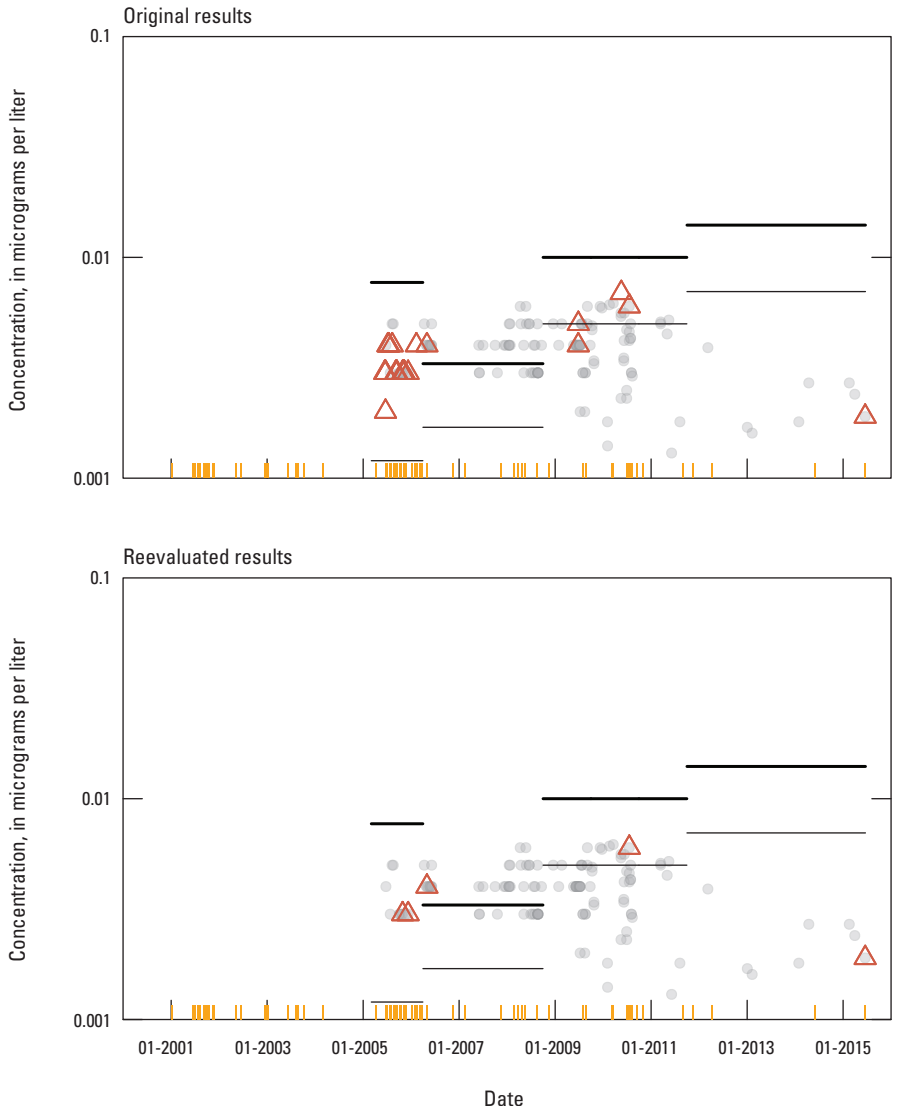
G. Tefluthrin



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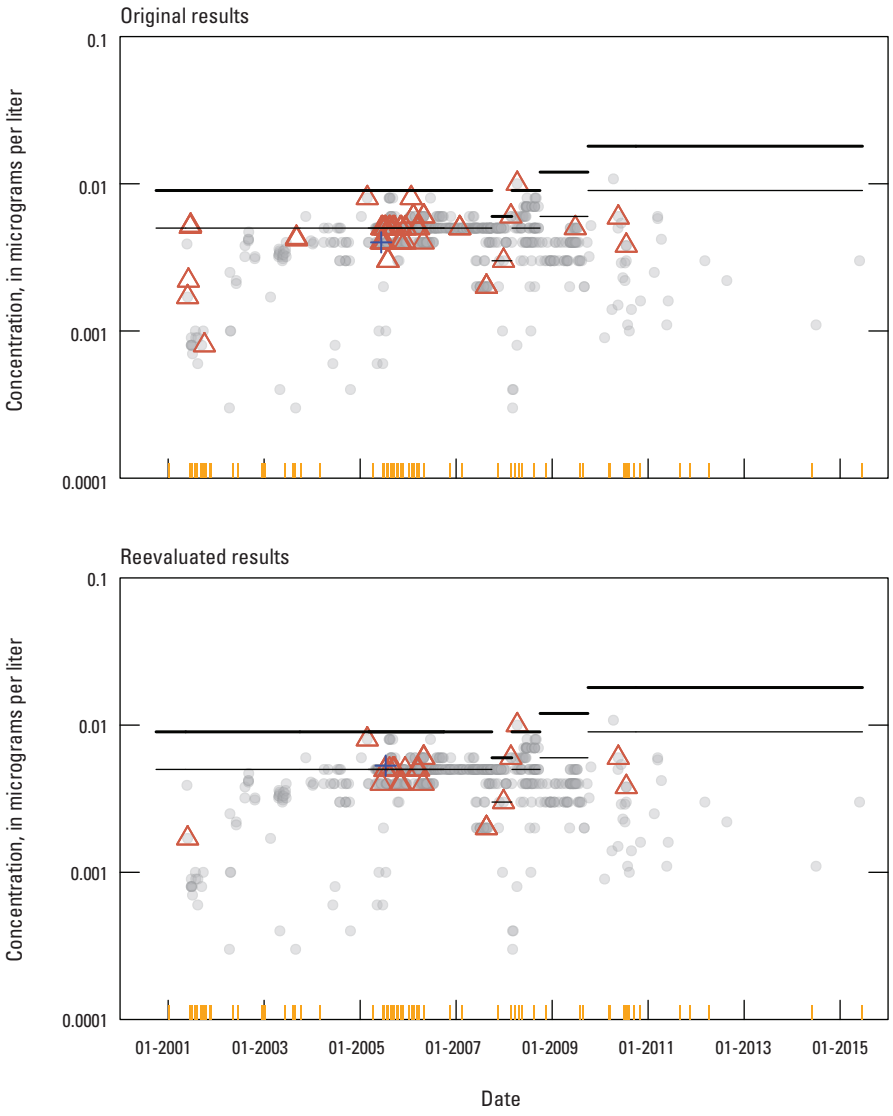
***H.* Trifluralin**



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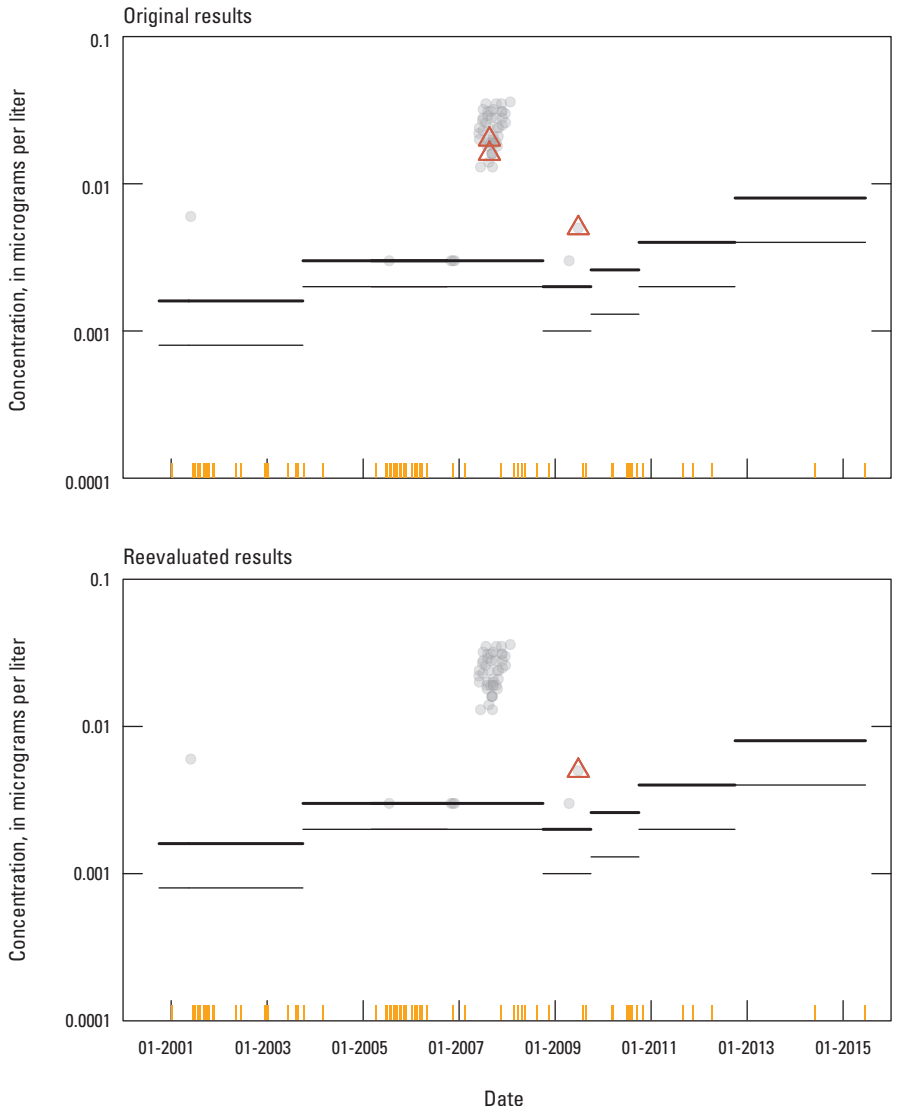
***I.* Molinate**



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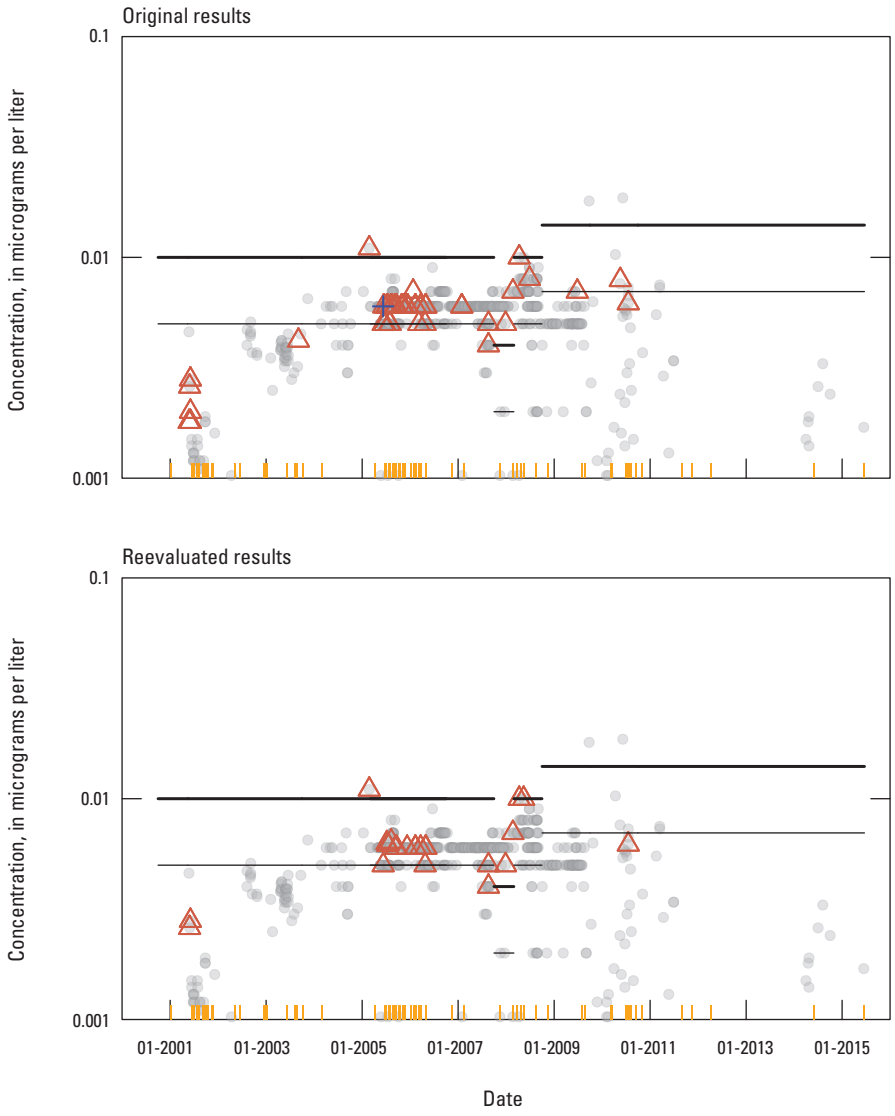
***J.* Benfluralin**



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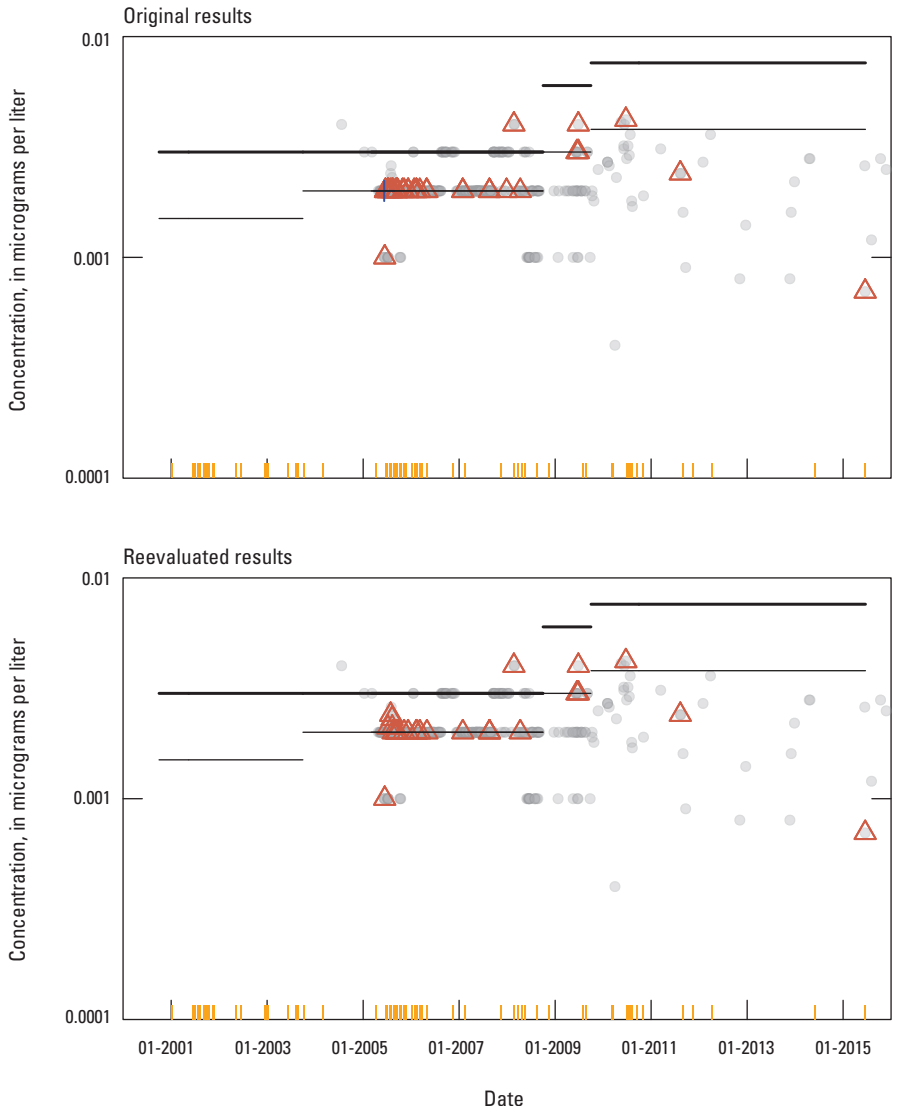
K. **Dacthal**



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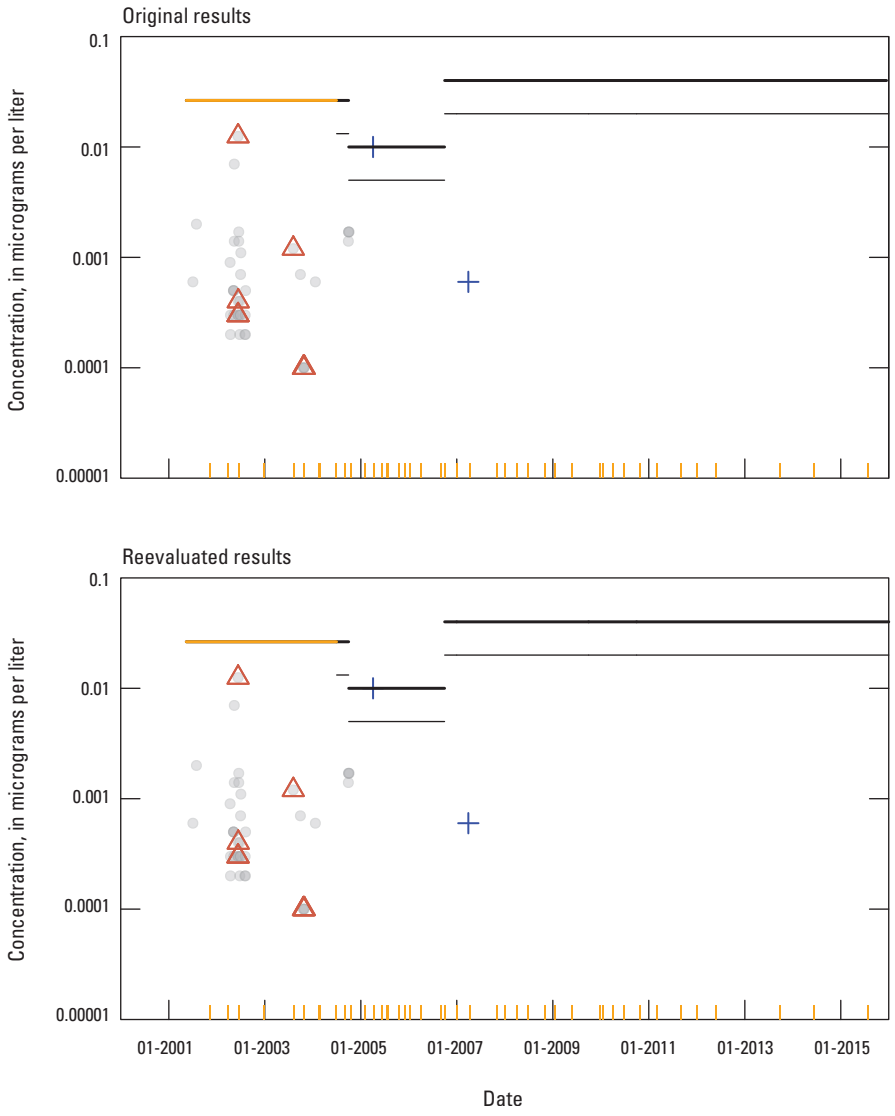
L. **Diphenamid**



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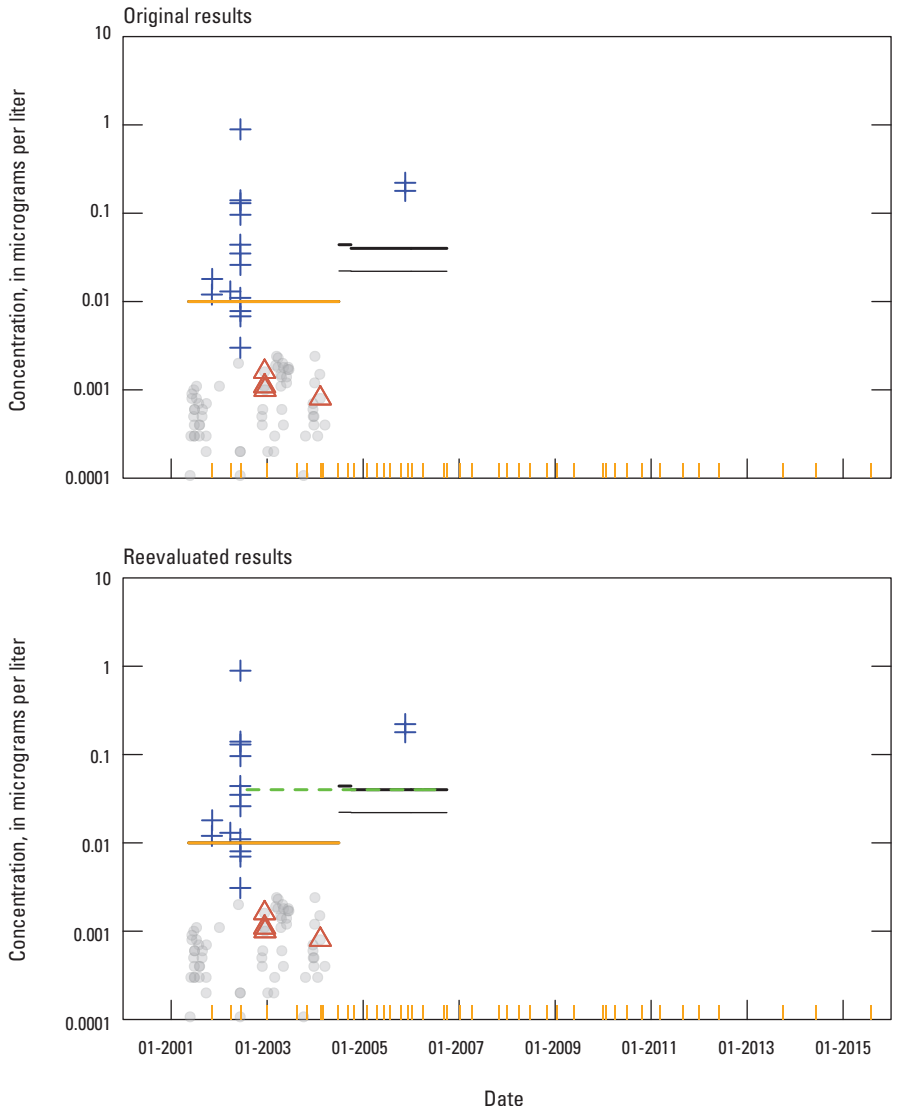
***M.* 2-Chloro-4,6-diamino-s-triazine (CAAT)**



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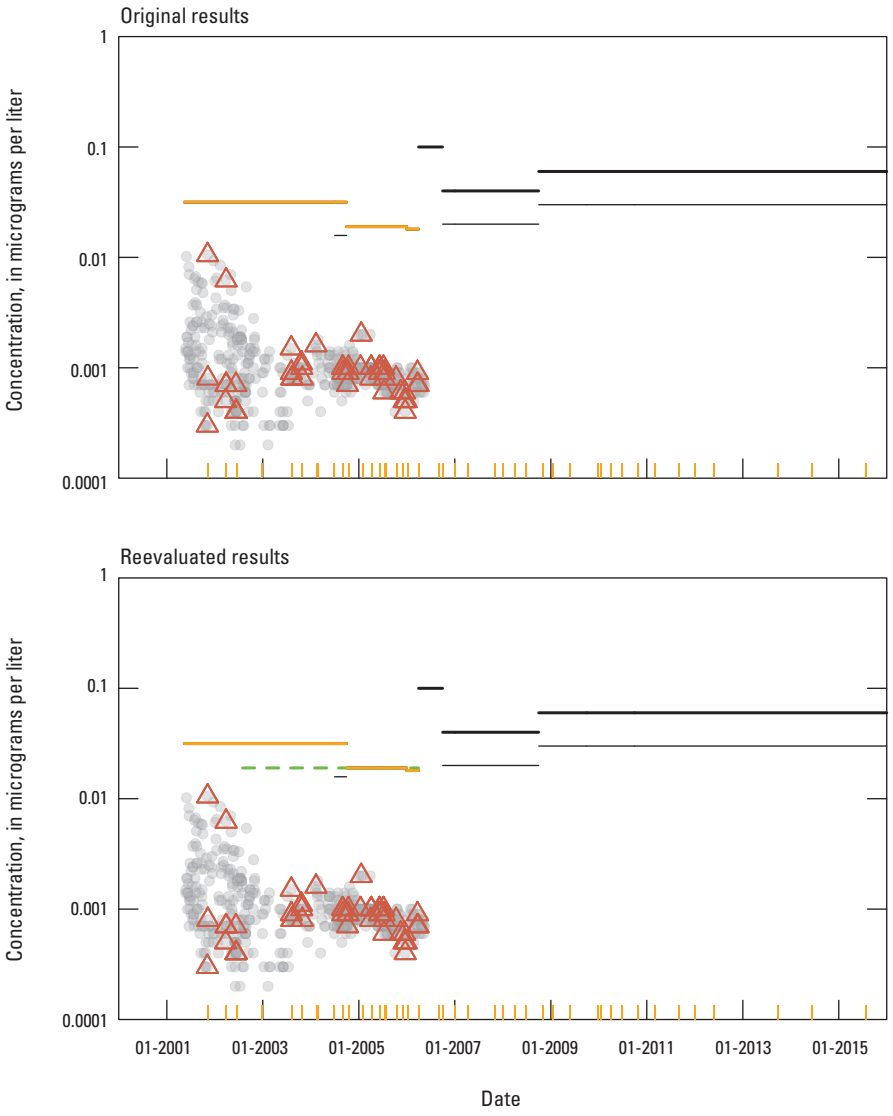
***N.* Fenuron**



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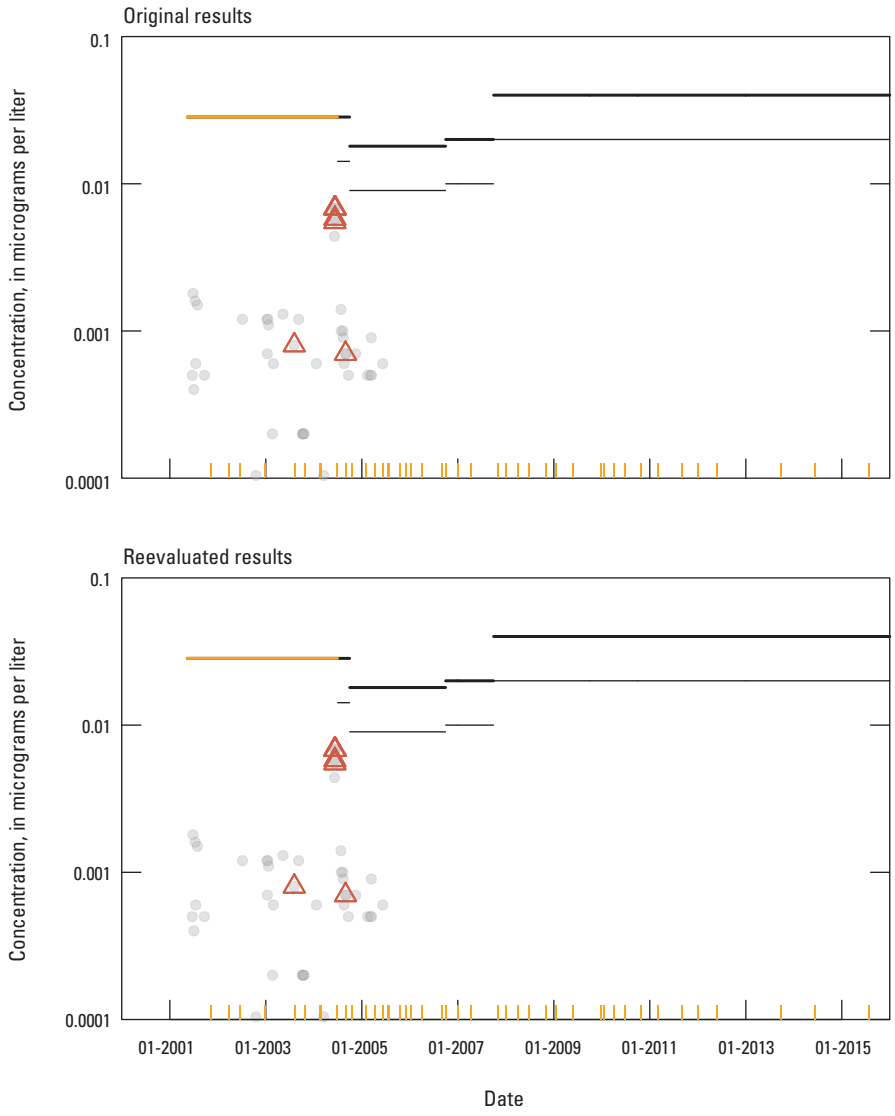
O. Carbaryl



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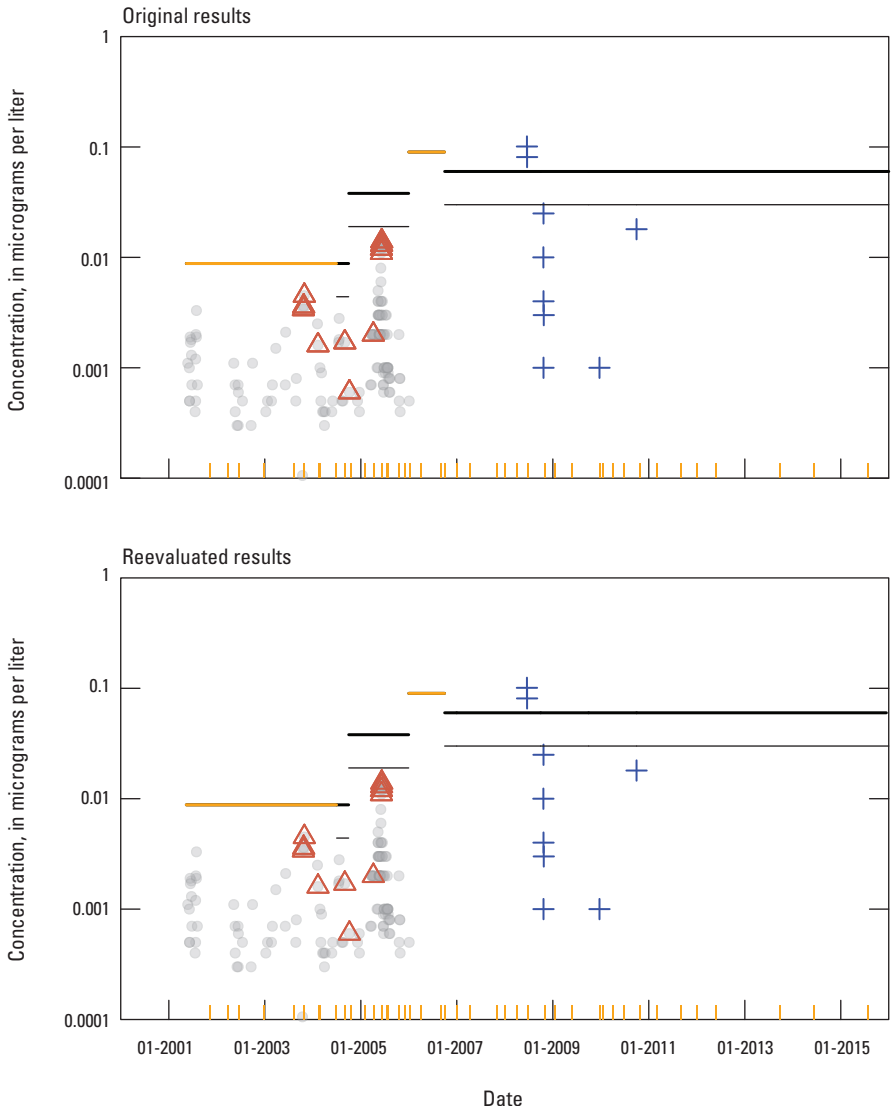
P. **Sulfometuron-methyl**



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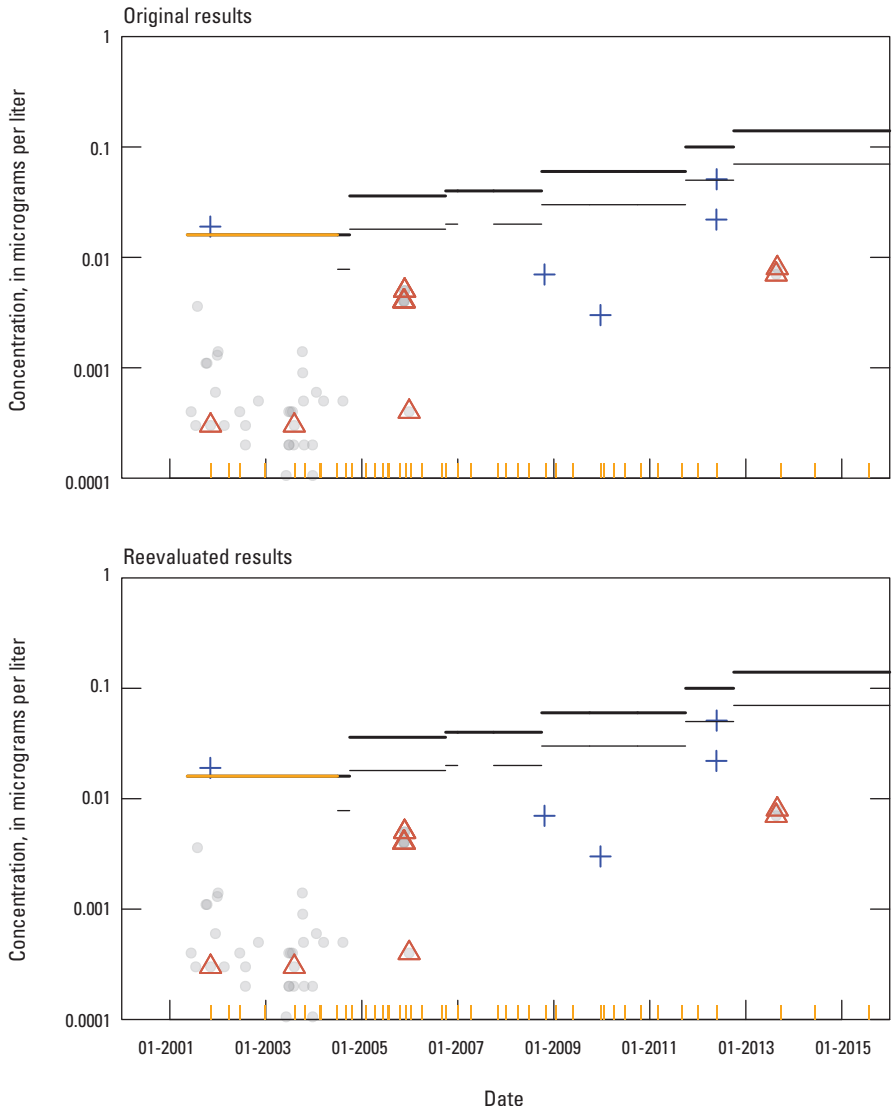
Q. Imazaquin



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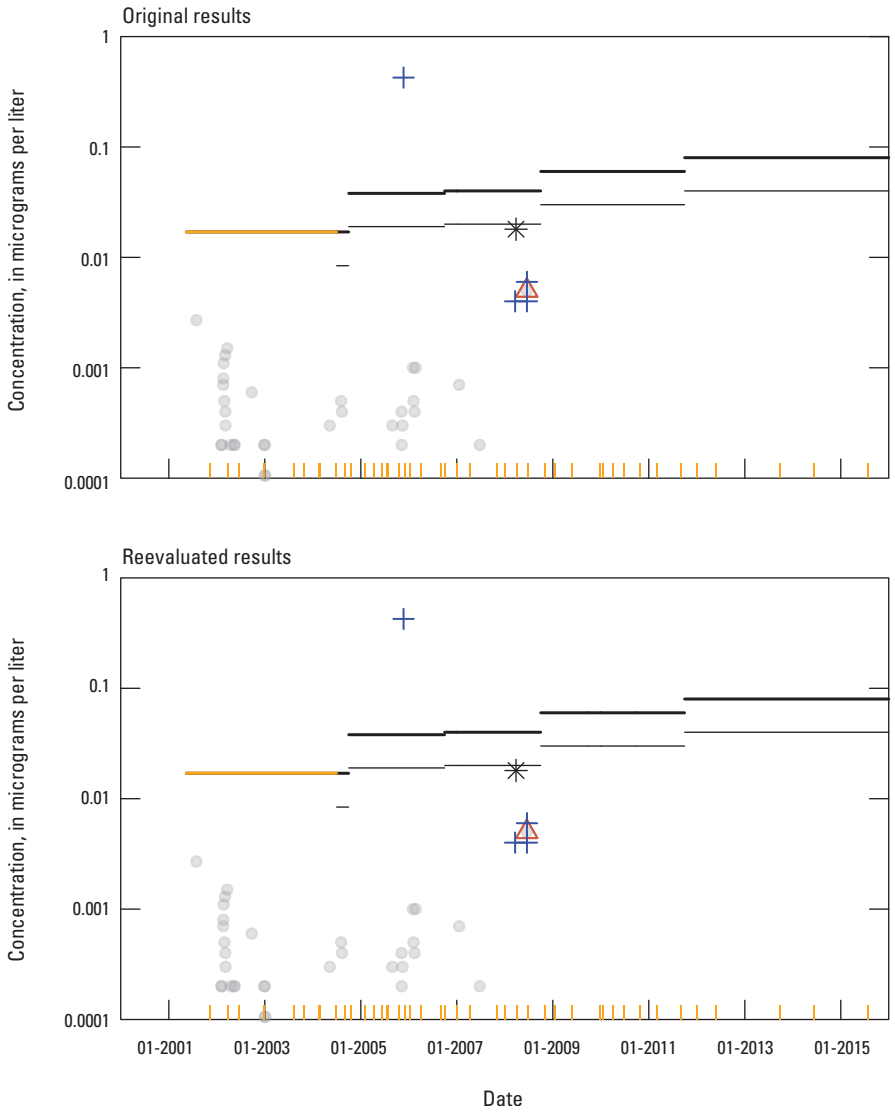
***R.* Imazethapyr**



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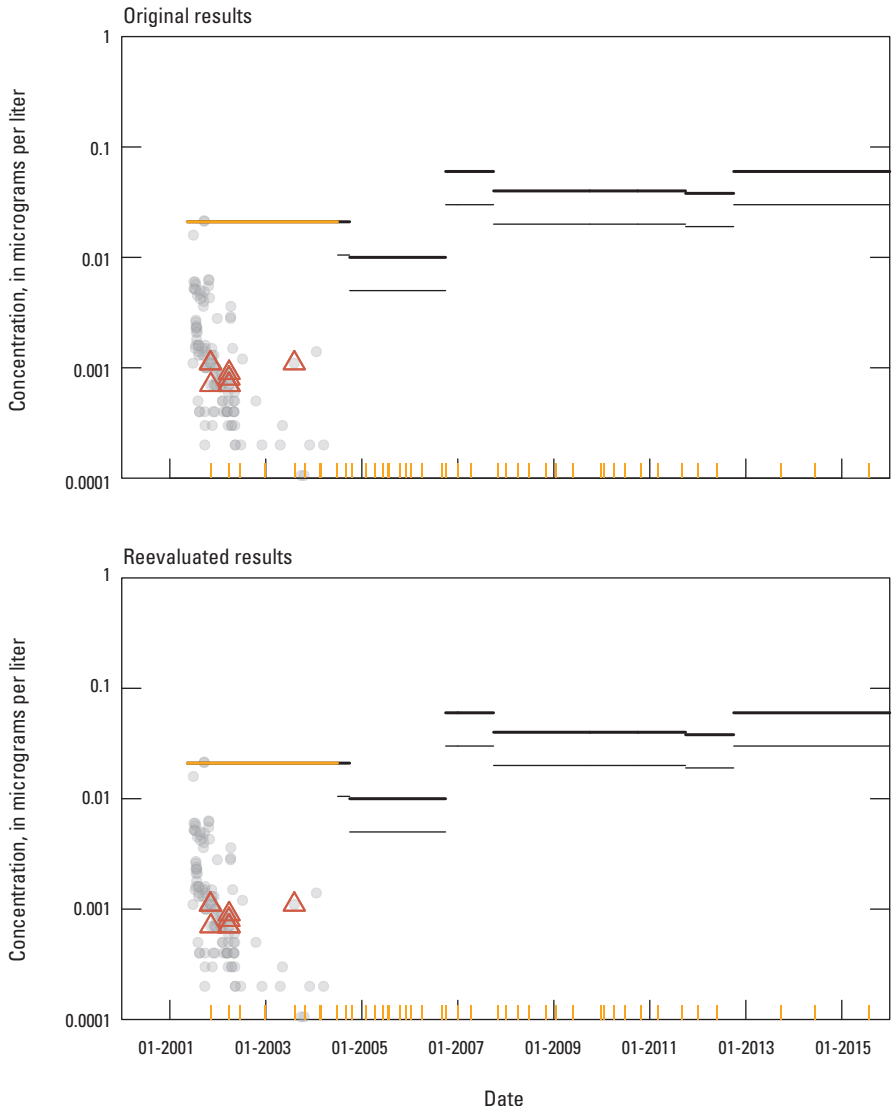
S. Propiconazole



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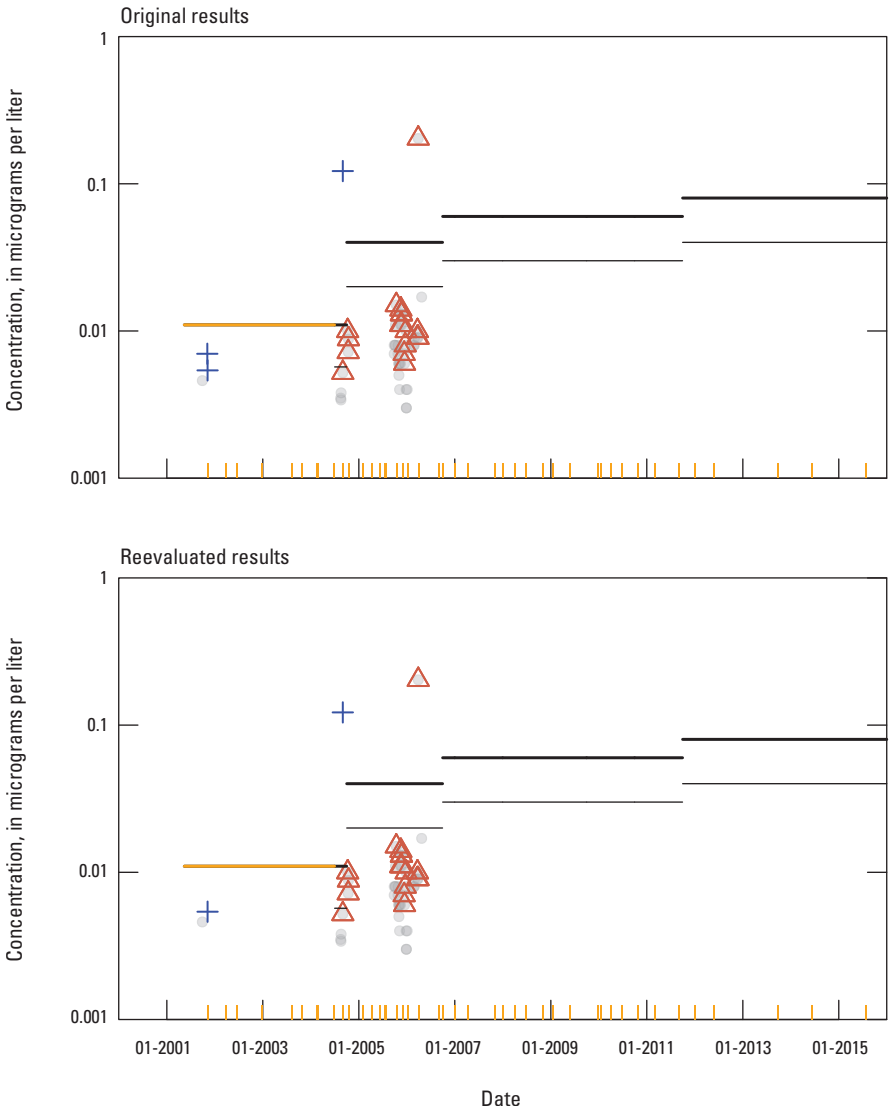
***T.* Flumetsulam**



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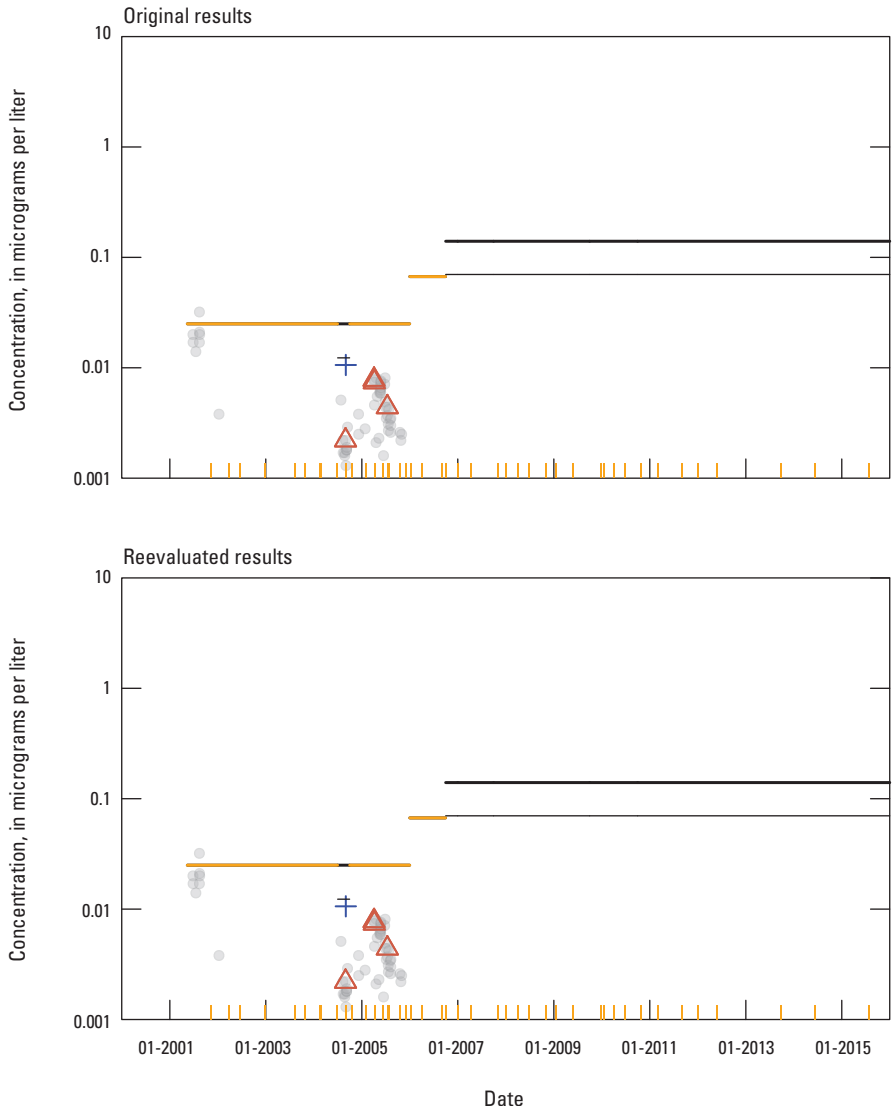
U. **Metsulfuron-methyl**



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EXPLANATION

Reporting level

Long-term method detection limit (LT-MDL)

Minimum reporting level

Detection from liquid chromatography/mass spectrometry methods (figs. 3*L* through 3*U* and 4*L* through 4*U*)

From data reload—See Rapi-Note 2007.05 (app. 2)

Detection in set blank

In 113 reviewed batches

All batches (includes 113 batches reviewed)

Detection in environmental result

Detection in field-blank result

Detection in blind-blank result

Date of reviewed instrument batch included in this report

***A. p,p'*-DDE**

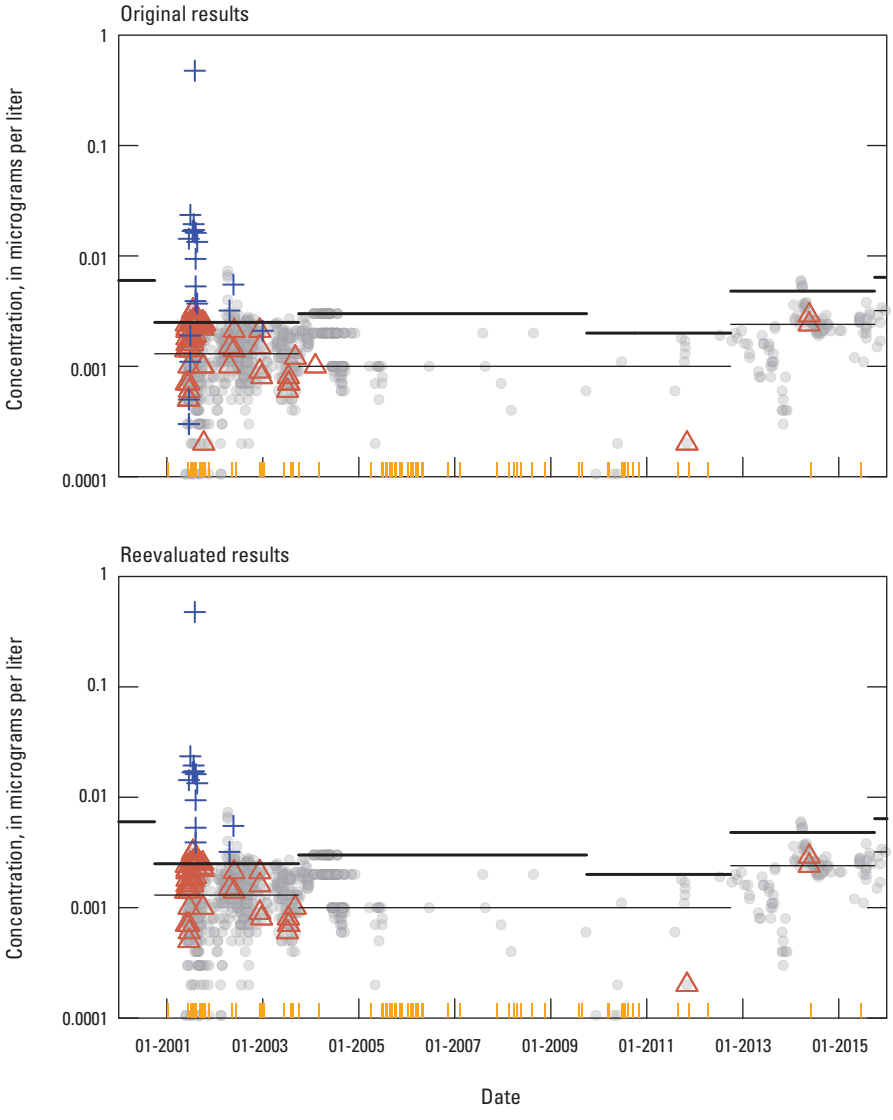
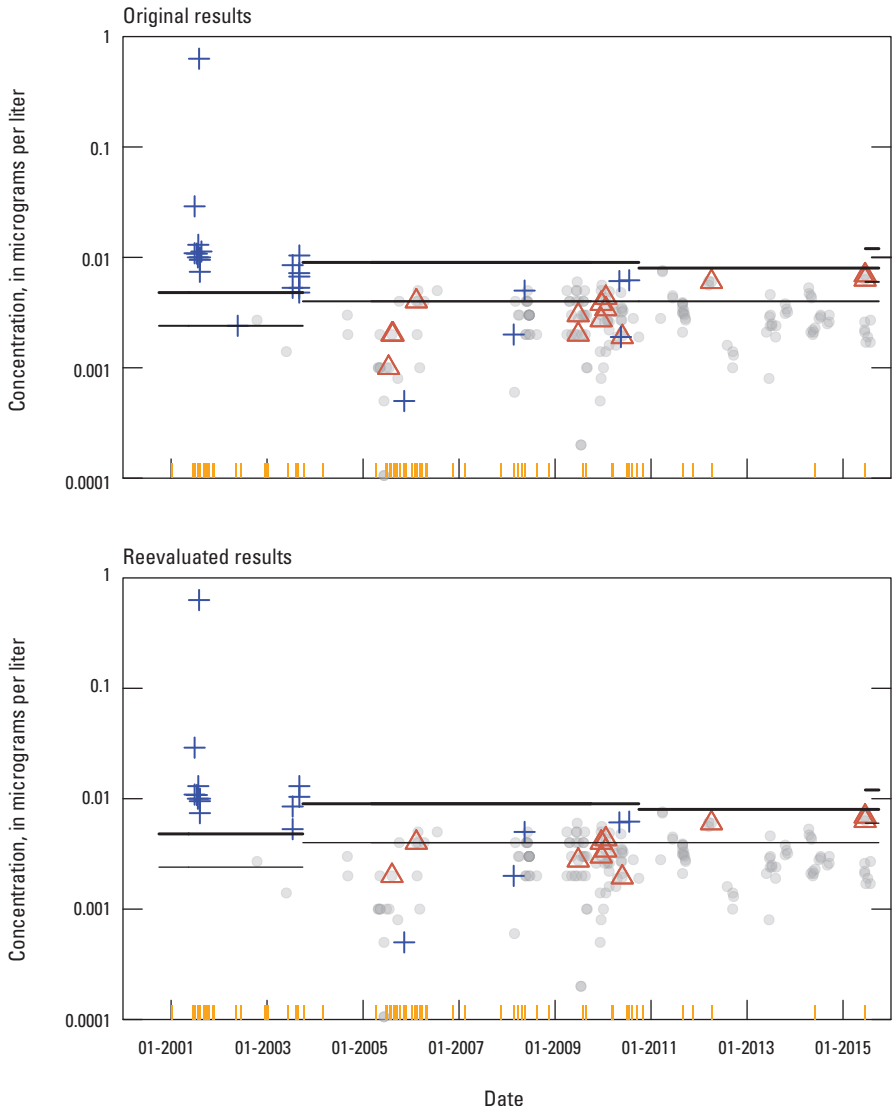


Figure 4. Concentrations of detections in surface-water samples and blanks (set, field, and blind samples from the U.S. Geological Survey Quality Systems Branch) for selected gas or liquid chromatography/mass spectrometry compounds for original and reevaluated results from a subset of instrument batches and from all set blanks analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p,p'*–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl.

***B.* Dieldrin**



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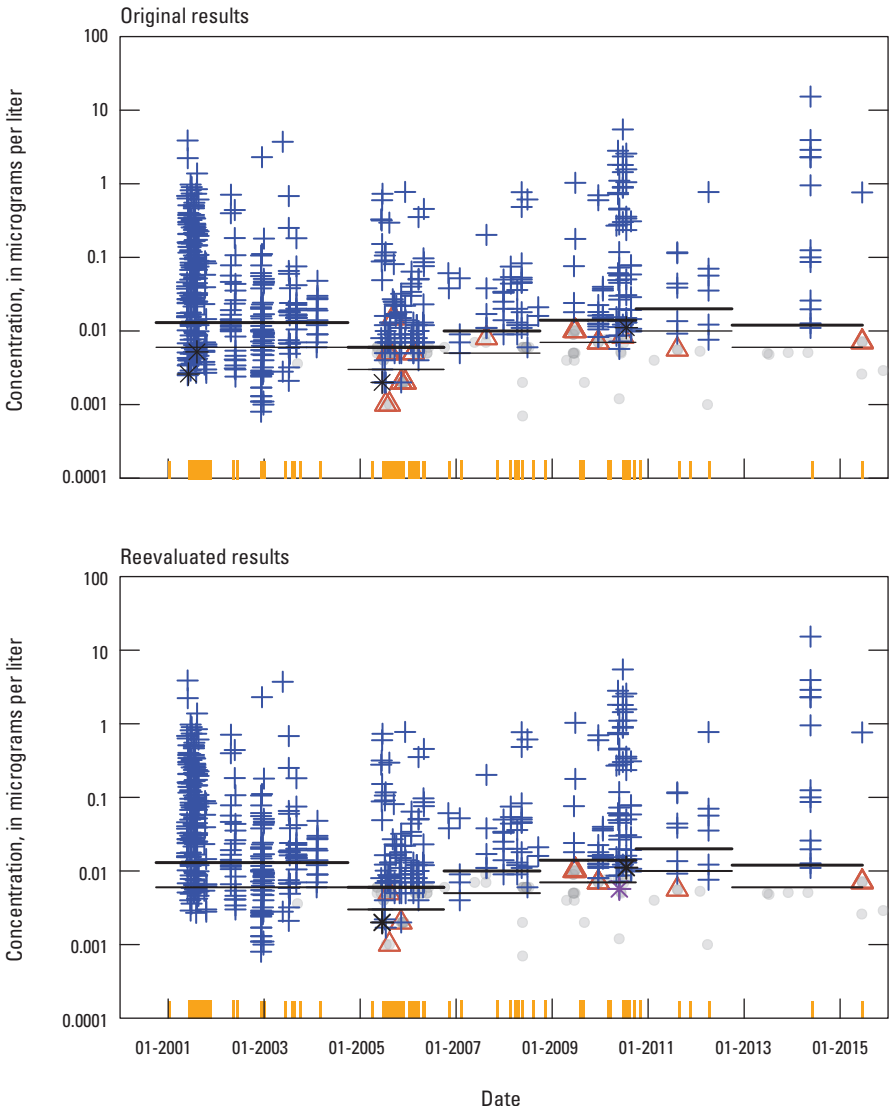
C. Metolachlor



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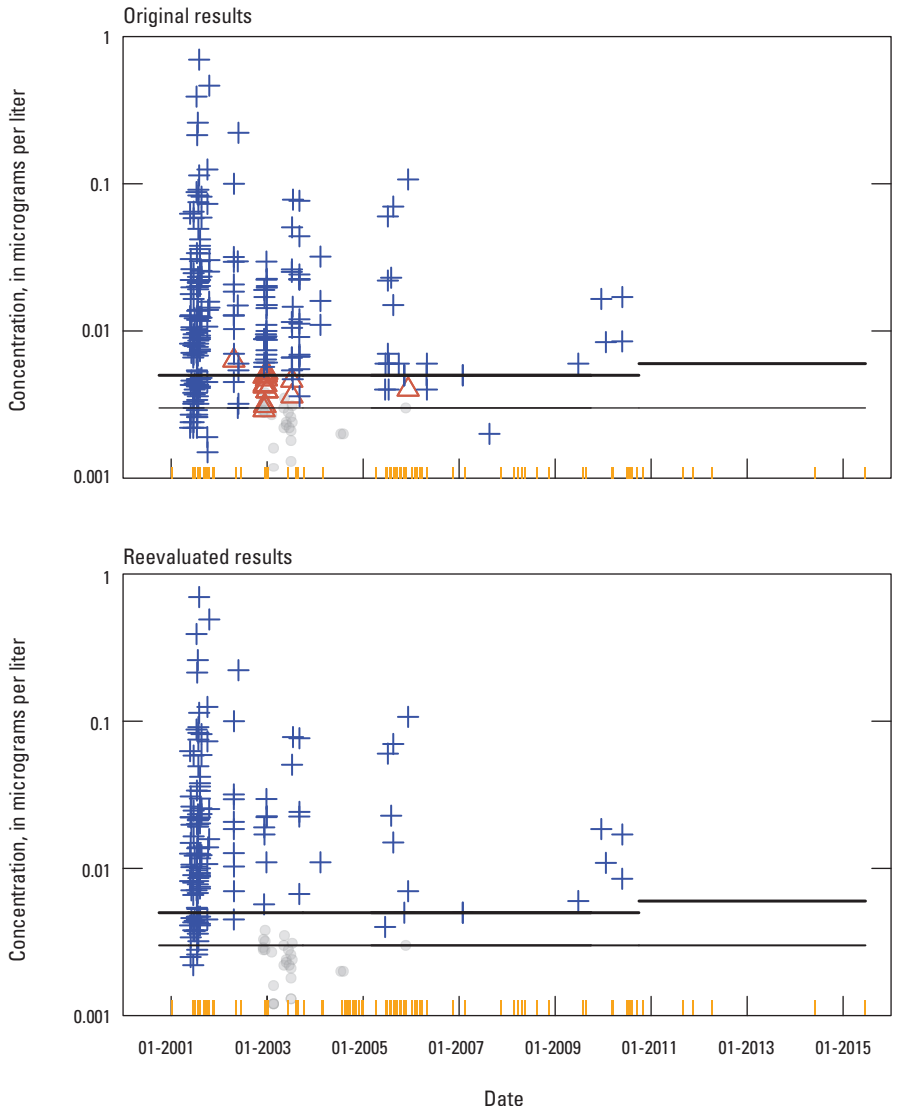
D. Diazinon



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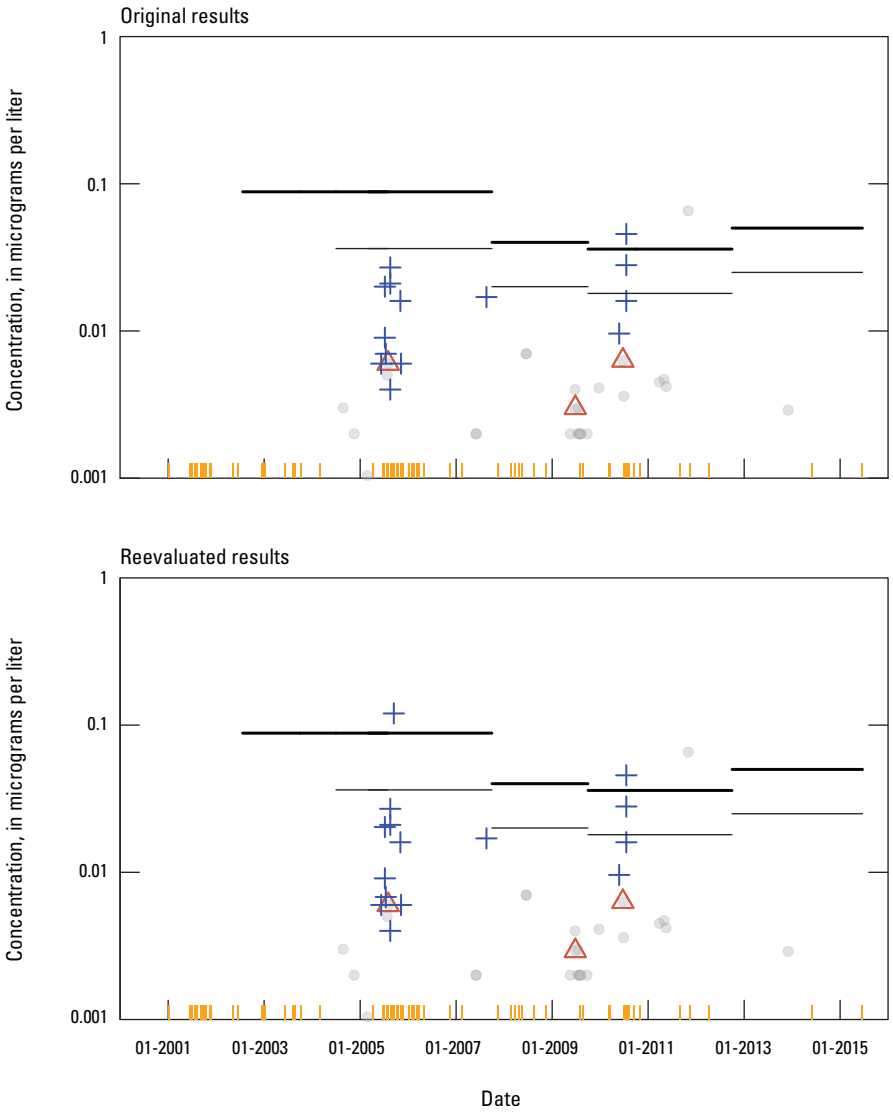
***E.* 1-Naphthol**



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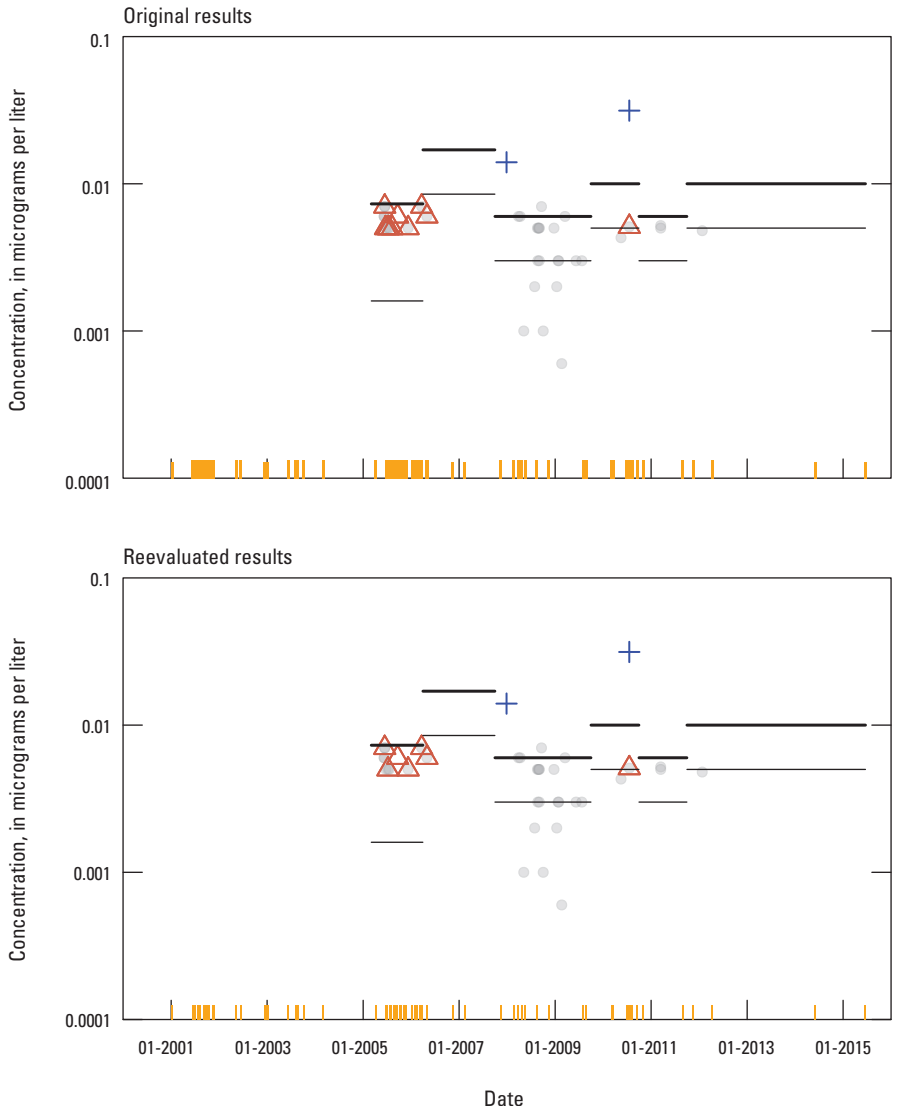
F. Oxyfluorfen



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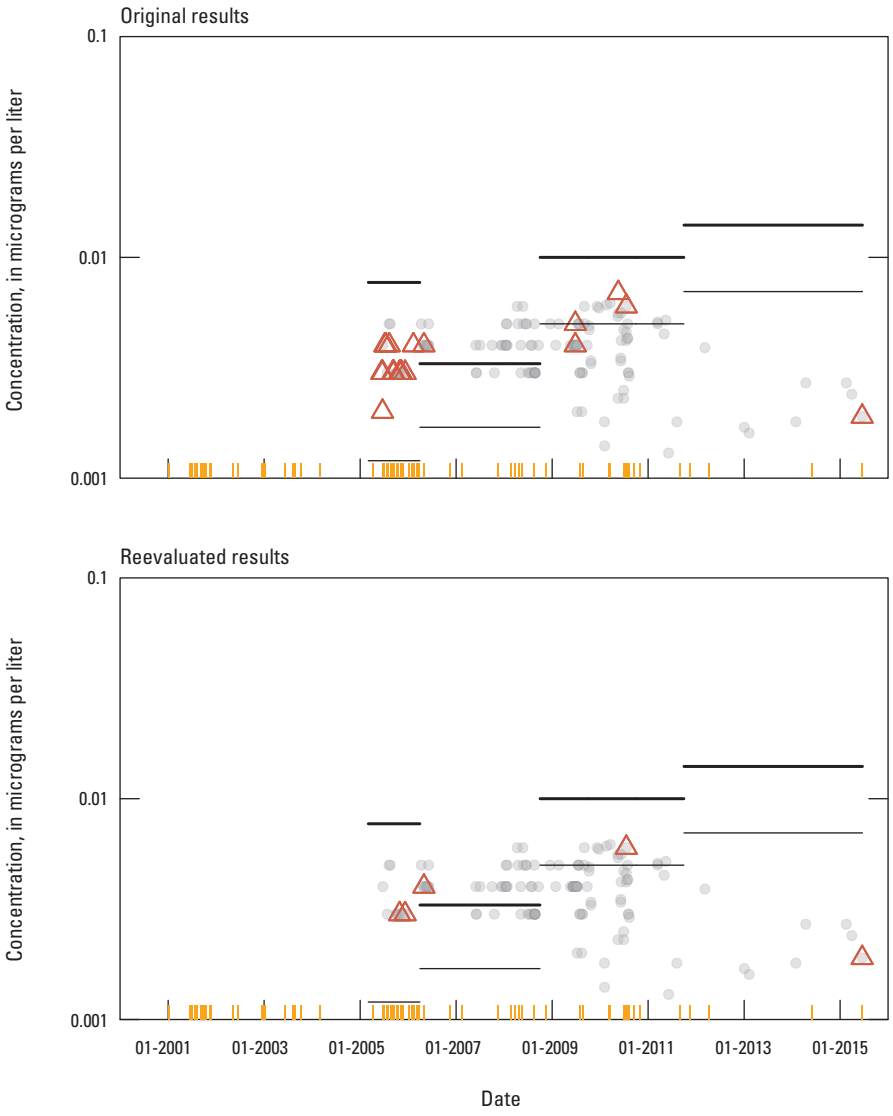
***G.* Tefluthrin**



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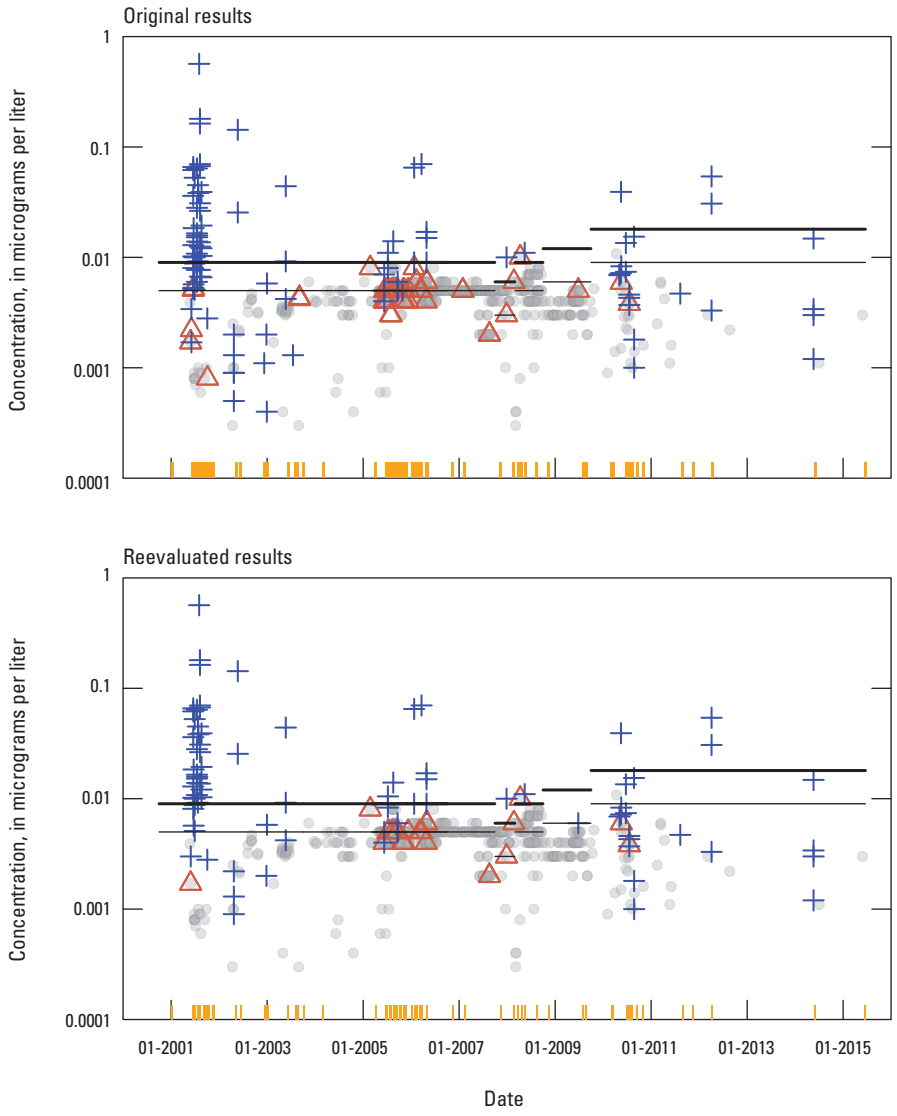
H. Trifluralin



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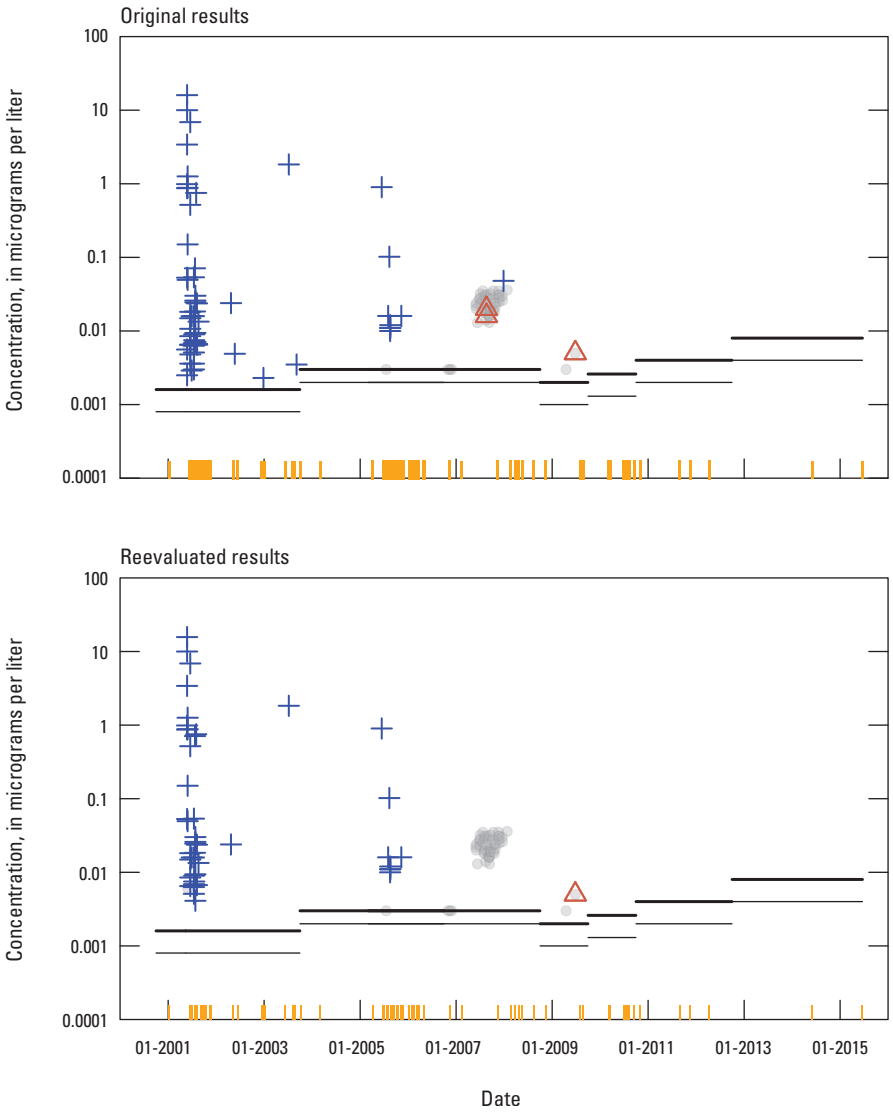
I. Molinate



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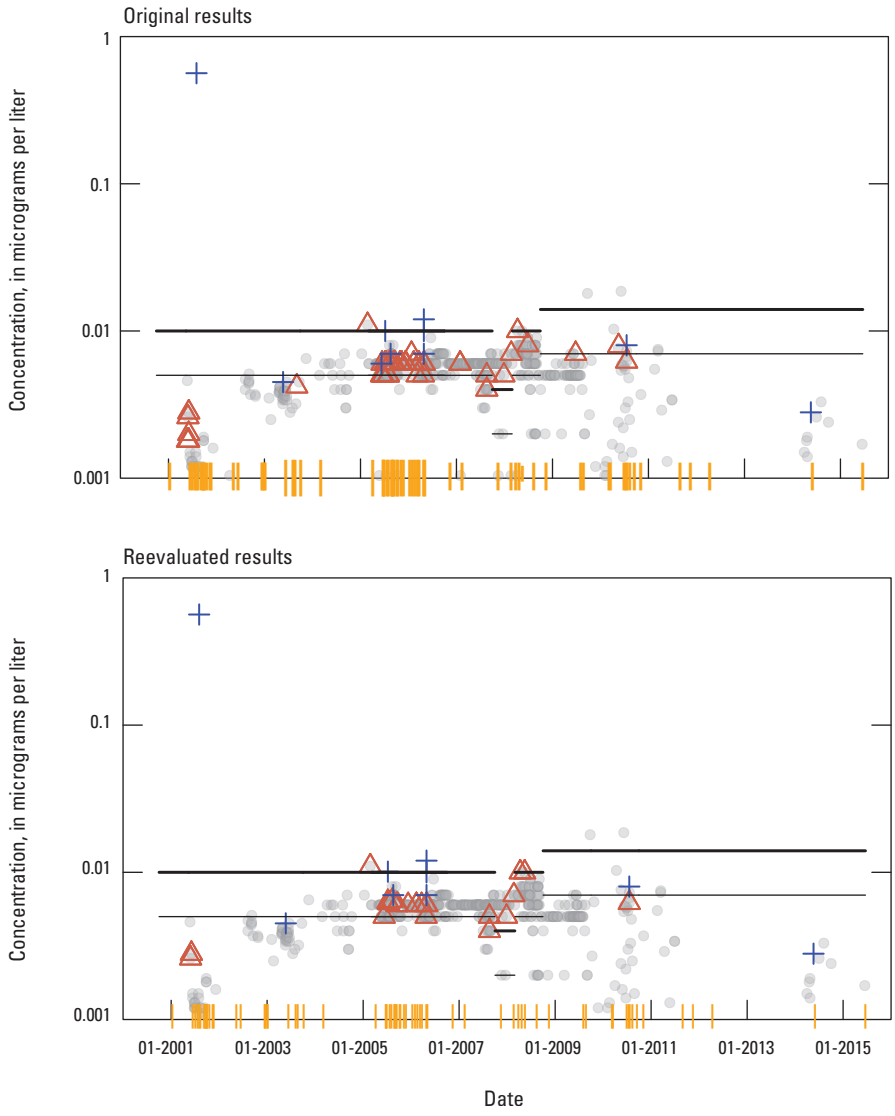
J. Benfluralin



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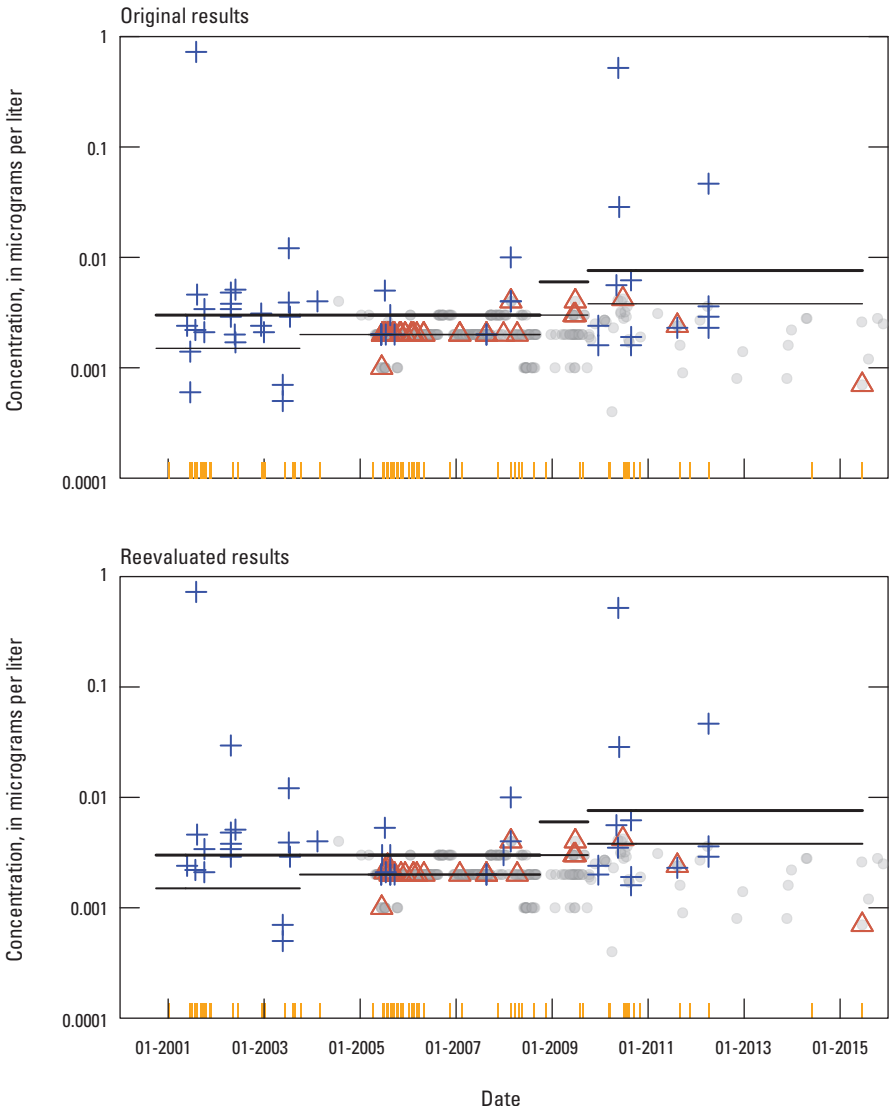
***K.* Dacthal**



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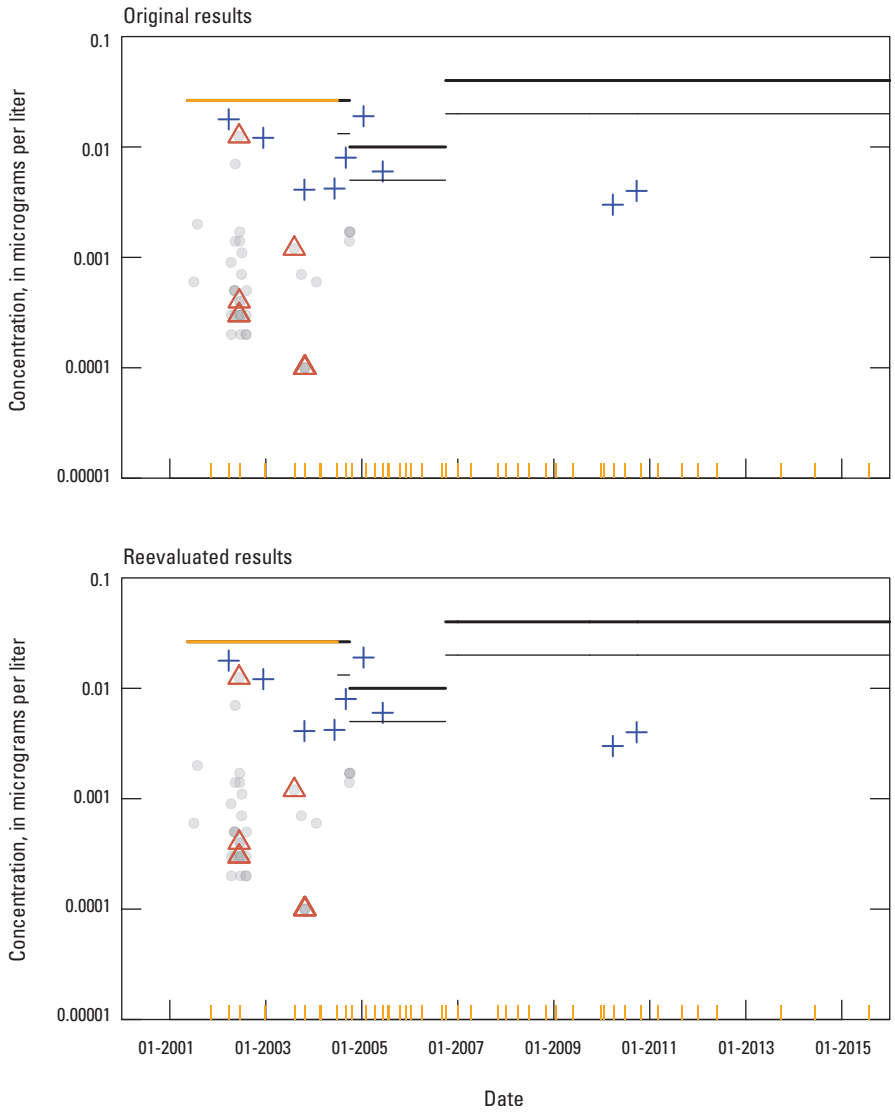
L. Diphenamid



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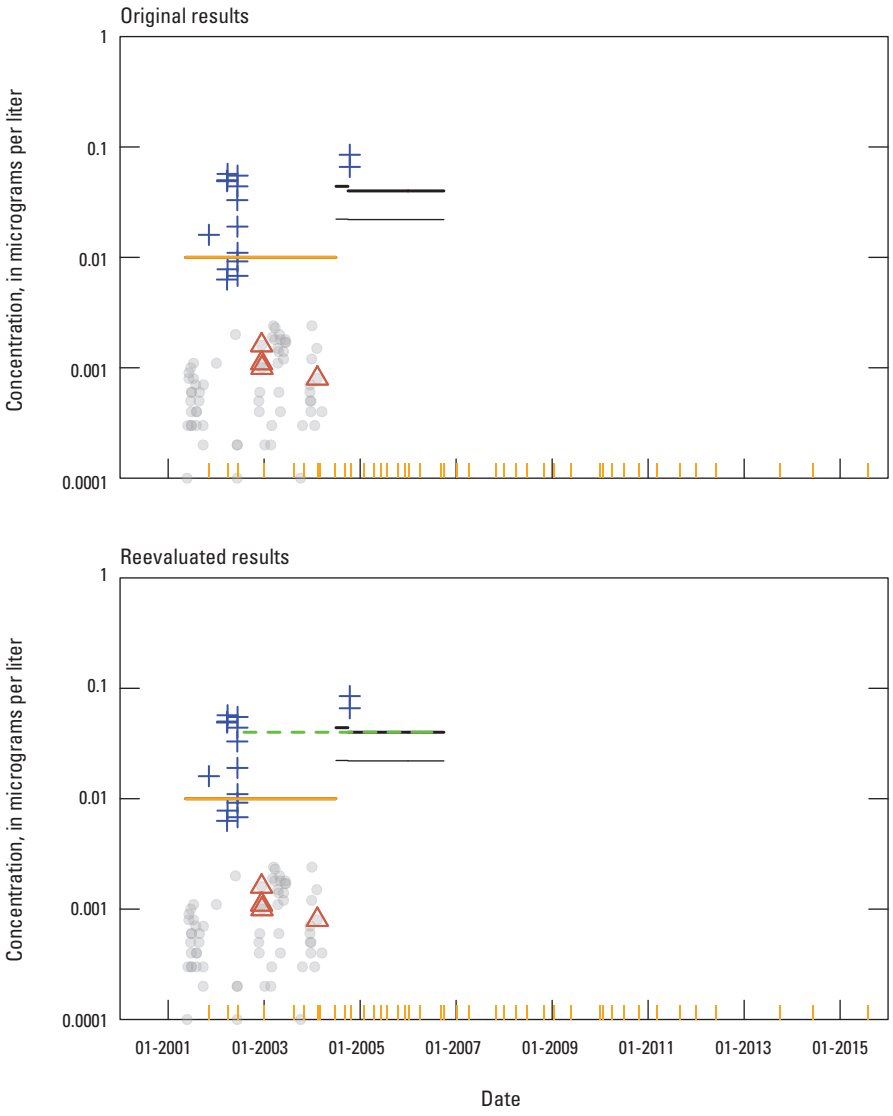
***M.* 2-Chloro-4,6-diamino-s-triazine (CAAT)**



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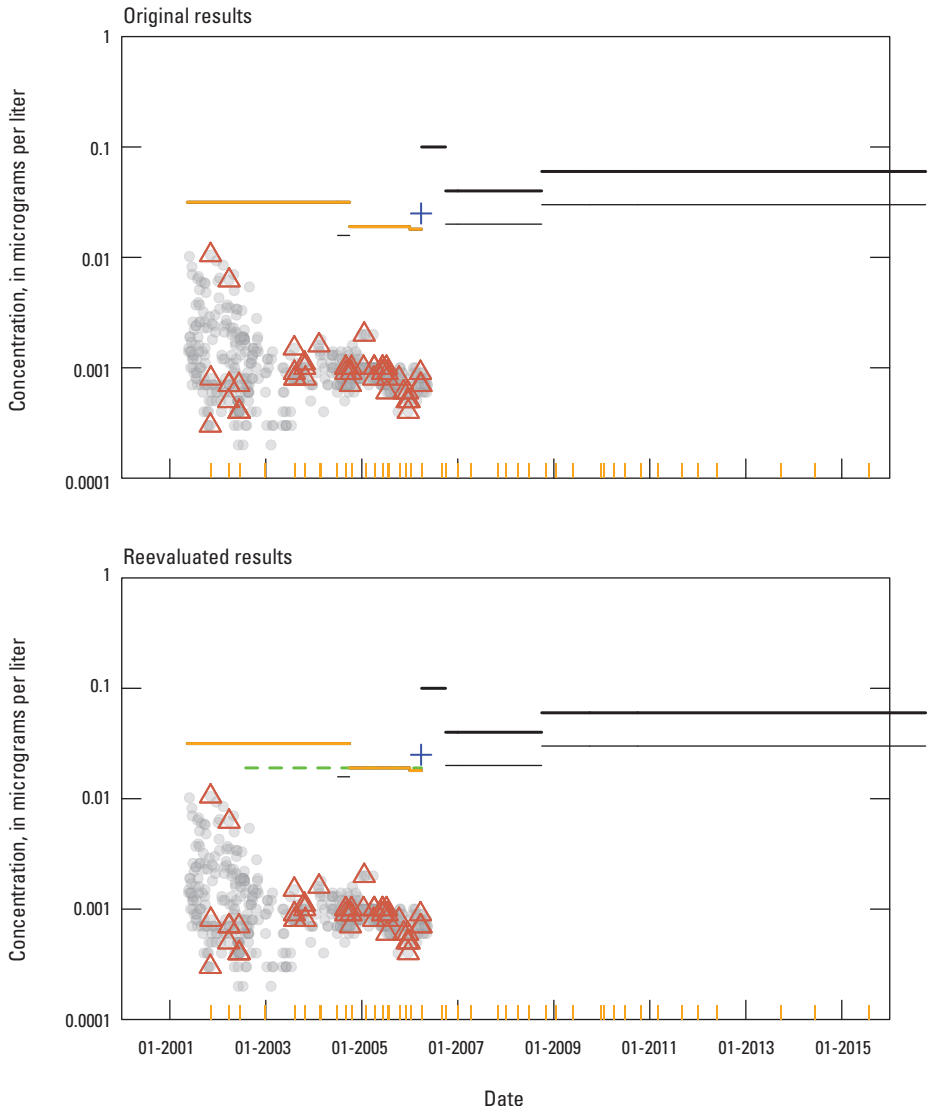
***N.* Fenuron**



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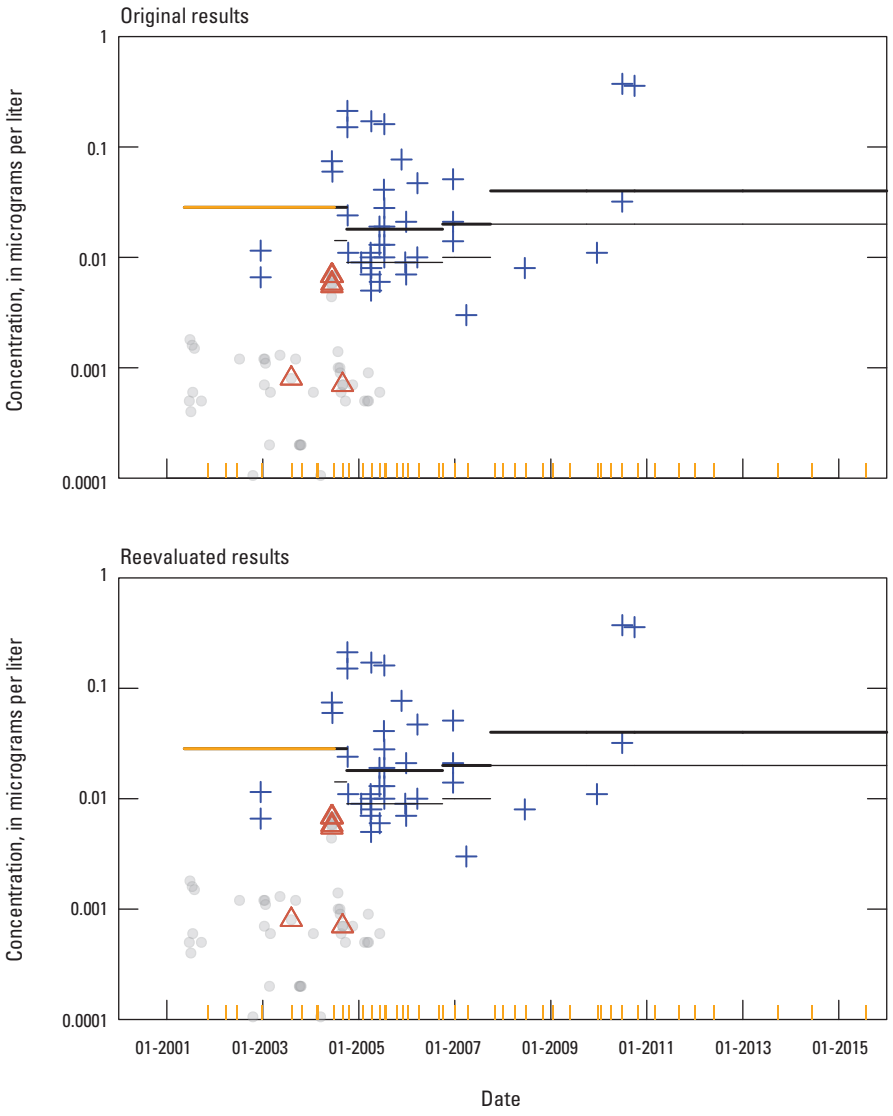
***O.* Carbaryl**



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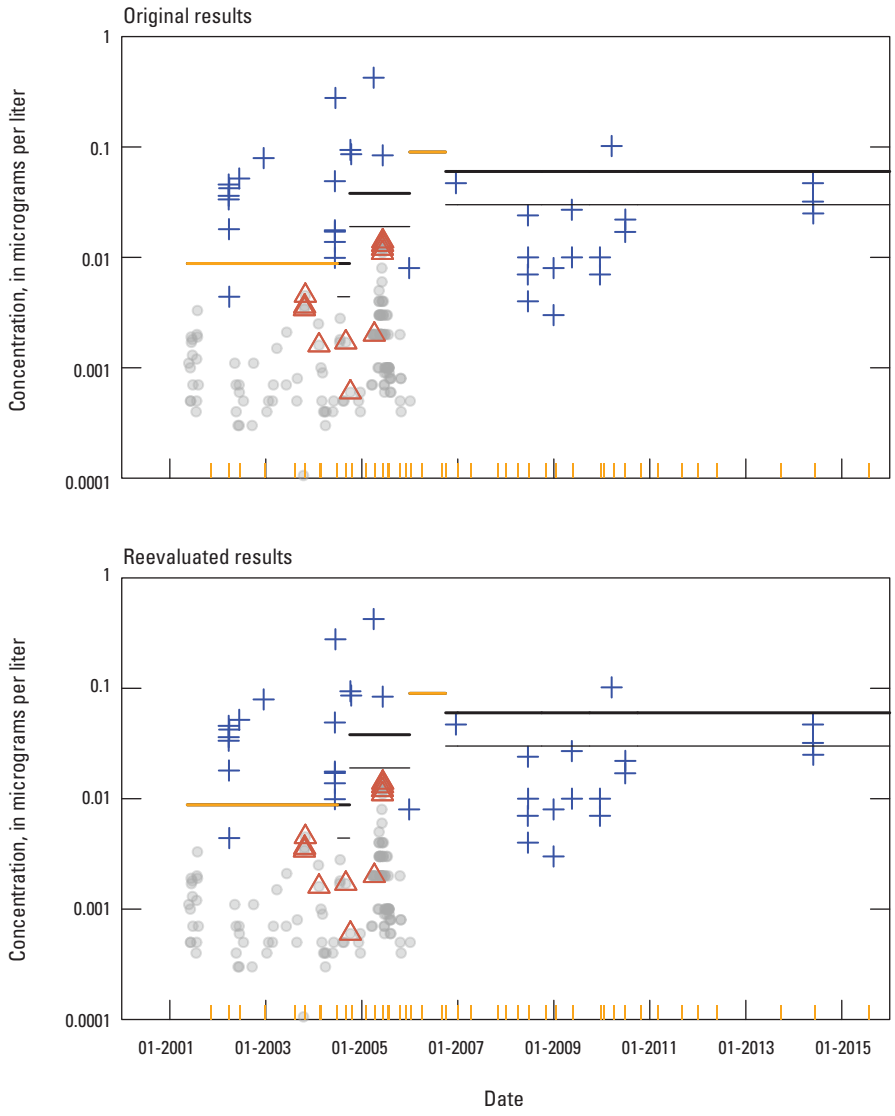
P. **Sulfometuron-methyl**



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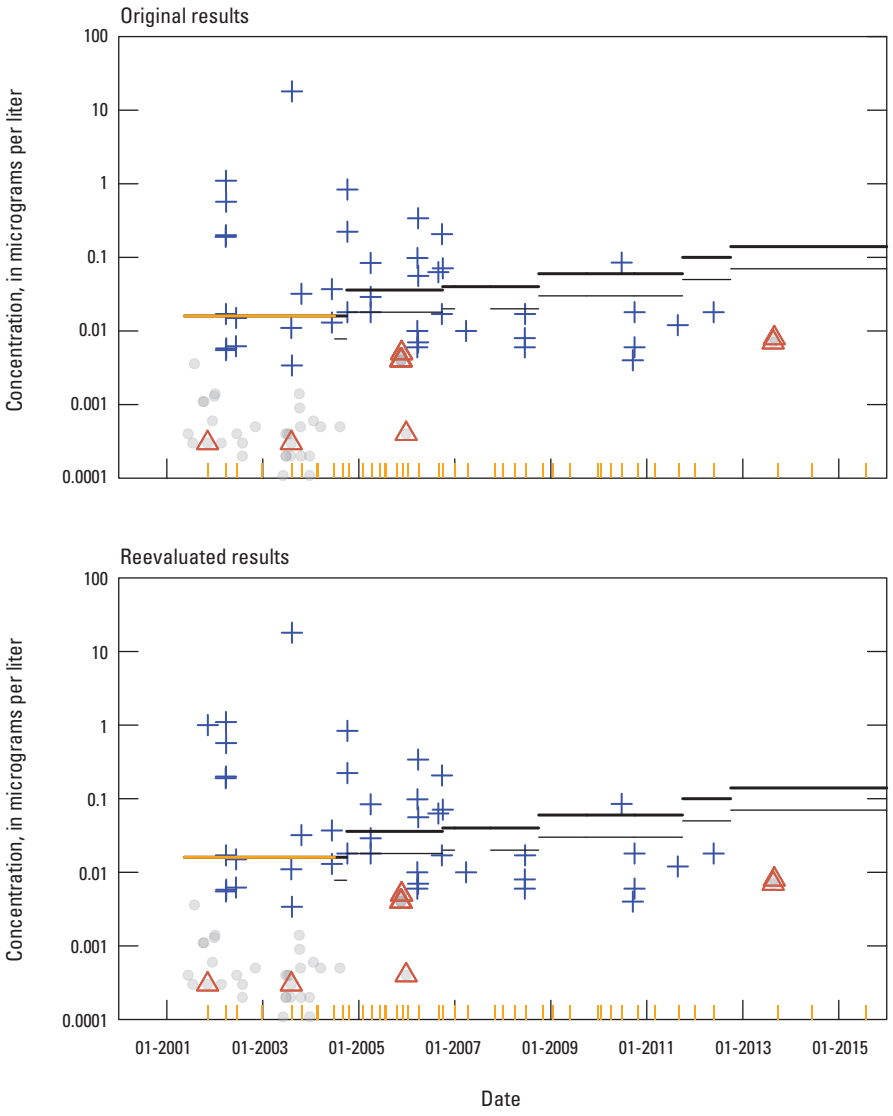
***Q* Imazaquin**



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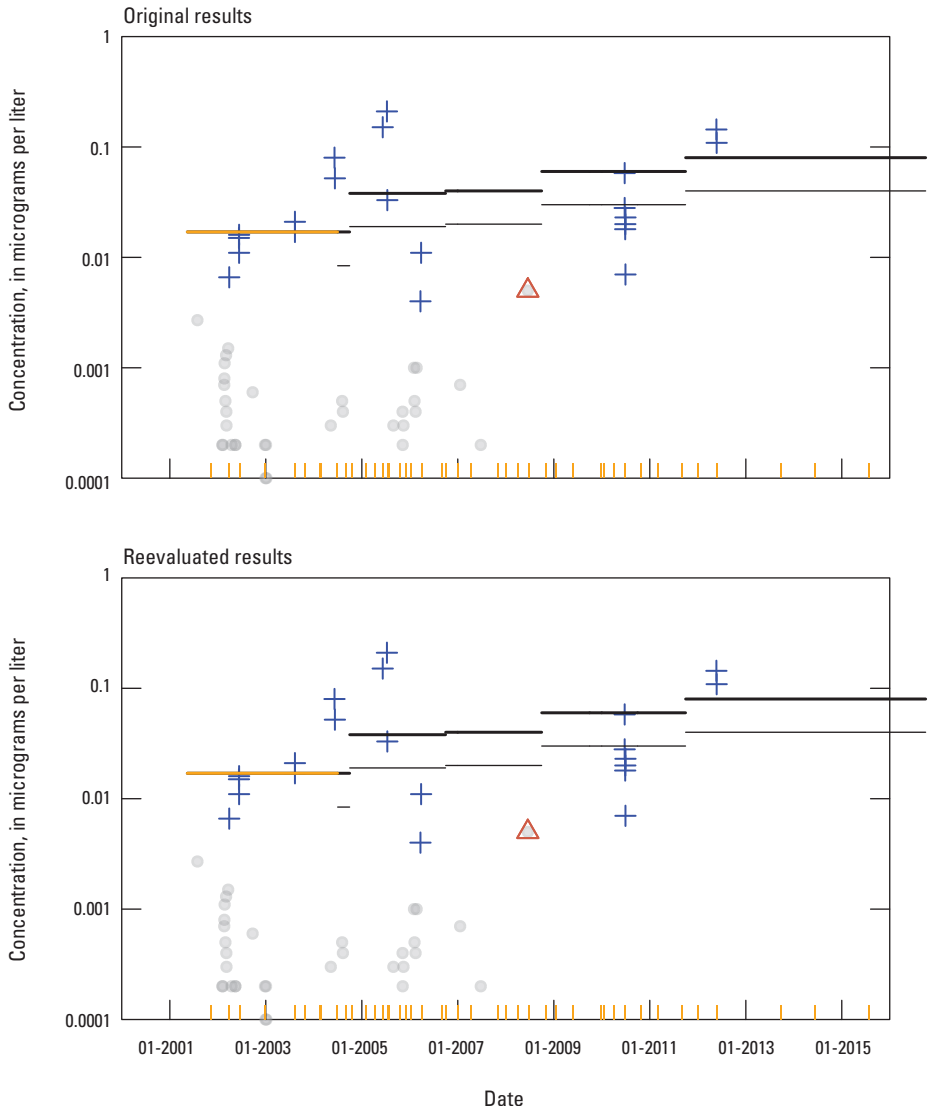
R. **Imazethapyr**



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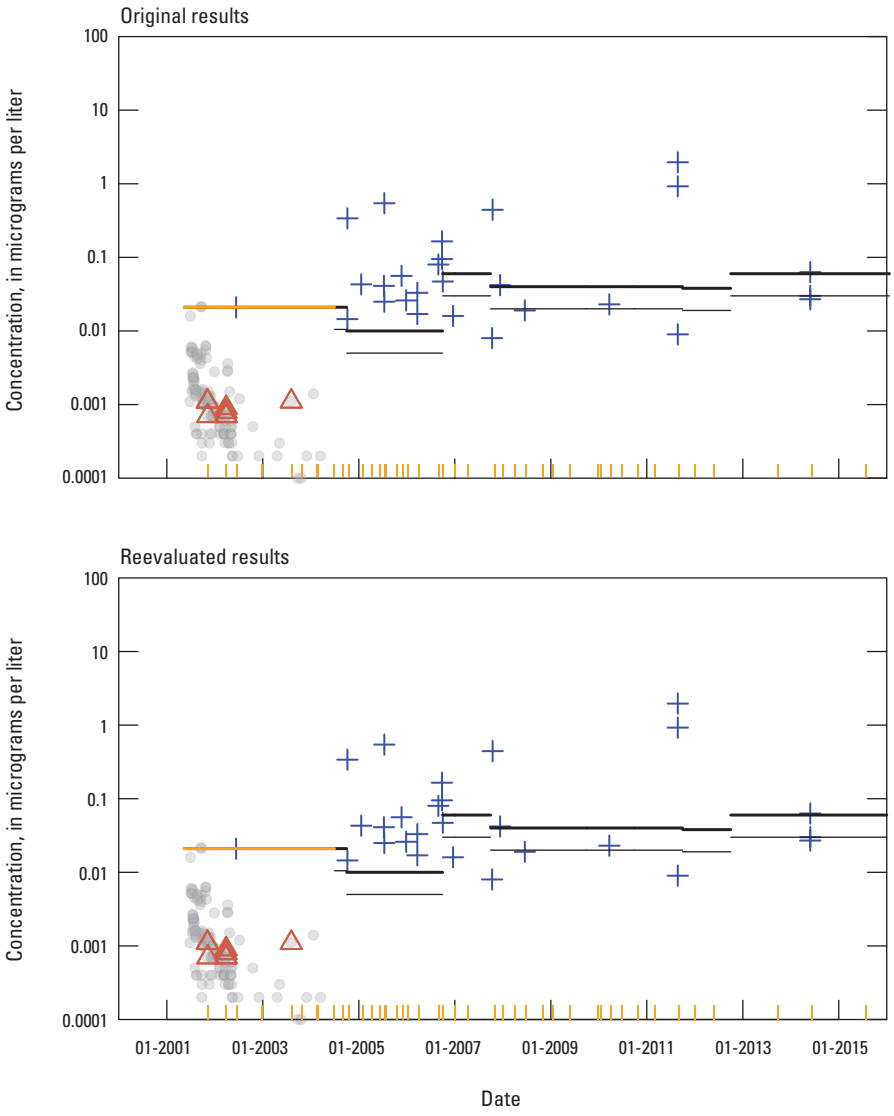
S. Propiconazole



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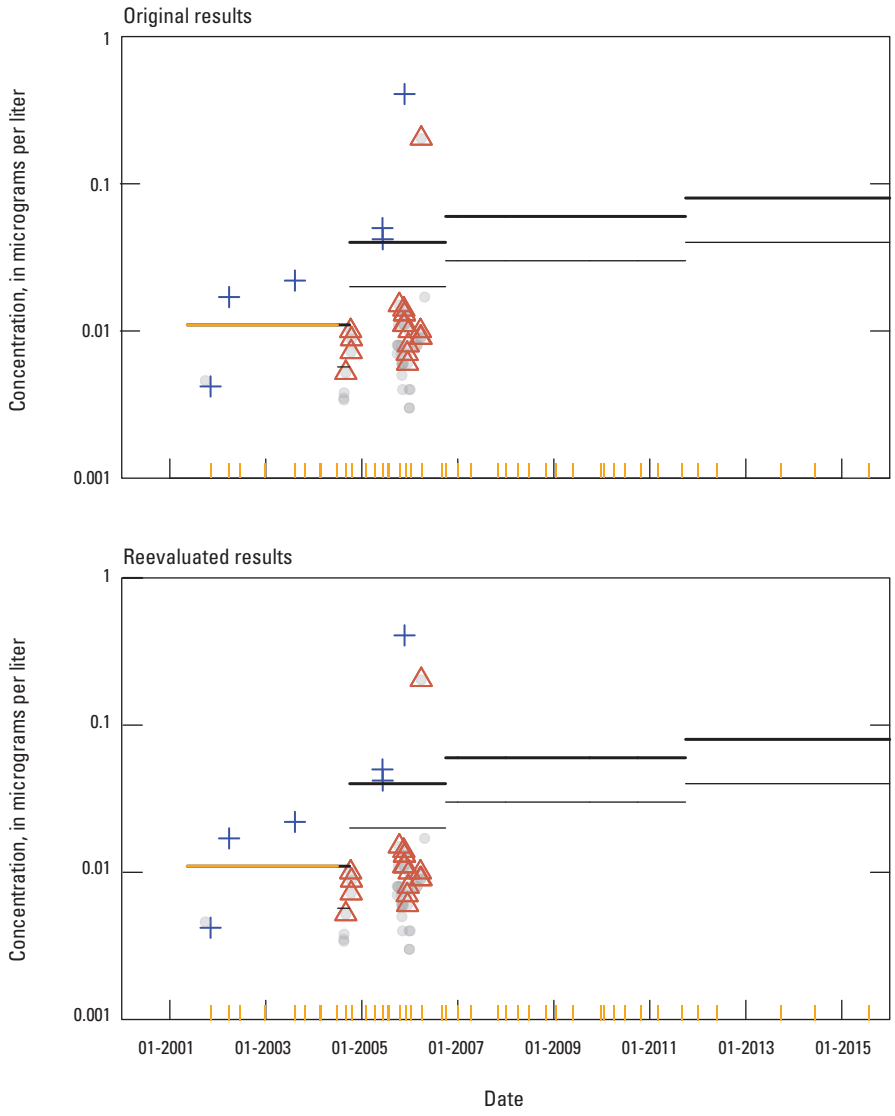
***T.* Flumetsulam**



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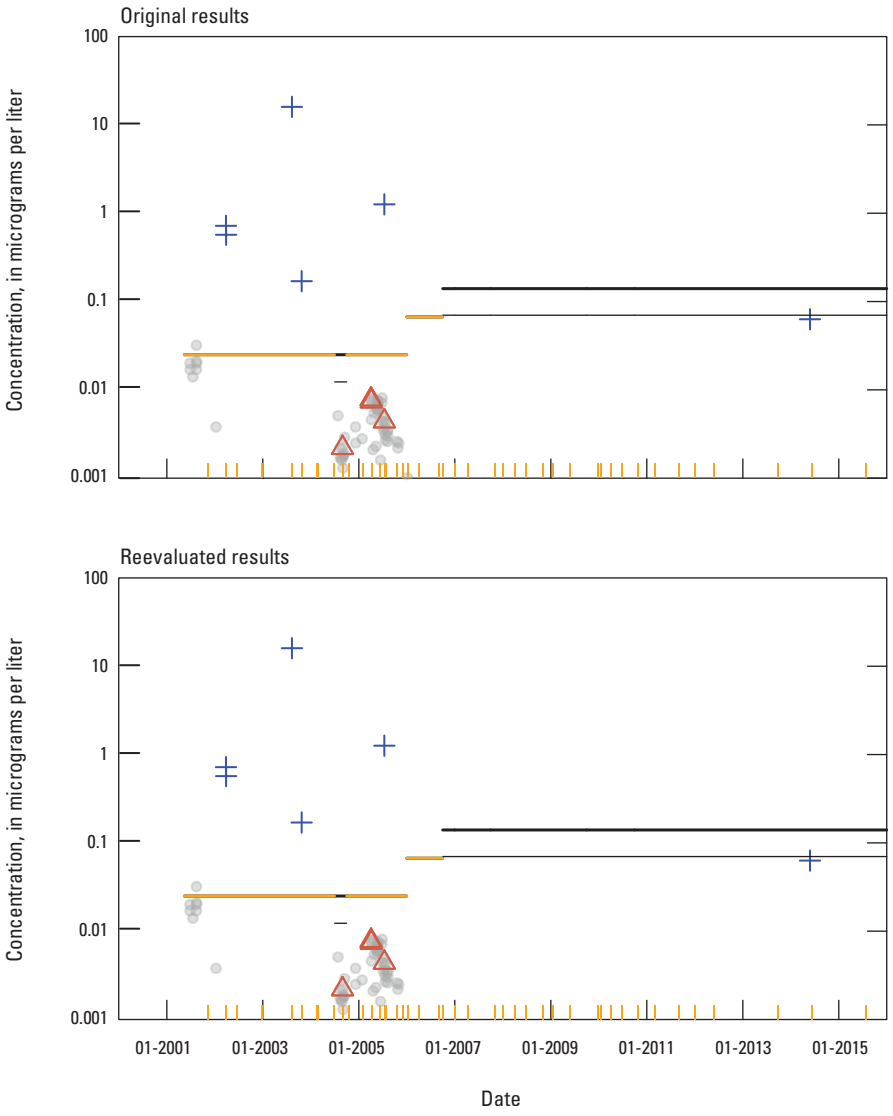
***U.* Metsulfuron-methyl**



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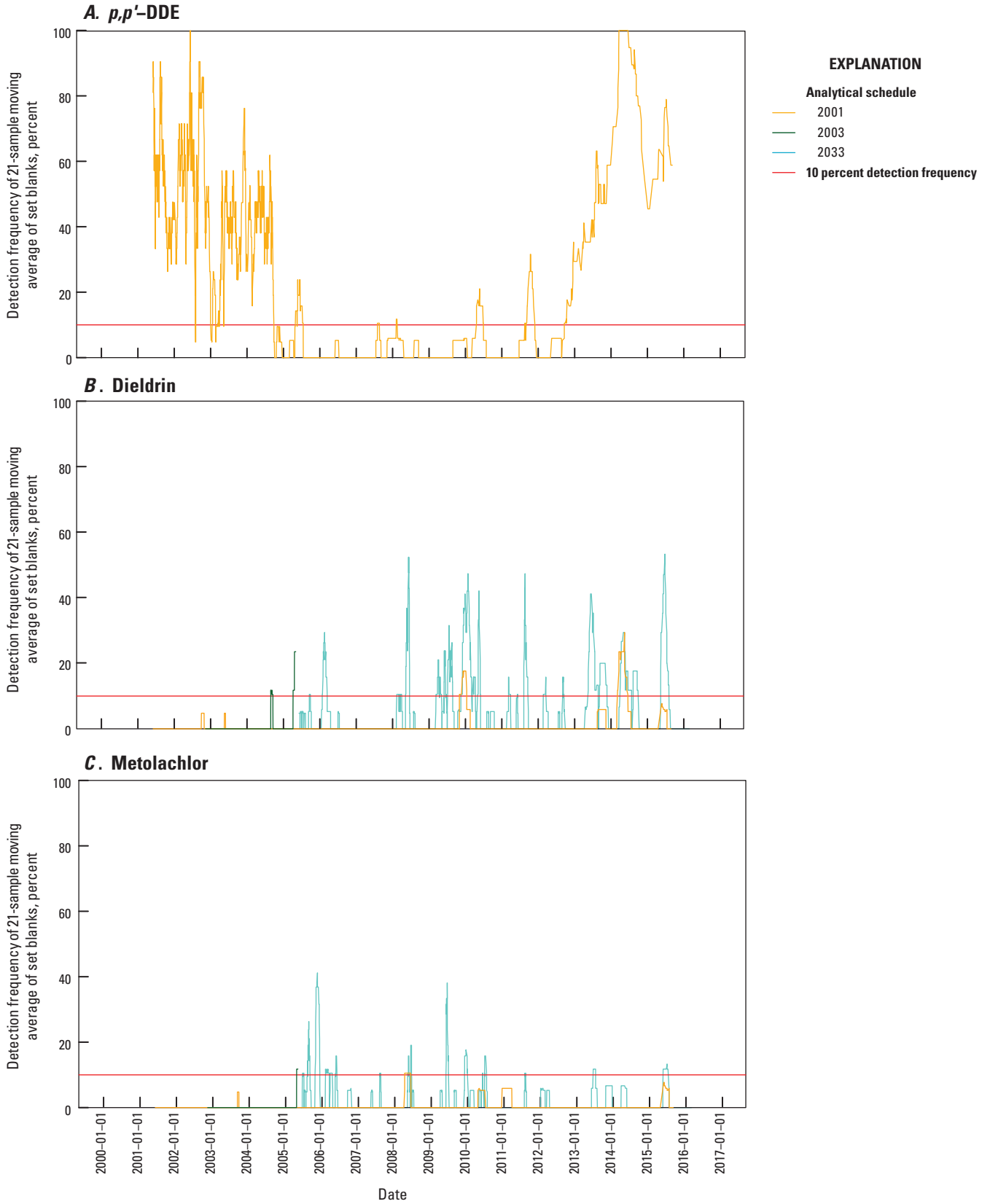
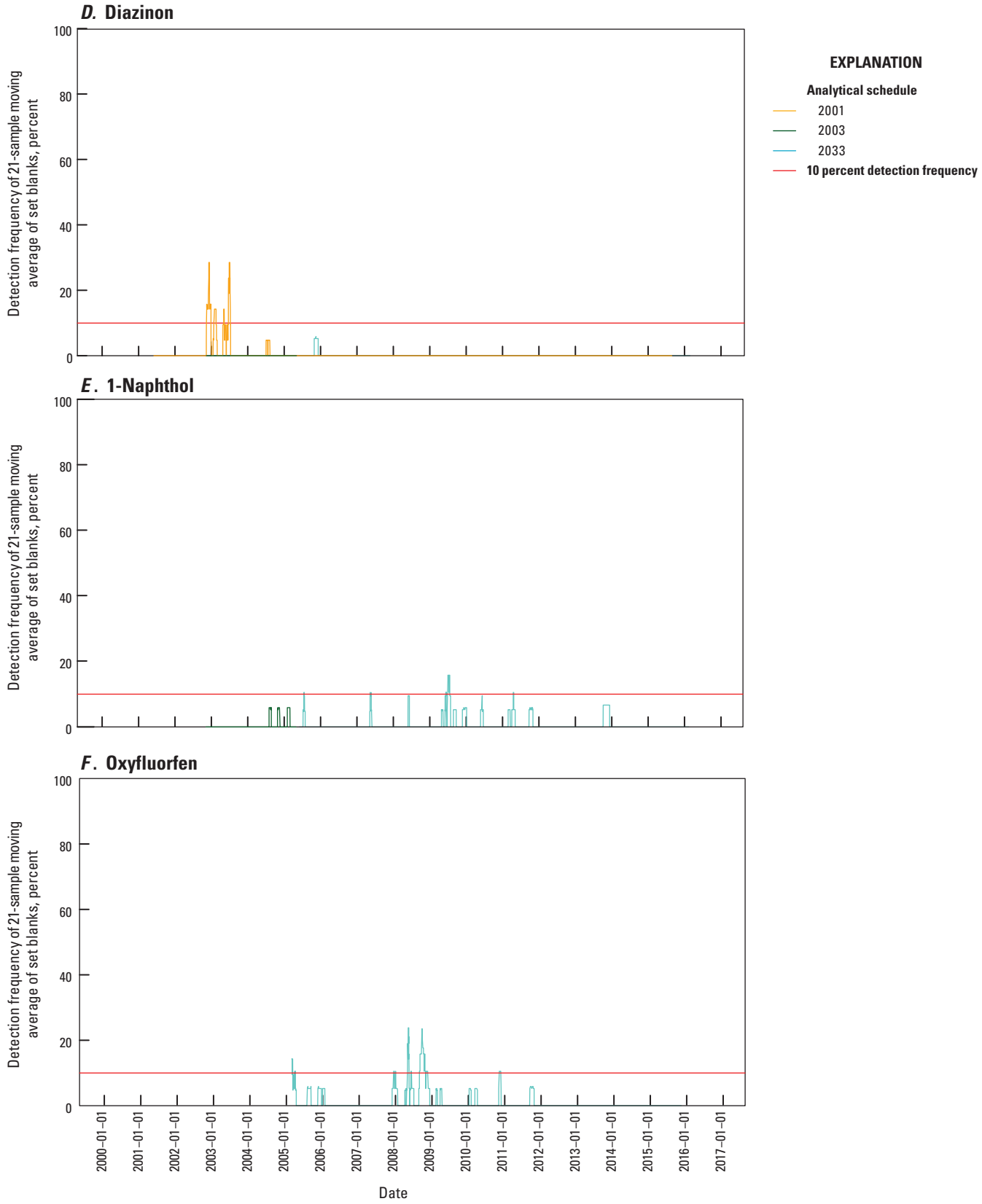


Figure 5. Moving averages of detection frequencies of set blanks to identify periods of time with random and episodic laboratory contamination for gas or liquid chromatography/mass spectrometry compounds for results from all set blanks analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p,p'*–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl.



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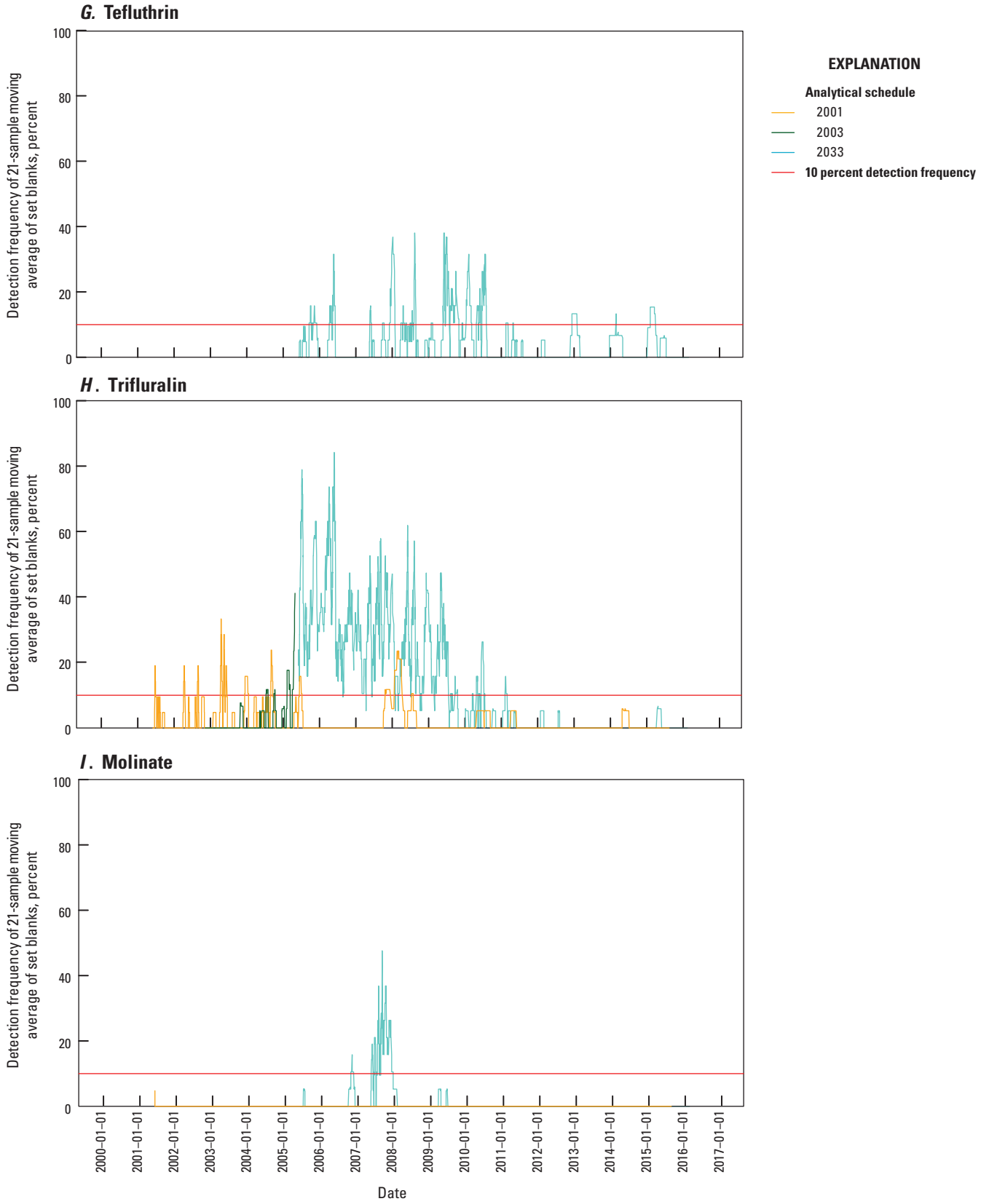

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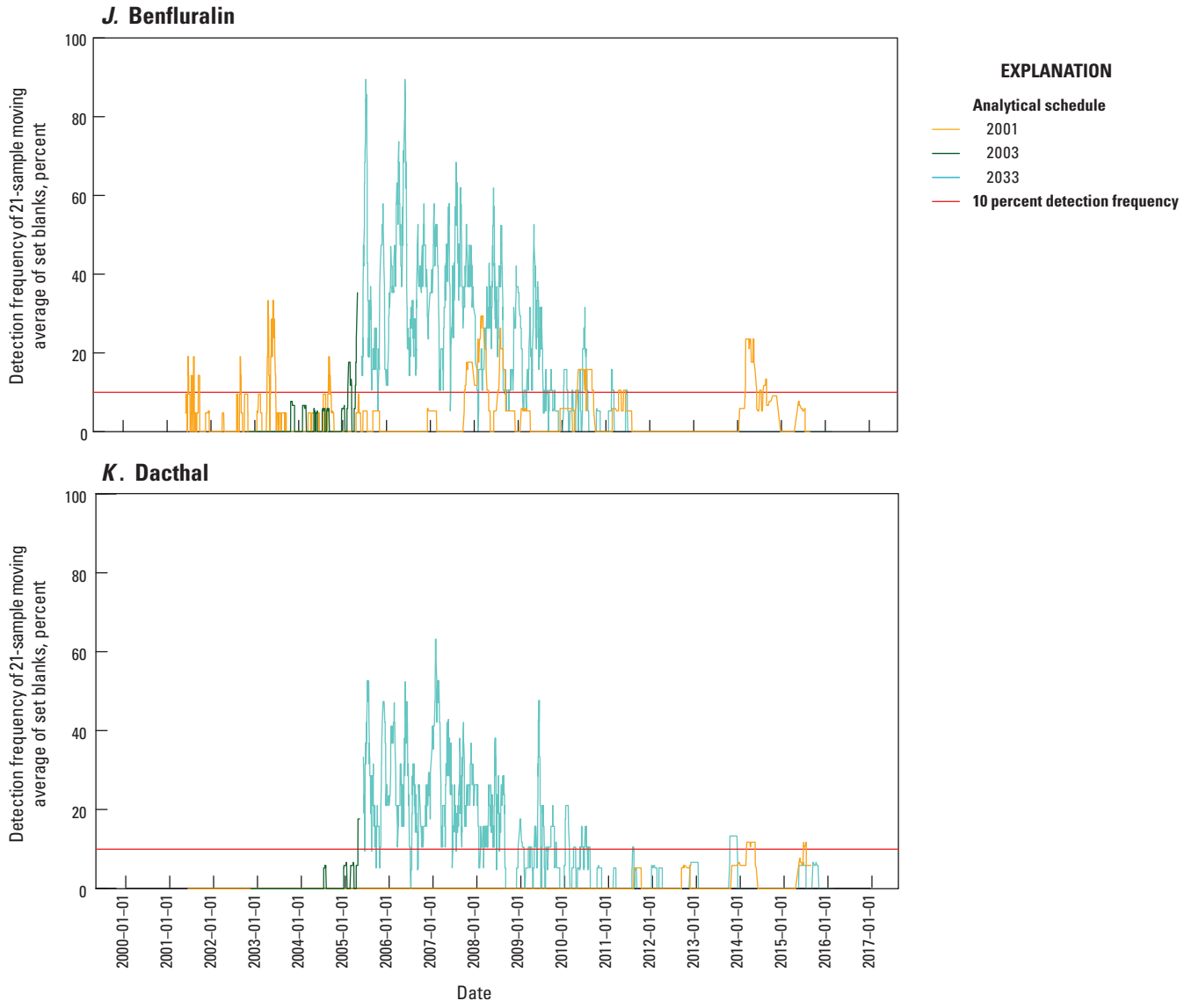

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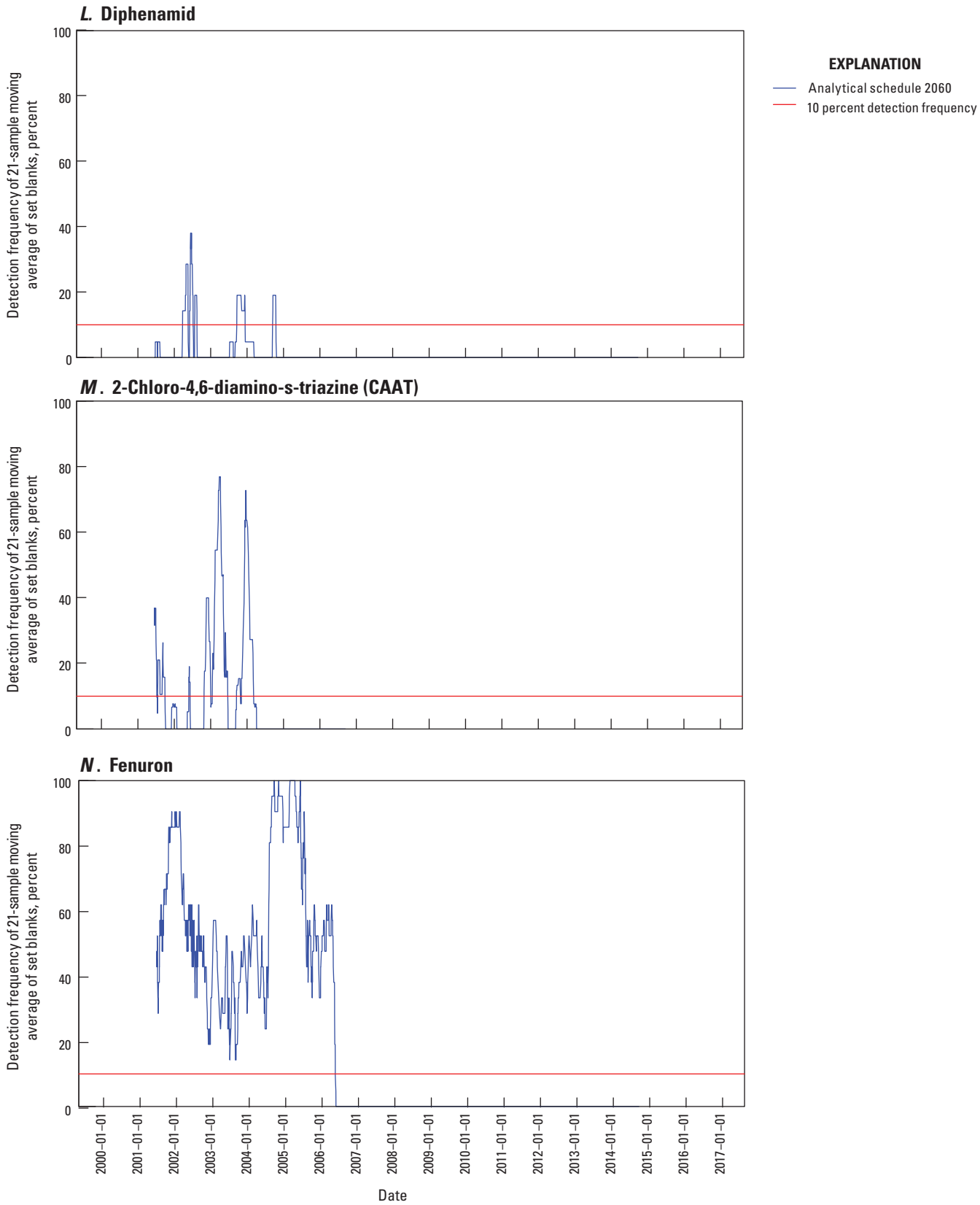

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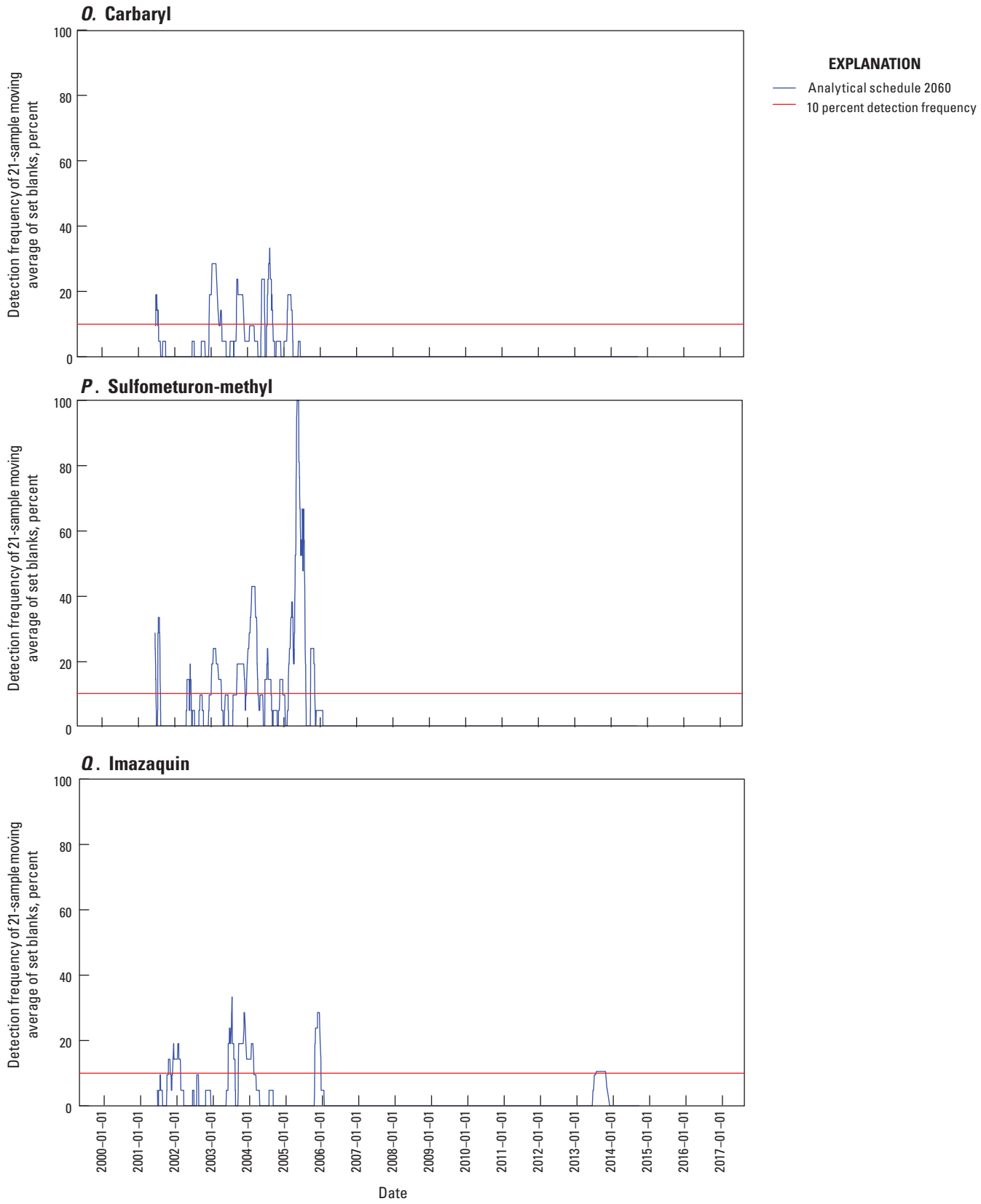

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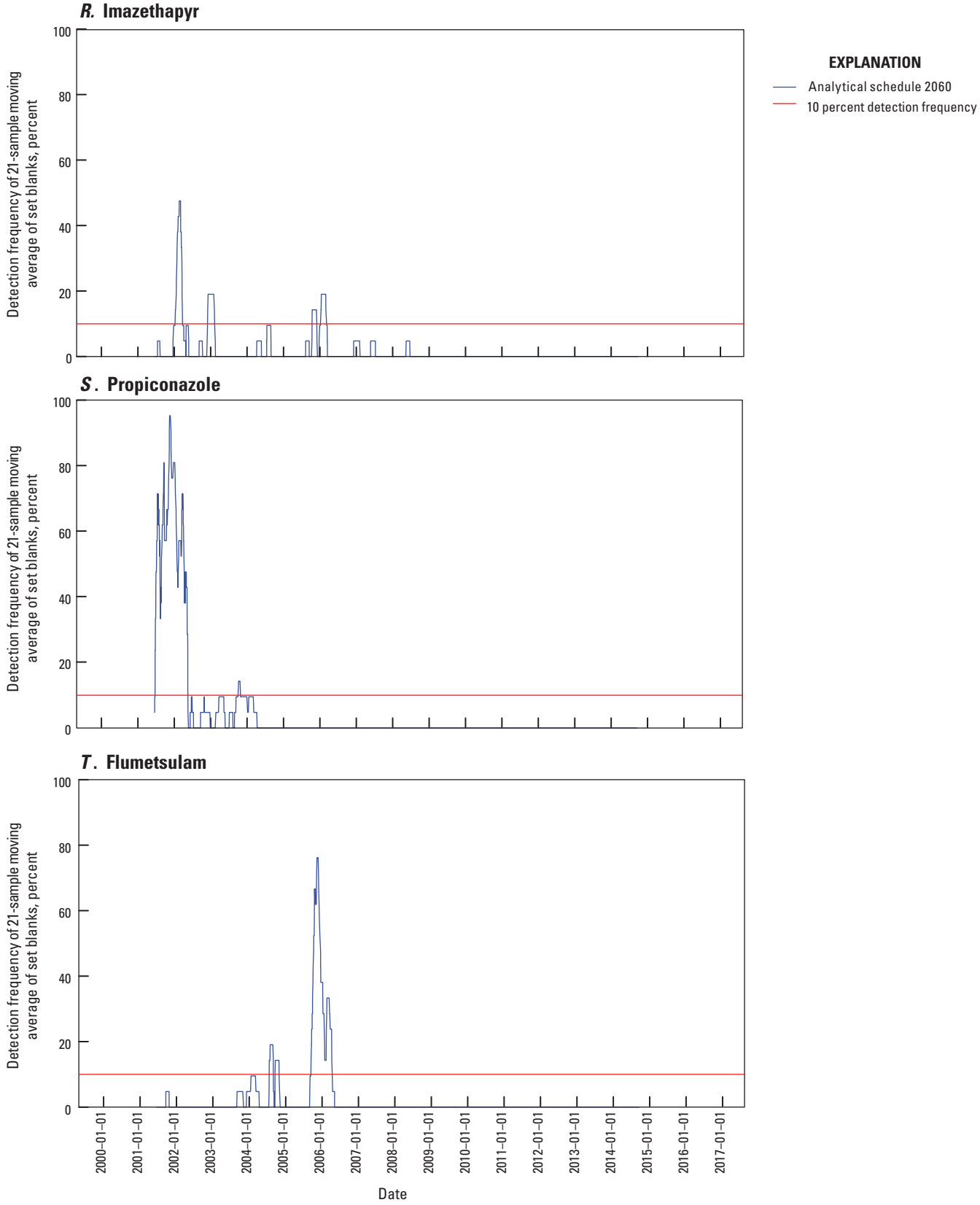

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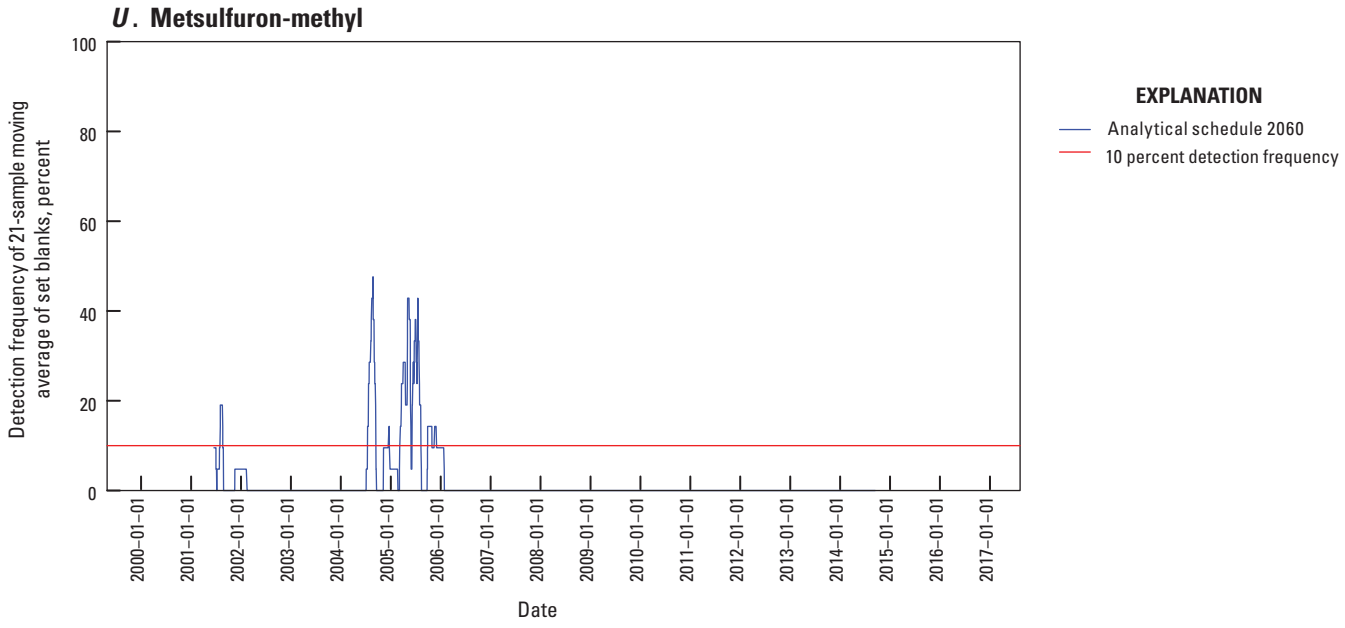

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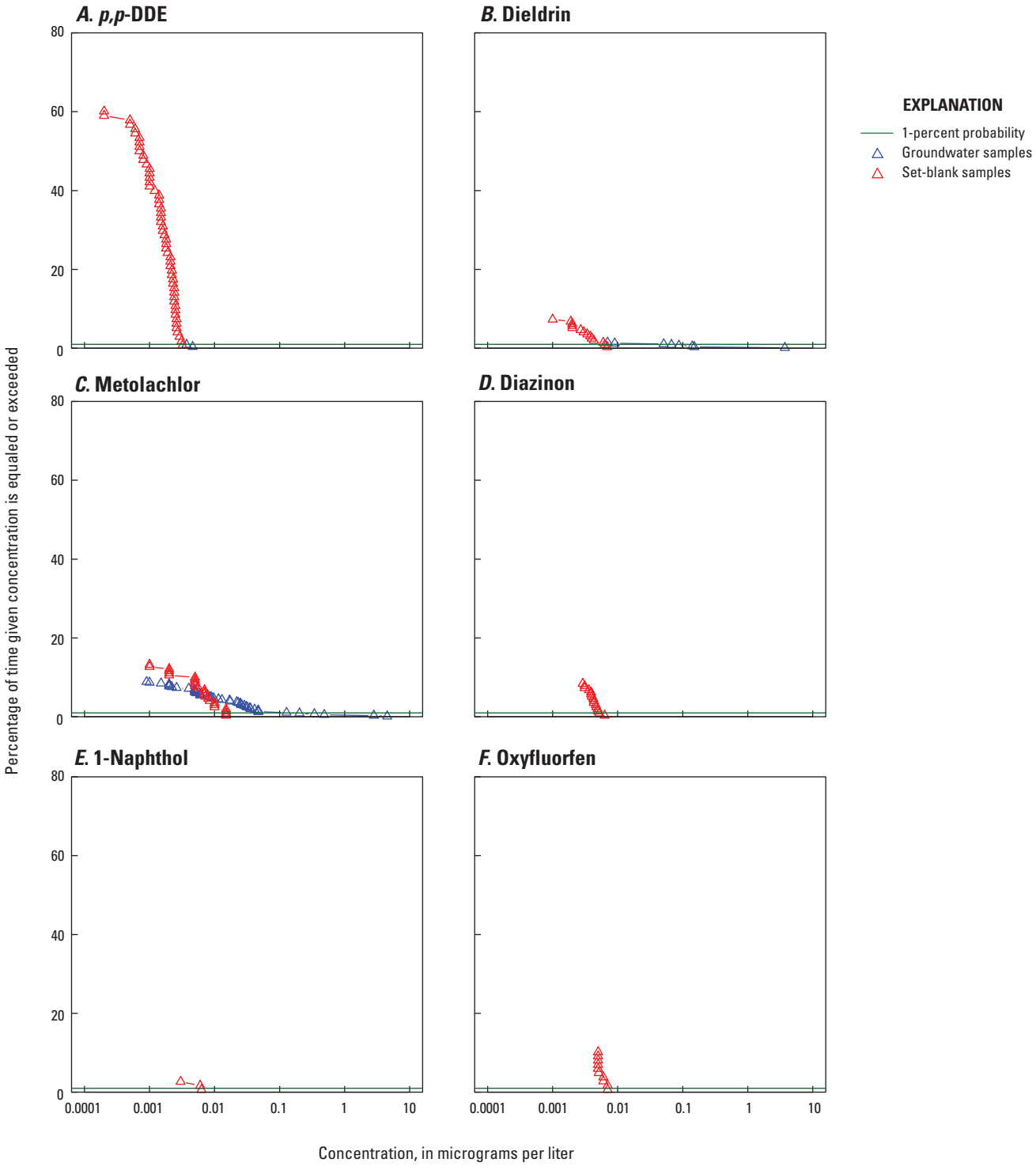
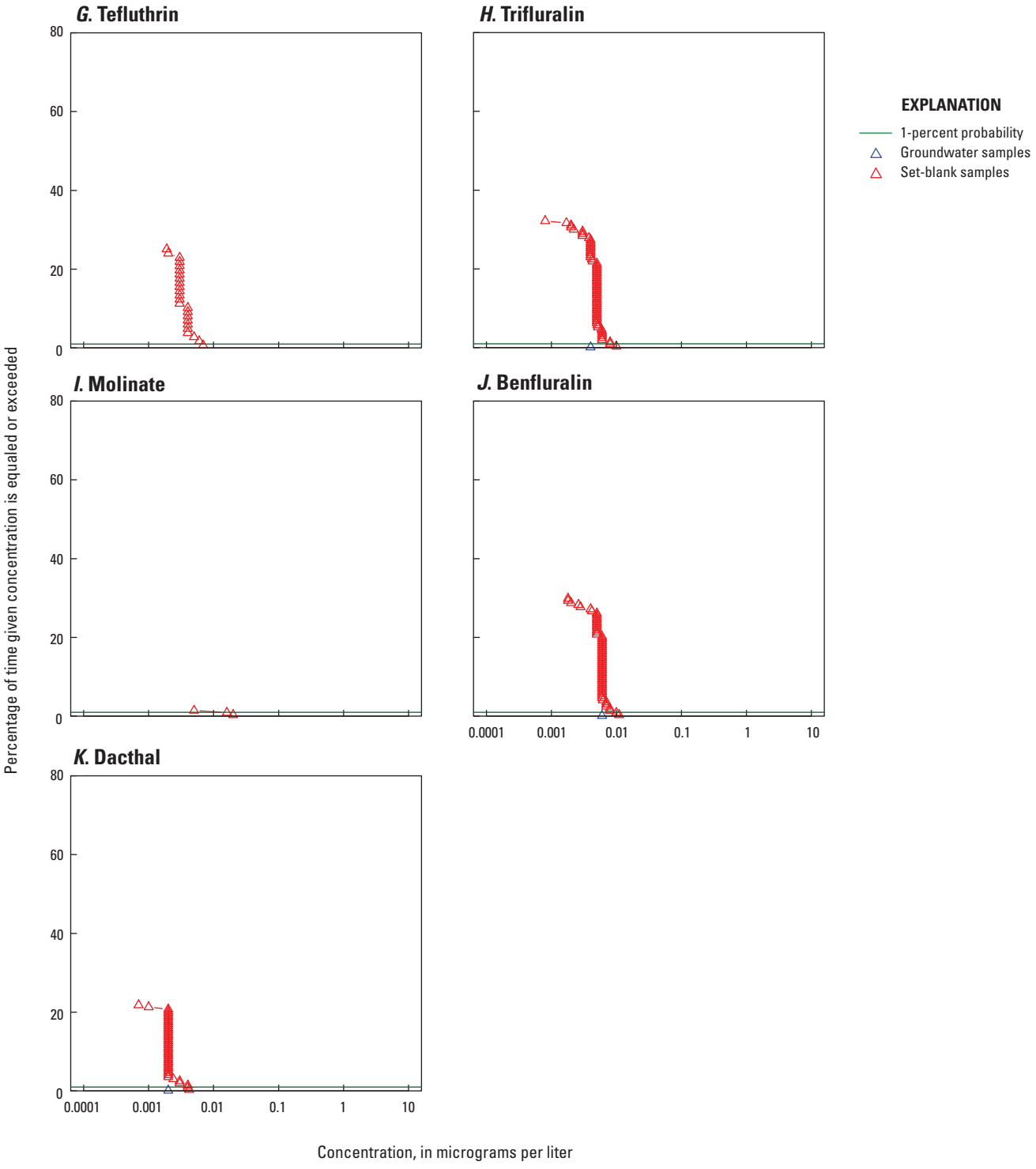


Figure 6. Cumulative distribution function of concentrations of detections in groundwater samples and set blanks of selected gas or liquid chromatography/mass spectrometry compounds, 2001–15. *A*, *p,p*'–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl. This figure is based on data in the Laboratory Information Management System of the National Water Quality Laboratory (Riskin and others, 2019).



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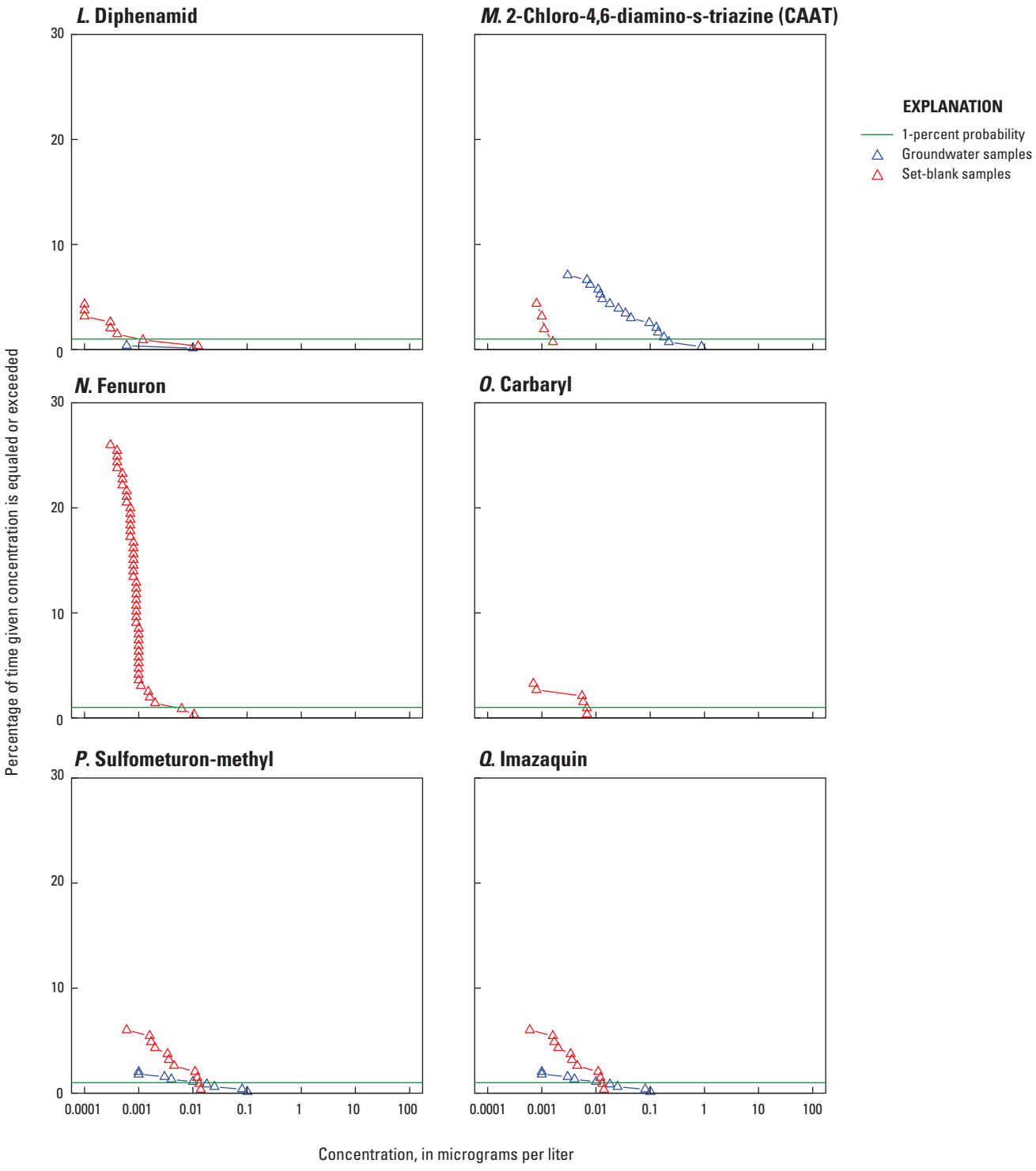

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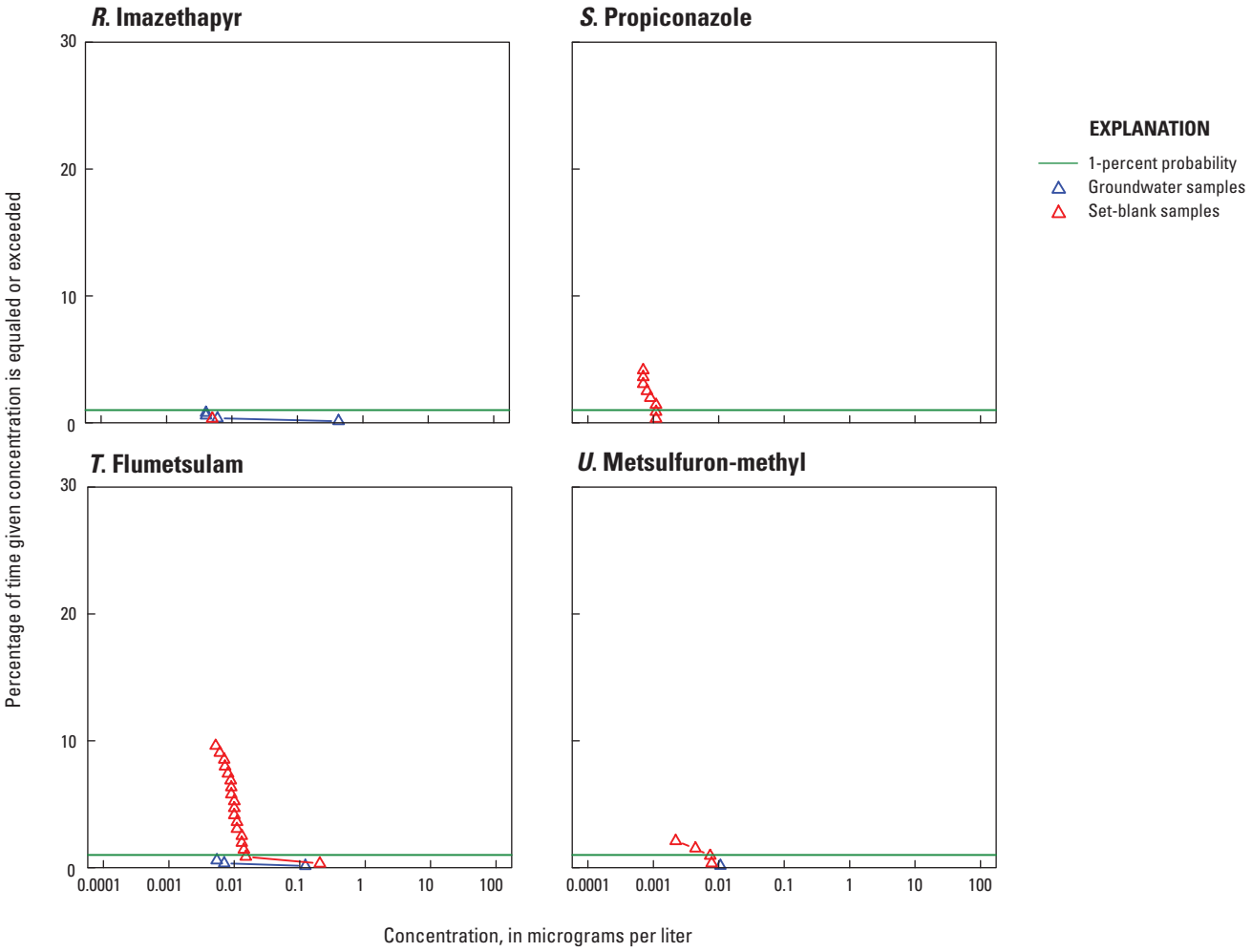

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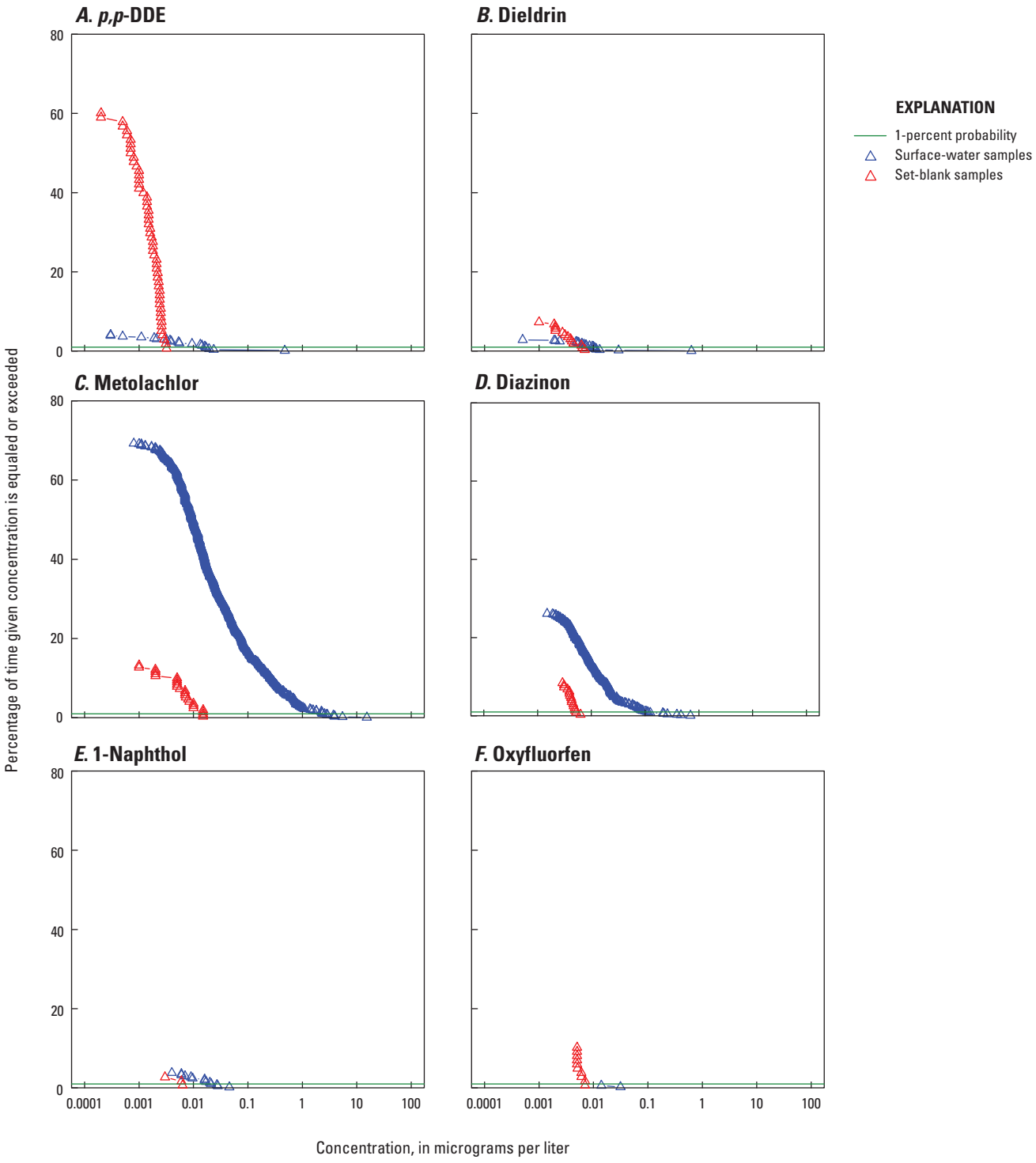
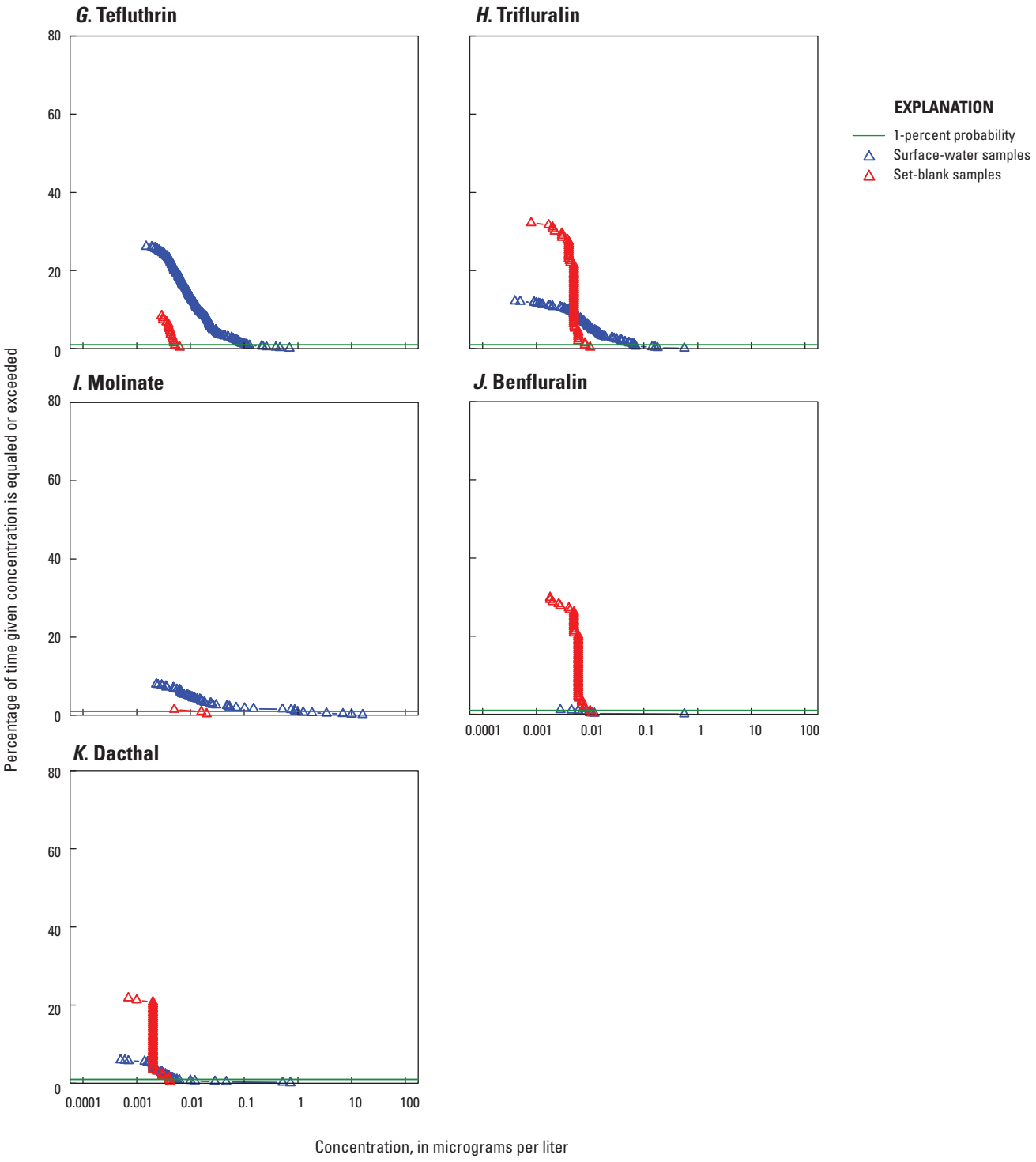


Figure 7. Cumulative distribution function of concentrations of detections in surface-water samples and set blanks of selected gas or liquid chromatography/mass spectrometry compounds analyzed at the National Water Quality Laboratory from 2001 to 2015 for *A*, *p,p'*–DDE; *B*, dieldrin; *C*, metolachlor; *D*, diazinon; *E*, 1-naphthol; *F*, oxyfluorfen; *G*, tefluthrin; *H*, trifluralin; *I*, molinate; *J*, benfluralin; *K*, dacthal; *L*, diphenamid; *M*, 2-chloro-4,6-diamino-s-triazine (CAAT); *N*, fenuron; *O*, carbaryl; *P*, sulfometuron-methyl; *Q*, imazaquin; *R*, imazethapyr; *S*, propiconazole; *T*, flumetsulam; and *U*, metsulfuron-methyl. Based on data in Riskin and others (2019).



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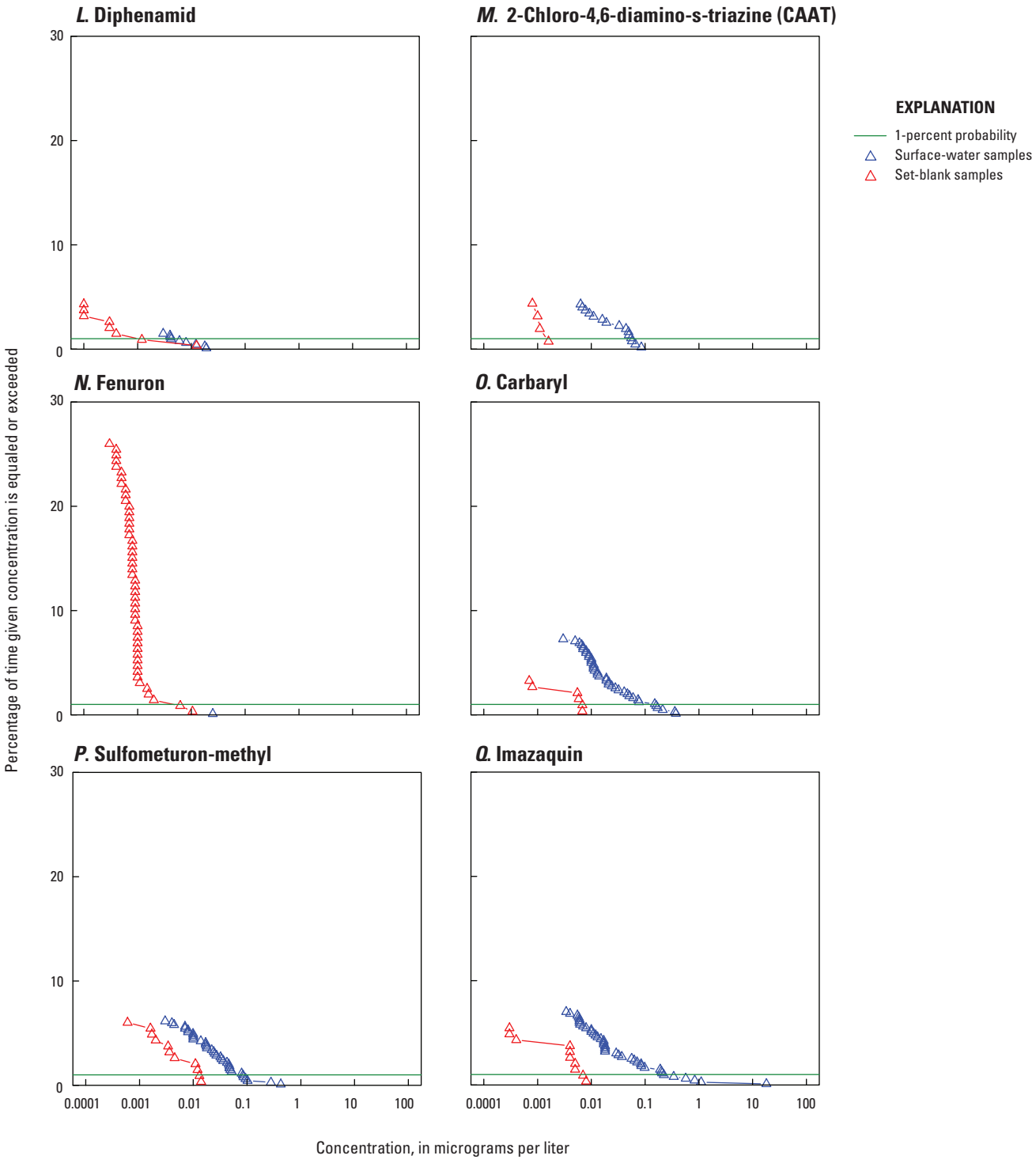

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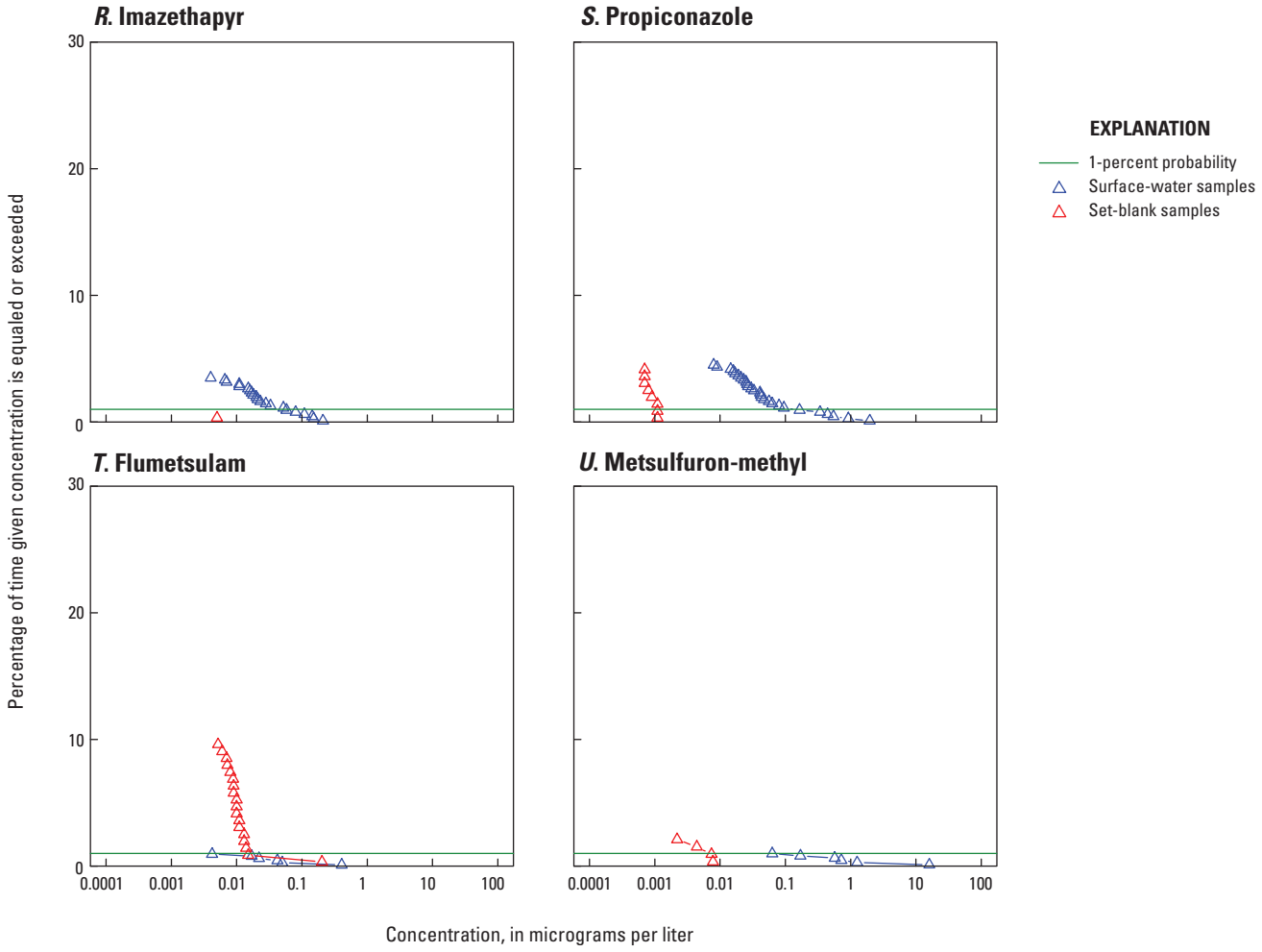

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Glossary

analytical schedule A collection of tests, analytes, variables, or any combination that is defined by the National Water Quality Laboratory (NWQL) as a routine or customer-defined request.

batch Composed of two or more sets of samples, where each set includes environmental and quality-control (QC) samples, run in sequence in an instrument batch at the NWQL. (Also called instrument batch)

batch blank A blank sample analyzed as part of an instrument batch but that is not specifically prepared (extracted) with a given set of associated environmental samples. (*See also* table 3; (Also called instrument blank)

blind sample A QC sample submitted for analysis for which the identity of the sample as well as the concentration of the individual components within the sample is unknown to the analyst.

calibration standard Calibration in analytical chemistry is the operation that determines the functional relationship between measured values (signal intensities at certain signal positions) and analytical quantities characterizing the types of analytes and their amount (content and concentration; Danzer and Currie, 1998). Experimental calibrations are mainly carried out by measurement of a set of calibration samples ("standards") containing the analyte under investigation in suitably graduated amounts.

censoring The process of changing detected results that are below a concentration threshold to nondetections.

detection level (DL) A generic term to describe any possible detection-level conventions or procedures that the NWQL has used in the past to minimize false-positive risk, including the U.S. Environmental Protection Agency method detection limit (MDL), the long-term method detection limit (LT–MDL), or procedures used with the ASTM International (2016) DQCALC software (app. 1).

deterministic contamination Laboratory contamination from a known source that affects every sample (of all types) in the analytical set. In this report, the term "deterministic contamination" also includes "semideterministic contamination."

environmental sample Groundwater or surface-water sample typically collected as part of a water-quality assessment for which a chemical or physical property is measured.

episodic contamination Laboratory contamination, as determined by detections in set blanks, that occur in clusters or episodes in time and defined specifically in this report by calculation of detection frequencies of set blanks above 10 percent for a variable-sample moving average window. Episodic contamination describes most of the laboratory contamination seen at the NWQL for the compounds in this study.

false negative A result that indicates a substance is not present (was not found) in a sample when the substance was present (Keith, 1992). The NWQL provides a "less than" (<) reporting level concentration instead of reporting "not present" or "not detected." Therefore, a false negative occurs when the analyte is reported as less than the reporting level (that is, less than laboratory reporting level [LRL], less than minimum reporting level [MRL], or less than other concentration) when the true concentration is at or above that reporting level concentration.

false positive A result that indicates a substance is present in a sample when it is not (Keith, 1992).

instrument blank A blank sample analyzed as part of an instrument batch but that is not specifically prepared (extracted) with a given set of associated environmental samples. (*See also* table 3; (Also called batch blank)

integration The measurement of the chromatographic peak area of the mass spectral quantitation and qualifier ions that are determined by the analytical instrument software. The analyst can manually override

the automatic integration done by the software for cases of incorrect integrations of chromatographic peak area, which could happen if the baseline in the chromatogram is noisy or irregular or if an interfering compound only partially coelutes.

interferent The presence of a signal (peak or noise) in the ion chromatogram that is not from the compound of interest. Generally, this is from another chemical in the sample that elutes near the compound of interest and produces an instrument response for the same monitored ion. This signal is referred to as "interference" or "chemical noise" and is determined not to be from the compound of interest because not all the qualitative identification criteria are met to confirm the identification of the compound. (*Also called* **interference**.)

interim reporting level (IRL) Used for time periods when the pesticide schedule applied the LRL convention but the detection levels for some or all method analytes had not yet been or never were established or verified by the LT–MDL procedure.

laboratory contamination Contamination of a sample that is generated during preparation, processing, or instrument analysis in a laboratory. In this report, laboratory contamination is described as semideterministic, episodic, or random.

laboratory reporting level (LRL) Typically set at twice the LT–MDL. The chance of falsely reporting a nondetection for a sample in which the analyte is present at a concentration equal to or greater than the LRL is 1 percent or less (Childress and others, 1999).

long-term method detection limit (LT–MDL) A detection level derived by determining the standard deviation of a minimum of 24 MDL spike sample measurements or at least 50 blind-blank measurements during an extended period. LT–MDL data are collected on a continuous basis to assess year-to-year variations in the LT–MDL (Childress and others, 1999).

lowest reportable concentration (LRC) Applies to compounds analyzed by mass spectrometry and has typically been established as either 1 percent (through September 30, 2009) or 10 percent (beginning October 1, 2009) of the detection limit.

method detection limit (MDL) The minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than 0 microgram per liter. It is determined from the analysis of a sample in a given matrix containing the analyte, in accordance with the U.S. Environmental Protection Agency's definition and procedure for the determination of the method detection limit (U.S. Environmental Protection Agency, 2011). At the MDL concentration, the risk of a false positive is predicted to be less than or equal to 1 percent.

minimum reporting level (MRL) The smallest measured concentration of a constituent that may be reliably measured by using a given analytical method (Childress and others, 1999).

minimum reporting level censoring A minimum reporting level convention at the NWQL for analytes that exhibit performance limitations. Between October 1, 2000, and November 30, 2009, quantified results could be reported below the MRL concentration only if the result included an "E" remark code in the National Water Information System (U.S. Geological Survey, 2017a); beginning December 1, 2009, any detections that are less than the MRL concentration are censored and reported as less than the MRL.

original result Original results are data that were retrieved from the NWQL internal database called the Laboratory Information Management System (LIMS). These data were reviewed and released by the NWQL to scientists in U.S. Geological Survey (USGS) water science centers across the Nation that originally collected and submitted the samples for analysis. Original results are subject to NWQL applied censoring based on detections in set blanks or, in some cases, batch blanks to address potential laboratory contamination.

quality-control sample Sample used to identify and measure bias and variability of the analytical method. Quality-control samples include samples collected in the field (blanks, replicates, spikes) and samples generated in a laboratory setting (set blanks, instrument blanks, set spikes, blind-spikes, blind-blanks).

raised reporting level (RRL) A concentration whose "less than" concentration is greater than the default reporting level. The most common reasons for applying a raised reporting level are the presence of an

interferent, the presence of the analyte in the associated set blank, or insufficient sample volume.

random contamination Laboratory contamination that is no more likely to occur at any one time than any other time.

reagent-grade water Purified water that does not contain analytes to be determined or substances that interfere in the analytical method. It is used to prepare QC samples (blank and spike samples).

recovery The primary indicator of the analytical bias of a measurement. Recovery of 100 percent indicates no bias.

reevaluated result For data presented in this study, the NWQL reevaluated every result from 70 batches of samples analyzed with gas chromatography/mass spectrometry methods and 43 batches of samples analyzed with liquid chromatography/mass spectrometry methods, using protocols for identification and reporting of detections updated in 2017 and consistently applied criteria for the qualitative identification of pesticides. Some reevaluated results are different from original results. No changes for reevaluated results have been made to data in the LIMS or published in the NWIS.

reporting level (RL) The "less than" concentration provided when the analyte is not detected or is detected below a minimum (censor-limit-based) concentration, which might be at or below the reporting level value.

semideterministic contamination Laboratory contamination that affects most but not necessarily all samples in the analytical set or batch. In this report, "semideterministic contamination" is included in the term "deterministic contamination."

set A sequence of environmental and QC samples that are prepared (extracted) and run together at the NWQL; also called "preparation set."

set blank A specific type of laboratory blank sample (also called method, reagent, or preparation blank) that is used to assess possible contamination for a set of samples during preparation, processing, and instrument analysis. Set blanks are processed in the same way as all other samples in the set.

set censoring Procedures for reporting analytical results at the NWQL to address laboratory contamination whereby environmental and field quality-control samples are censored (reported as less than the reporting level) based on detections in set blanks.

Appendixes 1–4

Appendix 1. Detection Levels and Reporting Conventions Applied to Pesticide Analysis by the National Water Quality Laboratory From 2001 to 2015

During the period from 2001 to 2015, the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) used either the laboratory reporting level (LRL) or the minimum reporting level (MRL) convention for reporting pesticide results (fig. 1.1; tables 1.1 to 1.5). Phased implementation of a new method for estimating detection levels using the ASTM International DQCALC software and for establishing reporting levels based on DQCALC (RLDQC) began in 2014.

Table 1.1. Detection and reporting levels for National Water Quality Laboratory Analytical Schedule 2001, 1994–2015.

[This table is available for download at https://doi.org/10.3111/sir20195055 in Microsoft Excel and comma delimited (CSV) formats]

Table 1.2. Detection and reporting levels for National Water Quality Laboratory Analytical Schedule 2003, 2001–15.

[This table is available for download at https://doi.org/10.3111/sir20195055 in Microsoft Excel and comma delimited (CSV) formats]

Table 1.3. Detection and reporting levels for National Water Quality Laboratory Analytical Schedule 2032, 2001–15.

[This table is available for download at https://doi.org/10.3111/sir20195055 in Microsoft Excel and comma delimited (CSV) formats]

Table 1.4. Detection and reporting levels for National Water Quality Laboratory Analytical Schedule 2033, 2001–15.

[This table is available for download at https://doi.org/10.3111/sir20195055 in Microsoft Excel and comma delimited (CSV) formats]

Table 1.5. Detection and reporting levels for National Water Quality Laboratory Analytical Schedule 2060, 2001–15.

[This table is available for download at https://doi.org/10.3111/sir20195055 in Microsoft Excel and comma delimited (CSV) formats]

Laboratory Reporting Level (LRL) Convention

The LRL, used with the long-term method detection level (LT–MDL) procedure, was adopted by the NWQL because of limitations of the U.S. Environmental Protection Agency (EPA) method detection limit (MDL) procedure and the use of the MDL as the reporting level—namely, the inability to adequately minimize false-negative risk when the reporting level is set equal to the detection level (Childress and others, 1999). The LT–MDL procedure was overseen initially by the NWQL and subsequently by the USGS Quality Systems Branch (QSB) LT–MDL project. The procedure primarily used blind QC samples of reagent-grade water spiked at low concentrations near the detection level to estimate the LT–MDL. In subsequent years and for some pesticide schedules, these spike-based LT–MDL determinations were supplemented by inferences from results of blind blanks and additional low-level spikes submitted to the NWQL by the QSB and sometimes by examination of NWQL set blanks (primarily for inorganic methods). For analytes with more frequent (generally greater than 20 percent) detections in blind blanks, the detection level was estimated by QSB to be the 99th percentile concentration in the set of blind blanks. Over time, the LRL convention was applied to all NWQL pesticide schedules that used gas chromatography/mass spectrometry, liquid chromatography/photodiode-array ultraviolet, and liquid chromatography/mass spectrometry methods of analysis.

The following applies to those analytes reported by using the LRL convention (fig. 1.1*A*):

- The detection level was estimated and annually verified by using the LT–MDL procedure. The LT–MDL procedure corresponds to the classic definition of "detection;" that is, detections with concentrations at the LT–MDL should, in theory, have no more than a 1-percent probability of being false-positive detections (based on detection-limit assessments using spiked reagent-water matrix).
- The National Water Information System (NWIS) reporting level code associated with the result for most method analytes was either LRL or interim reporting level (IRL). The IRL code was used for time periods when the pesticide schedule applied the LRL convention but the detection levels for some or all method analytes had not yet been or never were established or verified by using the LT–MDL procedure.
- LT–MDLs typically are higher than those previously estimated by using the EPA MDL procedure and, thus, are presumed better at reducing false-positive risk to the desired probability of 1 percent or less at the detection level.
- The LRL was set to twice the LT–MDL for most analytes. Setting the reporting level at twice the detection level has continued to be standard protocol at the NWQL for many organic analytes to the present [2019].
- For a few analytes, the LRL was set to a higher concentration because of performance considerations (for example, lower method recovery or inability to reliably achieve qualitative identification at twice the LT–MDL).

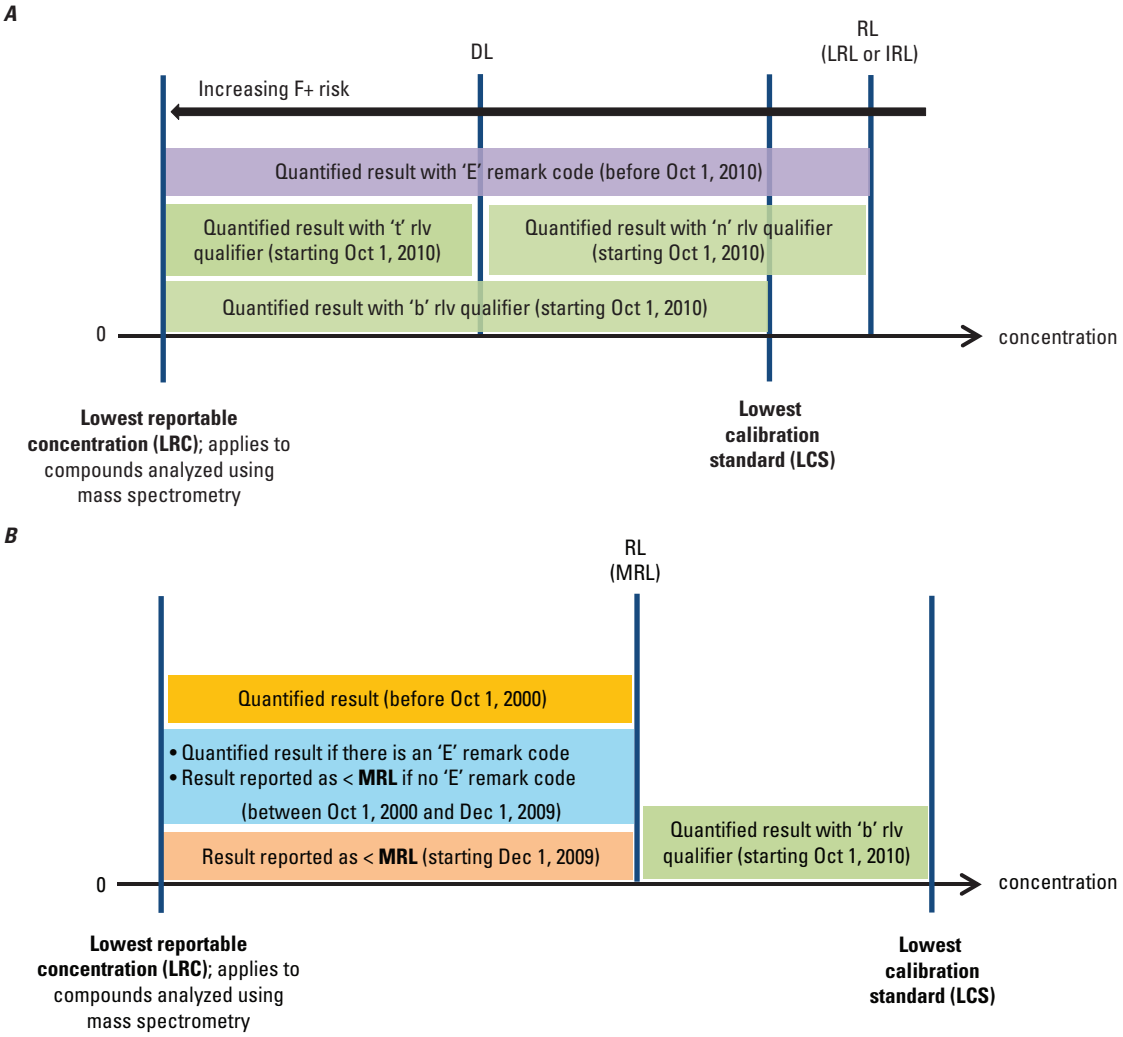

Figure 1.1. Reporting conventions at the National Water Quality Laboratory and result-level value-qualifier codes used in the National Water Information System for water-quality results that meet qualitative identification criteria when the report-level type is *A*, the laboratory or interim reporting level and *B*, the minimum reporting level. Use of result-level value-qualifier codes began October 1, 2010, for compounds analyzed by organic methods as described in U.S. Geological Survey (2010). Terms in bold type are defined in the glossary of this report.

- The LRL was designed to minimize the risks of both false positives and false negatives. The LRL corresponds to the concentration threshold at which a nondetection reported as less than the LRL in theory has no more than 1 percent probability of being a false negative (based on detection-level assessment using a reagent-water matrix and assuming an average percent analyte recovery of 100 when the LRL was set at or greater than twice the LT–MDL). U.S. Geological Survey (2010, attachment C) addresses the setting of RLs relative to false-negative risk and analyte recovery.
- Nondetections were reported as <LRL.
- Any reported results below the LRL included an estimated ("E") remark code to denote increased quantitative (not qualitative) uncertainty. The mass spectrometric detection methods have a two-part process for reporting results: identification and quantitation. The identification is based on qualitative identification criteria for chromatographic retention time and ratios of characteristic mass-spectral fragment ions. If the compound meets qualitative identification criteria, the concentration is determined and reported. Concentrations less than the detection level are usually below the lowest calibration standard, so the "E" remark was used to signify the larger potential bias in the reported concentration.
- To minimize the risk of false negatives at the LRL concentration, concentrations between the LRL and LT–MDL were reported.
- Detections meeting qualification criteria that were below the LT–MDL were reported for those methods classified as being "information rich" that use mass spectrometry (pertains to all analytes in this report) or photodiode-array ultraviolet detection.
- The threshold below which no results were reported for the information-rich methods was set to 1 percent of the detection level for most analytes. This was an arbitrarily chosen censoring threshold not mentioned in Childress and others (1999). This censoring threshold is referred to as the lowest reportable concentration (LRC) in this report.

Minimum Reporting Level (MRL) Convention

Data-reporting conventions for those compounds with reporting level code MRL (tables 1.1 to 1.5) changed over time (fig. 1.1*B*). Before implementation of the LRL convention to the pesticide methods in the 2001–04 timeframe, the reporting level for all compounds was coded and referred to by the NWQL as the MRL, with applicable pesticide method results reported using the following conventions:

- The MRL typically was set at the detection level determined by using the EPA MDL procedure as described in Childress and others (1999).
- Nondetections were reported as <MRL.
- Any detection that was less than the MRL concentration was reported, typically with inclusion of the "E" remark code.
- Reporting level type codes and reporting level values were not populated in NWIS before 2000; routine entry of this metadata began in 2001 with full implementation of NWIS version 4.1.

Once the LRL convention was implemented for a schedule, most analytes were reported by using the LRL convention. However, for a few analytes in these schedules that exhibited performance limitations (for example, detection frequency in set blanks being 20 percent or more), results were reported by using a modified MRL convention, as follows:

- NWIS report-level code is MRL (tables 1.1 to 1.5).
- The MRL was set to a value of twice the detection level or higher on the basis of other performance information, such as results from set blanks.
- Nondetections were reported as less than the MRL.
- Detections that were less than the MRL concentration were reported only if the value also included the "E" remark code; values less than the MRL without the "E" remark code were censored and reported as <MRL.

Beginning on December 1, 2009, the MRL convention was further modified for all compounds with the NWIS report-level type code MRL (U.S. Geological Survey, 2015) as follows:

- Detected values below the MRL were automatically censored by the Laboratory Information Management System (LIMS) regardless of the applied remark code and were reported as less than the MRL.
- The MRL became the smallest (lowest) concentration that is reported for the analyte.

Other Modifications to Detection-Level Determinations and Data Reporting

In 2000, the QSB began using blind-blank samples to estimate or verify detection levels, primarily for inorganic methods but also for some organic methods and analytes. Application of blind-blank results to evaluation of detection levels for analytes in the pesticide schedules was uncommon because detections in blind blanks for most pesticides were infrequent or possibly censored by the analyst on the basis of detections in the corresponding set blank. [The batch set blank is another sample-preparation set blank that is included with

the instrument batch but is distinct from the specific set blank that was prepared along with the blind-blank sample or other samples within that preparation set. For example, the blank for preparation set 2 in table 3 is considered to be the batch set blank for preparation set 1 and the blank for preparation set 1 is considered to be the batch set blank for preparation set 2.] Beginning on October 1, 2009, the LRC value was increased to 10 percent of the DL concentration for those pesticide schedules active at that time, except for compounds in NWQL schedule 2060 whose LRCs varied by analyte between eight-one-thousandths and one-quarter of the detection level.

Beginning on October 1, 2010, the NWQL implemented modifications to reporting conventions for organic methods as described in U.S. Geological Survey (2010). The modifications involved application of NWIS result-level value-qualifier codes instead of the "E" remark code to reduce the number of reasons for applying the "E" code to results (fig. 1.1). Implementation dates of these modifications can be determined in tables 1.1 to 1.5 where "2" was appended to the LRL, IRL, or MRL report-level code (the "2" was appended to these report-level codes only for results in LIMS, not in NWIS). Detections are reported as follows:

- Detections between the detection level and reporting level are reported with an "n" result-level value-qualifier code.
- Detections below the detection level are reported with a "t" result-level value-qualifier code. Only methods that use mass spectrometry (including all pesticide compounds in schedules 2001, 2003, 2032, 2033, and 2060) provide results below the detection level.
- Detections that are below the lowest calibration standard are reported with the "b" result-level value-qualifier code.

Beginning on January 1, 2012, the NWQL began routinely applying the NWIS "v" result-level value-qualifier code and "E" remark code to results, where applicable, to denote that the concentration might be influenced by detections in corresponding set blanks as detailed in U.S. Geological Survey (2011).

In June 2012, the NWQL terminated annual evaluations and verifications of detection levels using the LT–MDL procedure and began exploring alternative procedures for estimating detection levels. In October 2013, the NWQL expanded the use of the "i" result-level value-qualifier code (i-code) for all analyses performed by the NWQL, especially for organic methods. The i-code is used when the result may be affected by interference (Dupré and others, 2013, app. A, table 11). The i-code is applied to a reported detection when the quantitative measurement includes a contribution from sources other than the target analyte. Interferences typically add to a measurement. Thus, results with i-codes could be biased high (positive bias), although steps taken by an analyst to minimize the effect of the interference on the measured area (response) of a chromatographic peak, for example, might result in a negative bias. Use of the i-code is not contingent upon knowing the source of the interference. Potential sources of interferences are the sample matrix, an unknown compound, a known compound, or an electronic noise. The "E" remark code is included with the reported concentration whenever the i-code is applied. The i-code is applied under conditions when instrument (signal) interference affects a measurement, thereby introducing a likely result bias. The analyst is confident in the qualitative identification of the compound but uncertain about the quantitative reliability of the result. Application of the i-code for nondetections adheres to the following conventions:

- For situations when the measured result is above the compound's reporting level but the compound's qualitative identification cannot be confirmed because of signal interference, the result can include both the "less than" (<) remark code and the i-code to denote interference. This is a raised reporting level scenario (fig. 2), and the result is interpreted as a nondetection at this elevated level.
- If a qualitatively uncertain result is subject to interference but the concentration is below the RL, the i-code is not applied. This is the conventional, nondetected result. Although reporting a less-than reporting level (raised or not) is interpreted as a nondetection, it does not mean that the analyte was not present in the sample at a lower concentration.

In March 2014, the NWQL began a phased implementation of the ASTM International (2013) standard D7782–13 (multiconcentration procedure for estimating detection levels) and use of the associated calculator DQCALC (detailed in the ASTM International standard D7510–10(2016)e1; ASTM International, 2016). In June 2015, the NWQL released Technical Memorandum 2015.02 (U.S. Geological Survey, 2015), which describes and defines the following:

- Implementation of ASTM D7782–13 (previously D6091–07) and DQCALC and their relation to the LT–MDL and MDL; the new NWIS detection-level code is DLDQC.
- Expanded use of set-blank data to either establish detection levels or verify detection levels determined by using spike-based procedures for those analytes frequently detected in set blanks; the new NWIS blank-based detection-level code is DLBLK.
- Similar to determination of the LT–MDL, the detection and reporting levels are reevaluated annually by using either of or both the new detection-level procedures; changes, if needed, generally are implemented at the start of the water year (October).

New NWIS reporting level codes and corresponding data-reporting conventions include the following:

- New reporting level codes relevant to the pesticide schedules are RLDQC and RLBLK for schedules or

analytes where the detection level is established or verified by using DQCALC or blank-based procedures, respectively.

- Reporting conventions for RLDQC and RLBLK follow those used by the LRL convention and continue use of the NWIS result-level value-qualifier codes (b, i, n, t, and v).
- Some blank-limited analytes coded as DLBLK might be reported by using the MRL convention instead of the RLBLK convention, where nondetections and detections below the MRL concentration are reported as <MRL.
- As of January 2018, pesticide schedule 2437 has been the only pesticide schedule evaluated by using the DQCALC and blank-based detection-level procedures. All schedule 2437 analytes currently are reported by using reporting level code RLDQC. Evaluation of other pesticide schedules is pending.

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U.S. Geological Survey, 2015, Changes to National Water Quality Laboratory (NWQL) procedures used to establish and verify laboratory detection and reporting limits: U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 2015.02, accessed December 19, 2017, at https://nwql.usgs.gov/tech_memos/nwql.2015-02.pdf.

Appendix 2. Documentation by the National Water Quality Laboratory for the Reload of Data for Analytical Schedule 2060

Rapi-Notes are the mechanism used by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) to disseminate information internally to USGS users of water-quality data. Information in Rapi-Notes is not typically available to the public. Documentation for data (Riskin and others, 2019) used in this report related to the data reload for analytical schedule 2060 is found in Rapi-Note 07–005 (fig. 2.1) and in the associated information on changes to specific analytes (fig. 2.2) reloaded in the National Water Information System (U.S. Geological Survey, 2017). Hyperlinks in the original documents are disabled.

References Cited

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U.S. Geological Survey, 2017, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed December 27, 2017, at https://doi.org/10.5066/F7P55KJN.

Date: March 6, 2007

Subject: Analyte Changes Summary for 2060 Reload

This Rapi-Note is additional information relating to Rapi-Note 06-020 that was issued on June 27, 2006 which finalized the 2060 reload of data.

The NWQL has summarized the analytical changes for the 2060 compounds that were reloaded on June 27, 2006. The summary can be found on the NWQL's Technical Information web page, under Schedules and has the header "Analyte Reporting Information Changes for 2060 Reload Compounds" (http://wwwnwql.cr.usgs.gov/USGS/rapi-notes/2060AnalyteInformation.pdf).

If your Water Science Center has not applied the reload in Rapi-Note 06-020, please do so and send a notice of completion to labhelp@usgs.gov. The WSCs will need to process the reload files into their respective NWIS database per the instructions found in the Attachment. Since some samples go back to 2002, the "override DQI" option must be used. If you cannot find the files, please contact labhelp@usgs.gov to request the files be placed on your server for processing.

Attachment: Processing the Reload into NWIS Version 4.6.

Please check that your reload status is correct on the NWQL Reload web page. If you have processed the reload and the status page does not show it, please email your corrected status to labhelp@usgs.gov.

The NWQL has modified the Sample Status page to show the original and reloaded (updated) results for samples that were involved in the 2060 reload. The 2060 analytes are under the 'pst2' (pesticides 2) link. The "Result" and "Final Result" fields are the original (pre-reload) results. The "Updated NWISREM" and "Updated NWISVAL" fields are the reloaded results.

Examples of analyte changes to look for are:

- Results that originally had an "E" on the "Final Result" and did not have an "E" after the reload
- Results that originally did not have an "E" on the "Final Result" and did have an "E" after the reload

Figure 2.1. U.S. Geological Survey Rapi-Note 07-005, Dated March 6, 2007, on Analyte Changes Summary for Data Reload for Analytical Schedule 2060.

Analyte Changes for 2060 Reload Compounds

October 1, 2006

Date range of the reload: 08-01-2002 thru 03-31-2006

NWIS User Manual – Appendix A. Codes Used in Water-Quality Processing System – http://wwwnwis.er.usgs.gov/currentdocs/qw/QW-AppxA.pdf

Definition requested – Table Number in above link – Definition – Description
NWIS definition for remark code "E" – (Table 10) – Estimated Value – Value is estimated.
NWIS definition for value qualifier "m" – (Table 16) – Value is highly variable by this method –
Highly variable compound using this method, questionable precision and (or) accuracy.
Citation of OFR or NWQL Technical Memo in result comment.
NWIS definition for value qualifier "v" – (Table 16) – Analyte detected in laboratory blank –
Analyte detected in laboratory blank

Reload criteria(s) by parameter code.

Parameter code: 04029 (Bromacil)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 04029 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.033 µg/L
Any value less than 0.003 will be reported as < 0.033
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.018 µg/L
Any value below 0.003 will be reported as <0.018
Detected values greater than or equal to 0.003 and less than 0.018 will have an 'E' code
Detected values greater than or equal to 0.018 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 04031 (Cycloate)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.

Comment of ‘The parameter 04031 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.013 µg/L
Any value less than 0.003 will be reported as < 0.013
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.014 µg/L
Any value below 0.003 will be reported as <0.014
Detected values greater than or equal to 0.003 and less than 0.014 will have an ‘E’ code
Detected values greater than or equal to 0.014 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results prior to 4/1/2006

Parameter code: 04032 (Terbacil)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 04032 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0098 µg/L
Any value less than 0.003 will be reported as < 0.0098
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 10/1/2004 to 3/31/2006
Action: Laboratory Report Level (LRL) = 0.016 µg/L
Any value below 0.003 will be reported as <0.016
Detected values greater than or equal to 0.003 and less than 0.016 will have an ‘E’ code
Detected values greater than or equal to 0.016 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 4/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.026 µg/L
Any value below 0.003 will be reported as <0.026
Detected values greater than or equal to 0.003 and less than 0.026 will have an ‘E’ code
Detected values greater than or equal to 0.026 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'

Parameter code: 04038 (2-Chloro-6-ethylamino-4-amino-s-triazine, {CEAT} aka Deisopropylatrazine)

Date range: 8/1/2002 to 6/30/2004
Action: Interim Report Level (IRL) = 0.044 µg/L
Any value below 0.003 will be reported as <0.044
Detected values greater than or equal to 0.003 and less than 0.044 will have an 'E' code
Detected values greater than or equal to 0.044 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 7/01/2004 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 04038 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.01 µg/L
Any value less than 0.003 will be reported as < 0.01
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/01/2004 to 12/31/2005
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 04038 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.08 µg/L
Any value less than 0.003 will be reported as < 0.08
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 01/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.08 µg/L
Any value below 0.003 will be reported as <0.08
Detected values greater than or equal to 0.003 and less than 0.08 will have an 'E' code
Detected values greater than or equal to 0.08 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Parameter code: 04039 (Chlordiamino-s-triazine, {CAAT} aka Deethyldeisopropyl atrazine)

Date range: 8/1/2002 to 3/31/2006

Action: Any result will have a result qualifier of 'v' added, and a comment of 'detected in lab blank'
Values above Report Level Value should have an 'E' remark code and a value qualifier of 'm' and a
Comment of 'The parameter 04039 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Method Report Level (MRL) = 0.04 µg/L
All detections below the MRL will be set to <0.04
Detected values greater than or equal to 0.04 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 04/1/2006 to present

Action: Laboratory Report Level (LRL) = 0.04 µg/L
Any value below 0.022 will be reported as <0.04
Detected values greater than or equal to 0.022 and less than 0.04 will have an 'E' code
Detected values greater than or equal to 0.04 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 04040 (2-Chloro-4-isopropylamino-6-amino-s-triazine, {CIAT} aka Deethylatrazine)

Date range: 8/1/2002 to 9/30/2004

Action: Interim Report Level (IRL) = 0.0282 µg/L
Any value below 0.003 will be reported as <0.0282
Detected values greater than or equal to 0.003 and less than 0.0282 will have an 'E' code
Detected values greater than or equal to 0.0282 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to present

Action: Laboratory Report Level (LRL) = 0.028 µg/L
Any value below 0.003 will be reported as <0.028
Detected values greater than or equal to 0.003 and less than 0.028 will have an 'E' code
Detected values greater than or equal to 0.028 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Parameter code: 38487 (MCPB)

Date range: 8/1/2002 to 9/30/2004
- Action: Interim Report Level (IRL) = 0.015 µg/L
- Any value below 0.003 will be reported as <0.015
- Detected values greater than or equal to 0.003 and less than 0.015 will have an 'E' code
- Detected values greater than or equal to 0.015 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to 3/31/2006
- Action: Laboratory Report Level (LRL) = 0.01 µg/L
- Any value below 0.003 will be reported as <0.01
- Detected values greater than or equal to 0.003 and less than 0.01 will have an 'E' code
- Detected values greater than or equal to 0.01 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 4/1/2006 to present
- Action: Method Report Level (MRL) = 0.10 µg/L
- All detections below the MRL will be set to <0.10
- Detected values greater than or equal to 0.10 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any bench 'E' remark codes remain 'E'
- Any bench '<' values will remain '<'

Parameter code: 38501 (Methiocarb)

Date range: 8/1/2002 to 9/30/2004
- Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
- Comment of 'The parameter 38501 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
- Interim Report Level (IRL) = 0.008 µg/L
- Any value less than 0.003 will be reported as < 0.008
- Detected values greater than or equal to 0.003 will have an 'E' remark code
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to 3/31/2006
- Action: Laboratory Report Level (LRL) = 0.01 µg/L
- Any value below 0.003 will be reported as <0.01
- Detected values greater than or equal to 0.003 and less than 0.01 will have an 'E' code
- Detected values greater than or equal to 0.01 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 4/1/2006 to present:
Action: Laboratory Report Level (LRL) = 0.034 µg/L
Any value below 0.003 will be reported as <0.034
Detected values greater than or equal to 0.003 and less than 0.034 will have an ‘E’ code
Detected values greater than or equal to 0.034 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Parameter code: 38711 (Bentazon)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 38711 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.011 µg/L
Any value less than 0.003 will be reported as < 0.011
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 10/1/2004 to 3/31/2006
Action: Laboratory Report Level (LRL) = 0.012 µg/L
Any value below 0.003 will be reported as <0.012
Detected values greater than or equal to 0.003 and less than 0.012 will have an ‘E’ code
Detected values greater than or equal to 0.012 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 4/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.024 µg/L
Any value below 0.003 will be reported as <0.024
Detected values greater than or equal to 0.003 and less than 0.024 will have an ‘E’ code
Detected values greater than or equal to 0.024 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Parameter code: 38746 (2,4-DB)

Date range: 8/1/2002 to 9/30/2004
- Action: Interim Report Level (IRL) = 0.016 µg/L
- Any value below 0.003 will be reported as <0.016
- Detected values greater than or equal to 0.003 and less than 0.016 will have an 'E' code
- Detected values greater than or equal to 0.016 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to present
- Action: Laboratory Report Level (LRL) = 0.02 µg/L
- Any value below 0.003 will be reported as <0.02
- Detected values greater than or equal to 0.003 and less than 0.02 will have an 'E' code
- Detected values greater than or equal to 0.02 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 38866 (Oxamyl)

Date range: 8/1/2002 to 9/30/2004
- Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
- Comment of 'The parameter 38866 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
- Interim Report Level (IRL) = 0.0122 µg/L
- Any value less than 0.003 will be reported as < 0.0122
- Detected values greater than or equal to 0.003 will have an 'E' remark code
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to 3/31/2006
- Action: Laboratory Report Level (LRL) = 0.03 µg/L
- Any value below 0.003 will be reported as <0.03
- Detected values greater than or equal to 0.003 and less than 0.03 will have an 'E' code
- Detected values greater than or equal to 0.03 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'

Date range: 4/1/2006 to present
- Action: Laboratory Report Level (LRL) = 0.05 µg/L
- Any value below 0.003 will be reported as <0.05
- Detected values greater than or equal to 0.003 and less than 0.05 will have an 'E' code
- Detected values greater than or equal to 0.05 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Any value > or equal to 1 will have 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 49292 (Oryzalin)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49292 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0176 µg/L
Any value less than 0.003 will be reported as < 0.0176
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to 3/31/2006
Action: Laboratory Report Level (LRL) = 0.012 µg/L
Any value below 0.003 will be reported as <0.012
Detected values greater than or equal to 0.003 and less than 0.012 will have an 'E' code
Detected values greater than or equal to 0.012 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 4/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.023 µg/L
Any value below 0.003 will be reported as <0.023
Detected values greater than or equal to 0.003 and less than 0.023 will have an 'E' code
Detected values greater than or equal to 0.023 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 49293 (Norflurazon)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49293 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.016 µg/L
Any value less than 0.003 will be reported as < 0.016
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.02 µg/L
Any value below 0.003 will be reported as <0.02
Detected values greater than or equal to 0.003 and less than 0.02 will have an 'E' code
Detected values greater than or equal to 0.02 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 49296 (Methomyl)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49296 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0044 µg/L
Any value less than 0.003 will be reported as < 0.0044
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to 3/31/2006
Action: Laboratory Report Level (LRL) = 0.02 µg/L
Any value below 0.003 will be reported as <0.02
Detected values greater than or equal to 0.003 and less than 0.02 will have an 'E' code
Detected values greater than or equal to 0.02 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 4/1/2006 to present
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49296 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.07 µg/L
Any value below 0.003 will be reported as <0.07
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 49297 (Fenuron)

Date range: 8/1/2002 to 9/30/2004
Action: Any result will have a result qualifier of 'v' added, and a comment of 'detected in lab blank'

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Values above Report Level Value should have an ‘E’ remark code and a value qualifier of ‘m’ and a
Comment of ‘The parameter 49297 is a highly variable compound in schedule 12060’ for each result Method Report Level (MRL) = 0.019 µg/L
All detections below the MRL will be set to <0.019
Detected values greater than or equal to 0.019 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 10/1/2004 to 3/31/2006
Action: Method Report Level (MRL) = 0.019 µg/L
All detections below the MRL will be set to <0.019
Detected values greater than or equal to 0.019 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results

Date range: 4/1/2006 to present
Action: Method Report Level (MRL) = 0.10 µg/L
Any value less than 0.10 will be reported as <0.10
Detected values greater than or equal to 0.10 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Parameter code: 49300 (Diuron)

Date range: 8/1/2002 to 3/31/2006
Action: Any result will have a result qualifier of ‘v’ added, and a comment of ‘detected in lab blank’
Method Report Level (MRL) = 0.015 µg/L
All detections below the MRL will be set to <0.015
Detected values greater than or equal to 0.015 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any bench ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results prior to 4/1/2006

Date range: 4/1/2006 to present
Action: Method Report Level (MRL) = 0.016 µg/L
All detections below the MRL will be set to <0.016
Detected values greater than or equal to 0.016 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Parameter code: 49301 (Dinoseb)

Date range: 8/1/2002 to 9/30/2004
- Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
- Comment of 'The parameter 49301 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
- Interim Report Level (IRL) = 0.012 µg/L
- Any value less than 0.003 will be reported as < 0.012
- Detected values greater than or equal to 0.003 will have an 'E' remark code
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to present
- Action: Laboratory Report Level (LRL) = 0.038 µg/L
- Any value below 0.003 will be reported as <0.038
- Detected values greater than or equal to 0.003 and less than 0.038 will have an 'E' code
- Detected values greater than or equal to 0.038 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
- Any value > or equal to 1 will have 'E' remark code
- Any original 'E' remark codes from the bench remained 'E'
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 49306 (Chlorothalonil)

Date range: 8/1/2002 to 12/31/2005
- Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
- Comment of 'The parameter 49306 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
- Interim Report Level (IRL) = 0.035 µg/L
- Any value less than 0.003 will be reported as < 0.035
- Detected values greater than or equal to 0.003 will have an 'E' remark code
- Any original '<' values will remain '<'
- Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 1/1/2006 to present
- Action: Dropped compound from schedule.

Parameter code: 49311 (Bromoxynil)

Date range: 8/1/2002 to 9/30/2004
- Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
- Comment of 'The parameter 49311 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
- Interim Report Level (IRL) = 0.017 µg/L
- Any value less than 0.003 will be reported as < 0.017
- Detected values greater than or equal to 0.003 will have an 'E' remark code
- Any original '<' values will remain '<'

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to 3/31/2006

Action: Laboratory Report Level (LRL) = 0.028 µg/L
Any value below 0.003 will be reported as <0.028
Detected values greater than or equal to 0.003 and less than 0.028 will have an 'E' code
Detected values greater than or equal to 0.028 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Date range: 4/1/2006 to present

Action: Laboratory Report Level (LRL) = 0.044 µg/L
Detected values greater than or equal to 0.003 and less than 0.044 will have an 'E' code
Detected values greater than or equal to 0.044 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 49312 (Aldicarb)

Date range: 8/1/2002 to 3/31/2006

Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49312 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.04 µg/L
Any value less than 0.003 will be reported as < 0.04
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Date range: 4/1/2006 to present

Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49312 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (MRL) = 0.015 µg/L
All detections below the MRL will be set to <0.015
Detected values greater than or equal to 0.015 will have an 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'

Parameter code: 49313 (Aldicarb sulfone)

Date range: 8/1/2002 to 9/30/2004

Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Comment of 'The parameter 49313 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.02 µg/L
Any value less than 0.003 will be reported as < 0.02
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.018 µg/L
Any value below 0.003 will be reported as <0.018
Detected values greater than or equal to 0.003 and less than 0.018 will have an 'E' code
Detected values greater than or equal to 0.018 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 49314 (Aldicarb sulfoxide)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49314 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0082 µg/L
Any value less than 0.003 will be reported as < 0.0082
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 10/1/2004 to 3/31/2006
Action: Laboratory Report Level (LRL) = 0.022 µg/L
Any value below 0.003 will be reported as <0.022
Detected values greater than or equal to 0.003 and less than 0.022 will have an 'E' code
Detected values greater than or equal to 0.022 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Date range: 4/1/2006 to present
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 49314 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.10 µg/L
Any value below 0.003 will be reported as <0.10
Detected values greater than or equal to 0.003 will have an 'E' remark code

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Parameter code: 50295 (3-Ketocarbofuran)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 50295 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.014 µg/L
Any value less than 0.003 will be reported as < 0.014
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 10/1/2004 to 12/31/2005
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 50295 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.02 µg/L
Any value less than 0.003 will be reported as < 0.02
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 1/1/2006 to present
Action: Dropped compound from schedule.

Parameter code: 50300 (Benomyl)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 50300 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0038 µg/L
Any value less than 0.003 will be reported as < 0.0038
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.022 µg/L
Any value below 0.003 will be reported as <0.022
Any value below 0.003 will be reported as <0.022
Detected values greater than or equal to 0.003 and less than 0.022 will have an ‘E’ code
Detected values greater than or equal to 0.022 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 50306 (Chlorimuron-ethyl)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50306 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0096 µg/L
Any value less than 0.003 will be reported as < 0.0096
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50306 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.032 µg/L
Any value less than 0.003 will be reported as < 0.032
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 50355 (2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine, {OIET} aka Hydroxyatrazine)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50355 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.008 µg/L
Any value less than 0.003 will be reported as < 0.008
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.032 µg/L
Any value below 0.003 will be reported as <0.032
Detected values greater than or equal to 0.003 and less than 0.032 will have an 'E' code
Detected values greater than or equal to 0.032 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 50356 (Imazaquin)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50356 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.016 µg/L
Any value less than 0.003 will be reported as < 0.016
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50356 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.036 µg/L
Any value less than 0.003 will be reported as < 0.036
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 50364 (Nicosulfuron)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50364 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.013 µg/L
Any value less than 0.003 will be reported as < 0.013
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to 12/31/2005
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50364 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Laboratory Report Level (LRL) = 0.04 µg/L
Any value less than 0.003 will be reported as < 0.04
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Date range: 1/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.04 µg/L
Any value below 0.003 will be reported as <0.04
Detected values greater than or equal to 0.003 and less than 0.04 will have an 'E' code
Detected values greater than or equal to 0.04 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any bench 'E' remark codes remain 'E'
Any bench '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 50407 (Imazethapyr)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 50407 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.017 µg/L
Any value less than 0.003 will be reported as < 0.017
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.038 µg/L
Any value below 0.003 will be reported as <0.038
Detected values greater than or equal to 0.003 and less than 0.038 will have an 'E' code
Detected values greater than or equal to 0.038 and < 1 will not have an 'E' remark code (unless the 'E' came from the bench)
Any value > or equal to 1 will have 'E' remark code
Any original 'E' remark codes from the bench remained 'E'
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results prior to 4/1/2006

Parameter code: 61188 (Chloramben, methyl ester)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an 'E' remark code, a value qualifier of 'm', and a
Comment of 'The parameter 61188 is a highly variable compound in schedule 12060' for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.018 µg/L
Any value less than 0.003 will be reported as < 0.018
Detected values greater than or equal to 0.003 will have an 'E' remark code
Any original '<' values will remain '<'
Comment of 'NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006' added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.024 µg/L
Any value below 0.003 will be reported as <0.024

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Detected values greater than or equal to 0.003 and less than 0.024 will have an ‘E’ code
Detected values greater than or equal to 0.024 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results prior to 4/1/2006

Parameter code: 61693 (Bensulfuron-methyl)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 61693 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.0158 µg/L
Any value less than 0.003 will be reported as < 0.0158
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.018 µg/L
Any value below 0.003 will be reported as <0.018
Detected values greater than or equal to 0.003 and less than 0.018 will have an ‘E’ code
Detected values greater than or equal to 0.018 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results prior to 4/1/2006

Parameter code: 61694 (Flumetsulam)

Date range: 8/1/2002 to 9/30/2004
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 61694 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.011 µg/L
Any value less than 0.003 will be reported as < 0.011
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 10/1/2004 to present
Action: Laboratory Report Level (LRL) = 0.04 µg/L
Any value below 0.003 will be reported as <0.04

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Detected values greater than or equal to 0.003 and less than 0.04 will have an ‘E’ code
Detected values greater than or equal to 0.04 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘E’ remark codes from the bench remained ‘E’
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results prior to 4/1/2006

Parameter code: 61697 (Metsulfuron methyl)

Date range: 8/1/2002 to 12/31/2005
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 61697 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Interim Report Level (IRL) = 0.025 µg/L
Any value less than 0.003 will be reported as < 0.025
Detected values greater than or equal to 0.003 will have an ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 1/1/2006 to present
Action: All detected values should have an ‘E’ remark code, a value qualifier of ‘m’, and a
Comment of ‘The parameter 61697 is a highly variable compound in schedule 12060’ for all results (12060 is schedule 2060)
Method Report Level (MRL) = 0.067 µg/L
All detections below the MRL will be set to < 0.067
Detected values greater than or equal to 0.067 will have an ‘E’ remark code

Parameter code: 82670 (Tebuthiuron)

Date range: 8/1/2002 to 3/31/2006;
Action: Any result will have a result qualifier of ‘v’ added, and a comment of ‘detected in lab blank’
Method Report Level (MRL) = 0.026 µg/L
All detections below the MRL will be set to <0.026
Detected values greater than or equal to 0.026 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any original ‘<’ values will remain ‘<’
Comment of ‘NWQL Tech Memo 2005.03, NWQL Rapi-Note 06-006’ added to all results
Date range: 4/1/2006 to present
Action: Laboratory Report Level (LRL) = 0.026 µg/L Any value below 0.013 will be reported as <0.026
Detected values greater than or equal to 0.013 and less than 0.026 will have an ‘E’ code
Detected values greater than or equal to 0.026 and < 1 will not have an ‘E’ remark code (unless the ‘E’ came from the bench)
Any value > or equal to 1 will have ‘E’ remark code
Any bench ‘E’ remark codes remain ‘E’
Any bench ‘<’ values will remain ‘<’

Figure 2.2. Information for Specific Analytes Processed by the U.S. Geological Survey National Water Quality Laboratory Under Analytical Schedule 2060.—Continued

Appendix 3. Additional Considerations for Using Pesticide Data of the National Water Quality Laboratory

This appendix lists considerations for choosing a reporting level or other censoring threshold to apply to U.S. Geological Survey National Water Quality Laboratory (NWQL) data. General areas of additional consideration pertain to limiting the probability of false-positive and false-negative reporting of results, as specified in project-specific data-quality objectives (U.S. Environmental Protection Agency, 2006).

1. If the data-quality objectives for the project include a high-priority concern for limiting the probability of false-positive detections to the standard probability of no more than 1 percent, then data can be censored to the detection level that directly meets that criterion. For pesticides without detections in set blanks, that level is the long-term method detection limit (LT–MDL; or the detection limit calculated by the DQCALC software [DLDQC] and phased in beginning during 2014). The LT–MDL is half of the laboratory reporting level (LRL; or the reporting limit calculated by the DQCALC software [RLDQC]) for many analytes. For pesticides that have detections in set blanks, it may be necessary to use blank data to determine a detection level that likely would be higher than the LT–MDL (or DLDQC). NWQL Technical Memorandum 2015.02 (U.S. Geological Survey, 2015) outlines the approaches the NWQL uses to calculate a blank-based detection level (coded as DLBLK).

2. If the data-quality objectives for the project include a high-priority concern to limit the false-positive risk to well below 1 percent (this is different from the LT–MDL or DQCALC procedure listed above), then data can be censored to a higher concentration than the LT–MDL, such as the reporting level.

3. If the data-quality objectives for the project include a high-priority concern for limiting the probability of false negatives to the standard probability of no more than 1 percent, then results between the reporting level and the detection level also must be used. If those results are not used, simply censoring all results to less than the reporting level will not provide a false-negative probability of less than or equal to 1 percent. This is because the distribution of measured concentrations will not all lie at or above the reporting level when the true concentration is at the reporting level (U.S. Geological Survey, 2010, attachment C).

4. If the data-quality objectives for the project include a high-priority concern for limiting the probability of false positives to much less than 1 percent and for limiting false negatives to the standard probability of no more than 1 percent, then the first step is to choose a higher concentration to use as both the reporting level and detection level. A factor greater than two as the difference between the detection and reporting levels would further ensure a false-negative risk of less than or equal to 1 percent.

5. If the objectives of the project are to cast a wide net for determining what pesticides may be in groundwater or surface water, and if having a false-positive rate greater than 1 percent meets the data-quality objectives, then it is appropriate to use reported results with no additional censoring. For datasets that span multiple years, an additional consideration is how to handle multiple detection and reporting levels over time.

Some examples of applications of various censoring thresholds are as follows:

- Censor data below the highest reporting level. This is one of the most conservative approaches and would likely unnecessarily remove valid results. It also creates a high false-negative risk, which is unavoidable when applying this censoring scenario (for example, Paul and others, 2007).

- Use the most common detection level and reporting level in the dataset as criteria for determining which data (if any) to censor (for example, Medalie and Martin, 2016, fig. 4).

- Keep all detections as reported and provide detection frequencies using different censoring levels (for example, Toccalino and others, 2014).

- Keep all data and employ statistical tools for computing concentration statistics (median and percentile concentrations) such as the Kaplan-Meier method on left-censored data (Helsel, 2012). Such statistical methods involve no assumptions about the underlying distribution of a dataset and can handle complex datasets with multiple reporting levels and detected concentrations that are less than the reporting level (for example, Heckathorn and Deetz, 2012; Berndt and Crandall, 2009).

- Consider a variety of ancillary information when evaluating pesticide detections, including the land use in the vicinity of the collected sample, pesticide usage practices, the presence of additional manmade contaminants, and so on. For groundwater samples, information such as well depth, well type, and groundwater age also are important explanatory factors for evaluating contaminant detections. For surface-water samples, flow rates, seasonality, and other factors contribute towards the overall assessment of pesticide occurrence. These approaches generally are appropriate for

evaluating low-level detections after the sample data have undergone reviews of long-term laboratory and field QC data and where some evidence leads the data analyst to believe that the sample in question should not show that the analyte is present.

- Censor data on the basis of study objectives that strive to balance a conservative approach (such as to censor data below the highest reporting level) with preservation of data for trends analysis (for example, Ryberg and others, 2010; Oelsner and others, 2017).

- Censor data based on characterization of laboratory contamination (detections in set blanks). If laboratory contamination is not random and is not sufficiently addressed with existing censoring to meet specific project data-quality objectives, additional censoring could be applied to environmental samples for dates when the moving average detection frequency in set blanks is greater than a user-designated threshold such as 5 or 10 percent (for example, Fram and Belitz, 2011; or a modified Fram and Belitz approach described in "Objective 1: Determine the Characteristics of Laboratory Contamination Over Time" of the "Methods" section of this report). For data users who prefer to follow the modified Fram and Belitz approach described in this report and who might not have access to information about which analytical schedule is associated with environmental data, a conservative approach for defining periods of episodic laboratory contamination for the compounds analyzed with gas chromatography/mass spectrometry methods based on this study is to consider episodes such as those identified for analytical schedule 2001 from May 2001 through June 2005 and for analytical schedule 2033 from June 2005 through April 2016; the selection of those compounds is because the majority of environmental samples were determined by these schedules during those periods. The attribute "schedule" is included with environmental and set-blank data in Riskin and others (2019); however, the analytical schedule is generally not part of the data retrieved through the National Water Information System (https://waterdata.usgs.gov/) or the Water Quality Portal (https://www.waterqualitydata.us/).

- Establish a censoring threshold using a binomial probability method based on one-sided, nonparametric upper confidence limits. First, a desired probability of reporting results for environmental samples without false-positive detections and a confidence level in that probability are defined. Then, a binomial distribution is used to calculate the number of field blanks (or set blanks) in a dataset of field or set blanks that must be uncontaminated in order to meet the desired probability and confidence level (for example, Olsen and others [2010], Fram and others [2012]).

- Establish a censoring threshold equal to or greater than three times (U.S. Geological Survey, 2011) the maximum concentration (or a high percentile, such as the 95th or 99th) in field blanks, or in the set blank during periods of episodic contamination.

- Censor environmental detections below the MRL because for results produced after October 1, 2000, the MRL type of reporting level was generally used by the NWQL to indicate performance limitations (app. 1).

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Appendix 4. Policy and Guidance on Making Changes to Laboratory Results in the QWDATA Subsystem of the National Water Information System

United States Department of the Interior

U.S. GEOLOGICAL SURVEY
Reston, VA 20192

In Reply Refer
To: Mail Stop 412

April 21, 2017

OFFICE OF WATER QUALITY TECHNICAL MEMORANDUM 2017.05
SUBJECT: Policy and guidance on making changes to laboratory results in the QWDATA Subsystem (QWDATA) of the National Water Information System (NWIS)

Purpose:

This memorandum reiterates the U.S. Geological Survey (USGS) and Office of Water Quality (OWQ) policies, practices, and procedures that data reviewers and approvers in USGS Water Science Centers (Centers) should follow in reviewing and changing laboratory results in QWDATA. These rules are important because NWISWeb, the publicly available version of NWIS, does not fully track changes made by USGS in QWDATA. These policies help protect public users of NWISWeb from retrieving different versions of laboratory data with minimal explanation as to why the changes were made.

Policy

OWQ Technical Memorandum (TM) 2008.05 requires that original scientific data be stored in NWIS for archival and other purposes. Follow USGS and OWQ policies and procedures on data management when laboratory results are reviewed for quality-control purposes prior to approval in QWDATA. Follow OWQ TM 2017.03 on documenting data revisions and changes applied after data have been approved.

By definition, the results from a synthesis of non-interpretive data are interpretive data when new findings are reached (Survey Manual, SM 502.8). QWDATA is a USGS approved database and should contain only non-interpretive scientific data. USGS Fundamental Science Practices provide definitions of non-interpretive and interpretive data and the appropriate outlets for their publication, respectively (SM 205.18).

1. Laboratory results stored in QWDATA should not be changed by data reviewers and approvers in Centers based on interpretation of laboratory and/or field quality-control results collected over time, but should remain as non-interpretive scientific data. Regardless of the outlet used for release of interpreted data, the laboratory data upon which they are based should be stored as appropriate in QWDATA, where they should appear as originally reported by the laboratory in almost all circumstances.

   For example, data reviewers and approvers may seek to change laboratory results in QWDATA based on analysis of laboratory and field quality-control data sets collected over time. The changes would address concerns that public users of NWISWeb may retrieve results that are either at or below the method reporting level (RL) for selected methods.

USGS reporting conventions allow for reporting laboratory results below the RL if data are created using information-rich laboratory methods (as defined in Childress and others, 1999). As a remedy for these concerns, some Centers have sought to add a less than remark code (<) and/or to raise the concentration value to the laboratory RL (for example changing E0.1 to <0.1 or <1). Both changes would alter the original laboratory result in QWDATA.

The recommended approach to report interpreted data as described in the preceding example should be in data-series reports, open-file reports, supplemental materials, data releases, and other approved information products with appropriate supporting analyses and metadata (SM 1100.3, Appendix A).

2. The specific circumstances under which a data reviewer or approver in a USGS Center may change result-level laboratory data in QWDATA are identified in two OWQ technical memoranda. Only under the following conditions should data reviewers and approvers in USGS Centers make changes to result-level laboratory data and metadata in QWDATA.

   In the event that any of these conditions warrant a change to QWDATA, the Center must investigate the source of the problem and take corrective action so that changes to laboratory results in QWDATA are rare.

   a. OWQ TM 1997.08 identifies the case of systematic or incidental field contamination. Use a "V" remark code with a laboratory result when there is documented evidence that sample results are directly affected by field contamination. However, the associated concentration (value) should *not* be changed in QWDATA. V-coded data are released to the public in NWISWeb.

      In practice, a V remark code indicates that the sample result can be used with caution for some purposes. For example, a V-coded result that is well below that of a water-quality criterion may still be useful for comparison to the criterion even though the sample result may not meet the original objectives of the project for which it was collected and analyzed.

   b. OWQ TM 2002.15 describes "poor-quality" results that are misleading about environmental conditions. In this case, the result would lead to incorrect data interpretations in all cases. These results may necessitate use of the Data Quality Indicator (DQI) code "Q" in QWDATA. All results identified as "poor quality" using the Q code need to have additional information stored with the results in QWDATA describing why the quality was considered poor. The Q code indicates that the results have been reviewed and rejected. Q-coded results are not released to the public in NWISWeb.

      For example, the Q code is used when a dilution error at the laboratory is suspected because results are outside what was expected but a rerun of the laboratory analysis is not possible. If a sample container was compromised in shipment and noted as such when received at the laboratory, the Q code can be used. Strong evidence of a laboratory or field mix-up due to sample labeling errors also may indicate an appropriate use of the Q code. This is indicated by anomalous results showing that the expected sample type was not received by the laboratory.

Guidance

Techniques and Methods Book 4, Chapter C4 (TM4-C4) "Design, Analysis, and Interpretation of Field Quality-Control Data for Water-Sampling Projects" provides guidance on how to analyze and report quality-control data and associated water-quality results. TM4-C4 stresses the importance of not changing sample results in QWDATA based on analysis of field blanks and other types of quality-control data (Mueller and others, 2015, p. 19, 45). This report provides several examples of how field blank contamination, for example, can be described in a data- series report.

Other Remedies

To help public users understand the reporting conventions used with data produced at the NWQL and other laboratories, the following italicized statement will be added to the NWISWeb Water-Quality Data help system for public data retrievals:

Prior to 2010, the USGS reported sample values below the reporting level (RL) from selected information-rich laboratory methods with the "E" or "estimated" remark code. The E remark code was assigned to sample values because even though the identification criterion was met, the quantitation was estimated. Since 2010, reported values below the RL are remarked with an "n" value qualifier code indicating that the value is below the RL but at or above the detection level. A "t" value qualifier code indicates that the value is below the detection level. The t value qualifier code is reported only for selected information-rich methods. Concentrations reported below the RL have an increased risk (>1 percent) of being a false positive, even for information- rich methods that provide enhanced analyte identification capabilities. Additional information on RL procedures are available from the USGS in Office of Water Quality Technical Memorandum 2010.07 and National Water Quality Laboratory Technical Memorandum 2015.02.

Future modernization of QWDATA and NWISWeb may provide for versioning and tracking of changes to laboratory results in QWDATA. Until that time, the policy and guidelines outlined in this OWQ TM will remain in effect.

If you have questions or concerns about this policy or know of data that have been changed in QWDATA, please contact the OWQ through the representative of the Water-Quality User Group (pmruhl@usgs.gov) or the Water Science Field Team (Callie Oblinger, oblinger@usgs.gov; Tim Oden, toden@usgs.gov; Michael Rosen, mrosen@usgs.gov; or Lisa Olsen, ldolsen@usgs.gov).

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References:

Fundamental Science Practices - Distinctions between New Research or Interpretive Information Products, Previously Published or Noninterpretive Information Products, and Scientific Data. This Web page provides definitions of non-interpretive and interpretive scientific data used by the Bureau. Available at https://www2.usgs.gov/fsp/interpretive_definitions_and_examples.asp

Mueller, D.K., Schertz, T.L., Martin, J.D., and Sandstrom, M.W., 2015, Design, analysis, and interpretation of field quality-control data for water-sampling projects: U.S. Geological Survey Techniques and Methods book 4, chapter C4, 54 p., Available at http://dx.doi.org/10.3133/tm4C4.

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Office of Water Quality Technical Memorandum 2017.03. Procedures for Identifying and Documenting Revisions to USGS Water Data. This memo establishes new policy and procedures to identify and document revisions to U.S. Geological Survey (USGS) approved time-series and discrete water data. Available at https://water.usgs.gov/admin/memo/QW/qw2017.03.pdf

Survey Manual 1100.3 - U.S. Geological Survey Publication Series. The purpose of this chapter is to define general policies and requirements governing the use of the U.S. Geological Survey (USGS) publication series. Available at https://www2.usgs.gov/usgs- manual/1100/1100-3.html

Survey Manual 205.18 – Authority to Approve Information Products. This policy makes a distinction related to approval authority between New Research or Interpretive Information Products and Previously Published or Noninterpretive Information Products. Available at https://www2.usgs.gov/usgs-manual/200/205-18.html

Survey Manual 502.8 – Fundamental Science Practices: Review and Approval of Scientific Data for Release (SM 502.8). This chapter provides requirements and procedures for review and approval of U.S. Geological Survey (USGS) scientific data prior to release. Available at: https://www2.usgs.gov/usgs-manual/500/502-8.html

Figure 4.1. U.S. Geological Survey Office of Water Quality Technical Memorandum 2017.05, dated April 21, 2017, on policies, practices, and procedures that data reviewers and approvers in the USGS should follow in reviewing and changing laboratory results in the water-quality subsystem (QWDATA) of the National Water Information System (NWIS).

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