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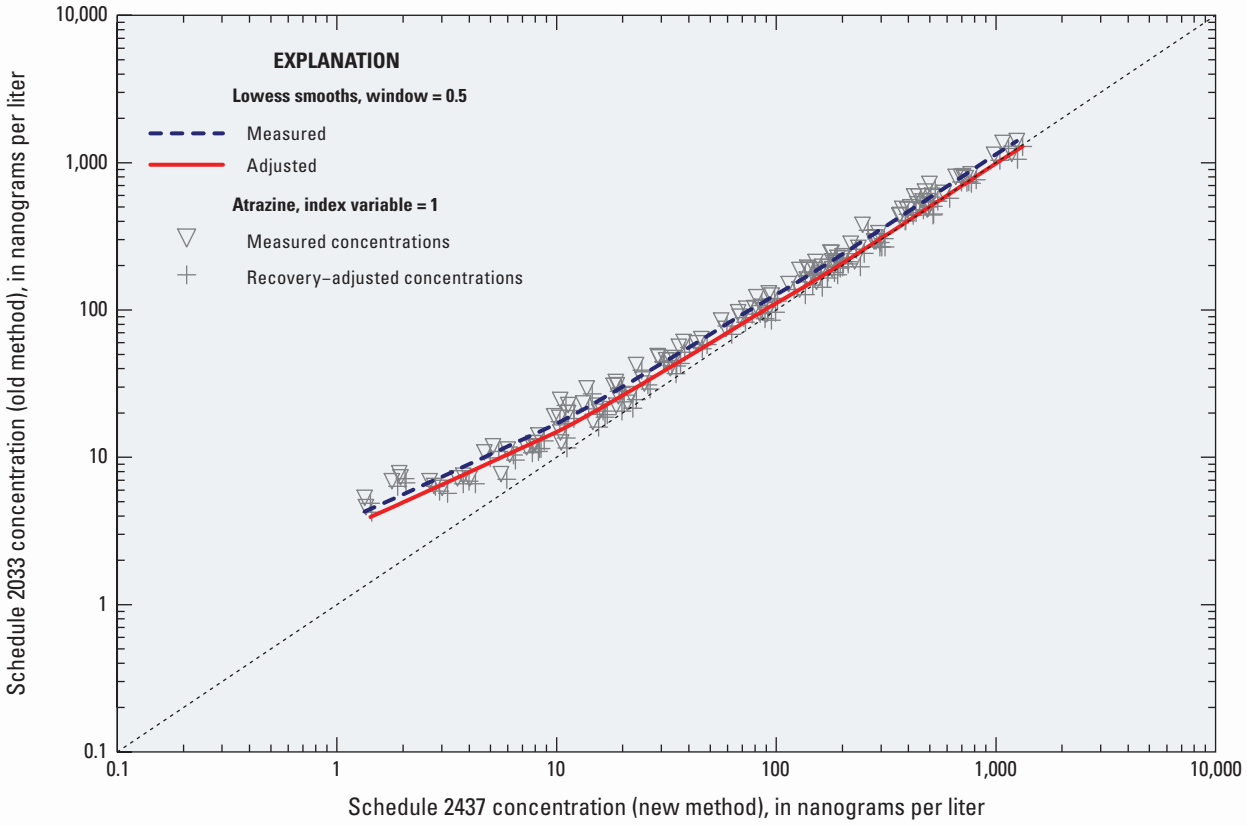
National Water-Quality Assessment

A Field Study of Selected U.S. Geological Survey Analytical Methods for Measuring Pesticides in Filtered Stream Water, June–September 2012



Scientific Investigations Report 2017–5049

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

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U.S. Department of the Interior
RYAN K. ZINKE, Secretary

U.S. Geological Survey
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U.S. Geological Survey, Reston, Virginia: 2017

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Foreword

Sustaining the quality of the Nation's water resources and the health of our diverse ecosystems depends on the availability of sound water-resources data and information to develop effective, science-based policies. Effective management of water resources also brings more certainty and efficiency to important economic sectors. Taken together, these actions lead to immediate and long-term economic, social, and environmental benefits that make a difference to the lives of the almost 400 million people projected to live in the United States by 2050.

In 1991, Congress established the National Water-Quality Assessment (NAWQA) to address where, when, why, and how the Nation's water quality has changed, or is likely to change in the future, in response to human activities and natural factors. Since then, NAWQA has been a leading source of scientific data and knowledge used by national, regional, State, and local agencies to develop science-based policies and management strategies to improve and protect water resources used for drinking water, recreation, irrigation, energy development, and ecosystem needs (https://water.usgs.gov/nawqa/applications/). Plans for the third decade of NAWQA (2013–23) address priority water-quality issues and science needs identified by NAWQA stakeholders, such as the Advisory Committee on Water Information and the National Research Council, and are designed to meet increasing challenges related to population growth, increasing needs for clean water, and changing land-use and weather patterns.

U.S. Geological Survey monitoring programs extensively used two analytical methods, gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry, to measure pesticides in filtered water samples during 1992–2012. In October 2012, the monitoring programs began using direct aqueous-injection liquid chromatography tandem mass spectrometry as a new analytical method for pesticides. A field study was designed to document performance of the new method in a variety of stream-water matrices and to quantify any potential changes in measurement bias or variability that could be attributed to changes in analytical methods. The results of the field study identified several challenges for the analysis and interpretation of data produced by both old and new methods, particularly when data span the change in methods and are combined for analysis of temporal trends in water quality. All NAWQA reports are available online at https://water.usgs.gov/nawqa/bib/.

We hope this publication will provide you with insights and information to meet your water-resource needs and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters. The information in this report is intended primarily for those interested or involved in resource management and protection, conservation, regulation, and policymaking at the regional and national levels.

Dr. Donald W. Cline
Associate Director for Water
U.S. Geological Survey

Contents

Figures

Tables

Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
microliter (µL)	0.3882×10^{-4}	ounce, fluid (fl. oz)
	Mass	
microgram (µg)	0.3527×10^{-7}	ounce, avoirdupois (oz)
nanogram (ng)	0.3527×10^{-10}	ounce, avoirdupois (oz)

Supplemental Information

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

Abbreviations

ASR	analytical services request form
BQS	Branch of Quality Systems
DAI	direct aqueous-injection
GC–MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatograph
LC–MS	liquid chromatography/mass spectrometry
LC–MS/MS	liquid chromatography tandem mass spectrometry
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
NFM	National Field Manual
NMN	National Monitoring Network
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OBW	organic blank water
QA	quality assurance
QC	quality control
RSD	relative standard deviation
SD	standard deviation
USGS	U.S. Geological Survey

A Field Study of Selected U.S. Geological Survey Analytical Methods for Measuring Pesticides in Filtered Stream Water, June–September 2012

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Abstract

U.S. Geological Survey monitoring programs extensively used two analytical methods, gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry, to measure pesticides in filtered water samples during 1992–2012. In October 2012, the monitoring programs began using direct aqueous-injection liquid chromatography tandem mass spectrometry as a new analytical method for pesticides. The change in analytical methods, however, has the potential to inadvertently introduce bias in analysis of datasets that span the change.

A field study was designed to document performance of the new method in a variety of stream-water matrices and to quantify any potential changes in measurement bias or variability that could be attributed to changes in analytical methods. The goals of the field study were to (1) summarize performance (bias and variability of pesticide recovery) of the new method in a variety of stream-water matrices; (2) compare performance of the new method in laboratory blank water (laboratory reagent spikes) to that in a variety of stream-water matrices; (3) compare performance (analytical recovery) of the new method to that of the old methods in a variety of stream-water matrices; (4) compare pesticide detections and concentrations measured by the new method to those of the old methods in a variety of stream-water matrices; (5) compare contamination measured by field blank water samples in old and new methods; (6) summarize the variability of pesticide detections and concentrations measured by the new method in field duplicate water samples; and (7) identify matrix characteristics of environmental water samples that adversely influence the performance of the new method. Stream-water samples and a variety of field quality-control samples were collected at 48 sites in the U.S. Geological Survey monitoring networks during June–September 2012. Stream sites were located across the United States and included sites in agricultural and urban land-use settings, as well as sites on major rivers.

The results of the field study identified several challenges for the analysis and interpretation of data analyzed by both old and new methods, particularly when data span the change in methods and are combined for analysis of temporal trends in water quality. The main challenges identified are large (greater than 30 percent), statistically significant differences in analytical recovery, detection capability, and (or) measured concentrations for selected pesticides. These challenges are documented and discussed, but specific guidance or statistical methods to resolve these differences in methods are beyond the scope of the report. The results of the field study indicate that the implications of the change in analytical methods must be assessed individually for each pesticide and method.

Understanding the possible causes of the systematic differences in concentrations between methods that remain after recovery adjustment might be necessary to determine how to account for the differences in data analysis. Because recoveries for each method are independently determined from separate reference standards and spiking solutions, the differences might be due to an error in one of the reference standards or solutions or some other basic aspect of standard procedure in the analytical process. Further investigation of the possible causes is needed, which will lead to specific decisions on how to compensate for these differences in concentrations in data analysis. In the event that further investigations do not provide insight into the causes of systematic differences in concentrations between methods, the authors recommend continuing to collect and analyze paired environmental water samples by both old and new methods. This effort should be targeted to seasons, sites, and expected concentrations to supplement those concentrations already assessed and to compare the ongoing analytical recovery of old and new methods to those observed in the summer and fall of 2012.

Introduction

The National Water-Quality Assessment (NAWQA) and National Stream Quality Accounting Network (NASQAN) are U.S. Geological Survey (USGS) monitoring programs that measure pesticide concentrations in the Nation's streams and rivers, herein collectively referred to as streams. NAWQA began monitoring pesticides in 1992 and NASQAN began monitoring pesticides in 1995. The programs were recently

merged to form the USGS National Water Quality Network for Rivers and Streams. Water samples are analyzed for pesticides by the USGS National Water Quality Laboratory (NWQL) using methods developed by the NWQL's Methods Research and Development team. Two analytical methods for pesticides, gas chromatography/mass spectrometry (GC–MS) and liquid chromatography/mass spectrometry (LC–MS), were historically used to measure pesticides in filtered water samples. In October 2012, both programs changed analytical methods and began using a new analytical method for pesticides. The new analytical method is direct aqueous-injection (DAI) liquid chromatography tandem mass spectrometry (LC–MS/MS). The new analytical method (DAI LC–MS/MS) has many advantages over the previously used methods, including small sample volumes, no sample preparation or extraction procedures, and many more pesticides and pesticide degradates analyzed (Sandstrom and others, 2015, p. 46). The change in analytical methods, however, has the potential to inadvertently introduce bias in analysis of datasets that span the change.

Purpose and Scope

A field study was designed and implemented to help assess potential measurement bias between old and new analytical methods. A variety of environmental and quality-control water samples were collected by field teams during summer and fall of 2012 and were submitted for analyses by both old and new analytical methods. This report statistically assesses measurement bias and variability of the analytical methods during summer and fall of 2012, describes general patterns of bias and variability between methods, and provides detailed information in tables and appendixes for the hundreds of pesticides assessed. In addition, datasets supporting this analysis are provided in Martin and Baker (2017).

Study Design and Methods

This section describes pesticide analytical methods and schedules, the design of the field study, compilation and review of data, and calculations and statistical methods used to summarize and compare analytical results from the three pesticide methods.

Pesticide Analytical Methods and Schedules

The USGS monitoring programs have extensively used two analytical methods (GC–MS and LC–MS) to measure pesticides and pesticide degradates (hereafter called pesticides) in water from 1992 to 2012. USGS field teams select the analytical method for the samples they submit by requesting NWQL analytical "schedules," which are specific lists of pesticides that are analyzed by particular types of instrumentation and methods (Timme, 1995, p. 22). Knowledge of the NWQL schedule is particularly important for the GC–MS method because, even though the analytical method is the same, the particular lists of pesticides measured changes among the schedules.

The most widely used method was GC–MS, where pesticides are isolated from 1-liter filtered water samples by solid-phase extraction and analyzed by capillary-column GC–MS with selected-ion monitoring (Zaugg and others, 1995; Lindley and others, 1996; Madsen and others, 2003). This version of the GC–MS method is known as NWQL schedule 2001, provides measurements of 52 pesticides, and was used primarily from 1992 to 2004. In 1999, the same GC–MS analytical techniques and instrumentation were used to measure 77 different pesticides (Sandstrom and others, 2001). This version of the GC–MS method is known as NWQL schedule 2002 and it had moderate use from 1999 to 2003. Subsequent GC–MS schedules combined pesticides from NWQL schedules 2001 and 2002. NWQL schedule 2003 (64 pesticides) was used primarily in 2003–05 and NWQL schedule 2033 (83 pesticides) was used primarily from 2005 to 2012. Schedule 2033 is the version of the GC–MS method used in this report.

The second most widely used method was LC–MS, where pesticides are isolated from 1-liter filtered water samples by graphitized carbon-based solid-phase extraction and analyzed by liquid chromatography with electrospray ionization/mass spectrometry (Furlong and others, 2001). The LC–MS method is known as NWQL schedule 2060, provides measurements of 60 pesticides, and was used primarily from 1999 to 2012.

The new analytical method is direct aqueous-injection liquid chromatography tandem mass spectrometry (DAI LC–MS/MS) (Sandstrom and others, 2015). Unlike the old methods, the new analytical method only requires a 20-milliliter filtered sample. No other sample preparation procedures (extraction) other than filtration are required, so differences in bias and variability were expected. The DAI method is known as NWQL schedule 2437, provides measurements of 119 pesticides and 120 pesticide degradates, and has been used as the primary analytical method since October 2012. Subsequent to the field study and final method approval by USGS, 12 analytes were deleted from the new method for poor performance (U.S. Geological Survey, 2015). Data for these poor-performing analytes are presented in this report and these poor-performing analytes are identified in table 5.[1]

The three analytical methods discussed in this report do not have specified "detection limits" for each pesticide analyte. Compounds detected and conclusively identified by retention time and mass spectral characteristics are quantified and reported (Zaugg and others, 1995, p. 19–21; Furlong and others, 2001, p. 37; Sandstrom and others, 2015, p. 17). Nondetections of pesticides (analyses that do not meet identification criteria based on retention time and mass

[1]The three relevant schedules for the field study will be abbreviated as sh2033, sh2060, and sh2437 in the subsequent text.

spectral characteristics) are reported as less than the reporting level for that method and analyte (for example, less than [<] 5 nanograms per liter [ng/L]). The numerical values of the reporting levels are method- and analyte-specific and are based on estimates of the Long-Term Method Detection Level (Childress and others, 1999; Sandstrom and others, 2015, p. 21–22). Reporting levels may change through time, typically at the start of the water year, in response to changes in the ability of the method to quantify low-level concentrations in laboratory reagent-water spikes. Reporting levels for sh2437 typically are similar to those for sh2033 but are smaller than those for sh2060. A small number of environmental samples have "matrix effects" (characteristics of the environmental water sample) or other analytical difficulties that interfere with the measurement of pesticide retention time or mass spectral characteristics. Under conditions of interference, pesticides (1) cannot be identified/detected if they are present at concentrations less than the level of interference and (2) are reported as nondetections less than a "raised" reporting level (for example, <30 ng/L, six times greater than the reporting level discussed above). Nondetections at raised reporting levels indicate the maximum possible concentration of the pesticide that could be present based on the magnitude of the interference.

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

Pesticide data quality is routinely monitored by the collection of field QC samples. Field QC procedures are presented in Mueller and others (1997) and require the collection of field blank water samples, field replicate (duplicate) water samples, and field matrix-spike water samples. Data quality for the GC–MS method for selected periods has been published previously. Contamination in field blank water samples was summarized for 1992–95 in Martin and others (1999). Variability of pesticide detections and concentrations in field replicate water samples was summarized for 1992–97 in Martin (2002). Pesticide recovery in laboratory reagent spikes and field matrix spikes was summarized for 1992–2006 in Martin and others (2009) and for 1992–2010 in Martin and Eberle (2011). Field QC assessments for the LC–MS method have not been published.

Method Comparison Field Study

Changes in analytical methods may introduce changes in data quality. A field study was designed to document performance of the new method in a variety of stream-water matrices and to quantify any potential changes in measurement bias or variability that could be attributed to changes in analytical methods. The goals of the field study were to (1) summarize performance (bias and variability of pesticide recovery) of the new method in a variety of stream-water matrices; (2) compare performance of the new method in laboratory blank water (laboratory reagent spikes) to that in a variety of stream-water matrices; (3) compare performance of the new method (sh2437) to that of the old methods (sh2033 and sh2060) in a variety of stream-water matrices; (4) compare pesticide detections and concentrations measured by the new method to those of the old methods in a variety of stream-water matrices; (5) compare contamination measured by field blank water samples in old and new methods; (6) summarize the variability of pesticide detections and concentrations measured by the new method in field duplicate water samples; and (7) identify matrix characteristics of environmental water samples that adversely influence the performance of the new method.

Stream-water samples were collected at 48 sites in the USGS monitoring network during June–September 2012. Stream sites were located across the United States and included sites in agricultural and urban land-use settings, as well as sites on major rivers and reference sites (fig. 1, tables 1 and 2). Most sites were sampled on three dates (site visits) for a total of 150 site visits (table 3). Instructions for the collection and processing of the field-study samples are provided in appendix 1.

For each site visit, a single, large-volume water sample was collected and processed into three sets of two samples (an environmental sample and a matrix spike). A method-specific spike solution (100 microliters [µL]) was added to each matrix spike sample. The three sets of samples were then analyzed, each by one of the three analytical methods—sh2437, sh2033, and sh2060. At one site visit for each site, additional QC samples were collected: (1) three field blank water samples (one for each analytical method), (2) a duplicate environmental water sample for analysis by sh2437, and (3) a duplicate field matrix spike for analysis by sh2437.[2]

Spiking typically increased the concentration of pesticides by approximately 0.1 microgram per liter (µg/L) in sh2033 samples, by 0.25 µg/L in sh2060 samples, and by 250 ng/L (0.25 µg/L) in sh2437 samples. The types of water samples, analytical schedules, and data-management strategy for samples collected for the field study are described in table 4.

[2]Except for the section "Variability of Pesticides Analyzed by Schedule 2437," duplicate water samples and duplicate field matrix spikes were not used in statistical summaries or tests to avoid biasing results to the specific sites and conditions when the duplicates were collected.

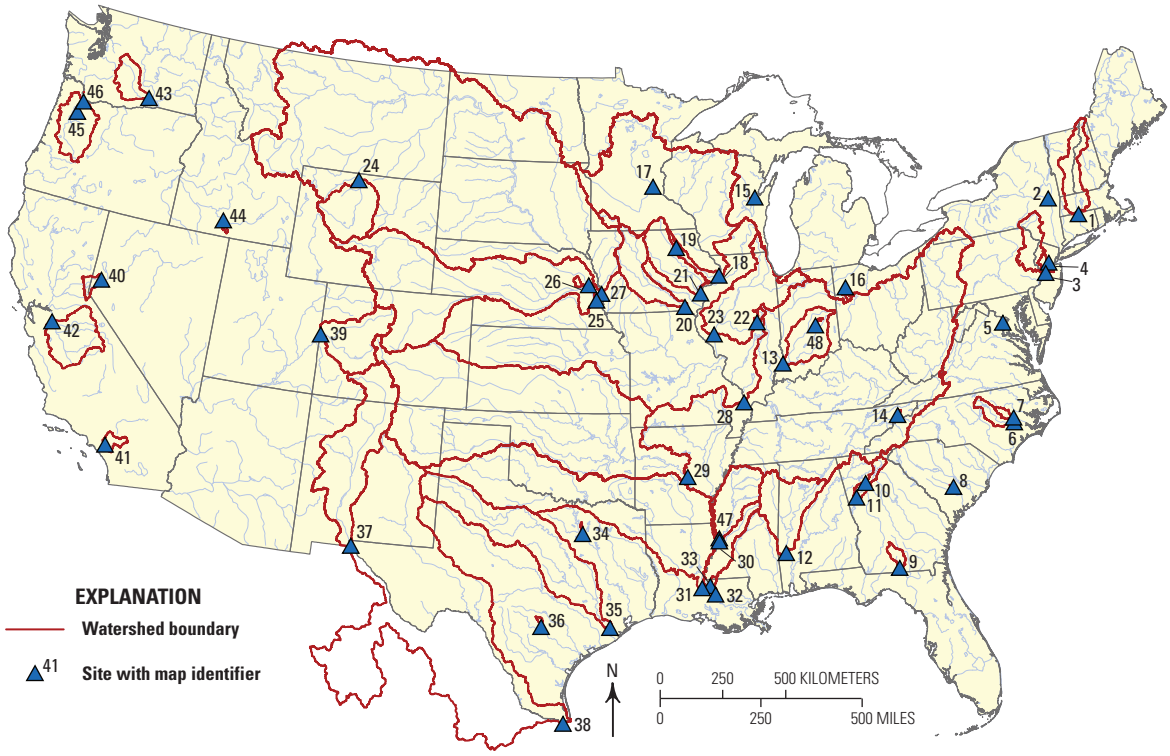

Figure 1. Location of stream-water sites selected for the field study.

Table 1. National Water-Quality Assessment study-unit identifiers.

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

Table 2. Stream-water sites selected for the field study.

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. CT., Connecticut; NY, New York; NJ, New Jersey; VA, Virginia; NC, North Carolina; SC, South Carolina; US, United States; GA, Georgia; R, river; BL, below; L&D, lock and dam; IN, Indiana; TN, Tennessee; WI, Wisconsin; OH, Ohio; MN, Minnesota; IA, Iowa; IL, Illinois; WY, Wyoming; NE, Nebraska; NEBR., Nebraska; @, at; AR, Arkansas; NR, near; MS, Mississippi; ST., Saint; LA, Louisiana; (COE), Corps of Engineers; RV, River; TX, Texas; CK, creek; NV, Nevada; CA, California; WA, Washington; AB, above; HWY, Highway; XING, crossing; ID, Idaho; MT, Mount; OR, Oregon; CO RD, county road; S, south]

Map number (fig. 1)	Station number	Study unit[1] abbreviation (table 1)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
1	01184000	CONN	MIXED	9,660	CONNECTICUT RIVER AT THOMPSONVILLE, CT.
2	01356190	HDSN	URBAN	16	LISHA KILL NORTHWEST OF NISKAYUNA NY
3	01403300	LINJ	MIXED	804	RARITAN RIVER AT QUEENS BRIDGE AT BOUND BROOK NJ
4	01463500	DELR	MIXED	6,780	DELAWARE RIVER AT TRENTON NJ
5	01654000	PODL	URBAN	24	ACCOTINK CREEK NEAR ANNANDALE, VA
6	02089500	ALBE	MIXED	2,692	NEUSE RIVER AT KINSTON, NC
7	02091500	ALBE	MIXED	733	CONTENTNEA CREEK AT HOOKERTON, NC
8	02174250	SANT	AG	23	COW CASTLE CREEK NEAR BOWMAN, SC
9	02318500	GAFL	MIXED	1,480	WITHLACOOCHEE RIVER AT US 84 NEAR QUITMAN, GA
10	02335870	ACFB	URBAN	31	SOPE CREEK NEAR MARIETTA, GA
11	02338000	ACFB	MIXED	2,430	CHATTAHOOCHEE RIVER NEAR WHITESBURG, GA
12	02469762	MOBL	MIXED	18,417	TOMBIGBEE R BL COFFEEVILLE L&D NEAR COFFEEVILLE
13	03374100	WHMI	MIXED	11,305	WHITE RIVER AT HAZLETON, IN
14	03466208	TENN	AG	79	BIG LIMESTONE CREEK NEAR LIMESTONE, TN
15	04072050	WMIC	AG	96	DUCK CREEK AT SEMINARY ROAD NEAR ONEIDA, WI
16	04186500	LERI	AG	332	AUGLAIZE RIVER NEAR FORT JENNINGS OH
17	05288705	UMIS	URBAN	28	SHINGLE CREEK AT QUEEN AVE IN MINNEAPOLIS, MN
18	05420500	NSQN	OTHER	85,600	MISSISSIPPI RIVER AT CLINTON, IA
19	05420680	EIWA	AG	346	WAPSIPINICON RIVER NEAR TRIPOLI, IA
20	05465500	EIWA	MIXED	12,500	IOWA RIVER AT WAPELLO, IA
21	05490500	EIWA	OTHER	14,038	DES MOINES RIVER AT KEOSAUQUA, IA
22	05572000	LIRB	AG	550	SANGAMON RIVER AT MONTICELLO, IL
23	05586100	LIRB	MIXED	26,743	ILLINOIS RIVER AT VALLEY CITY, IL
24	06279500	YELL	MIXED	15,762	BIGHORN RIVER AT KANE, WY
25	06610000	NSQN	OTHER	322,800	MISSOURI RIVER AT OMAHA, NE
26	06800000	CNBR	AG	368	MAPLE CREEK NEAR NICKERSON, NEBR.
27	06805500	CNBR	MIXED	85,370	PLATTE RIVER AT LOUISVILLE, NEBR.
28	07022000	NSQN	OTHER	713,200	MISSISSIPPI RIVER AT THEBES, IL
29	07263620	NSQN	OTHER	158,429	AR RIVER@DAVID D TERRY L&D BELOW LITTLE ROCK, AR
30	07288955	MISE	MIXED	13,355	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
31	07373420	NSQN	OTHER	1,125,300	MISSISSIPPI R NR ST. FRANCISVILLE, LA
32	07374000	NSQN	OTHER	1,125,810	MISSISSIPPI RIVER AT BATON ROUGE, LA
33	07381495	NSQN	OTHER	93,316	(COE) ATCHAFALAYA RIVER AT MELVILLE, LA
34	08057410	TRIN	MIXED	6,278	TRINITY RV BL DALLAS, TX
35	08116650	NSQN	OTHER	45,339	BRAZOS RV NR ROSHARON, TX
36	08178800	SCTX	URBAN	189	SALADO CK AT LOOP 13, SAN ANTONIO, TX
37	08364000	RIOG	MIXED	32,210	RIO GRANDE AT EL PASO, TX
38	08475000	NSQN	OTHER	176,333	RIO GRANDE NR BROWNSVILLE, TX

Table 2. Stream-water sites selected for the field study.—Continued

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. CT., Connecticut; NY, New York; NJ, New Jersey; VA, Virginia; NC, North Carolina; SC, South Carolina; US, United States; GA, Georgia; R, river; BL, below; L&D, lock and dam; IN, Indiana; TN, Tennessee; WI, Wisconsin; OH, Ohio; MN, Minnesota; IA, Iowa; IL, Illinois; WY, Wyoming; NE, Nebraska; NEBR., Nebraska; @, at; AR, Arkansas; NR, near; MS, Mississippi; ST., Saint; LA, Louisiana; (COE), Corps of Engineers; RV, River; TX, Texas; CK, creek; NV, Nevada; CA, California; WA, Washington; AB, above; HWY, Highway; XING, crossing; ID, Idaho; MT, Mount; OR, Oregon; CO RD, county road; S, south]

Map number (fig. 1)	Station number	Study unit[1] abbreviation (table 1)	Drainage basin land-use class	Drainage area (square miles)	Name of stream-water site
39	09163500	UCOL	MIXED	17,849	COLORADO RIVER NEAR COLORADO-UTAH STATE LINE
40	10350340	NVBR	MIXED	1,580	TRUCKEE RV NR TRACY, NV
41	11074000	SANA	MIXED	2,258	SANTA ANA R BL PRADO DAM CA
42	11303500	SANJ	MIXED	13,536	SAN JOAQUIN R NR VERNALIS CA
43	12510500	CCYK	MIXED	5,615	YAKIMA RIVER AT KIONA, WA
44	13092747	USNK	AG	259	ROCK CREEK AB HWY 30/93 XING AT TWIN FALLS ID
45	14201300	WILL	AG	15	ZOLLNER CREEK NEAR MT ANGEL, OR
46	14211720	WILL	MIXED	11,200	WILLAMETTE RIVER AT PORTLAND, OR
47	322023090544500	NSQN	OTHER		MISSISSIPPI RIVER ABOVE VICKSBURG AT MILE 438, MS
48	394340085524601	WHMI	AG	93	SUGAR CREEK AT CO RD 400 S AT NEW PALESTINE, IN

[1]National Stream Quality Accounting Network sites are coded "NSQN."

Table 3. Site-visit sequence number for graphs in figures 6 and 8.

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. GA, Georgia; NC, North Carolina; WA, Washington; NEBR., Nebraska; CT., Connecticut; NJ, New Jersey; IA, Iowa; US, United States; NY, New York; OH, Ohio; IL, Illinois; BL, below; NR, near; MS, Mississippi; R, river; L&D, lock and dam; NE, Nebraska; @, at; AR, Arkansas; ST., Saint; LA, Louisiana; COE, Corps of Engineers; RV, River; TX, Texas; NV, Nevada; VA, Virginia; CA, California; SC, South Carolina; CK, Creek; TN, Tennessee; MN, Minnesota; AB, above; HWY, Highway; XING, crossing; ID, Idaho; IN, Indiana; CO RD, County Road; S, south; MT, Mount; OR, Oregon; WI, Wisconsin; WY, Wyoming]

Site-visit sequence number	Map number (fig. 1)	Study unit[1] abbreviation (table 1)	Station number	Date of site visit (month/day/year)	Name of stream-water site
1	10	ACFB	02335870	6/27/2012	SOPE CREEK NEAR MARIETTA, GA
2	10	ACFB	02335870	7/25/2012	SOPE CREEK NEAR MARIETTA, GA
3	10	ACFB	02335870	8/23/2012	SOPE CREEK NEAR MARIETTA, GA
4	11	ACFB	02338000	7/10/2012	CHATTAHOOCHEE RIVER NEAR WHITESBURG, GA
5	11	ACFB	02338000	8/9/2012	CHATTAHOOCHEE RIVER NEAR WHITESBURG, GA
6	11	ACFB	02338000	9/6/2012	CHATTAHOOCHEE RIVER NEAR WHITESBURG, GA
7	6	ALBE	02089500	7/10/2012	NEUSE RIVER AT KINSTON, NC
8	6	ALBE	02089500	8/9/2012	NEUSE RIVER AT KINSTON, NC
9	6	ALBE	02089500	9/4/2012	NEUSE RIVER AT KINSTON, NC
10	7	ALBE	02091500	7/10/2012	CONTENTNEA CREEK AT HOOKERTON, NC
11	7	ALBE	02091500	8/9/2012	CONTENTNEA CREEK AT HOOKERTON, NC
12	7	ALBE	02091500	9/4/2012	CONTENTNEA CREEK AT HOOKERTON, NC
13	43	CCYK	12510500	7/10/2012	YAKIMA RIVER AT KIONA, WA
14	43	CCYK	12510500	8/6/2012	YAKIMA RIVER AT KIONA, WA
15	43	CCYK	12510500	9/5/2012	YAKIMA RIVER AT KIONA, WA
16	26	CNBR	06800000	6/27/2012	MAPLE CREEK NEAR NICKERSON, NEBR.
17	26	CNBR	06800000	7/24/2012	MAPLE CREEK NEAR NICKERSON, NEBR.

Table 3. Site-visit sequence number for graphs in figures 6 and 8.—Continued

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. GA, Georgia; NC, North Carolina; WA, Washington; NEBR., Nebraska; CT., Connecticut; NJ, New Jersey; IA, Iowa; US, United States; NY, New York; OH, Ohio; IL, Illinois; BL, below; NR, near; MS, Mississippi; R, river; L&D, lock and dam; NE, Nebraska; @, at; AR, Arkansas; ST., Saint; LA, Louisiana; COE, Corps of Engineers; RV, River; TX, Texas; NV, Nevada; VA, Virginia; CA, California; SC, South Carolina; CK, Creek; TN, Tennessee; MN, Minnesota; AB, above; HWY, Highway; XING, crossing; ID, Idaho; IN, Indiana; CO RD, County Road; S, south; MT, Mount; OR, Oregon; WI, Wisconsin; WY, Wyoming]

Site-visit sequence number	Map number (fig. 1)	Study unit[1] abbreviation (table 1)	Station number	Date of site visit (month/day/year)	Name of stream-water site
18	26	CNBR	06800000	8/21/2012	MAPLE CREEK NEAR NICKERSON, NEBR.
19	26	CNBR	06800000	9/4/2012	MAPLE CREEK NEAR NICKERSON, NEBR.
20	27	CNBR	06805500	7/11/2012	PLATTE RIVER AT LOUISVILLE, NEBR.
21	27	CNBR	06805500	8/9/2012	PLATTE RIVER AT LOUISVILLE, NEBR.
22	27	CNBR	06805500	9/5/2012	PLATTE RIVER AT LOUISVILLE, NEBR.
23	1	CONN	01184000	7/10/2012	CONNECTICUT RIVER AT THOMPSONVILLE, CT.
24	1	CONN	01184000	8/2/2012	CONNECTICUT RIVER AT THOMPSONVILLE, CT.
25	1	CONN	01184000	9/4/2012	CONNECTICUT RIVER AT THOMPSONVILLE, CT.
26	4	DELR	01463500	7/11/2012	DELAWARE RIVER AT TRENTON NJ
27	4	DELR	01463500	8/9/2012	DELAWARE RIVER AT TRENTON NJ
28	4	DELR	01463500	9/5/2012	DELAWARE RIVER AT TRENTON NJ
29	19	EIWA	05420680	6/25/2012	WAPSIPINICON RIVER NEAR TRIPOLI, IA
30	19	EIWA	05420680	7/23/2012	WAPSIPINICON RIVER NEAR TRIPOLI, IA
31	19	EIWA	05420680	8/27/2012	WAPSIPINICON RIVER NEAR TRIPOLI, IA
32	20	EIWA	05465500	7/10/2012	IOWA RIVER AT WAPELLO, IA
33	20	EIWA	05465500	8/2/2012	IOWA RIVER AT WAPELLO, IA
34	20	EIWA	05465500	9/5/2012	IOWA RIVER AT WAPELLO, IA
35	21	EIWA	05490500	7/6/2012	DES MOINES RIVER AT KEOSAUQUA, IA
36	21	EIWA	05490500	8/8/2012	DES MOINES RIVER AT KEOSAUQUA, IA
37	21	EIWA	05490500	9/6/2012	DES MOINES RIVER AT KEOSAUQUA, IA
38	9	GAFL	02318500	7/10/2012	WITHLACOOCHEE RIVER AT US 84 NEAR QUITMAN, GA
39	9	GAFL	02318500	8/7/2012	WITHLACOOCHEE RIVER AT US 84 NEAR QUITMAN, GA
40	9	GAFL	02318500	9/6/2012	WITHLACOOCHEE RIVER AT US 84 NEAR QUITMAN, GA
41	2	HDSN	01356190	6/25/2012	LISHA KILL NORTHWEST OF NISKAYUNA NY
42	2	HDSN	01356190	7/23/2012	LISHA KILL NORTHWEST OF NISKAYUNA NY
43	2	HDSN	01356190	8/22/2012	LISHA KILL NORTHWEST OF NISKAYUNA NY
44	16	LERI	04186500	6/26/2012	AUGLAIZE RIVER NEAR FORT JENNINGS OH
45	16	LERI	04186500	7/24/2012	AUGLAIZE RIVER NEAR FORT JENNINGS OH
46	16	LERI	04186500	8/21/2012	AUGLAIZE RIVER NEAR FORT JENNINGS OH
47	3	LINJ	01403300	6/28/2012	RARITAN RIVER AT QUEENS BRIDGE AT BOUND BROOK NJ
48	3	LINJ	01403300	7/25/2012	RARITAN RIVER AT QUEENS BRIDGE AT BOUND BROOK NJ
49	3	LINJ	01403300	8/22/2012	RARITAN RIVER AT QUEENS BRIDGE AT BOUND BROOK NJ
50	22	LIRB	05572000	7/9/2012	SANGAMON RIVER AT MONTICELLO, IL
51	22	LIRB	05572000	8/6/2012	SANGAMON RIVER AT MONTICELLO, IL
52	22	LIRB	05572000	9/6/2012	SANGAMON RIVER AT MONTICELLO, IL
53	23	LIRB	05586100	6/13/2012	ILLINOIS RIVER AT VALLEY CITY, IL
54	23	LIRB	05586100	6/27/2012	ILLINOIS RIVER AT VALLEY CITY, IL
55	23	LIRB	05586100	8/21/2012	ILLINOIS RIVER AT VALLEY CITY, IL
56	30	MISE	07288955	6/26/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
57	30	MISE	07288955	7/11/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
58	30	MISE	07288955	7/25/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS

Table 3. Site-visit sequence number for graphs in figures 6 and 8.—Continued

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. GA, Georgia; NC, North Carolina; WA, Washington; NEBR., Nebraska; CT., Connecticut; NJ, New Jersey; IA, Iowa; US, United States; NY, New York; OH, Ohio; IL, Illinois; BL, below; NR, near; MS, Mississippi; R, river; L&D, lock and dam; NE, Nebraska; @, at; AR, Arkansas; ST., Saint; LA, Louisiana; COE, Corps of Engineers; RV, River; TX, Texas; NV, Nevada; VA, Virginia; CA, California; SC, South Carolina; CK, Creek; TN, Tennessee; MN, Minnesota; AB, above; HWY, Highway; XING, crossing; ID, Idaho; IN, Indiana; CO RD, County Road; S, south; MT, Mount; OR, Oregon; WI, Wisconsin; WY, Wyoming]

Site-visit sequence number	Map number (fig. 1)	Study unit[1] abbreviation (table 1)	Station number	Date of site visit (month/day/year)	Name of stream-water site
59	30	MISE	07288955	8/8/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
60	30	MISE	07288955	8/23/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
61	30	MISE	07288955	9/6/2012	YAZOO RIVER BL STEELE BAYOU NR LONG LAKE, MS
62	12	MOBL	02469762	7/10/2012	TOMBIGBEE R BL COFFEEVILLE L&D NEAR COFFEEVILLE
63	12	MOBL	02469762	8/20/2012	TOMBIGBEE R BL COFFEEVILLE L&D NEAR COFFEEVILLE
64	12	MOBL	02469762	9/5/2012	TOMBIGBEE R BL COFFEEVILLE L&D NEAR COFFEEVILLE
65	18	NSQN	05420500	6/12/2012	MISSISSIPPI RIVER AT CLINTON, IA
66	18	NSQN	05420500	6/26/2012	MISSISSIPPI RIVER AT CLINTON, IA
67	25	NSQN	06610000	6/11/2012	MISSOURI RIVER AT OMAHA, NE
68	25	NSQN	06610000	6/25/2012	MISSOURI RIVER AT OMAHA, NE
69	25	NSQN	06610000	7/23/2012	MISSOURI RIVER AT OMAHA, NE
70	25	NSQN	06610000	8/27/2012	MISSOURI RIVER AT OMAHA, NE
71	28	NSQN	07022000	6/25/2012	MISSISSIPPI RIVER AT THEBES, IL
72	28	NSQN	07022000	7/24/2012	MISSISSIPPI RIVER AT THEBES, IL
73	28	NSQN	07022000	8/21/2012	MISSISSIPPI RIVER AT THEBES, IL
74	29	NSQN	07263620	6/12/2012	AR RIVER@DAVID D TERRY L&D BELOW LITTLE ROCK, AR
75	29	NSQN	07263620	8/14/2012	AR RIVER@DAVID D TERRY L&D BELOW LITTLE ROCK, AR
76	31	NSQN	07373420	6/11/2012	MISSISSIPPI R NR ST. FRANCISVILLE, LA
77	31	NSQN	07373420	6/25/2012	MISSISSIPPI R NR ST. FRANCISVILLE, LA
78	31	NSQN	07373420	8/6/2012	MISSISSIPPI R NR ST. FRANCISVILLE, LA
79	32	NSQN	07374000	6/11/2012	MISSISSIPPI RIVER AT BATON ROUGE, LA
80	32	NSQN	07374000	8/6/2012	MISSISSIPPI RIVER AT BATON ROUGE, LA
81	33	NSQN	07381495	6/12/2012	(COE) ATCHAFALAYA RIVER AT MELVILLE, LA
82	33	NSQN	07381495	6/27/2012	(COE) ATCHAFALAYA RIVER AT MELVILLE, LA
83	33	NSQN	07381495	8/9/2012	(COE) ATCHAFALAYA RIVER AT MELVILLE, LA
84	35	NSQN	08116650	6/27/2012	BRAZOS RV NR ROSHARON, TX
85	35	NSQN	08116650	7/18/2012	BRAZOS RV NR ROSHARON, TX
86	35	NSQN	08116650	8/21/2012	BRAZOS RV NR ROSHARON, TX
87	38	NSQN	08475000	8/6/2012	RIO GRANDE NR BROWNSVILLE, TX
88	38	NSQN	08475000	8/21/2012	RIO GRANDE NR BROWNSVILLE, TX
89	38	NSQN	08475000	9/5/2012	RIO GRANDE NR BROWNSVILLE, TX
90	47	NSQN	322023090544500	6/13/2012	MISSISSIPPI RIVER ABOVE VICKSBURG AT MILE 438, MS
91	47	NSQN	322023090544500	8/23/2012	MISSISSIPPI RIVER ABOVE VICKSBURG AT MILE 438, MS
92	40	NVBR	10350340	7/11/2012	TRUCKEE RV NR TRACY, NV
93	40	NVBR	10350340	8/9/2012	TRUCKEE RV NR TRACY, NV
94	40	NVBR	10350340	9/4/2012	TRUCKEE RV NR TRACY, NV
95	5	PODL	01654000	6/28/2012	ACCOTINK CREEK NEAR ANNANDALE, VA
96	5	PODL	01654000	7/12/2012	ACCOTINK CREEK NEAR ANNANDALE, VA
97	5	PODL	01654000	7/19/2012	ACCOTINK CREEK NEAR ANNANDALE, VA
98	5	PODL	01654000	7/26/2012	ACCOTINK CREEK NEAR ANNANDALE, VA
99	5	PODL	01654000	8/22/2012	ACCOTINK CREEK NEAR ANNANDALE, VA

Table 3. Site-visit sequence number for graphs in figures 6 and 8.—Continued

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. GA, Georgia; NC, North Carolina; WA, Washington; NEBR., Nebraska; CT., Connecticut; NJ, New Jersey; IA, Iowa; US, United States; NY, New York; OH, Ohio; IL, Illinois; BL, below; NR, near; MS, Mississippi; R, river; L&D, lock and dam; NE, Nebraska; @, at; AR, Arkansas; ST., Saint; LA, Louisiana; COE, Corps of Engineers; RV, River; TX, Texas; NV, Nevada; VA, Virginia; CA, California; SC, South Carolina; CK, Creek; TN, Tennessee; MN, Minnesota; AB, above; HWY, Highway; XING, crossing; ID, Idaho; IN, Indiana; CO RD, County Road; S, south; MT, Mount; OR, Oregon; WI, Wisconsin; WY, Wyoming]

Site-visit sequence number	Map number (fig. 1)	Study unit[1] abbreviation (table 1)	Station number	Date of site visit (month/day/year)	Name of stream-water site
100	5	PODL	01654000	9/6/2012	ACCOTINK CREEK NEAR ANNANDALE, VA
101	37	RIOG	08364000	6/12/2012	RIO GRANDE AT EL PASO, TX
102	37	RIOG	08364000	7/12/2012	RIO GRANDE AT EL PASO, TX
103	37	RIOG	08364000	8/15/2012	RIO GRANDE AT EL PASO, TX
104	41	SANA	11074000	7/10/2012	SANTA ANA R BL PRADO DAM CA
105	41	SANA	11074000	8/16/2012	SANTA ANA R BL PRADO DAM CA
106	41	SANA	11074000	9/4/2012	SANTA ANA R BL PRADO DAM CA
107	42	SANJ	11303500	7/23/2012	SAN JOAQUIN R NR VERNALIS CA
108	42	SANJ	11303500	8/23/2012	SAN JOAQUIN R NR VERNALIS CA
109	42	SANJ	11303500	9/6/2012	SAN JOAQUIN R NR VERNALIS CA
110	8	SANT	02174250	7/10/2012	COW CASTLE CREEK NEAR BOWMAN, SC
111	8	SANT	02174250	8/6/2012	COW CASTLE CREEK NEAR BOWMAN, SC
112	8	SANT	02174250	9/5/2012	COW CASTLE CREEK NEAR BOWMAN, SC
113	36	SCTX	08178800	7/23/2012	SALADO CK AT LOOP 13, SAN ANTONIO, TX
114	36	SCTX	08178800	8/20/2012	SALADO CK AT LOOP 13, SAN ANTONIO, TX
115	14	TENN	03466208	6/27/2012	BIG LIMESTONE CREEK NEAR LIMESTONE, TN
116	14	TENN	03466208	7/24/2012	BIG LIMESTONE CREEK NEAR LIMESTONE, TN
117	14	TENN	03466208	8/22/2012	BIG LIMESTONE CREEK NEAR LIMESTONE, TN
118	34	TRIN	08057410	6/26/2012	TRINITY RV BL DALLAS, TX
119	34	TRIN	08057410	7/25/2012	TRINITY RV BL DALLAS, TX
120	34	TRIN	08057410	8/20/2012	TRINITY RV BL DALLAS, TX
121	34	TRIN	08057410	9/5/2012	TRINITY RV BL DALLAS, TX
122	39	UCOL	09163500	7/11/2012	COLORADO RIVER NEAR COLORADO-UTAH STATE LINE
123	39	UCOL	09163500	8/8/2012	COLORADO RIVER NEAR COLORADO-UTAH STATE LINE
124	39	UCOL	09163500	9/6/2012	COLORADO RIVER NEAR COLORADO-UTAH STATE LINE
125	17	UMIS	05288705	7/12/2012	SHINGLE CREEK AT QUEEN AVE IN MINNEAPOLIS, MN
126	17	UMIS	05288705	8/9/2012	SHINGLE CREEK AT QUEEN AVE IN MINNEAPOLIS, MN
127	17	UMIS	05288705	8/20/2012	SHINGLE CREEK AT QUEEN AVE IN MINNEAPOLIS, MN
128	17	UMIS	05288705	9/5/2012	SHINGLE CREEK AT QUEEN AVE IN MINNEAPOLIS, MN
129	44	USNK	13092747	7/9/2012	ROCK CREEK AB HWY 30/93 XING AT TWIN FALLS ID
130	44	USNK	13092747	8/6/2012	ROCK CREEK AB HWY 30/93 XING AT TWIN FALLS ID
131	44	USNK	13092747	9/4/2012	ROCK CREEK AB HWY 30/93 XING AT TWIN FALLS ID
132	13	WHMI	03374100	6/27/2012	WHITE RIVER AT HAZLETON, IN
133	13	WHMI	03374100	7/24/2012	WHITE RIVER AT HAZLETON, IN
134	13	WHMI	03374100	8/24/2012	WHITE RIVER AT HAZLETON, IN
135	48	WHMI	394340085524601	6/28/2012	SUGAR CREEK AT CO RD 400 S AT NEW PALESTINE, IN
136	48	WHMI	394340085524601	7/25/2012	SUGAR CREEK AT CO RD 400 S AT NEW PALESTINE, IN
137	48	WHMI	394340085524601	8/20/2012	SUGAR CREEK AT CO RD 400 S AT NEW PALESTINE, IN
138	45	WILL	14201300	7/11/2012	ZOLLNER CREEK NEAR MT ANGEL, OR
139	45	WILL	14201300	7/25/2012	ZOLLNER CREEK NEAR MT ANGEL, OR
140	45	WILL	14201300	9/5/2012	ZOLLNER CREEK NEAR MT ANGEL, OR

Table 3. Site-visit sequence number for graphs in figures 6 and 8.—Continued

[Sequence numbers were assigned by sorting sites by study unit abbreviation, station number, and date. GA, Georgia; NC, North Carolina; WA, Washington; NEBR., Nebraska; CT., Connecticut; NJ, New Jersey; IA, Iowa; US, United States; NY, New York; OH, Ohio; IL, Illinois; BL, below; NR, near; MS, Mississippi; R, river; L&D, lock and dam; NE, Nebraska; @, at; AR, Arkansas; ST., Saint; LA, Louisiana; COE, Corps of Engineers; RV, River; TX, Texas; NV, Nevada; VA, Virginia; CA, California; SC, South Carolina; CK, Creek; TN, Tennessee; MN, Minnesota; AB, above; HWY, Highway; XING, crossing; ID, Idaho; IN, Indiana; CO RD, County Road; S, south; MT, Mount; OR, Oregon; WI, Wisconsin; WY, Wyoming]

Site-visit sequence number	Map number (fig. 1)	Study unit[1] abbreviation (table 1)	Station number	Date of site visit (month/day/year)	Name of stream-water site
141	46	WILL	14211720	7/12/2012	WILLAMETTE RIVER AT PORTLAND, OR
142	46	WILL	14211720	8/21/2012	WILLAMETTE RIVER AT PORTLAND, OR
143	46	WILL	14211720	9/4/2012	WILLAMETTE RIVER AT PORTLAND, OR
144	15	WMIC	04072050	6/26/2012	DUCK CREEK AT SEMINARY ROAD NEAR ONEIDA, WI
145	15	WMIC	04072050	7/24/2012	DUCK CREEK AT SEMINARY ROAD NEAR ONEIDA, WI
146	15	WMIC	04072050	8/23/2012	DUCK CREEK AT SEMINARY ROAD NEAR ONEIDA, WI
147	15	WMIC	04072050	9/6/2012	DUCK CREEK AT SEMINARY ROAD NEAR ONEIDA, WI
148	24	YELL	06279500	6/14/2012	BIGHORN RIVER AT KANE, WY
149	24	YELL	06279500	7/9/2012	BIGHORN RIVER AT KANE, WY
150	24	YELL	06279500	8/9/2012	BIGHORN RIVER AT KANE, WY

[1]National Stream Quality Accounting Network sites are coded "NSQN."

Table 4. Types of water samples, analytical schedules, and data-management strategy for samples collected for the field study.

[Jcode, a code assigned by the authors to facilitate the identification of sample type and analytical method; sample time offset, the number of minutes added to the initial sample time; NWIS, National Water Information System; WS, environmental surface water; WSQ, quality-control surface water; OAQ, quality-control artificial]

Jcode	Analytical schedule	Type of water sample	Sample time offset	NWIS sample medium code	NWIS sample type code	Sample collected every site visit?
a	2033	Environmental	0	WS	9	Yes
b	2033	Matrix spike	0	WSQ	1	Yes
c	2033	Field blank	0	OAQ	2	No
d	2060	Environmental	1	WS	9	Yes
e	2060	Matrix spike	1	WSQ	1	Yes
f	2060	Field blank	1	OAQ	2	No
g	2437	Environmental	2	WSQ	7 or B	Yes
h	2437	Matrix spike	3	WSQ	1	Yes
i	2437	Field blank	4	OAQ	2	No
j	2437	Field replicate[1]	4	WSQ	7	No
k	2437	Matrix spike replicate[1]	4	WSQ	1	No

[1]Except for the section "Variability of Pesticides Analyzed by Schedule 2437," duplicate water samples and duplicate field-matrix spikes were not used in statistical summaries or tests to avoid biasing results to the specific sites and conditions when the duplicates were collected.

Data Compilation, Data Review, and Calculation of Recovery

Water-quality data collected for USGS monitoring programs are stored in USGS National Water Information System (NWIS) databases located in the individual State Water Science Centers (WSCs). Water-quality data are periodically retrieved from the individual NWIS systems and aggregated into the NAWQA Data Warehouse (DWH) located in the Wisconsin WSC (the DWH is no longer active). Data aggregations are subjected to automated data-checking routines intended to identify erroneous or incomplete sample coding. Analytical data for the field study were retrieved from the DWH on July 29, 2013. Pesticide recovery in sh2437 laboratory reagent set spikes for the period of analysis of field-study samples were provided by NWQL on March 31, 2014.

Analytical data for the field study were reviewed to ensure that samples had the appropriate pesticides measured by the appropriate schedules. The number of detections in a sample was assessed to ensure that environmental samples, field blanks, and matrix spikes were analyzed by the appropriate schedule and had a reasonable number of detections, and that matrix spike samples were spiked with the appropriate spike solutions and amount of spike solution. Data-review issues were resolved by changes in sample coding (variable jcode, table 4), or samples and (or) analytical results were flagged in the large data set (Martin and Baker, 2017, dataset 1) and not selected for use in the smaller data set used for the field study (Martin and Baker, 2017, dataset 2). The metadata for dataset 1 explains the wide variety of reasons why samples or results were not selected for use in the field study.

Recovery is the ratio of a measured concentration divided by a theoretical or "expected" concentration and is the principal measure of analytical method performance. The expected concentration of a pesticide in a spiked sample is calculated as

$$Cexpected = Csolution \times Vsolution / Vsample \quad (1)$$

where

Cexpected is the expected or theoretical concentration of the pesticide in the spiked sample, in micrograms (or nanograms) per liter;

Csolution is the concentration of the pesticide in the spike solution, in micrograms (or nanograms) per milliliter;

Vsolution is the volume of spike solution added to the spiked sample, in milliliters; and

Vsample is the volume of water in the spiked sample, in liters.

Recovery in field matrix spikes must account for the concentrations of pesticides in the environmental water sample before the spike solution is added. These "background" concentrations are determined by analysis of the associated, unspiked, environmental water sample. Recovery in field matrix spikes is calculated as follows:

$$R = [(Cspiked - Cunspiked) / Cexpected] \times 100\% \quad (2)$$

where

R is pesticide recovery, in percent;

Cspiked is the measured concentration of the pesticide in the spiked sample, in micrograms (or nanograms) per liter;

Cunspiked is the measured concentration of the pesticide in the unspiked sample, in micrograms (or nanograms) per liter; and

Cexpected is the expected concentration of the pesticide in the spiked sample, in micrograms (or nanograms) per liter.

Nondetections of pesticides in the samples were assumed to be zero concentration for the calculation of recovery.

High background concentrations of pesticides resulted in invalid estimates of recovery for some matrix spikes. In the presence of high background concentrations, the additional concentration from spiking may be indistinguishable from the normal analytical variability of measurements at high concentrations. Recoveries calculated from matrix spikes under these conditions may be much higher or lower (even negative) than is typical for the method. Martin and others (2009, p. 6) determined that the incidence of very high or low recoveries for the GC–MS method was more common when background concentrations were more than 5 times the expected concentrations. On the basis of plots of recovery versus background concentration for the field study, a lower threshold for background concentration is used in this report. Calculated recoveries where background concentrations were greater than 3 times the expected concentration were flagged in the dataset and not selected for use in the analysis of recovery for the field study.

Adjustment of Environmental Pesticide Concentrations for Recovery

Large differences in analytical recovery between old and new methods could be a cause of differences in measured concentrations between methods. Comparisons of environmental concentrations between methods were made using both recovery-adjusted concentrations and the original (unadjusted) concentrations. Concentrations were adjusted using a similar procedure to that used in Martin and others (2009, p. 17), except that the median recovery, rather than the lowess-modeled recovery, was used to adjust concentrations. Lowess-modeled recovery was not done for the field study because the 3-month time frame was very short and the lowess model was very sensitive to the recoveries measured at the start and

end of the 3-month period. Concentrations were adjusted as follows:

$$Cadjusted = (Cmeasured / [Rmedian / 100]) \quad (3)$$

where

Cadjusted is the recovery-adjusted concentration of the pesticide in the water sample, in micrograms (or nanograms) per liter;

Cmeasured is the measured concentration of the pesticide in the water sample, in micrograms (or nanograms) per liter; and

Rmedian is the median recovery of field matrix spikes, in percent (the medians reported in appendixes 3 and 4).[3]

Censored concentrations (nondetections) at the routine reporting level were not adjusted for recovery. Censored concentrations at raised reporting levels were adjusted for recovery (Martin and others, 2009, p. 15–17).

Pesticides Analyzed in the Field Study

The three analytical schedules used in the field study provided data for 283 pesticides (table 5). Analytical data stored in NWIS and DWH are primarily managed by a 5-digit numerical parameter code. Parameter codes for the common pesticides measured by sh2437 are different than those for sh2033 and sh2060 because the units of measurement are different for sh2437 (nanograms per liter) than for sh2033 or sh2060 (micrograms per liter). A variable (index) was created to facilitate management of data for pesticides with different parameter codes (table 5). Indexes 1–6 are pesticides common to all three schedules. Indexes 7–61 are pesticides common to sh2437 and sh2033 (61 common pesticides). Indexes 62–93 are pesticides common to sh2437 and sh2060 (38 common pesticides). Indexes 94–283 are pesticides analyzed only by sh2437, sh2033, or sh2060 (table 5).

Statistical Methods

The UNIVARIATE procedure of SAS, version 8 (SAS Institute, Inc., 1990, p. 617–634) was used to calculate the mean, median, standard deviation (SD), relative standard deviation (RSD), percentiles, and other common descriptive statistics for the data in this report. S-PLUS, version 8.1.1 (Venables and Ripley, 1999) was used to produce boxplots (Tukey, 1977; Helsel and Hirsch, 1992, p. 24–25) of the distributions of recovery. Boxplots are explained in figure 2. The lowess procedure (Cleveland, 1979; Cleveland and McGill, 1985, p. 833), as implemented in S-PLUS, was used to show the relation between two variables in scatterplots. The lowess smoothing window used was a function of the number of data points in the plots: 1 for 4–25 points, 0.75 for 26–45 points, and 0.5 for more than 45 points. No lowess smooth was done for less than 4 points. S-PLUS was used to make all graphs in the report.

SAS was used to calculate one-sided, 90-percent upper confidence bounds for the percentage of duplicate sets with inconsistent detections (Hahn and Meeker, 1991, p. 104–105; Mueller and others, 2015, p. 32). Pooled estimates of SD and RSD were calculated using the procedure given in Anderson (1987, p. 44–45). SAS was used to calculate one-sided, 90-percent upper confidence bounds for the pooled estimates of SD and RSD (Hahn and Meeker, 1991, p. 55–56; Anderson, 1987, p. 47–50).

The NPAR1WAY procedure of SAS (SAS Institute, Inc., 1999, p. 2,507–2,552) was used to calculate the Wilcoxon rank-sum test (Helsel and Hirsch, 1992, p. 118–121), which tests whether one group tends to produce larger values than the second group and was used to identify differences in median recovery between field matrix spikes and laboratory reagent spikes. The sign test (Helsel and Hirsch, 1992, p. 137–142) tests whether one group tends to produce larger values than the second group, but is used for paired samples. The sign test was used to determine if recovery in paired field matrix spikes analyzed by old and new methods was different. The sign test also was used to identify differences in pesticide detections and concentrations in paired environmental water samples analyzed by old and new methods. The UNIVARIATE procedure of SAS (SAS Institute, Inc., 1990, p. 629) was used to calculate the sign test.

Differences in variance of recovery between field matrix spikes and laboratory reagent spikes and between field matrix spikes analyzed by old and new methods were identified by Levene's test for equality of variance (Levene, 1960). Levene's test was done using the GLM procedure (SAS Institute, Inc., 1999, p. 1,553–1,554). The magnitude of differences in concentrations in paired environmental water samples analyzed by old and new methods was estimated by calculating the logical relative percent difference (Tornqvist and others, 1985). Differences in the percentages of field blank water samples with detections of pesticides analyzed by old and new methods were assessed using the method of Natrella (1963, p. 8–16).

A threshold of 5 percent (alpha = 0.05) was used to identify statistically significant differences for the tests described above.

[3]The median recoveries reported in tables 9 and 11 are for paired matrix spikes analyzed by old and new methods and are slightly different than the medians for all matrix spikes.

Table 5. Pesticides analyzed for the field study.

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Index	Pesticide short name	NWQL schedule 2437		NWQL schedule 2033		NWQL schedule 2060		CAS	Type of pesticide	Parent pesticide (if degradate)	Pesticide name
		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
1	Atrazine	65065	LCM60	39632	GCM35	39632	LCM29	1912-24-9	Herbicide	NA	Atrazine
2	Carbaryl	65069	LCM60	82680	GCM35	49310	LCM29	63-25-2	Insecticide	NA	Carbaryl
3	Carbofuran	65070	LCM60	82674	GCM35	49309	LCM29	1563-66-2	Insecticide	NA	Carbofuran
4	Deethylatrazine	68552	LCM60	04040	GCM35	04040	LCM29	6190-65-4	Degradate	Atrazine	Deethylatrazine
5	Metalaxyl	68437	LCM60	61596	GCM39	50359	LCM29	57837-19-1	Fungicide	NA	Metalaxyl
6	Tebuthiuron	68695	LCM60	82670	GCM35	82670	LCM29	34014-18-1	Herbicide	NA	Tebuthiuron
7	2-Chloro-2,6-d_ilide	68525	LCM60	61618	GCM39	NA	NA	6967-29-9	Degradate	Alachlor	2-Chloro-2,6-diethylacetanilide
8	Acetochlor	68520	LCM60	49260	GCM33	NA	NA	34256-82-1	Herbicide	NA	Acetochlor
9	Alachlor	65064	LCM60	46342	GCM35	NA	NA	15972-60-8	Herbicide	NA	Alachlor
10	Azinphos-methyl	65066	LCM60	82686	GCM35	NA	NA	86-50-0	Insecticide	NA	Azinphos-methyl
11	Azinphos-methyl-oxon	68211	LCM60	61635	GCM39	NA	NA	961-22-8	Degradate	Azinphos-methyl	Azinphos-methyl-oxon
12	Chlorpyrifos	65072	LCM60	38933	GCM35	NA	NA	2921-88-2	Insecticide	NA	Chlorpyrifos
13	Chlorpyrifos_oxon	68216	LCM60	61636	GCM39	NA	NA	5598-15-2	Degradate	Chlorpyrifos	Chlorpyrifos oxon
14	Cyanazine	66592	LCM60	04041	GCM35	NA	NA	21725-46-2	Herbicide	NA	Cyanazine
15	Desulfinylfipro_mide	68570	LCM60	62169	GCM29	NA	NA	ND	Degradate	Fipronil	Desulfinylfipronil amide
16	Desulfinylfipronil	66607	LCM60	62170	GCM29	NA	NA	ND	Degradate	Fipronil	Desulfinylfipronil
17	Diazinon	65078	LCM60	39572	GCM35	NA	NA	333-41-5	Insecticide	NA	Diazinon
18	Diazoxon	68236	LCM60	61638	GCM14	NA	NA	962-58-3	Degradate	Diazinon	Diazoxon
19	Dichlorvos	68572	LCM60	38775	GCM39	NA	NA	62-73-7	Insecticide/fumigant/ degradate	Naled	Dichlorvos
20	Dicrotophos	68573	LCM60	38454	GCM39	NA	NA	141-66-2	Insecticide	NA	Dicrotophos
21	Dimethoate	66596	LCM60	82662	GCM40	NA	NA	60-51-5	Insecticide	NA	Dimethoate
22	Disulfoton	67595	LCM60	82677	GCM35	NA	NA	298-04-4	Insecticide	NA	Disulfoton
23	Disulfoton_sulfone	68589	LCM60	61640	GCM39	NA	NA	2497-06-5	Degradate	Disulfoton	Disulfoton sulfone
24	EPTC	65080	LCM60	82668	GCM35	NA	NA	759-94-4	Herbicide	NA	EPTC
25	Ethoprophos	68596	LCM60	82672	GCM35	NA	NA	13194-48-4	Insecticide	NA	Ethoprophos
26	Fenamiphos	68599	LCM60	61591	GCM39	NA	NA	22224-92-6	Nematocide	NA	Fenamiphos
27	Fenamiphos_sulfone	68600	LCM60	61645	GCM39	NA	NA	31972-44-8	Degradate	Fenamiphos	Fenamiphos sulfone
28	Fenamiphos_sulfoxide	68601	LCM60	61646	GCM39	NA	NA	31972-43-7	Degradate	Fenamiphos	Fenamiphos sulfoxide
29	Fipronil	66604	LCM60	62166	GCM29	NA	NA	120068-37-3	Insecticide	NA	Fipronil
30	Fipronil_sulfide	66610	LCM60	62167	GCM29	NA	NA	120067-83-6	Degradate	Fipronil	Fipronil sulfide
31	Fipronil_sulfone	66613	LCM60	62168	GCM29	NA	NA	120068-36-2	Degradate	Fipronil	Fipronil sulfone
32	Fonofos	65084	LCM60	04095	GCM35	NA	NA	944-22-9	Insecticide	NA	Fonofos
33	Hexazinone	65085	LCM60	04025	GCM39	NA	NA	51235-04-2	Herbicide	NA	Hexazinone
34	Malaoxon	68240	LCM60	61652	GCM39	NA	NA	1634-78-2	Degradate	Malathion	Malaoxon
35	Malathion	65087	LCM60	39532	GCM35	NA	NA	121-75-5	Insecticide	NA	Malathion
36	Methidathion	65088	LCM60	61598	GCM39	NA	NA	950-37-8	Insecticide	NA	Methidathion
37	Metolachlor	65090	LCM60	39415	GCM35	NA	NA	51218-45-2	Herbicide	NA	Metolachlor

Table 5. Pesticides analyzed for the field study.—Continued

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Index	Pesticide short name	NWQL schedule 2437		NWQL schedule 2033		NWQL schedule 2060		CAS	Type of pesticide	Parent pesticide (if degradate)	Pesticide name
		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
38	Metribuzin	68652	LCM60	82630	GCM35	NA	NA	21087-64-9	Herbicide	NA	Metribuzin
39	Molinate	65091	LCM60	82671	GCM35	NA	NA	2212-67-1	Herbicide	NA	Molinate
40	Myclobutanil	66632	LCM60	61599	GCM39	NA	NA	88671-89-0	Fungicide	NA	Myclobutanil
41	Oxyfluorfen	65093	LCM60	61600	GCM39	NA	NA	42874-03-3	Herbicide	NA	Oxyfluorfen
42	Paraoxon-methyl	68648	LCM60	61664	GCM39	NA	NA	950-35-6	Degradate	Methyl_parathion	Paraoxon-methyl
43	Parathion-methyl[1]	65089	LCM60	82667	GCM35	NA	NA	298-00-0	Insecticide	NA	Parathion-methyl
44	Pendimethalin	65098	LCM60	82683	GCM35	NA	NA	40487-42-1	Herbicide	NA	Pendimethalin
45	Phorate	68668	LCM60	82664	GCM35	NA	NA	298-02-2	Insecticide	NA	Phorate
46	Phorate_oxon	68669	LCM60	61666	GCM39	NA	NA	2600-69-3	Degradate	Phorate	Phorate oxon
47	Phosmet[1]	65101	LCM60	61601	GCM39	NA	NA	732-11-6	Insecticide	NA	Phosmet
48	Phosmet_oxon[1]	68674	LCM60	61668	GCM39	NA	NA	3735-33-9	Degradate	Phosmet	Phosmet oxon
49	Prometon	67702	LCM60	04037	GCM35	NA	NA	1610-18-0	Herbicide	NA	Prometon
50	Prometryn	65103	LCM60	04036	GCM39	NA	NA	7287-19-6	Herbicide	NA	Prometryn
51	Propanil	66641	LCM60	82679	GCM35	NA	NA	709-98-8	Herbicide	NA	Propanil
52	Propargite	68677	LCM60	82685	GCM35	NA	NA	2312-35-8	Acaricide	NA	Propargite
53	Propyzamide	67706	LCM60	82676	GCM35	NA	NA	23950-58-5	Herbicide	NA	Propyzamide
54	Simazine	65105	LCM60	04035	GCM35	NA	NA	122-34-9	Herbicide	NA	Simazine
55	Tebuconazole	66649	LCM60	62852	GCM14	NA	NA	107534-96-3	Fungicide	NA	Tebuconazole
56	Terbufos	68699	LCM60	82675	GCM35	NA	NA	13071-79-9	Insecticide	NA	Terbufos
57	Terbufos_sulfo_nalog	68701	LCM60	61674	GCM39	NA	NA	56070-15-6	Degradate	Terbufos	Terbufos sulfone oxygen analog
58	Terbuthylazine	66651	LCM60	04022	GCM39	NA	NA	5915-41-3	Herbicide	NA	Terbuthylazine
59	Thiobencarb	65107	LCM60	82681	GCM35	NA	NA	28249-77-6	Herbicide	NA	Thiobencarb
60	Tribuphos	68711	LCM60	61610	GCM39	NA	NA	78-48-8	Defoliant	NA	Tribuphos
61	cis-Permethrin	68769	LCM60	82687	GCM35	NA	NA	61949-76-6	Insecticide	NA	cis-Permethrin
62	2,4-D	68500	LCM60	NA	NA	39732	LCM29	94-75-7	Herbicide	NA	2,4-D
63	2-Hydroxyatrazine	68660	LCM60	NA	NA	50355	LCM29	2163-68-0	Degradate	Atrazine	2-Hydroxyatrazine
64	3-Hydroxycarbofuran	68508	LCM60	NA	NA	49308	LCM29	16655-82-6	Degradate	Carbofuran	3-Hydroxycarbofuran
65	Aldicarb	68528	LCM60	NA	NA	49312	LCM29	116-06-3	Insecticide	NA	Aldicarb
66	Aldicarb_sulfone	68529	LCM60	NA	NA	49313	LCM29	1646-88-4	Degradate	Aldicarb	Aldicarb sulfone
67	Aldicarb_sulfoxide	68530	LCM60	NA	NA	49314	LCM29	1646-87-3	Degradate	Aldicarb	Aldicarb sulfoxide
68	Bentazon	68538	LCM60	NA	NA	38711	LCM29	25057-89-0	Herbicide	NA	Bentazon
69	Bromacil	68542	LCM60	NA	NA	04029	LCM29	314-40-9	Herbicide	NA	Bromacil
70	Bromoxynil	68543	LCM60	NA	NA	49311	LCM29	1689-84-5	Herbicide	NA	Bromoxynil
71	Chlorimuron-ethyl	68872	LCM60	NA	NA	50306	LCM29	90982-32-4	Herbicide	NA	Chlorimuron-ethyl
72	Dacthal_monoacid	68560	LCM60	NA	NA	49304	LCM29	887-54-7	Degradate	Dacthal	Dacthal monoacid
73	Deisopropylatrazine	68550	LCM60	NA	NA	04038	LCM29	1007-28-9	Degradate	Atrazine/Cyanazine/ Simazine	Deisopropylatrazine

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74	Dicamba	68571	LCM60	NA	NA	38442	LCM29	1918-00-9	Herbicide	NA	Dicamba
75	Diuron	66598	LCM60	NA	NA	49300	LCM29	330-54-1	Herbicide	NA	Diuron
76	Flumetsulam	61679	LCM60	NA	NA	61694	LCM29	98967-40-9	Herbicide	NA	Flumetsulam
77	Fluometuron	68608	LCM60	NA	NA	38811	LCM29	2164-17-2	Herbicide	NA	Fluometuron
78	Imazaquin	61682	LCM60	NA	NA	50356	LCM29	81335-37-7	Herbicide	NA	Imazaquin
79	Imazethapyr	61683	LCM60	NA	NA	50407	LCM29	81335-77-5	Herbicide	NA	Imazethapyr
80	Imidacloprid	68426	LCM60	NA	NA	61695	LCM29	138261-41-3	Insecticide	NA	Imidacloprid
81	Linuron	68639	LCM60	NA	NA	38478	LCM29	330-55-2	Herbicide	NA	Linuron
82	MCPA	68641	LCM60	NA	NA	38482	LCM29	94-74-6	Herbicide	NA	MCPA
83	Methomyl	68645	LCM60	NA	NA	49296	LCM29	16752-77-5	Insecticide	NA	Methomyl
84	Nicosulfuron	61685	LCM60	NA	NA	50364	LCM29	111991-09-4	Herbicide	NA	Nicosulfuron
85	Norflurazon	67685	LCM60	NA	NA	49293	LCM29	27314-13-2	Herbicide	NA	Norflurazon
86	Oryzalin	68663	LCM60	NA	NA	49292	LCM29	19044-88-3	Herbicide	NA	Oryzalin
87	Oxamyl	68664	LCM60	NA	NA	38866	LCM29	23135-22-0	Insecticide	NA	Oxamyl
88	Propiconazole	66643	LCM60	NA	NA	50471	LCM29	60207-90-1	Fungicide	NA	Propiconazole
89	Propoxur	68679	LCM60	NA	NA	38538	LCM29	114-26-1	Insecticide	NA	Propoxur
90	Siduron	68686	LCM60	NA	NA	38548	LCM29	1982-49-6	Herbicide	NA	Siduron
91	Sulfometuron-methyl	68688	LCM60	NA	NA	50337	LCM29	74222-97-2	Herbicide	NA	Sulfometuron-methyl
92	Terbacil	68698	LCM60	NA	NA	04032	LCM29	5902-51-2	Herbicide	NA	Terbacil
93	Triclopyr	68712	LCM60	NA	NA	49235	LCM29	55335-06-3	Herbicide	NA	Triclopyr
94	1H-1,2,4-Triazole	68498	LCM60	NA	NA	NA	NA	116421-29-5	Degradate	Propiconazole	1H-1,2,4-Triazole
95	2-(1-Hydroxyeth_line	68611	LCM60	NA	NA	NA	NA	196611-19-5	Degradate	Acetochlor/Metolachlor	2-(1-Hydroxyethyl)-6-methylaniline
96	2-Amino-N-isopr_mide	68503	LCM60	NA	NA	NA	NA	30391-89-0	Degradate	Bentazon	2-Amino-N-isopropylbenzamide
97	2-Aminobenzimidazole	68502	LCM60	NA	NA	NA	NA	934-32-7	Degradate	Benomyl	2-Aminobenzimidazole
98	2-Isopropyl-6-m_inol	68505	LCM60	NA	NA	NA	NA	2814-20-2	Degradate	Diazinon	2-Isopropyl-6-methyl-4-pyrimidinol
99	2-[(2-Ethyl-6-m_anol	68595	LCM60	NA	NA	NA	NA	61520-53-4	Degradate	Metolachlor	2-[(2-Ethyl-6-methylphenyl)amino]-1-propanol
100	3,4-Dichlorophe_urea	68226	LCM60	NA	NA	NA	NA	2327-02-8	Degradate	Diuron	3,4-Dichlorophenylurea
101	3-Ketocarbofuran[1]	68509	LCM60	NA	NA	NA	NA	16709-30-1	Degradate	Carbofuran	3-Ketocarbofuran
102	3-Phenoxybenzoi_acid	68873	LCM60	NA	NA	NA	NA	3739-38-6	Degradate	Permethrin	3-Phenoxybenzoic acid
103	4-(Hydroxymeth_halin	68511	LCM60	NA	NA	NA	NA	56750-76-6	Degradate	Pendimethalin	4-(Hydroxymethyl)pendimethalin
104	4-Chlorobenzylm_xide	68514	LCM60	NA	NA	NA	NA	934-73-6	Degradate	Thiobencarb	4-Chlorobenzylmethyl sulfoxide
105	4-Hydroxy_molinate	68515	LCM60	NA	NA	NA	NA	66747-12-4	Degradate	Molinate	4-Hydroxy molinate
106	4-Hydroxychloro_onil	68336	LCM60	NA	NA	NA	NA	28343-61-5	Degradate	Chlorothalonil	4-Hydroxychlorothalonil
107	4-Hydroxyhexazi_ne_A	68517	LCM60	NA	NA	NA	NA	72576-13-7	Degradate	Hexazinone	4-Hydroxyhexazinone A
108	7-Hydroxycarbofuran[1]	68518	LCM60	NA	NA	NA	NA	1563-38-8	Degradate	Carbofuran	7-Hydroxycarbofuran
109	Acephate	68519	LCM60	NA	NA	NA	NA	30560-19-1	Pesticide	NA	Acephate
110	Acet/Met_sec_amide	68521	LCM60	NA	NA	NA	NA	32428-71-0	Degradate	Acetochlor/Metolachlor	Acetochlor/Metolachlor secondary amide

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		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
111	Acetochlor_ESA	68523	LCM60	NA	NA	NA	NA	187022-11-3	Degradate	Acetochlor	Acetochlor ethane sulfonic acid
112	Acetochlor_OXA	68522	LCM60	NA	NA	NA	NA	194992-44-4	Degradate	Acetochlor	Acetochlor oxanilic acid
113	Acetochlor_SAA	68524	LCM60	NA	NA	NA	NA	618113-86-3	Degradate	Acetochlor	Acetochlor sulfynilacetic acid
114	Alachlor_ESA	68871	LCM60	NA	NA	NA	NA	142363-53-9	Degradate	Alachlor	Alachlor ethane sulfonic acid
115	Alachlor_OXA	68526	LCM60	NA	NA	NA	NA	171262-17-2	Degradate	Alachlor	Alachlor oxanilic acid
116	Alachlor_SAA	68527	LCM60	NA	NA	NA	NA	494847-39-1	Degradate	Alachlor	Alachlor sulfynilacetic acid
117	Ametryn	68533	LCM60	NA	NA	NA	NA	834-12-8	Herbicide	NA	Ametryn
118	Aminopyralid[1]	68534	LCM60	NA	NA	NA	NA	150114-71-9	Pesticide	NA	Aminopyralid
119	Ammelide[1]	68535	LCM60	NA	NA	NA	NA	645-93-2	Degradate	Atrazine	Ammelide
120	Asulam	68536	LCM60	NA	NA	NA	NA	3337-71-1	Pesticide	NA	Asulam
121	Azoxystrobin	66589	LCM60	NA	NA	NA	NA	131860-33-8	Pesticide	NA	Azoxystrobin
122	Bifenazate[1]	68540	LCM60	NA	NA	NA	NA	149877-41-8	Pesticide	NA	Bifenazate
123	Bifenazate_diazene[1]	68541	LCM60	NA	NA	NA	NA	149878-40-0	Degradate	Bifenazate	Bifenazate diazene
124	Bifenthrin	65067	LCM60	NA	NA	NA	NA	82657-04-3	Insecticide	NA	Bifenthrin
125	Butralin	68545	LCM60	NA	NA	NA	NA	33629-47-9	Pesticide	NA	Butralin
126	Butylate	65068	LCM60	NA	NA	NA	NA	2008-41-5	Herbicide	NA	Butylate
127	Carbendazim	68548	LCM60	NA	NA	NA	NA	10605-21-7	Degradate	Benomyl	Carbendazim
128	Carboxy_molinate	68549	LCM60	NA	NA	NA	NA	66747-13-5	Degradate	Molinate	Carboxy molinate
129	Chlorosulfonami_acid	68551	LCM60	NA	NA	NA	NA	130-45-0	Degradate	Halosulfuron-methyl	Chlorosulfonamide acid
130	Chlorsulfuron	61678	LCM60	NA	NA	NA	NA	64902-72-3	Pesticide	NA	Chlorsulfuron
131	Dechlorofipronil	68561	LCM60	NA	NA	NA	NA	ND	Degradate	Fipronil	Dechlorofipronil
132	Dechlorometolachlor	68562	LCM60	NA	NA	NA	NA	126605-22-9	Degradate	Metolachlor	Dechlorometolachlor
133	Deethylhydroxy_azine	68659	LCM60	NA	NA	NA	NA	19988-24-0	Degradate	Atrazine/Cyanazine/ Simazine	Deethylhydroxyatrazine
134	Deiodo_flubendiamide	68563	LCM60	NA	NA	NA	NA	ND	Degradate	Flubendiamide	Deiodo flubendiamide
135	Deisopropyl_pr_etryn	68564	LCM60	NA	NA	NA	NA	4147-57-3	Degradate	Prometryn	Deisopropyl prometryn
136	Deisopropylhyd_azine	68656	LCM60	NA	NA	NA	NA	7313-54-4	Degradate	Atrazine/Cyanazine/ Simazine	Deisopropylhydroxyatrazine
137	Deisopropyliprodione[1]	68565	LCM60	NA	NA	NA	NA	79076-80-5	Degradate	Iprodione	Deisopropyliprodione
138	Demethyl_fluometuron	68591	LCM60	NA	NA	NA	NA	3032-40-4	Degradate	Fluometuron	Demethyl fluometuron
139	Demethyl_hexazi_ne_B	68566	LCM60	NA	NA	NA	NA	56611-54-2	Degradate	Hexazinone	Demethyl hexazinone B
140	Demethyl_norflurazon	68567	LCM60	NA	NA	NA	NA	23576-24-1	Degradate	Norflurazon	Demethyl norflurazon
141	Desamino-diketo_uzin	68569	LCM60	NA	NA	NA	NA	52236-30-3	Degradate	Metribuzin	Desamino-diketo metribuzin
142	Didealkylatrazine	68547	LCM60	NA	NA	NA	NA	3397-62-4	Degradate	Atrazine	Didealkylatrazine
143	Didemethyl_hexa_ne_F	68574	LCM60	NA	NA	NA	NA	ND	Degradate	Hexazinone	Didemethyl hexazinone F
144	Diflubenzuron	68576	LCM60	NA	NA	NA	NA	35367-38-5	Pesticide	NA	Diflubenzuron
145	Diflufenzopyr	68577	LCM60	NA	NA	NA	NA	109293-97-2	Pesticide	NA	Diflufenzopyr

Table 5. Pesticides analyzed for the field study.—Continued

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		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
146	Diketonitrile-i_tole	68578	LCM60	NA	NA	NA	NA	143701-75-1	Degradate	Isoxaflutole	Diketonitrile-isoxaflutole
147	Dimethenamid	68580	LCM60	NA	NA	NA	NA	87674-68-8	Herbicide	NA	Dimethenamid
148	Dimethenamid_ESA	68582	LCM60	NA	NA	NA	NA	205939-58-8	Degradate	Dimethenamid	Dimethenamid ethane sulfonic acid
149	Dimethenamid_OXA	68581	LCM60	NA	NA	NA	NA	ND	Degradate	Dimethenamid	Dimethenamid oxanilic acid
150	Dimethenamid_SAA	68583	LCM60	NA	NA	NA	NA	ND	Degradate	Dimethenamid	Dimethenamid SAA
151	Dimethoate_oxyg_alog	68661	LCM60	NA	NA	NA	NA	1113-02-6	Degradate	Dimethoate	Dimethoate oxygen analog
152	Disulfoton_oxon	68586	LCM60	NA	NA	NA	NA	126-75-0	Degradate	Disulfoton	Disulfoton oxon
153	Disulfoton_oxon_fone	68588	LCM60	NA	NA	NA	NA	2496-91-5	Degradate	Disulfoton	Disulfoton oxon sullfone
154	Disulfoton_oxon_xide	68587	LCM60	NA	NA	NA	NA	2496-92-6	Degradate	Disulfoton	Disulfoton oxon sulfoxide
155	Disulfoton_sulfoxide	68590	LCM60	NA	NA	NA	NA	2497-07-6	Degradate	Disulfoton	Disulfoton sulfoxide
156	EPTC_degradate_48722	68594	LCM60	NA	NA	NA	NA	ND	Degradate	EPTC	EPTC degradate R248722
157	Etoxazole	68598	LCM60	NA	NA	NA	NA	153233-91-1	Pesticide	NA	Etoxazole
158	Famoxadone	67609	LCM60	NA	NA	NA	NA	131807-57-3	Pesticide	NA	Famoxadone
159	Fenbutatin_oxide	68602	LCM60	NA	NA	NA	NA	13356-08-6	Pesticide	NA	Fenbutatin oxide
160	Fentin	68603	LCM60	NA	NA	NA	NA	668-34-8	Pesticide	NA	Fentin
161	Fipronil_amide	68604	LCM60	NA	NA	NA	NA	ND	Degradate	Fipronil	Fipronil amide
162	Fipronil_sulfonate	68605	LCM60	NA	NA	NA	NA	209248-72-6	Degradate	Fipronil	Fipronil sulfonate
163	Flubendiamide	68606	LCM60	NA	NA	NA	NA	272451-65-7	Pesticide	NA	Flubendiamide
164	Flumiclorac[1]	68607	LCM60	NA	NA	NA	NA	87546-18-7	Pesticide	NA	Flumiclorac
165	Formetanate[1]	68609	LCM60	NA	NA	NA	NA	22259-30-9	Pesticide	NA	Formetanate
166	Halosulfuron-methyl	61680	LCM60	NA	NA	NA	NA	100784-20-1	Pesticide	NA	Halosulfuron-methyl
167	Hexazinone_Tran_ct_C	68612	LCM60	NA	NA	NA	NA	72585-88-7	Degradate	Hexazinone	Hexazinone Transformation Product C
168	Hexazinone_Tran_ct_D	68613	LCM60	NA	NA	NA	NA	30243-77-7	Degradate	Hexazinone	Hexazinone Transformation Product D
169	Hexazinone_Tran_ct_E	68614	LCM60	NA	NA	NA	NA	72576-14-8	Degradate	Hexazinone	Hexazinone Transformation Product E
170	Hexazinone_Tran_ct_G	68713	LCM60	NA	NA	NA	NA	ND	Degradate	Hexazinone	Hexazinone Transformation Product G
171	Hydroxy_didemet_uron	68619	LCM60	NA	NA	NA	NA	ND	Degradate	Fluometuron	Hydroxy didemethyl fluometuron
172	Hydroxy_monodem_uron	68617	LCM60	NA	NA	NA	NA	ND	Degradate	Fluometuron	Hydroxy monodemethyl fluometuron
173	Hydroxyacetochlor	68615	LCM60	NA	NA	NA	NA	60090-47-3	Degradate	Acetochlor	Hydroxyacetochlor
174	Hydroxyalachlor	68616	LCM60	NA	NA	NA	NA	56681-55-1	Degradate	Alachlor	Hydroxyalachlor
175	Hydroxydiazinon	68618	LCM60	NA	NA	NA	NA	29820-16-4	Degradate	Diazinon	Hydroxydiazinon
176	Hydroxyfluometuron	68620	LCM60	NA	NA	NA	NA	ND	Degradate	Fluometuron	Hydroxyfluometuron
177	Hydroxymetolachlor	68622	LCM60	NA	NA	NA	NA	131068-72-9	Degradate	Metolachlor	Hydroxymetolachlor
178	Hydroxyphthalazinone	68623	LCM60	NA	NA	NA	NA	ND	Degradate	Diflufenzopyr	Hydroxyphthalazinone
179	Hydroxysimazine	68624	LCM60	NA	NA	NA	NA	2599-11-3	Degradate	Simazine	Hydroxysimazine
180	Hydroxytebuthurion	68621	LCM60	NA	NA	NA	NA	59962-54-8	Degradate	Tebuthiuron	Hydroxytebuthurion
181	Imazamox	68625	LCM60	NA	NA	NA	NA	114311-32-9	Pesticide	NA	Imazamox
182	Indoxacarb	68627	LCM60	NA	NA	NA	NA	173584-44-6	Pesticide	NA	Indoxacarb

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		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
183	Isoxaflutole	68632	LCM60	NA	NA	NA	NA	141112-29-0	Herbicide	NA	Isoxaflutole
184	Isoxaflutole_ac_3328	68633	LCM60	NA	NA	NA	NA	142994-06-7	Degradate	Isoxaflutole	Isoxaflutole acid metabolite RPA 203328
185	Kresoxim-methyl	67670	LCM60	NA	NA	NA	NA	143390-89-0	Pesticide	NA	Kresoxim-methyl
186	Lactofen	68638	LCM60	NA	NA	NA	NA	77501-63-4	Pesticide	NA	Lactofen
187	Metconazole	66620	LCM60	NA	NA	NA	NA	125116-23-6	Pesticide	NA	Metconazole
188	Methamidophos	68644	LCM60	NA	NA	NA	NA	10265-92-6	Pesticide	NA	Methamidophos
189	Methomyl_oxime	68646	LCM60	NA	NA	NA	NA	13749-94-5	Degradate	Methomyl	Methomyl oxime
190	Methoxyfenozide	68647	LCM60	NA	NA	NA	NA	161050-58-4	Pesticide	NA	Methoxyfenozide
191	Metolachlor_ESA	68651	LCM60	NA	NA	NA	NA	171118-09-5	Degradate	Metolachlor	Metolachlor ethane sulfonic acid
192	Metolachlor_OXA	68650	LCM60	NA	NA	NA	NA	152019-73-3	Degradate	Metolachlor	Metolachlor oxanilic acid
193	Metolachlor_hyd_none	68649	LCM60	NA	NA	NA	NA	61520-54-5	Degradate	Metolachlor	Metolachlor hydroxy morpholinone
194	Metribuzin-desamino	68568	LCM60	NA	NA	NA	NA	35045-02-4	Degradate	Metribuzin	Metribuzin-desamino
195	Metribuzin_DK	68653	LCM60	NA	NA	NA	NA	56507-37-0	Degradate	Metribuzin	Metribuzin DK
196	N-(3,4-Dichloro_urea	68231	LCM60	NA	NA	NA	NA	3567-62-2	Degradate	Diuron	N-(3,4-Dichlorophenyl)-N'-methylurea
197	Naled	68654	LCM60	NA	NA	NA	NA	300-76-5	Pesticide	NA	Naled
198	Novaluron	68655	LCM60	NA	NA	NA	NA	116714-46-6	Pesticide	NA	Novaluron
199	O-Ethyl-O-methy_oate	68597	LCM60	NA	NA	NA	NA	76960-87-7	Degradate	Ethoprop	O-Ethyl-O-methyl-S-propylphosphorothioate
200	O-Ethyl-S-methy_oate	68657	LCM60	NA	NA	NA	NA	ND	Degradate	Ethoprop	O-Ethyl-S-methyl-S-propyl phosphorodithioate
201	O-Ethyl-S-propy_oate	68658	LCM60	NA	NA	NA	NA	31110-62-0	Degradate	Ethoprop	O-Ethyl-S-propylphosphorothioate
202	Orthosulfamuron	68662	LCM60	NA	NA	NA	NA	213464-77-8	Pesticide	NA	Orthosulfamuron
203	Oxamyl_oxime	68665	LCM60	NA	NA	NA	NA	30558-43-1	Degradate	Oxamyl	Oxamyl oxime
204	Paraoxon-ethyl	68666	LCM60	NA	NA	NA	NA	311-45-5	Insecticide/Degradate	Parathion	Paraoxon-ethyl
205	Phorate_oxon_su_xide	68671	LCM60	NA	NA	NA	NA	2588-05-8	Degradate	Phorate	Phorate oxon sulfoxide
206	Phorate_oxygen_fone	68670	LCM60	NA	NA	NA	NA	2588-06-9	Degradate	Phorate	Phorate oxygen analog sulfone
207	Phorate_sulfone	68672	LCM60	NA	NA	NA	NA	2588-04-7	Degradate	Phorate	Phorate sulfone
208	Phorate_sulfoxide	68673	LCM60	NA	NA	NA	NA	2588-03-6	Degradate	Phorate	Phorate sulfoxide
209	Phthalazinone	68675	LCM60	NA	NA	NA	NA	ND	Degradate	Diflufenzopyr	Phthalazinone
210	Piperonyl_butoxide	65102	LCM60	NA	NA	NA	NA	51-03-6	Synergist	NA	Piperonyl butoxide
211	Profenofos	68676	LCM60	NA	NA	NA	NA	41198-08-7	Insecticide	NA	Profenofos
212	Propazine	68678	LCM60	NA	NA	NA	NA	139-40-2	Herbicide	NA	Propazine
213	Prosulfuron	61687	LCM60	NA	NA	NA	NA	94125-34-5	Pesticide	NA	Prosulfuron
214	Pymetrozine	68680	LCM60	NA	NA	NA	NA	123312-89-0	Pesticide	NA	Pymetrozine
215	Pyraclostrobin	66646	LCM60	NA	NA	NA	NA	175013-18-0	Pesticide	NA	Pyraclostrobin
216	Pyridaben	68682	LCM60	NA	NA	NA	NA	96489-71-3	Pesticide	NA	Pyridaben
217	Pyriproxyfen	68683	LCM60	NA	NA	NA	NA	95737-68-1	Pesticide	NA	Pyriproxyfen
218	Sulfentrazone	68687	LCM60	NA	NA	NA	NA	122836-35-5	Pesticide	NA	Sulfentrazone
219	Sulfosulfuron	68689	LCM60	NA	NA	NA	NA	141776-32-1	Pesticide	NA	Sulfosulfuron

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		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
220	Sulfosulfuron_e_fone	68690	LCM60	NA	NA	NA	NA	ND	Degradate	Sulfosulfuron	Sulfosulfuron ethyl sulfone
221	TCPSA_ethyl_ester	68691	LCM60	NA	NA	NA	NA	65600-62-6	Degradate	Triallate	TCPSA ethyl ester
222	Tebufenozide	68692	LCM60	NA	NA	NA	NA	112410-23-8	Pesticide	NA	Tebufenozide
223	Tebupirimfos	68693	LCM60	NA	NA	NA	NA	96182-53-5	Insecticide	NA	Tebupirimfos
224	Tebupirimfos_oxon	68694	LCM60	NA	NA	NA	NA	ND	Degradate	Tebupirimfos	Tebupirimfos oxon
225	Tebuthiuron_TP_104	68575	LCM60	NA	NA	NA	NA	ND	Degradate	Tebuthiuron	Tebuthiuron TP 104
226	Tebuthiuron_TP_108	68696	LCM60	NA	NA	NA	NA	39222-73-6	Degradate	Tebuthiuron	Tebuthiuron TP 108
227	Tebuthiuron_TP_109	68697	LCM60	NA	NA	NA	NA	ND	Degradate	Tebuthiuron	Tebuthiuron TP 109
228	Tebuthiuron_Tra_106	68714	LCM60	NA	NA	NA	NA	ND	Degradate	Tebuthiuron	Tebuthiuron Transformation Product 106
229	Terbufos_oxon	68700	LCM60	NA	NA	NA	NA	56070-14-5	Degradate	Terbufos	Terbufos oxon
230	Terbufos_oxon_s_xide	68702	LCM60	NA	NA	NA	NA	56165-57-2	Degradate	Terbufos	Terbufos oxon sulfoxide
231	Terbufos_sulfone	68703	LCM60	NA	NA	NA	NA	56070-16-7	Degradate	Terbufos	Terbufos sulfone
232	Terbufos_sulfoxide	68704	LCM60	NA	NA	NA	NA	10548-10-4	Degradate	Terbufos	Terbufos sulfoxide
233	Tetraconazole	66654	LCM60	NA	NA	NA	NA	112281-77-3	Pesticide	NA	Tetraconazole
234	Triallate	68710	LCM60	NA	NA	NA	NA	2303-17-5	Herbicide	NA	Triallate
235	Trifloxystrobin	66660	LCM60	NA	NA	NA	NA	141517-21-7	Pesticide	NA	Trifloxystrobin
236	cis-Bifenthrin_acid	68553	LCM60	NA	NA	NA	NA	68127-59-3	Degradate	Bifenthrin/lambda-cyhalothrin/Tefluthrin	cis-Bifenthrin acid/cis-Cyhalothrin acid/cis-Tefluthrin acid
237	sec-Acetochlor_OXA	68684	LCM60	NA	NA	NA	NA	152019-74-4	Degradate	Acetochlor/Metolachlor	sec-Acetochlor oxanilic acid
238	sec-Alachlor_OXA	68685	LCM60	NA	NA	NA	NA	ND	Degradate	Alachlor	sec-Alachlor oxanilic acid
239	trans-Permethrin	68708	LCM60	NA	NA	NA	NA	61949-77-7	ND	ND	trans-Permethrin
240	1-Naphthol	NA	NA	49295	GCM39	NA	NA	90-15-3	Degradate	Carbaryl/napropamide	1-Naphthol
241	2,6-Diethylaniline	NA	NA	82660	GCM35	NA	NA	579-66-8	Degradate	Alachlor	2,6-Diethylaniline
242	2-Ethyl-6-meth_iline	NA	NA	61620	GCM39	NA	NA	24549-06-2	Degradate	Metolachlor	2-Ethyl-6-methylaniline
243	3,4-Dichloroaniline	NA	NA	61625	GCM39	NA	NA	95-76-1	Degradate	Diuron	3,4-Dichloroaniline
244	3,5-Dichloroaniline	NA	NA	61627	GCM39	NA	NA	626-43-7	Degradate	Iprodione	3,5-Dichloroaniline
245	4-Chloro-2-met_henol	NA	NA	61633	GCM39	NA	NA	1570-64-5	Degradate	MCPA	4-Chloro-2-methylphenol
246	Benfluralin	NA	NA	82673	GCM35	NA	NA	1861-40-1	Herbicide	NA	Benfluralin
247	Cyfluthrin	NA	NA	61585	GCM39	NA	NA	68359-37-5	Insecticide	NA	Cyfluthrin
248	Cypermethrin	NA	NA	61586	GCM39	NA	NA	52315-07-8	Insecticide	NA	Cypermethrin
249	Dacthal	NA	NA	82682	GCM35	NA	NA	1861-32-1	Herbicide	NA	Dacthal
250	Dieldrin	NA	NA	39381	GCM35	NA	NA	60-57-1	Insecticide	NA	Dieldrin
251	Endosulfan_sulfate	NA	NA	61590	GCM39	NA	NA	1031-07-8	Degradate	alpha-Endosulfan/beta-Endosulfan	Endosulfan sulfate
252	Ethion	NA	NA	82346	GCM40	NA	NA	563-12-2	Insecticide	NA	Ethion
253	Ethion_monoxon	NA	NA	61644	GCM39	NA	NA	17356-42-2	Degradate	Ethion	Ethion monoxon
254	Iprodione	NA	NA	61593	GCM39	NA	NA	36734-19-7	Fungicide	NA	Iprodione

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		NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code	NWIS parameter code	NWIS method code				
255	Isofenphos	NA	NA	61594	GCM39	NA	NA	25311-71-1	Insecticide	NA	Isofenphos
256	Tefluthrin	NA	NA	61606	GCM39	NA	NA	79538-32-2	Insecticide	NA	Tefluthrin
257	Trifluralin	NA	NA	82661	GCM35	NA	NA	1582-09-8	Herbicide	NA	Trifluralin
258	alpha-Endosulfan	NA	NA	34362	GCM39	NA	NA	959-98-8	Insecticide	NA	alpha-Endosulfan
259	cis-Propiconazole	NA	NA	79846	GCM40	NA	NA	112721-87-6	Fungicide	NA	cis-Propiconazole
260	lambda-Cyhalothrin	NA	NA	61595	GCM39	NA	NA	91465-08-6	Insecticide	NA	lambda-Cyhalothrin
261	trans-Propiconazole	NA	NA	79847	GCM40	NA	NA	120523-07-1	Fungicide	NA	trans-Propiconazole
262	2,4-DB	NA	NA	NA	NA	38746	LCM29	94-82-6	Herbicide	NA	2,4-DB
263	2,4-D_methyl_ester	NA	NA	NA	NA	50470	LCM29	1928-38-7	Herbicide	NA	2,4-D methyl ester
264	2,4-D_plus_2,4-_ster	NA	NA	NA	NA	66496	CAL13	ND	Herbicide	NA	2,4-D plus 2,4-D methyl ester
265	3-(4-chlorophe_urea	NA	NA	NA	NA	61692	LCM29	5352-88-5	Degradate	Monuron/monolinuron	3-(4-chlorophenyl)-1-methyl urea
266	Acifluorfen	NA	NA	NA	NA	49315	LCM29	50594-66-6	Herbicide	NA	Acifluorfen
267	Bendiocarb	NA	NA	NA	NA	50299	LCM29	22781-23-3	Insecticide	NA	Bendiocarb
268	Benomyl	NA	NA	NA	NA	50300	LCM29	17804-35-2	Fungicide	NA	Benomyl
269	Bensulfuron-methyl	NA	NA	NA	NA	61693	LCM29	83055-99-6	Herbicide	NA	Bensulfuron-methyl
270	Caffeine	NA	NA	NA	NA	50305	LCM29	58-08-2	Stimulant	NA	Caffeine
271	Chloramben_met_ester	NA	NA	NA	NA	61188	LCM29	7286-84-2	Herbicide	NA	Chloramben methyl ester
272	Clopyralid	NA	NA	NA	NA	49305	LCM29	1702-17-6	Herbicide	NA	Clopyralid
273	Cycloate	NA	NA	NA	NA	04031	LCM29	1134-23-2	Herbicide	NA	Cycloate
274	Dichlorprop	NA	NA	NA	NA	49302	LCM29	120-36-5	Herbicide	NA	Dichlorprop
275	Dinoseb	NA	NA	NA	NA	49301	LCM29	88-85-7	Herbicide	NA	Dinoseb
276	Diphenamid	NA	NA	NA	NA	04033	LCM29	957-51-7	Herbicide	NA	Diphenamid
277	Fenuron	NA	NA	NA	NA	49297	LCM29	101-42-8	Herbicide	NA	Fenuron
278	MCPB	NA	NA	NA	NA	38487	LCM29	94-81-5	Herbicide	NA	MCPB
279	Methiocarb	NA	NA	NA	NA	38501	LCM29	2032-65-7	Insecticide	NA	Methiocarb
280	Metsulfuron-methyl	NA	NA	NA	NA	61697	LCM29	74223-64-6	Herbicide	NA	Metsulfuron-methyl
281	Neburon	NA	NA	NA	NA	49294	LCM29	555-37-3	Herbicide	NA	Neburon
282	Picloram	NA	NA	NA	NA	49291	LCM29	1918-02-1	Herbicide	NA	Picloram
283	Propham	NA	NA	NA	NA	49236	LCM29	122-42-9	Herbicide	NA	Propham

[1]Pesticide subsequently deleted from schedule 2437.

Tables, Figures, and Datasets in Appendixes

The large number of pesticides, analytical methods, and comparisons in this report provides challenges for presenting the information concisely in the text. Figures comparing recovery in field matrix spikes and laboratory reagent spikes; and comparing recovery, detections, or concentrations by pesticides analyzed by old and new analytical methods generated hundreds of pages of figures. For these figures, one example pesticide (atrazine) is provided in the text but all pesticides are shown in the figures in the appendixes. In general, pesticides in the figures and tables are presented by the index variable (table 5). In tables presenting statistical results, however, pesticides are sorted by the test statistic. Data files used to calculate recovery from analytical data, to compare recovery among methods, to compare detections and concentrations among methods, to calculate variability of detections and concentrations for sh2437, and to investigate matrix effects that might influence recovery are provided in (Martin and Baker, 2017).

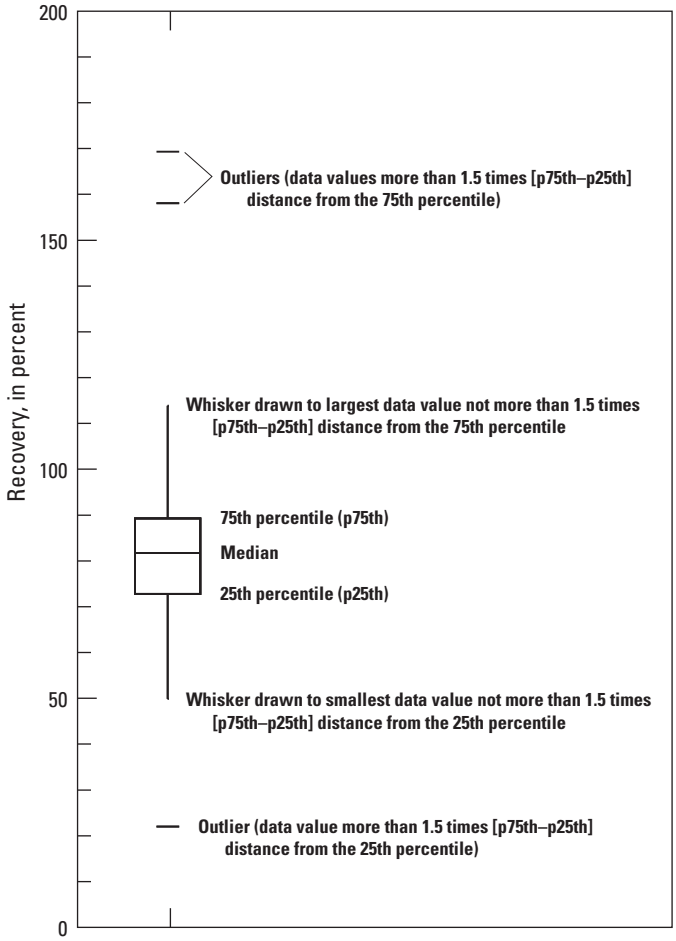

Figure 2. Explanation of a boxplot that is used to depict the distribution of recovery.

Results and Discussion

Recovery of Pesticides Analyzed by Schedule 2437

This section summarizes pesticide recovery in stream-water matrix spikes analyzed by sh2437, compares recovery in stream-water matrix spikes to recovery in laboratory reagent spikes, and presents a dataset for the analysis of matrix characteristics that might influence recovery.

Stream-Water Matrix Spikes

The median recoveries of pesticides in stream-water matrix spikes analyzed by sh2437 ranged from 0 percent for 3-ketocarbofuran,[4] ammelide,[4] and phosmet_oxon[4] to 209.6 percent for didealkylatrazine (table 6). The median recovery for 237 pesticides was 91.3 percent (there were no recovery data for acetochlor_ESA [index 111] or alachlor_ESA [index 114]). Relative standard deviations of pesticide recovery in stream-water matrix spikes analyzed by sh2437 ranged from 9.8 percent for hexazinone to 369.5 percent for ammelide[4] (RSD for phosmet_oxon[4] [index 48] could not be calculated because the mean and standard deviation of recovery were 0 percent). The distributions of pesticide recovery in stream-water matrix spikes analyzed by sh2437 are shown in figure 3.

Stream-Water Matrix Spikes versus Laboratory Reagent Spikes

Pesticide recovery in stream-water matrix spikes was compared to recovery in laboratory reagent spikes in order to determine if recovery in laboratory reagent spikes would suitably characterize recovery in stream water. Laboratory reagent spikes typically are more numerous than field matrix spikes and if recovery is similar between the types of spikes, laboratory QC data could be used to characterize performance in stream water. Martin and others (2009, p. 10) observed that recovery in matrix spikes was much greater than in laboratory reagent spikes for most pesticides analyzed by GC–MS. The distributions of recovery in field matrix spikes compared to laboratory reagent spikes are shown in side-by-side boxplots for 237 pesticides in appendix 2 and for atrazine in figure 4. The laboratory reagent spikes are those that were analyzed during the same time period as the field matrix spikes for the field study. Analytical data and calculated recoveries for all background environmental pesticide concentrations and for all the associated field matrix spikes are provided in Martin and Baker (2017, dataset 1). Analytical data and calculated recoveries for background environmental pesticide concentrations and for the associated field matrix spikes that met the criteria

[4]These compounds were subsequently deleted from the method.

Table 6. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437.

[Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated]

Index	Pesticide short name	Number of matrix spikes	Mean (percent)	Standard deviation (percent)	Relative standard deviation (percent)	Percentiles of recovery (percent)						
						Minimum	5th	25th	Median	75th	95th	Maximum
1	Atrazine	141	95.9	16.0	16.7	62.4	71.4	83.9	94.2	105.5	124.5	138.3
2	Carbaryl	145	80.4	21.5	26.7	2.7	46.4	69.8	82.9	92.6	110.1	135.5
3	Carbofuran	145	89.4	14.6	16.3	43.2	69.7	80.2	87.2	97.5	116.1	132.0
4	Deethylatrazine	145	89.2	16.3	18.2	54.6	64.7	79.0	85.0	99.5	120.0	138.2
5	Metalaxyl	145	97.0	14.7	15.1	62.3	74.6	87.9	96.3	106.3	121.3	151.0
6	Tebuthiuron	145	92.4	9.5	10.3	69.3	75.9	86.3	93.2	98.7	107.1	116.0
7	2-Chloro-2,6-d_ilide	145	91.1	16.9	18.5	55.0	64.9	79.5	91.3	99.8	120.1	134.5
8	Acetochlor	145	97.4	19.0	19.5	61.3	70.3	81.9	96.4	112.0	128.7	142.7
9	Alachlor	145	99.5	16.0	16.0	65.2	75.6	88.2	97.9	111.4	127.7	143.9
10	Azinphos-methyl	145	105.4	21.9	20.7	68.2	76.8	92.0	102.0	113.7	145.5	219.0
11	Azinphos-methyl-oxon	145	94.4	20.2	21.4	27.1	65.8	82.4	93.9	104.4	131.2	151.6
12	Chlorpyrifos	145	79.9	13.6	17.0	48.1	57.5	73.2	78.7	84.1	108.2	120.5
13	Chlorpyrifos_oxon	145	76.1	16.4	21.6	32.6	53.6	65.1	75.2	84.2	108.3	124.3
14	Cyanazine	100	104.1	16.9	16.3	66.6	78.2	91.7	102.9	115.7	131.6	139.7
15	Desulfinylfipro_mide	145	77.4	12.7	16.4	45.4	59.1	69.8	76.6	84.8	98.5	122.0
16	Desulfinylfipronil	145	87.5	10.9	12.4	62.6	74.7	80.4	85.2	92.4	111.1	118.8
17	Diazinon	145	94.8	17.2	18.2	57.3	69.4	83.0	94.4	104.5	125.2	157.3
18	Diazoxon	145	65.3	14.2	21.7	34.8	44.8	58.5	65.6	73.0	81.2	147.6
19	Dichlorvos	145	95.7	22.4	23.5	45.5	63.5	80.9	93.1	105.3	135.8	180.0
20	Dicrotophos	145	106.7	24.0	22.5	61.5	77.7	91.1	102.9	115.2	148.3	242.8
21	Dimethoate	145	103.4	22.2	21.5	58.5	79.5	89.6	100.0	112.3	148.5	218.9
22	Disulfoton	145	83.5	15.4	18.4	52.4	64.4	73.2	80.3	90.1	114.8	142.7
23	Disulfoton_sulfone	145	97.5	22.0	22.6	25.9	72.2	84.5	94.9	107.3	135.9	190.0
24	EPTC	145	105.6	24.7	23.4	49.9	62.6	91.3	103.6	117.9	148.9	182.5
25	Ethoprophos	145	96.4	16.0	16.6	60.4	75.5	85.2	94.3	102.9	131.5	154.2
26	Fenamiphos	145	94.9	14.7	15.5	61.1	76.4	85.1	92.3	101.8	124.8	149.8
27	Fenamiphos_sulfone	145	111.1	23.3	21.0	71.8	83.5	95.4	106.5	121.9	153.1	247.5
28	Fenamiphos_sulfoxide	145	112.8	25.8	22.9	71.3	81.2	97.3	108.5	124.1	154.4	258.5
29	Fipronil	145	93.3	13.5	14.5	66.0	75.6	83.9	90.3	99.4	120.6	130.0
30	Fipronil_sulfide	145	92.5	11.4	12.3	67.9	77.8	84.4	91.0	98.8	115.9	124.2
31	Fipronil_sulfone	145	87.1	11.3	13.0	62.2	71.8	77.7	86.0	94.8	107.1	116.5
32	Fonofos	145	95.0	17.1	18.0	57.3	74.7	83.6	92.5	101.8	130.9	161.7
33	Hexazinone	145	92.8	9.1	9.8	69.2	77.2	86.2	93.7	98.8	107.5	113.4
34	Malaoxon	145	60.2	26.0	43.2	0.0	14.1	46.0	61.1	74.3	101.5	132.9
35	Malathion	145	77.0	21.3	27.6	3.9	44.4	68.0	76.9	88.8	106.7	137.8
36	Methidathion	145	106.3	21.4	20.1	69.8	81.1	92.0	102.3	116.7	143.5	223.9
37	Metolachlor	137	96.1	11.2	11.7	69.3	79.6	87.9	95.3	104.0	115.1	124.2
38	Metribuzin	145	91.8	12.1	13.2	59.0	73.6	83.6	91.6	100.2	110.6	132.0
39	Molinate	145	96.8	24.5	25.3	52.6	66.8	78.2	89.9	108.2	142.8	176.3
40	Myclobutanil	145	94.9	18.1	19.1	63.2	69.8	80.9	91.3	108.5	125.1	156.0
41	Oxyfluorfen	145	106.8	41.0	38.4	0.0	49.4	77.5	101.0	136.6	176.1	215.6
42	Paraoxon-methyl	145	101.3	22.9	22.6	49.7	72.6	85.4	97.8	110.4	145.3	199.0
43	Parathion-methyl	145	97.5	64.1	65.8	0.0	0.0	58.8	95.8	134.9	208.4	307.3
44	Pendimethalin	145	88.8	15.3	17.2	46.6	65.1	79.7	87.8	99.2	113.3	139.8
45	Phorate	145	84.7	17.5	20.7	54.6	62.9	72.1	81.8	94.0	121.2	139.3
46	Phorate_oxon	145	87.8	20.3	23.1	51.7	63.7	74.5	85.3	95.8	127.8	182.4
47	Phosmet	122	34.7	12.8	36.9	16.1	20.2	23.8	32.0	40.7	59.6	72.7

Table 6. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437.—Continued

[Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated]

Index	Pesticide short name	Number of matrix spikes	Mean (percent)	Standard deviation (percent)	Relative standard deviation (percent)	Percentiles of recovery (percent)						
						Minimum	5th	25th	Median	75th	95th	Maximum
48	Phosmet_oxon	54	0.0	0.0	nc	0.0	0.0	0.0	0.0	0.0	0.0	0.0
49	Prometon	145	94.4	12.5	13.2	69.6	75.3	86.0	93.5	101.1	114.6	142.9
50	Prometryn	145	97.5	10.3	10.6	73.6	82.8	91.4	96.7	103.9	113.6	138.2
51	Propanil	145	101.5	18.6	18.4	56.9	70.8	90.3	101.7	113.0	130.7	150.4
52	Propargite	145	85.8	20.9	24.4	13.3	52.4	75.6	85.3	98.3	116.9	138.6
53	Propyzamide	145	99.6	17.5	17.6	59.8	69.0	89.4	100.6	111.0	128.7	140.6
54	Simazine	145	93.6	14.6	15.6	58.1	72.0	84.1	93.1	103.0	118.8	140.2
55	Tebuconazole	145	96.7	15.5	16.0	65.9	73.6	85.5	94.5	107.1	122.6	146.9
56	Terbufos	145	81.0	14.4	17.8	49.6	61.0	72.1	78.7	88.8	107.8	134.5
57	Terbufos_sulfo_nalog	145	85.8	20.9	24.4	7.8	58.0	77.1	86.3	96.2	116.4	146.6
58	Terbuthylazine	145	95.8	11.3	11.8	70.2	76.1	89.1	94.9	103.0	115.8	126.5
59	Thiobencarb	145	95.1	16.9	17.7	65.6	72.4	83.7	89.9	108.3	123.1	156.0
60	Tribuphos	145	97.7	18.5	19.0	17.2	67.2	90.1	98.0	105.6	130.0	156.1
61	cis-Permethrin	136	85.3	19.2	22.5	14.7	45.5	74.8	88.9	96.0	112.2	135.1
62	2,4-D	143	92.8	19.7	21.2	45.5	58.3	80.9	92.2	104.4	128.3	163.7
63	2-Hydroxyatrazine	145	96.0	19.1	19.9	53.1	71.1	83.5	93.7	104.9	128.6	178.5
64	3-Hydroxycarbofuran	145	71.5	18.2	25.4	6.4	44.2	62.3	73.1	82.4	100.3	128.0
65	Aldicarb	145	86.0	17.2	20.0	57.5	64.7	75.6	82.8	93.5	120.6	177.6
66	Aldicarb_sulfone	145	95.6	19.4	20.3	56.8	69.8	82.6	92.4	109.3	131.1	151.3
67	Aldicarb_sulfoxide	145	92.6	14.3	15.5	60.1	72.8	82.9	91.2	99.9	120.3	136.7
68	Bentazon	145	102.6	16.2	15.8	69.6	79.3	91.8	100.4	113.0	126.8	162.4
69	Bromacil	145	101.5	19.2	18.9	69.4	74.5	88.9	100.7	110.9	131.6	199.2
70	Bromoxynil	145	97.7	19.9	20.3	58.9	72.5	83.4	93.5	109.0	139.5	170.5
71	Chlorimuron-ethyl	145	52.1	17.7	34.1	4.3	21.4	41.1	55.9	64.1	74.8	91.7
72	Dacthal_monoacid	145	96.5	61.4	63.7	0.0	11.7	53.5	94.2	129.2	197.1	372.8
73	Deisopropylatrazine	145	94.3	19.5	20.6	62.2	66.9	81.3	92.4	102.7	134.9	177.1
74	Dicamba	144	115.4	52.3	45.3	21.5	61.3	82.9	106.7	140.0	208.6	409.0
75	Diuron	143	89.0	9.5	10.7	56.8	73.7	83.6	88.8	94.3	105.5	116.2
76	Flumetsulam	145	134.9	36.9	27.4	80.2	93.3	109.2	124.1	149.7	207.6	300.1
77	Fluometuron	145	90.9	9.5	10.4	69.3	76.3	85.0	91.1	96.6	106.8	116.9
78	Imazaquin	145	91.6	11.8	12.9	62.7	74.8	82.7	90.3	99.0	113.8	119.7
79	Imazethapyr	145	109.5	20.3	18.6	63.4	82.8	96.8	107.9	117.4	148.5	191.5
80	Imidacloprid	145	123.6	24.5	19.8	81.4	89.8	106.3	118.0	136.0	170.9	200.9
81	Linuron	145	93.0	10.2	11.0	59.1	77.2	85.6	93.5	100.3	108.1	118.1
82	MCPA	145	92.7	22.0	23.8	44.9	54.9	80.0	94.1	106.5	128.7	156.2
83	Methomyl	145	109.8	20.8	19.0	63.4	75.6	98.1	109.4	119.3	144.3	201.4
84	Nicosulfuron	145	58.1	17.9	30.7	6.2	25.8	48.7	60.2	68.8	88.2	98.8
85	Norflurazon	145	108.1	22.7	21.0	69.2	79.2	95.1	104.3	116.9	139.4	250.1
86	Oryzalin	145	106.0	21.2	20.0	59.1	77.1	89.5	105.8	120.6	139.9	182.9
87	Oxamyl	144	64.6	22.4	34.7	0.3	18.8	54.0	66.3	77.6	99.0	108.5
88	Propiconazole	145	95.8	16.8	17.5	58.8	74.9	83.5	91.4	107.7	123.7	157.2
89	Propoxur	145	96.6	14.4	15.0	61.0	75.1	86.1	95.3	104.0	121.7	142.5
90	Siduron	145	94.7	11.3	11.9	65.3	78.7	87.3	93.9	102.0	112.3	139.9
91	Sulfometuron-methyl	145	70.1	14.2	20.3	20.9	45.7	63.8	72.4	79.8	90.0	95.4
92	Terbacil	145	100.7	24.2	24.0	50.2	68.2	82.0	97.3	118.0	141.0	174.2
93	Triclopyr	145	93.1	20.4	21.9	45.1	63.9	77.7	91.9	108.7	124.7	148.2
94	1H-1,2,4-Triazole	115	45.4	23.9	52.8	-69.9	20.5	33.7	43.6	56.2	82.4	114.6
95	2-(1-Hydroxyeth_line	145	45.6	17.2	37.7	0.0	23.1	33.6	45.2	55.3	73.3	102.1

Table 6. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437.—Continued

[Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated]

Index	Pesticide short name	Number of matrix spikes	Mean (percent)	Standard deviation (percent)	Relative standard deviation (percent)	Percentiles of recovery (percent)						
						Minimum	5th	25th	Median	75th	95th	Maximum
96	2-Amino-N-isopr_mide	145	95.3	16.0	16.8	66.1	74.3	84.2	91.1	104.3	125.7	147.9
97	2-Aminobenzimidazole	145	112.6	14.6	13.0	80.7	90.2	102.6	111.1	120.8	137.0	178.9
98	2-Isopropyl-6-m_inol	145	114.9	43.1	37.5	25.8	77.3	94.8	107.8	122.9	162.9	497.8
99	2-[(2-Ethyl-6-m_anol	145	88.2	17.4	19.8	48.8	61.7	76.7	84.8	101.3	118.2	138.3
100	3,4-Dichlorophe_urea	145	92.7	14.1	15.2	63.4	70.0	82.1	93.3	102.6	114.7	129.8
101	3-Ketocarbofuran	54	6.9	13.9	201.4	0.0	0.0	0.0	0.0	0.0	34.9	58.0
102	3-Phenoxybenzoi_acid	145	87.1	9.9	11.4	63.6	72.9	80.6	86.2	93.6	103.5	111.5
103	4-(Hydroxymeth_halin	145	85.6	28.5	33.3	37.9	48.4	67.1	80.8	99.1	139.4	222.6
104	4-Chlorobenzylm_xide	145	101.7	18.2	17.8	62.6	77.7	87.9	99.2	111.2	134.3	158.9
105	4-Hydroxy_molinate	145	90.9	19.2	21.1	56.9	64.9	78.3	85.6	104.6	123.2	149.5
106	4-Hydroxychloro_onil	142	102.0	33.9	33.2	37.7	50.1	74.4	105.9	121.0	164.2	198.7
107	4-Hydroxyhexazi_ne_A	145	103.0	19.5	19.0	68.2	79.6	88.7	100.0	112.9	135.3	198.7
108	7-Hydroxycarbofuran	145	97.4	40.1	41.1	0.0	32.2	74.6	98.3	124.5	164.3	194.7
109	Acephate	141	111.7	25.7	23.0	69.5	84.1	96.6	106.0	118.6	164.5	256.0
110	Acet/Met_sec_amide	145	89.2	17.7	19.8	51.8	62.0	76.5	89.1	100.7	120.4	137.4
112	Acetochlor_OXA	142	96.7	21.0	21.7	38.9	70.4	83.7	95.3	107.7	129.5	180.9
113	Acetochlor_SAA	144	88.3	26.7	30.3	29.3	43.6	70.5	86.5	103.3	133.6	194.3
115	Alachlor_OXA	145	92.7	15.2	16.4	53.7	70.0	81.4	92.0	102.5	118.5	143.6
116	Alachlor_SAA	145	89.4	21.7	24.3	38.2	56.2	73.9	90.1	100.3	132.2	157.1
117	Ametryn	145	97.6	13.0	13.3	70.2	73.9	88.6	97.1	107.3	120.6	131.3
118	Aminopyralid	25	156.8	59.6	38.0	56.1	62.6	124.3	168.9	188.9	259.7	304.8
119	Ammelide	145	1.6	5.7	369.5	-16.6	0.0	0.0	0.0	0.0	15.3	36.8
120	Asulam	145	27.5	11.9	43.2	8.4	11.0	20.2	25.4	33.7	48.1	79.3
121	Azoxystrobin	145	95.7	17.9	18.6	62.7	71.7	83.7	91.2	110.2	124.2	154.8
122	Bifenazate	145	2.8	3.9	141.4	0.0	0.2	0.5	0.9	3.6	11.0	19.8
123	Bifenazate_diazene	145	4.9	10.0	205.1	0.0	0.0	0.0	0.8	4.6	30.8	54.9
124	Bifenthrin	137	88.3	24.3	27.5	12.4	39.0	75.3	94.7	104.1	122.9	143.2
125	Butralin	145	167.4	37.1	22.2	71.1	97.1	144.1	166.8	190.7	224.9	264.2
126	Butylate	145	97.3	19.3	19.9	66.0	74.1	83.5	91.4	112.3	129.2	163.9
127	Carbendazim	145	91.8	9.2	10.0	67.6	76.3	86.8	92.9	96.5	106.1	126.1
128	Carboxy_molinate	145	89.8	18.2	20.3	58.0	63.8	76.5	85.8	102.6	120.7	159.8
129	Chlorosulfonami_acid	145	98.9	77.6	78.5	0.0	21.3	46.5	77.4	131.7	252.9	447.1
130	Chlorsulfuron	145	73.9	15.6	21.1	21.3	43.3	65.1	73.8	83.7	98.8	120.5
131	Dechlorofipronil	145	86.8	13.6	15.6	59.4	69.8	78.4	85.4	93.4	111.0	133.7
132	Dechlorometolachlor	145	90.0	10.1	11.2	67.1	73.8	82.5	90.2	97.2	105.9	111.7
133	Deethylhydroxy_azine	144	114.2	29.3	25.7	61.5	74.7	93.4	111.7	127.5	172.9	198.3
134	Deiodo_flubendiamide	145	90.3	14.5	16.1	58.7	68.4	79.6	87.9	100.6	113.0	131.2
135	Deisopropyl_pr_etryn	145	89.0	8.9	10.0	64.8	72.6	83.4	89.4	95.0	102.8	108.4
136	Deisopropylhyd_azine	127	139.2	33.9	24.3	84.8	94.2	115.2	135.0	154.0	223.6	246.6
137	Deisopropyliprodione	145	196.2	72.6	37.0	74.7	105.3	144.8	181.1	234.1	341.9	474.3
138	Demethyl_fluometuron	145	85.7	8.9	10.3	63.0	70.0	79.6	85.8	91.6	100.3	106.1
139	Demethyl_hexazi_ne_B	145	88.4	8.8	9.9	62.1	74.2	82.8	88.5	93.6	102.1	109.4
140	Demethyl_norflurazon	145	93.3	11.2	12.1	67.6	76.6	87.2	91.8	100.2	113.6	126.8
141	Desamino-diketo_uzin	145	74.5	21.4	28.7	16.4	40.8	62.4	72.1	86.2	107.5	150.7
142	Didealkylatrazine	143	232.8	111.3	47.8	54.2	112.4	152.1	209.6	270.0	450.1	703.7
143	Didemethyl_hexa_ne_F	145	85.7	8.8	10.3	57.9	71.2	80.1	86.2	91.7	100.6	106.8
144	Diflubenzuron	145	86.7	10.4	12.0	62.0	69.4	80.7	87.1	93.2	102.3	120.0
145	Diflufenzopyr	145	92.9	28.3	30.5	20.3	51.9	73.2	90.6	108.1	134.7	195.7

Table 6. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437.—Continued

[Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated]

Index	Pesticide short name	Number of matrix spikes	Mean (percent)	Standard deviation (percent)	Relative standard deviation (percent)	Percentiles of recovery (percent)						
						Minimum	5th	25th	Median	75th	95th	Maximum
146	Diketonitrile-i_tole	145	147.3	50.1	34.0	71.8	86.6	112.8	137.1	168.8	234.2	366.0
147	Dimethenamid	143	100.2	17.5	17.5	62.0	71.4	88.7	100.4	111.9	130.8	145.3
148	Dimethenamid_ESA	145	86.7	15.1	17.4	35.6	60.7	76.2	86.5	98.2	108.1	122.9
149	Dimethenamid_OXA	145	94.1	14.5	15.4	58.7	71.4	84.0	93.9	103.9	116.6	136.5
150	Dimethenamid_SAA	145	79.8	21.9	27.5	22.3	48.4	64.5	79.1	91.0	113.5	170.8
151	Dimethoate_oxyg_alog	145	80.1	23.6	29.5	6.5	45.8	68.0	78.1	89.2	122.9	158.4
152	Disulfoton_oxon	145	109.3	22.8	20.8	68.2	82.1	95.3	105.9	116.7	151.3	232.6
153	Disulfoton_oxon_fone	145	83.9	21.7	25.9	5.9	53.3	74.6	83.7	94.3	110.7	154.5
154	Disulfoton_oxon_xide	145	109.8	22.3	20.3	64.5	81.1	94.5	106.5	119.1	148.5	220.5
155	Disulfoton_sulfoxide	145	115.3	24.2	21.0	76.0	86.8	99.7	110.3	125.1	155.1	241.8
156	EPTC_degradate_48722	145	94.3	17.8	18.9	59.0	69.4	82.1	89.7	105.7	124.5	160.9
157	Etoxazole	145	96.4	18.4	19.1	32.6	68.4	85.2	95.6	108.0	125.0	149.2
158	Famoxadone	122	21.2	21.5	101.6	0.0	0.0	0.0	15.0	34.5	66.4	86.2
159	Fenbutatin_oxide	145	87.8	34.6	39.5	23.1	43.1	65.9	83.3	103.7	150.8	268.0
160	Fentin	145	92.1	19.0	20.7	40.1	64.6	79.6	92.5	105.2	124.9	141.0
161	Fipronil_amide	145	92.7	19.0	20.5	37.7	65.0	79.7	93.3	103.2	130.9	154.5
162	Fipronil_sulfonate	145	109.3	33.4	30.6	45.4	60.6	86.2	104.6	132.4	166.1	232.3
163	Flubendiamide	145	130.2	29.3	22.5	67.0	88.4	108.9	130.2	149.7	181.3	198.8
164	Flumiclorac	54	3.4	5.1	148.5	0.0	0.0	1.0	1.2	2.8	18.5	19.8
165	Formetanate	122	12.0	10.6	88.5	0.0	1.7	3.9	7.2	18.0	33.8	42.0
166	Halosulfuron-methyl	145	63.4	14.0	22.0	18.3	40.5	55.2	66.5	72.7	82.6	89.0
167	Hexazinone_Tran_ct_C	145	107.6	22.1	20.6	63.0	78.5	93.4	104.1	117.1	149.6	222.9
168	Hexazinone_Tran_ct_D	145	98.6	33.8	34.3	24.1	54.7	76.5	92.2	116.4	158.7	200.1
169	Hexazinone_Tran_ct_E	145	62.8	19.2	30.6	14.8	30.9	49.1	62.0	76.3	94.1	109.6
170	Hexazinone_Tran_ct_G	145	83.9	11.4	13.6	56.0	64.7	76.4	83.3	92.0	101.5	124.8
171	Hydroxy_didemet_uron	145	73.7	19.0	25.8	0.0	44.6	61.0	73.2	85.8	104.8	125.8
172	Hydroxy_monodem_uron	145	63.6	19.2	30.2	11.5	32.1	51.4	64.7	76.6	95.2	105.7
173	Hydroxyacetochlor	145	90.6	18.8	20.8	51.4	61.0	76.6	89.7	104.3	122.3	139.9
174	Hydroxyalachlor	145	91.9	16.9	18.3	56.9	66.1	81.4	90.5	101.5	122.2	135.4
175	Hydroxydiazinon	145	87.2	15.1	17.3	55.8	70.2	76.7	84.5	93.6	118.9	143.7
176	Hydroxyfluometuron	145	49.5	25.2	50.9	1.8	8.1	31.8	52.0	67.8	89.6	99.0
177	Hydroxymetolachlor	145	92.1	11.6	12.6	64.9	76.4	85.2	89.5	99.2	113.9	138.1
178	Hydroxyphthalazinone	145	90.2	14.3	15.8	53.7	68.9	80.4	89.1	101.8	112.7	126.2
179	Hydroxysimazine	145	109.2	15.8	14.4	70.0	84.1	99.2	107.6	118.3	133.5	160.6
180	Hydroxytebuthurion	145	72.3	17.6	24.3	5.8	37.1	64.1	74.7	83.6	97.1	102.6
181	Imazamox	145	107.8	18.3	16.9	57.1	83.9	96.3	105.2	119.6	142.3	163.5
182	Indoxacarb	145	67.1	23.6	35.2	0.0	23.1	54.8	68.3	81.5	101.6	126.0
183	Isoxaflutole	145	74.7	21.3	28.4	4.5	39.5	63.1	77.6	89.8	104.7	124.6
184	Isoxaflutole_ac_3328	145	96.9	15.4	15.9	65.8	76.7	87.0	92.9	106.3	125.0	146.7
185	Kresoxim-methyl	145	78.0	19.5	25.0	12.8	55.8	66.4	77.3	93.2	107.8	122.6
186	Lactofen	145	70.3	26.2	37.2	1.3	19.1	55.9	72.0	85.8	113.5	138.3
187	Metconazole	145	95.8	15.0	15.6	63.4	75.4	85.5	92.1	107.0	121.5	154.7
188	Methamidophos	144	109.9	22.3	20.3	69.1	83.4	95.7	105.8	117.5	154.4	224.3
189	Methomyl_oxime	145	93.9	24.8	26.4	55.3	64.9	78.7	90.3	101.5	140.0	200.3
190	Methoxyfenozide	145	100.5	20.4	20.3	61.6	71.6	85.0	97.9	117.4	135.4	159.8
191	Metolachlor_ESA	136	88.7	25.9	29.2	0.8	46.8	76.2	89.2	101.4	130.5	165.6
192	Metolachlor_OXA	137	94.1	22.8	24.2	29.0	55.9	77.5	94.2	110.0	133.7	162.0
193	Metolachlor_hyd_none	145	91.9	18.9	20.6	56.6	66.7	78.7	89.0	102.9	127.4	160.7

Table 6. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437.—Continued

[Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated]

Index	Pesticide short name	Number of matrix spikes	Mean (percent)	Standard deviation (percent)	Relative standard deviation (percent)	Percentiles of recovery (percent)						
						Minimum	5th	25th	Median	75th	95th	Maximum
194	Metribuzin-desamino	145	87.5	10.4	11.8	60.0	70.5	81.0	88.6	93.8	104.1	115.7
195	Metribuzin_DK	145	73.8	20.9	28.3	21.3	38.3	60.7	73.5	88.3	108.6	130.8
196	N-(3,4-Dichloro_urea	144	85.9	9.6	11.1	58.3	70.9	79.0	86.1	93.0	102.3	107.7
197	Naled	145	28.6	20.5	71.8	0.0	1.9	12.4	24.3	42.1	67.7	83.3
198	Novaluron	145	67.3	19.9	29.6	5.5	21.7	59.0	69.7	81.7	92.1	116.2
199	O-Ethyl-O-methy_oate	145	112.0	23.9	21.3	69.3	84.3	97.4	109.2	120.6	157.9	238.4
200	O-Ethyl-S-methy_oate	145	110.6	22.7	20.5	68.0	83.5	97.8	106.1	118.6	150.9	241.7
201	O-Ethyl-S-propy_oate	145	119.0	34.4	28.9	68.7	78.1	96.3	113.4	135.4	172.7	300.7
202	Orthosulfamuron	145	37.6	18.2	48.4	1.1	8.5	23.5	39.5	47.6	70.4	80.7
203	Oxamyl_oxime	145	112.5	26.2	23.3	67.5	83.2	97.0	106.1	124.3	159.3	248.8
204	Paraoxon-ethyl	145	116.3	23.4	20.1	76.2	87.3	102.0	113.6	124.2	161.4	247.4
205	Phorate_oxon_su_xide	145	82.9	20.6	24.9	8.6	53.4	71.8	81.7	94.4	115.0	144.8
206	Phorate_oxygen_fone	145	76.6	21.6	28.2	3.5	47.0	65.1	76.5	87.2	111.6	147.5
207	Phorate_sulfone	145	112.7	22.9	20.3	71.3	83.4	97.8	109.9	123.6	160.9	205.4
208	Phorate_sulfoxide	145	113.0	23.1	20.4	71.4	84.0	98.4	109.0	123.4	156.4	243.5
209	Phthalazinone	145	91.0	13.6	14.9	63.4	69.8	81.8	90.6	99.4	116.2	129.2
210	Piperonyl_butoxide	137	89.6	16.3	18.2	43.5	68.2	79.0	86.5	98.8	119.7	148.4
211	Profenofos	145	77.8	18.9	24.3	12.1	46.5	69.7	77.3	88.3	105.9	126.8
212	Propazine	145	95.3	12.8	13.4	63.8	75.2	86.2	94.5	103.9	116.4	126.9
213	Prosulfuron	145	91.0	38.7	42.6	6.0	36.5	66.3	89.8	116.8	157.6	218.7
214	Pymetrozine	145	126.1	50.4	39.9	57.9	82.5	94.3	108.8	128.5	244.0	271.1
215	Pyraclostrobin	145	92.9	17.8	19.2	59.0	65.1	80.5	88.8	106.0	121.0	153.5
216	Pyridaben	145	97.8	19.7	20.1	28.8	67.9	87.9	99.0	109.3	128.6	153.8
217	Pyriproxyfen	145	96.2	15.8	16.4	62.6	74.8	85.4	93.2	106.7	122.3	153.1
218	Sulfentrazone	145	137.8	40.3	29.2	74.0	87.4	106.6	127.9	166.4	214.9	262.3
219	Sulfosulfuron	145	80.3	11.7	14.5	38.4	61.0	72.0	80.9	87.8	98.7	108.3
220	Sulfosulfuron_e_fone	145	90.6	11.5	12.7	64.2	73.3	82.6	89.7	97.2	109.0	129.4
221	TCPSA_ethyl_ester	145	87.1	12.6	14.4	54.3	66.8	78.8	86.2	95.0	107.9	123.6
222	Tebufenozide	145	101.0	17.9	17.7	66.3	75.5	88.5	97.8	114.7	128.8	160.5
223	Tebupirimfos	145	93.9	15.1	16.0	60.9	75.1	85.0	91.6	100.1	121.7	153.8
224	Tebupirimfos_oxon	145	94.7	15.4	16.3	59.1	75.9	84.5	93.0	99.3	126.9	156.6
225	Tebuthiuron_TP_104	145	100.3	16.1	16.1	68.4	77.6	89.6	99.1	106.2	132.8	173.3
226	Tebuthiuron_TP_108	145	80.7	9.7	12.1	50.3	63.3	75.1	80.7	87.1	96.7	107.2
227	Tebuthiuron_TP_109	145	93.1	45.2	48.5	12.7	48.7	73.1	86.9	101.5	139.6	407.1
228	Tebuthiuron_Tra_106	145	88.1	12.9	14.6	56.2	67.1	80.2	87.4	95.8	106.8	143.3
229	Terbufos_oxon	145	56.3	18.0	32.1	16.3	30.2	42.9	54.5	66.9	85.3	111.1
230	Terbufos_oxon_s_xide	145	94.2	20.6	21.9	18.1	68.4	84.5	93.4	104.1	133.1	156.7
231	Terbufos_sulfone	145	111.5	23.9	21.4	70.6	80.2	96.5	107.7	123.5	151.2	243.9
232	Terbufos_sulfoxide	145	113.0	21.8	19.3	75.7	87.0	99.2	109.4	122.3	154.9	233.0
233	Tetraconazole	145	93.1	19.9	21.4	62.1	67.4	77.7	86.4	110.7	126.5	152.8
234	Triallate	145	90.9	17.4	19.1	58.7	67.2	78.1	86.8	104.8	120.1	150.0
235	Trifloxystrobin	145	85.9	19.0	22.1	14.0	60.8	77.0	85.7	98.6	112.8	133.8
236	cis-Bifenthrin_acid	144	109.3	51.8	47.4	0.0	58.2	78.6	99.1	123.7	207.0	370.0
237	sec-Acetochlor_OXA	145	84.6	12.0	14.2	49.9	64.5	76.5	85.3	92.5	103.1	114.6
238	sec-Alachlor_OXA	145	86.4	12.3	14.2	60.2	65.0	77.6	86.5	96.0	105.9	110.9
239	trans-Permethrin	144	88.1	20.0	22.7	13.0	47.1	77.1	91.9	100.2	113.5	130.9

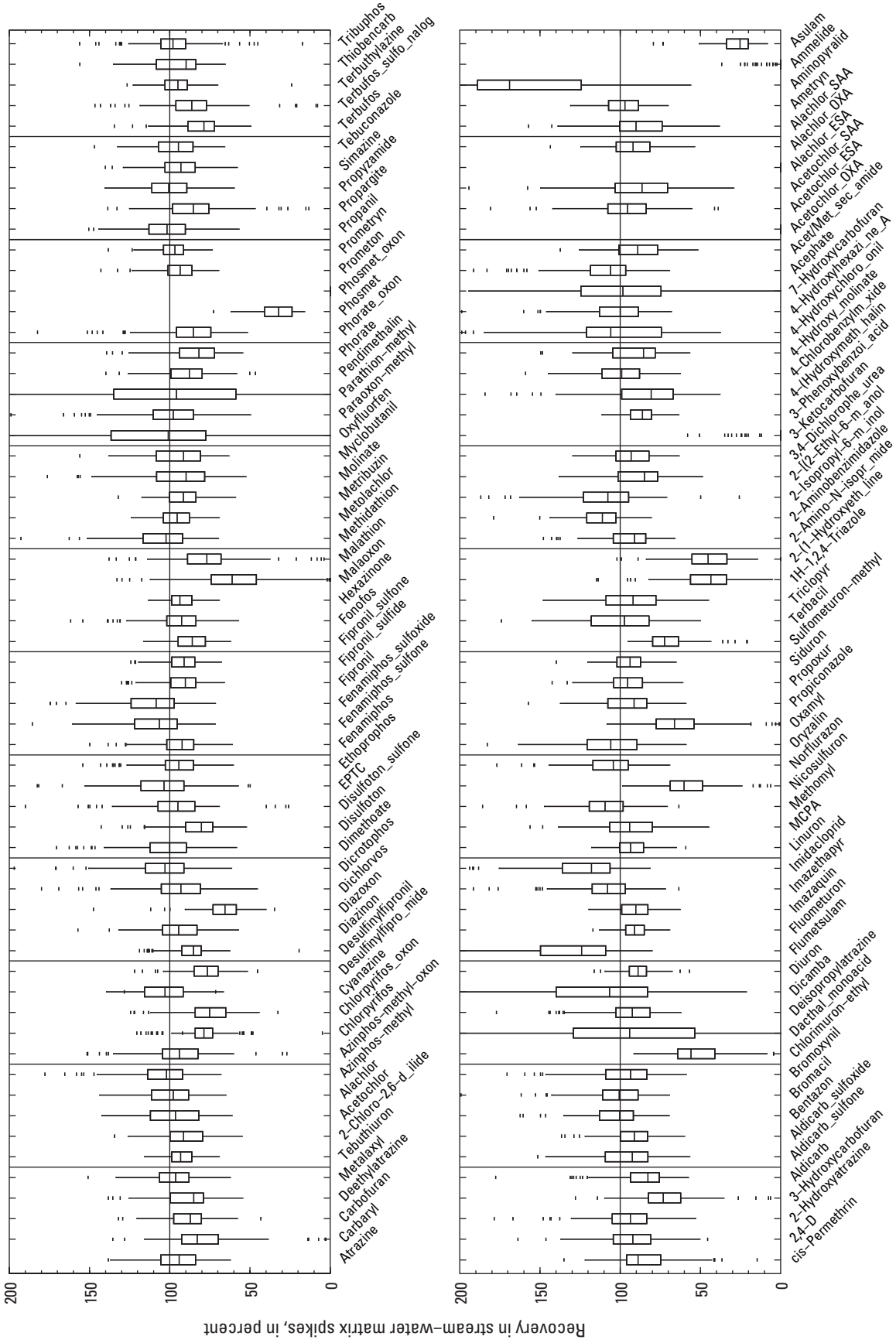

Figure 3. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437. Pesticides are sorted by the index variable (table 5). Boxplots are explained in figure 2. Recovery statistics are presented in table 6. Recoveries greater than 200 percent or less than 0 percent are not shown.

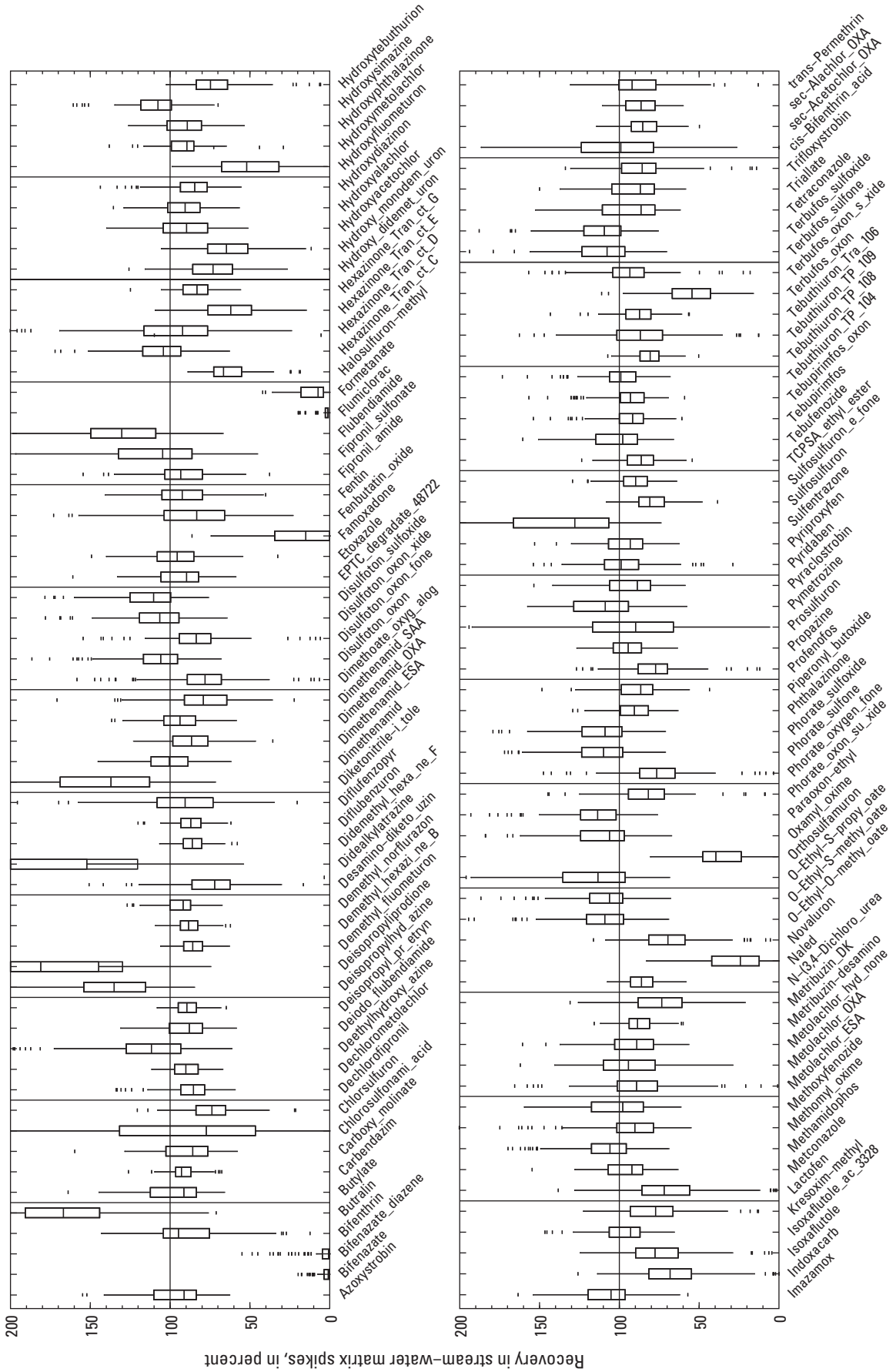

Figure 3. Recovery of pesticides in stream-water matrix spikes analyzed by schedule 2437. Pesticides are sorted by the index variable (table 5). Boxplots are explained in figure 2. Recovery statistics are presented in table 6. Recoveries greater than 200 percent or less than 0 percent are not shown.—Continued

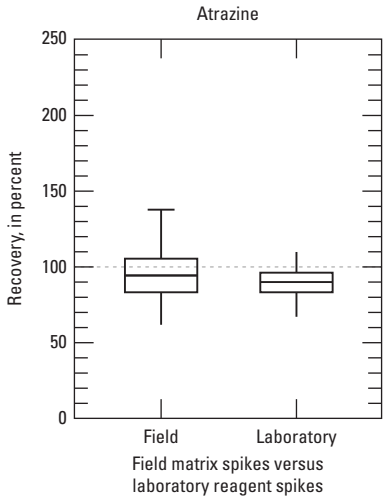

Figure 4. Distribution of recovery of atrazine in field matrix spikes and laboratory reagent spikes analyzed by the new analytical method (schedule 2437).

for use in this assessment are provided in Martin and Baker (2017, dataset 2). The metadata for Martin and Baker (2017, dataset 1) explains the wide variety of reasons why samples or results were not selected for use in the field study. Measurements of recovery in laboratory reagent spikes (and field matrix spikes selected for use in the assessment) are provided in Martin and Baker (2017, dataset 3).

The Wilcoxon rank-sum test was used to compare the median recovery of pesticides in field matrix spikes and laboratory reagent spikes. Of the 237 pesticides tested, median recovery was significantly greater in field matrix spikes for 50 pesticides and was significantly greater in laboratory reagent spikes for 58 pesticides (table 7). Although statistically significant, the difference in median recovery for 62 of the 108 pesticides was less than 15 percent. Levene's test was used to compare the variability of recovery of pesticides in field matrix spikes and laboratory reagent spikes. Of the 237 pesticides tested, recovery was significantly more variable in field matrix spikes for 30 pesticides and was significantly more variable in laboratory reagent spikes for 22 pesticides (table 8). On the basis of both of these test results, it is evident that field matrix spikes are preferable to laboratory reagent spikes for characterizing the performance of sh2437 in stream-water samples for many of the pesticides measured.

Stream-Water Matrix Characteristics that Influence Recovery

Analysis of the matrix characteristics that might influence recovery requires sophisticated regression analyses and model building that are beyond the scope of this report. Analytical water-quality data for the environmental stream-water matrix (for example, pH, specific conductance, organic carbon, and so forth) and the pesticide recovery in the associated field matrix spikes are provided in Martin and Baker, 2017, dataset 4 to support future work on matrix effects.

Comparisons of Pesticides Analyzed by Old and New Methods

This section compares median values and variability of pesticide recovery in stream-water matrix spikes analyzed by old and new methods, compares pesticide detections and concentrations in paired environmental stream-water samples analyzed by old and new methods, and compares detections in field blank water samples analyzed by old and new methods. Analytical data for paired environmental concentrations, for background environmental pesticide concentrations, and for concentrations and recovery in the associated field matrix spikes are provided in Martin and Baker (2017, datasets 5 and 6).

Recovery in Stream-Water Matrix Spikes

The distributions of recovery in field matrix spikes analyzed by sh2033 and sh2437 for the 61 pesticides common to both methods are shown in side-by-side boxplots in figure 5. These same data are shown by study unit, station number, and site visit sequence number in appendix 3 and for atrazine in figure 6. The sign test was used to determine if recovery in paired field matrix spikes analyzed by sh2033 and sh2437 were statistically different. Of the 61 pesticides common to both schedules, recovery was significantly greater in samples analyzed by sh2033 for 44 pesticides and was significantly greater in samples analyzed by sh2437 for 12 pesticides (table 9). Median recovery was closer to 100 percent for 17 pesticides analyzed by sh2033 and for 43 pesticides analyzed by sh2437.

Levene's test was used to compare the variability of recovery of pesticides analyzed by sh2033 and sh2437. Recovery was significantly more variable in spikes analyzed by sh2033 for 16 pesticides and was significantly more variable in spikes analyzed by sh2437 for 21 pesticides (table 10).

The distributions of recovery in field matrix spikes analyzed by sh2060 and sh2437 for the 38 pesticides common to both methods are shown in side-by-side boxplots in figure 7. Recovery also is shown by study unit, station number, and site visit sequence number in appendix 4 and for atrazine in figure 8. Of the 38 pesticides common to both schedules, recovery was significantly greater in samples analyzed by sh2060 for 12 pesticides and was significantly greater in samples analyzed by sh2437 for 18 pesticides (table 11). Median recovery was closer to 100 percent for 17 pesticides analyzed by sh2060 and for 21 pesticides analyzed by sh2437. Recovery was significantly more variable in spikes analyzed by sh2060 for 12 pesticides and was significantly more variable in spikes analyzed by sh2437 for 18 pesticides (table 12).

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.

[Pesticides are sorted by the test statistic. Probablity values less than 0.05 are shown in bold; <, less than]

Index	Pesticide short name	Median recovery in laboratory reagent spikes (percent)	Median recovery in field matrix spikes (percent)	Difference in median recovery (reagent-field) (percent)	Wilcoxon rank-sum test		Number of laboratory reagent spikes (percent)	Number of field matrix spikes (percent)
					Test statistic	2-sided *p*-value		
142	Didealkylatrazine	89.2	209.6	-120.4	-8.5814	**< 0.0001**	33	143
136	Deisopropylhyd_azine	82.7	135.0	-52.3	-8.4554	**< 0.0001**	33	127
125	Butralin	87.5	166.8	-79.3	-8.2276	**< 0.0001**	32	145
80	Imidacloprid	85.9	118.0	-32.1	-8.0176	**< 0.0001**	33	145
97	2-Aminobenzimidazole	91.1	111.1	-20.0	-6.5466	**< 0.0001**	33	145
60	Tribuphos	72.5	98.0	-25.5	-6.5314	**< 0.0001**	32	145
76	Flumetsulam	94.7	124.1	-29.4	-6.4268	**< 0.0001**	33	145
133	Deethylhydroxy_azine	81.1	111.7	-30.6	-6.0284	**< 0.0001**	33	144
167	Hexazinone_Tran_ct_C	87.0	104.1	-17.1	-5.8391	**< 0.0001**	33	145
79	Imazethapyr	85.1	107.9	-22.8	-5.3974	**< 0.0001**	33	145
239	trans-Permethrin	70.8	91.9	-21.1	-5.2722	**< 0.0001**	32	144
181	Imazamox	91.7	105.2	-13.5	-5.2702	**< 0.0001**	33	145
124	Bifenthrin	64.2	94.7	-30.5	-5.2626	**< 0.0001**	32	137
157	Etoxazole	76.6	95.6	-19.0	-4.9762	**< 0.0001**	32	145
83	Methomyl	89.0	109.4	-20.4	-4.8622	**< 0.0001**	33	145
216	Pyridaben	80.7	99.0	-18.3	-4.8161	**< 0.0001**	32	145
61	cis-Permethrin	69.8	88.9	-19.1	-4.8007	**< 0.0001**	32	136
163	Flubendiamide	108.3	130.2	-21.9	-4.7971	**< 0.0001**	34	145
31	Fipronil_sulfone	76.3	86.0	-9.7	-4.6095	**< 0.0001**	34	145
203	Oxamyl_oxime	93.6	106.1	-12.5	-4.4280	**< 0.0001**	33	145
30	Fipronil_sulfide	82.1	91.0	-8.9	-4.0726	**< 0.0001**	34	145
63	2-Hydroxyatrazine	82.2	93.7	-11.5	-3.9339	**< 0.0001**	33	145
107	4-Hydroxyhexazi_ne_A	88.9	100.0	-11.1	-3.7617	**0.0002**	33	145
14	Cyanazine	92.6	102.9	-10.3	-3.5189	**0.0004**	33	100
179	Hydroxysimazine	88.9	107.6	-18.7	-3.4660	**0.0005**	33	145
223	Tebupirimfos	86.8	91.6	-4.8	-3.3874	**0.0007**	33	145
214	Pymetrozine	92.6	108.8	-16.2	-3.3725	**0.0007**	33	145
109	Acephate	97.2	106.0	-8.8	-3.3053	**0.0009**	33	141
146	Diketonitrile-i_tole	116.1	137.1	-21.0	-3.2305	**0.0012**	34	145
96	2-Amino-N-isopr_mide	84.8	91.1	-6.3	-3.2227	**0.0013**	33	145
74	Dicamba	87.5	106.7	-19.2	-3.0916	**0.0020**	34	144
24	EPTC	95.5	103.6	-8.1	-2.7960	**0.0052**	33	145
50	Prometryn	92.6	96.7	-4.1	-2.6725	**0.0075**	33	145
201	O-Ethyl-S-propy_oate	102.6	113.4	-10.8	-2.5827	**0.0098**	33	145
28	Fenamiphos_sulfoxide	99.2	108.5	-9.3	-2.5490	**0.0108**	33	145
204	Paraoxon-ethyl	104.9	113.6	-8.7	-2.4667	**0.0136**	33	145
225	Tebuthiuron_TP_104	93.7	99.1	-5.4	-2.4505	**0.0143**	36	145
134	Deiodo_flubendiamide	82.0	87.9	-5.9	-2.4442	**0.0145**	33	145
27	Fenamiphos_sulfone	99.9	106.5	-6.6	-2.4217	**0.0154**	33	145
118	Aminopyralid	102.5	168.9	-66.4	-2.3569	**0.0184**	31	25
218	Sulfentrazone	115.6	127.9	-12.3	-2.3333	**0.0196**	34	145
159	Fenbutatin_oxide	68.6	83.3	-14.7	-2.2851	**0.0223**	32	145
29	Fipronil	87.2	90.3	-3.1	-2.2027	**0.0276**	34	145
117	Ametryn	92.3	97.1	-4.8	-2.2009	**0.0277**	33	145
36	Methidathion	97.2	102.3	-5.1	-2.1784	**0.0294**	33	145
70	Bromoxynil	88.8	93.5	-4.7	-2.1567	**0.0310**	34	145

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the test statistic. Probablity values less than 0.05 are shown in bold; <, less than]

Index	Pesticide short name	Median recovery in laboratory reagent spikes (percent)	Median recovery in field matrix spikes (percent)	Difference in median recovery (reagent-field) (percent)	Wilcoxon rank-sum test		Number of laboratory reagent spikes (percent)	Number of field matrix spikes (percent)
					Test statistic	2-sided *p*-value		
17	Diazinon	86.4	94.4	-8.0	-2.1560	**0.0311**	33	145
162	Fipronil_sulfonate	95.4	104.6	-9.2	-2.0317	**0.0422**	34	145
52	Propargite	81.1	85.3	-4.2	-1.9840	**0.0473**	32	145
188	Methamidophos	101.3	105.8	-4.5	-1.9718	**0.0486**	33	144
232	Terbufos_sulfoxide	103.4	109.4	-6.0	-1.8940	0.0582	33	145
155	Disulfoton_sulfoxide	102.9	110.3	-7.4	-1.8790	0.0602	33	145
82	MCPA	85.4	94.1	-8.7	-1.8736	0.0610	34	145
199	O-Ethyl-O-methy_oate	103.2	109.2	-6.0	-1.8603	0.0628	33	145
53	Propyzamide	94.9	100.6	-5.7	-1.8491	0.0644	33	145
200	O-Ethyl-S-methy_oate	102.3	106.1	-3.8	-1.8154	0.0695	33	145
49	Prometon	88.0	93.5	-5.5	-1.8116	0.0700	33	145
85	Norflurazon	99.6	104.3	-4.7	-1.8116	0.0700	33	145
231	Terbufos_sulfone	104.2	107.7	-3.5	-1.7630	0.0779	33	145
154	Disulfoton_oxon_xide	100.9	106.5	-5.6	-1.7480	0.0805	33	145
58	Terbuthylazine	91.6	94.9	-3.3	-1.7255	0.0844	33	145
126	Butylate	89.3	91.4	-2.1	-1.7068	0.0879	33	145
208	Phorate_sulfoxide	104.9	109.0	-4.1	-1.6881	0.0914	33	145
73	Deisopropylatrazine	86.9	92.4	-5.5	-1.6844	0.0921	33	145
212	Propazine	91.8	94.5	-2.7	-1.6582	0.0973	33	145
207	Phorate_sulfone	103.8	109.9	-6.1	-1.6282	0.1035	33	145
1	Atrazine	90.3	94.2	-3.9	-1.5855	0.1129	33	141
68	Bentazon	97.2	100.4	-3.2	-1.5647	0.1177	34	145
41	Oxyfluorfen	86.3	101.0	-14.7	-1.4770	0.1397	32	145
26	Fenamiphos	91.4	92.3	-0.9	-1.4748	0.1403	33	145
104	4-Chlorobenzylm_xide	96.8	99.2	-2.4	-1.2801	0.2005	33	145
37	Metolachlor	92.6	95.3	-2.7	-1.2765	0.2018	33	137
9	Alachlor	96.8	97.9	-1.1	-1.2427	0.2140	33	145
210	Piperonyl_butoxide	84.0	86.5	-2.5	-1.1780	0.2388	33	137
5	Metalaxyl	92.5	96.3	-3.8	-1.1716	0.2414	33	145
67	Aldicarb_sulfoxide	88.9	91.2	-2.3	-1.1491	0.2505	33	145
127	Carbendazim	92.5	92.9	-0.4	-1.0593	0.2895	33	145
100	3,4-Dichlorophe_urea	88.0	93.3	-5.3	-1.0406	0.2981	33	145
147	Dimethenamid	97.7	100.4	-2.7	-0.9779	0.3281	33	143
224	Tebupirimfos_oxon	90.9	93.0	-2.1	-0.9769	0.3286	33	145
25	Ethoprophos	94.1	94.3	-0.2	-0.9545	0.3398	33	145
51	Propanil	96.5	101.7	-5.2	-0.9545	0.3398	33	145
10	Azinphos-methyl	100.7	102.0	-1.3	-0.9395	0.3475	33	145
106	4-Hydroxychloro_onil	98.2	105.9	-7.7	-0.9350	0.3498	34	142
8	Acetochlor	94.6	96.4	-1.8	-0.9096	0.3631	33	145
152	Disulfoton_oxon	104.4	105.9	-1.5	-0.8983	0.3690	33	145
131	Dechlorofipronil	85.0	85.4	-0.4	-0.8623	0.3885	34	145
149	Dimethenamid_OXA	89.0	93.9	-4.9	-0.7704	0.4411	34	145
32	Fonofos	89.8	92.5	-2.7	-0.7336	0.4632	33	145
69	Bromacil	98.1	100.7	-2.6	-0.7149	0.4747	33	145
135	Deisopropyl_pr_etryn	87.7	89.4	-1.7	-0.7112	0.4770	33	145
192	Metolachlor_OXA	94.2	94.2	0.0	-0.7024	0.4824	34	137

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

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Index	Pesticide short name	Median recovery in laboratory reagent spikes (percent)	Median recovery in field matrix spikes (percent)	Difference in median recovery (reagent-field) (percent)	Wilcoxon rank-sum test		Number of laboratory reagent spikes (percent)	Number of field matrix spikes (percent)
					Test statistic	2-sided *p*-value		
217	Pyriproxyfen	91.6	93.2	-1.6	-0.6925	0.4886	33	145
42	Paraoxon-methyl	95.4	97.8	-2.4	-0.6737	0.5005	33	145
112	Acetochlor_OXA	95.2	95.3	-0.1	-0.6089	0.5426	34	142
20	Dicrotophos	100.7	102.9	-2.2	-0.5951	0.5517	33	145
193	Metolachlor_hyd_none	87.4	89.0	-1.6	-0.5727	0.5669	33	145
115	Alachlor_OXA	91.5	92.0	-0.5	-0.5498	0.5825	34	145
108	7-Hydroxycarbofuran	92.5	98.3	-5.8	-0.5205	0.6027	22	145
174	Hydroxyalachlor	89.5	90.5	-1.0	-0.4791	0.6319	33	145
116	Alachlor_SAA	86.7	90.1	-3.4	-0.4468	0.6550	34	145
66	Aldicarb_sulfone	92.0	92.4	-0.4	-0.4230	0.6723	33	145
173	Hydroxyacetochlor	89.5	89.7	-0.2	-0.4155	0.6778	33	145
78	Imazaquin	89.1	90.3	-1.2	-0.3930	0.6943	33	145
54	Simazine	91.5	93.1	-1.6	-0.3818	0.7026	33	145
62	2,4-D	91.8	92.2	-0.4	-0.3742	0.7082	34	143
132	Dechlorometolachlor	90.2	90.2	0.0	-0.3182	0.7504	33	145
160	Fentin	87.8	92.5	-4.7	-0.3107	0.7561	33	145
90	Siduron	93.4	93.9	-0.5	-0.2358	0.8136	33	145
194	Metribuzin-desamino	87.5	88.6	-1.1	-0.2059	0.8369	33	145
65	Aldicarb	81.8	82.8	-1.0	-0.1984	0.8427	33	145
110	Acet/Met_sec_amide	87.8	89.1	-1.3	-0.1460	0.8839	33	145
227	Tebuthiuron_TP_109	86.2	86.9	-0.7	-0.1347	0.8928	33	145
33	Hexazinone	93.5	93.7	-0.2	-0.1273	0.8987	33	145
81	Linuron	92.0	93.5	-1.5	-0.1273	0.8987	33	145
21	Dimethoate	98.6	100.0	-1.4	-0.1235	0.9017	33	145
168	Hexazinone_Tran_ct_D	91.8	92.2	-0.4	-0.1048	0.9165	34	145
209	Phthalazinone	89.8	90.6	-0.8	-0.0674	0.9463	33	145
7	2-Chloro-2,6-d_ilide	89.7	91.3	-1.6	-0.0374	0.9701	33	145
86	Oryzalin	104.8	105.8	-1.0	-0.0313	0.9751	34	145
186	Lactofen	71.9	72.0	-0.1	-0.0225	0.9821	33	145
236	cis-Bifenthrin_acid	100.4	99.1	1.3	0.0056	0.9956	34	144
190	Methoxyfenozide	100.9	97.9	3.0	0.0262	0.9791	33	145
234	Triallate	90.3	86.8	3.5	0.0487	0.9612	33	145
93	Triclopyr	92.4	91.9	0.5	0.0791	0.9370	34	145
175	Hydroxydiazinon	85.6	84.5	1.1	0.0823	0.9344	33	145
92	Terbacil	104.4	97.3	7.1	0.0823	0.9344	33	145
16	Desulfinylfipronil	86.2	85.2	1.0	0.1048	0.9165	34	145
4	Deethylatrazine	85.7	85.0	0.7	0.1123	0.9106	33	145
222	Tebufenozide	100.1	97.8	2.3	0.1235	0.9017	33	145
39	Molinate	95.9	89.9	6.0	0.1647	0.8692	33	145
187	Metconazole	95.5	92.1	3.4	0.1909	0.8486	33	145
235	Trifloxystrobin	87.1	85.7	1.4	0.1984	0.8427	33	145
215	Pyraclostrobin	90.8	88.8	2.0	0.2134	0.8311	33	145
189	Methomyl_oxime	90.6	90.3	0.3	0.2508	0.8020	33	145
55	Tebuconazole	96.1	94.5	1.6	0.2807	0.7789	33	145
228	Tebuthiuron_Tra_106	88.8	87.4	1.4	0.2882	0.7732	33	145
88	Propiconazole	92.8	91.4	1.4	0.2920	0.7703	33	145

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

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					Test statistic	2-sided *p*-value		
40	Myclobutanil	96.5	91.3	5.2	0.3556	0.7221	33	145
23	Disulfoton_sulfone	96.3	94.9	1.4	0.3930	0.6943	33	145
177	Hydroxymetolachlor	91.5	89.5	2.0	0.4117	0.6805	33	145
56	Terbufos	81.2	78.7	2.5	0.4304	0.6669	33	145
140	Demethyl_norflurazon	96.2	91.8	4.4	0.4342	0.6641	33	145
233	Tetraconazole	91.8	86.4	5.4	0.4566	0.6479	33	145
121	Azoxystrobin	94.4	91.2	3.2	0.5016	0.6160	33	145
59	Thiobencarb	91.8	89.9	1.9	0.5240	0.6003	33	145
45	Phorate	85.0	81.8	3.2	0.5577	0.5770	33	145
43	Parathion-methyl	102.4	95.8	6.6	0.6105	0.5415	33	145
18	Diazoxon	66.5	65.6	0.9	0.6139	0.5393	33	145
99	2-[(2-Ethyl-6-m_anol	87.4	84.8	2.6	0.6176	0.5368	33	145
145	Diflufenzopyr	98.7	90.6	8.1	0.6343	0.5259	34	145
128	Carboxy_molinate	91.7	85.8	5.9	0.6663	0.5052	33	145
3	Carbofuran	88.9	87.2	1.7	0.6999	0.4840	33	145
191	Metolachlor_ESA	89.9	89.2	0.7	0.7012	0.4832	34	136
105	4-Hydroxy_molinate	90.0	85.6	4.4	0.7336	0.4632	33	145
98	2-Isopropyl-6-m_inol	108.4	107.8	0.6	0.7598	0.4474	33	145
156	EPTC_degradate_48722	94.1	89.7	4.4	0.7748	0.4385	33	145
113	Acetochlor_SAA	89.6	86.5	3.1	0.7974	0.4252	34	144
89	Propoxur	99.7	95.3	4.4	0.8946	0.3710	33	145
72	Dacthal_monoacid	99.1	94.2	4.9	1.0646	0.2871	34	145
161	Fipronil_amide	94.5	93.3	1.2	1.0903	0.2756	34	145
170	Hexazinone_Tran_ct_G	85.1	83.3	1.8	1.1229	0.2615	33	145
184	Isoxaflutole_ac_3328	96.4	92.9	3.5	1.1970	0.2313	34	145
178	Hydroxyphthalazinone	94.8	89.1	5.7	1.2053	0.2281	33	145
22	Disulfoton	84.2	80.3	3.9	1.3512	0.1766	33	145
211	Profenofos	83.4	77.3	6.1	1.3550	0.1754	33	145
129	Chlorosulfonami_acid	92.4	77.4	15.0	1.3661	0.1719	34	145
137	Deisopropyliprodione	226.7	181.1	45.6	1.4286	0.1531	34	145
198	Novaluron	77.7	69.7	8.0	1.5758	0.1151	33	145
38	Metribuzin	94.2	91.6	2.6	1.5983	0.1100	33	145
103	4-(Hydroxymeth_halin	88.8	80.8	8.0	1.6015	0.1093	34	145
144	Diflubenzuron	88.9	87.1	1.8	1.6320	0.1027	33	145
102	3-Phenoxybenzoi_acid	91.2	86.2	5.0	1.6897	0.0911	34	145
44	Pendimethalin	95.0	87.8	7.2	1.7143	0.0865	33	145
6	Tebuthiuron	96.4	93.2	3.2	1.7517	0.0798	33	145
213	Prosulfuron	98.7	89.8	8.9	1.8405	0.0657	34	145
143	Didemethyl_hexa_ne_F	89.4	86.2	3.2	1.8416	0.0655	33	145
77	Fluometuron	95.3	91.1	4.2	1.8416	0.0655	33	145
75	Diuron	93.3	88.8	4.5	1.8459	0.0649	33	143
230	Terbufos_oxon_s_xide	98.9	93.4	5.5	1.9613	**0.0498**	33	145
150	Dimethenamid_SAA	85.6	79.1	6.5	1.9766	**0.0481**	34	145
139	Demethyl_hexazi_ne_B	92.3	88.5	3.8	1.9838	**0.0473**	33	145
221	TCPSA_ethyl_ester	90.0	86.2	3.8	2.0611	**0.0393**	34	145
220	Sulfosulfuron_e_fone	96.3	89.7	6.6	2.1298	**0.0332**	33	145

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

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					Test statistic	2-sided *p*-value		
138	Demethyl_fluometuron	88.8	85.8	3.0	2.1859	**0.0288**	33	145
148	Dimethenamid_ESA	93.3	86.5	6.8	2.2193	**0.0265**	34	145
141	Desamino-diketo_uzin	83.5	72.1	11.4	2.2524	**0.0243**	34	145
183	Isoxaflutole	85.3	77.6	7.7	2.3506	**0.0187**	33	145
19	Dichlorvos	103.1	93.1	10.0	2.4741	**0.0134**	33	145
11	Azinphos-methyl-oxon	101.7	93.9	7.8	2.5078	**0.0121**	33	145
182	Indoxacarb	78.7	68.3	10.4	2.5116	**0.0120**	33	145
2	Carbaryl	89.2	82.9	6.3	2.5864	**0.0097**	33	145
238	sec-Alachlor_OXA	93.8	86.5	7.3	2.6017	**0.0093**	34	145
95	2-(1-Hydroxyeth_line	53.7	45.2	8.5	2.6987	**0.0070**	33	145
196	N-(3,4-Dichloro_urea	93.5	86.1	7.4	2.8080	**0.0050**	33	144
12	Chlorpyrifos	84.3	78.7	5.6	3.1666	**0.0015**	33	145
237	sec-Acetochlor_OXA	90.6	85.3	5.3	3.2563	**0.0011**	34	145
195	Metribuzin_DK	89.2	73.5	15.7	3.3298	**0.0009**	34	145
185	Kresoxim-methyl	90.0	77.3	12.7	3.3313	**0.0009**	33	145
35	Malathion	86.8	76.9	9.9	3.6345	**0.0003**	33	145
171	Hydroxy_didemet_uron	87.1	73.2	13.9	3.8347	**0.0001**	33	145
153	Disulfoton_oxon_fone	93.2	83.7	9.5	3.8703	**0.0001**	33	145
219	Sulfosulfuron	89.5	80.9	8.6	4.0275	**< 0.0001**	33	145
151	Dimethoate_oxyg_alog	91.2	78.1	13.1	4.0574	**< 0.0001**	33	145
205	Phorate_oxon_su_xide	96.1	81.7	14.4	4.0986	**< 0.0001**	33	145
180	Hydroxytebuthurion	87.4	74.7	12.7	4.1827	**< 0.0001**	31	145
130	Chlorsulfuron	85.5	73.8	11.7	4.2109	**< 0.0001**	33	145
15	Desulfinylfipro_mide	89.2	76.6	12.6	4.3300	**< 0.0001**	34	145
46	Phorate_oxon	99.1	85.3	13.8	4.4392	**< 0.0001**	33	145
57	Terbufos_sulfo_nalog	97.9	86.3	11.6	4.4842	**< 0.0001**	33	145
47	Phosmet	56.9	32.0	24.9	4.6093	**< 0.0001**	33	122
64	3-Hydroxycarbofuran	87.6	73.1	14.5	4.6414	**< 0.0001**	33	145
87	Oxamyl	84.5	66.3	18.2	4.9700	**< 0.0001**	33	144
226	Tebuthiuron_TP_108	90.0	80.7	9.3	4.9895	**< 0.0001**	33	145
164	Flumiclorac	18.7	1.2	17.5	5.0509	**< 0.0001**	28	54
13	Chlorpyrifos_oxon	92.2	75.2	17.0	5.1729	**< 0.0001**	33	145
206	Phorate_oxygen_fone	93.2	76.5	16.7	5.1953	**< 0.0001**	33	145
101	3-Ketocarbofuran	67.6	0.0	67.6	5.6425	**< 0.0001**	20	54
34	Malaoxon	82.2	61.1	21.1	5.6557	**< 0.0001**	33	145
158	Famoxadone	64.5	15.0	49.5	5.7704	**< 0.0001**	33	122
165	Formetanate	28.5	7.2	21.3	5.8805	**< 0.0001**	31	122
48	Phosmet_oxon	12.0	0.0	12.0	5.9048	**< 0.0001**	10	54
172	Hydroxy_monodem_uron	87.1	64.7	22.4	5.9664	**< 0.0001**	33	145
176	Hydroxyfluometuron	84.7	52.0	32.7	6.4567	**< 0.0001**	33	145
197	Naled	68.7	24.3	44.4	6.5504	**< 0.0001**	33	145
94	1H-1,2,4-Triazole	81.8	43.6	38.2	6.7627	**< 0.0001**	33	115
229	Terbufos_oxon	79.7	54.5	25.2	6.8348	**< 0.0001**	33	145
84	Nicosulfuron	78.6	60.2	18.4	6.8834	**< 0.0001**	33	145
91	Sulfometuron-methyl	87.3	72.4	14.9	6.8947	**< 0.0001**	33	145
202	Orthosulfamuron	58.9	39.5	19.4	6.9246	**< 0.0001**	33	145

Table 7. Comparison of median recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the test statistic. Probablity values less than 0.05 are shown in bold; <, less than]

Index	Pesticide short name	Median recovery in laboratory reagent spikes (percent)	Median recovery in field matrix spikes (percent)	Difference in median recovery (reagent-field) (percent)	Wilcoxon rank-sum test		Number of laboratory reagent spikes (percent)	Number of field matrix spikes (percent)
					Test statistic	2-sided *p*-value		
169	Hexazinone_Tran_ct_E	93.3	62.0	31.3	7.0549	**< 0.0001**	34	145
71	Chlorimuron-ethyl	77.9	55.9	22.0	7.0781	**< 0.0001**	33	145
166	Halosulfuron-methyl	82.9	66.5	16.4	7.2615	**< 0.0001**	33	145
123	Bifenazate_diazene	25.4	0.8	24.6	8.0270	**< 0.0001**	32	145
122	Bifenazate	83.5	0.9	82.6	8.5988	**< 0.0001**	31	145
120	Asulam	97.1	25.4	71.7	8.9047	**< 0.0001**	33	145
119	Ammelide	77.3	0.0	77.3	11.2986	**< 0.0001**	34	145

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
13	Chlorpyrifos_oxon	145	33	16.4	16.4	Equal	0.0	0.9365
135	Deisopropyl_pr_etryn	145	33	8.9	8.9	Equal	0.0	0.9644
127	Carbendazim	145	33	9.2	37.5	Field matrix	116.2	**<0.0001**
119	Ammelide	145	34	5.7	32.9	Field matrix	71.5	**<0.0001**
164	Flumiclorac	54	28	5.1	37.0	Field matrix	31.9	**<0.0001**
137	Deisopropyliprodione	145	34	72.6	292.4	Field matrix	13.3	**0.0003**
125	Butralin	145	32	37.1	12.4	Field matrix	11.4	**0.0009**
176	Hydroxyfluometuron	145	33	25.2	16.1	Field matrix	10.4	**0.0015**
218	Sulfentrazone	145	34	40.3	20.7	Field matrix	9.2	**0.0027**
133	Deethylhydroxy_azine	144	33	29.3	12.6	Field matrix	8.1	**0.0049**
136	Deisopropylhyd_azine	127	33	33.9	10.9	Field matrix	8.1	**0.0052**
229	Terbufos_oxon	145	33	18.0	10.0	Field matrix	7.5	**0.0068**
34	Malaoxon	145	33	26.0	13.5	Field matrix	7.2	**0.0082**
213	Prosulfuron	145	34	38.7	21.1	Field matrix	6.9	**0.0093**
214	Pymetrozine	145	33	50.4	24.2	Field matrix	6.1	**0.0144**
234	Triallate	145	33	17.4	11.3	Field matrix	5.8	**0.0168**
172	Hydroxy_monodem_uron	145	33	19.2	12.5	Field matrix	5.7	**0.0178**
126	Butylate	145	33	19.3	12.7	Field matrix	5.4	**0.0208**
43	Parathion-methyl	145	33	64.1	41.0	Field matrix	5.1	**0.0253**
163	Flubendiamide	145	34	29.3	21.9	Field matrix	4.8	**0.0295**
9	Alachlor	145	33	16.0	11.6	Field matrix	4.8	**0.0297**
39	Molinate	145	33	24.5	16.5	Field matrix	4.6	**0.0330**

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
87	Oxamyl	144	33	22.4	13.7	Field matrix	4.4	**0.0367**
17	Diazinon	145	33	17.2	11.4	Field matrix	4.4	**0.0375**
35	Malathion	145	33	21.3	10.1	Field matrix	4.4	**0.0378**
129	Chlorosulfonami_acid	145	34	77.6	26.3	Field matrix	4.3	**0.0406**
45	Phorate	145	33	17.5	11.7	Field matrix	4.2	**0.0410**
96	2-Amino-N-isopr_mide	145	33	16.0	10.2	Field matrix	4.2	**0.0421**
24	EPTC	145	33	24.7	16.4	Field matrix	4.2	**0.0427**
77	Fluometuron	145	33	9.5	6.9	Field matrix	4.0	**0.0470**
76	Flumetsulam	145	33	36.9	15.8	Field matrix	4.0	**0.0484**
182	Indoxacarb	145	33	23.6	15.4	Field matrix	3.9	**0.0494**
151	Dimethoate_oxyg_alog	145	33	23.6	13.0	Field matrix	3.8	0.0534
192	Metolachlor_OXA	137	34	22.8	16.6	Field matrix	3.8	0.0536
105	4-Hydroxy_molinate	145	33	19.2	14.2	Field matrix	3.7	0.0547
206	Phorate_oxygen_fone	145	33	21.6	11.4	Field matrix	3.7	0.0561
153	Disulfoton_oxon_fone	145	33	21.7	10.5	Field matrix	3.6	0.0581
71	Chlorimuron-ethyl	145	33	17.7	13.1	Field matrix	3.6	0.0580
63	2-Hydroxyatrazine	145	33	19.1	10.1	Field matrix	3.5	0.0623
233	Tetraconazole	145	33	19.9	15.2	Field matrix	3.5	0.0630
211	Profenofos	145	33	18.9	11.6	Field matrix	3.5	0.0645
2	Carbaryl	145	33	21.5	11.7	Field matrix	3.4	0.0679
59	Thiobencarb	145	33	16.9	12.5	Field matrix	3.4	0.0681
86	Oryzalin	145	34	21.2	15.2	Field matrix	3.3	0.0701
54	Simazine	145	33	14.6	10.4	Field matrix	3.3	0.0731
215	Pyraclostrobin	145	33	17.8	13.2	Field matrix	3.2	0.0746
52	Propargite	145	32	20.9	13.2	Field matrix	3.2	0.0746
82	MCPA	145	34	22.0	16.6	Field matrix	3.2	0.0746
4	Deethylatrazine	145	33	16.3	11.8	Field matrix	3.2	0.0752
160	Fentin	145	33	19.0	14.2	Field matrix	3.2	0.0762
230	Terbufos_oxon_s_xide	145	33	20.6	12.1	Field matrix	3.2	0.0763
84	Nicosulfuron	145	33	17.9	12.8	Field matrix	3.2	0.0769
162	Fipronil_sulfonate	145	34	33.4	23.6	Field matrix	3.2	0.0775
93	Triclopyr	145	34	20.4	15.2	Field matrix	3.1	0.0788
216	Pyridaben	145	32	19.7	13.5	Field matrix	3.0	0.0868
167	Hexazinone_Tran_ct_C	145	33	22.1	11.0	Field matrix	2.9	0.0925
183	Isoxaflutole	145	33	21.3	14.6	Field matrix	2.8	0.0950
239	trans-Permethrin	144	32	20.0	13.8	Field matrix	2.8	0.0950
157	Etoxazole	145	32	18.4	13.4	Field matrix	2.7	0.1005
32	Fonofos	145	33	17.1	11.3	Field matrix	2.7	0.1013

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
178	Hydroxyphthalazinone	145	33	14.3	11.6	Field matrix	2.7	0.1035
107	4-Hydroxyhexazi_ne_A	145	33	19.5	11.5	Field matrix	2.7	0.1045
121	Azoxystrobin	145	33	17.9	13.6	Field matrix	2.7	0.1045
222	Tebufenozide	145	33	17.9	13.9	Field matrix	2.6	0.1060
62	2,4-D	143	34	19.7	14.4	Field matrix	2.6	0.1067
184	Isoxaflutole_ac_3328	145	34	15.4	11.4	Field matrix	2.6	0.1076
23	Disulfoton_sulfone	145	33	22.0	13.1	Field matrix	2.6	0.1081
235	Trifloxystrobin	145	33	19.0	11.8	Field matrix	2.6	0.1078
68	Bentazon	145	34	16.2	11.4	Field matrix	2.6	0.1123
146	Diketonitrile-i_tole	145	34	50.1	29.7	Field matrix	2.5	0.1135
79	Imazethapyr	145	33	20.3	13.2	Field matrix	2.5	0.1148
11	Azinphos-methyl-oxon	145	33	20.2	14.3	Field matrix	2.5	0.1180
190	Methoxyfenozide	145	33	20.4	16.6	Field matrix	2.4	0.1219
147	Dimethenamid	143	33	17.5	14.2	Field matrix	2.4	0.1243
156	EPTC_degradate_48722	145	33	17.8	13.8	Field matrix	2.3	0.1276
188	Methamidophos	144	33	22.3	13.1	Field matrix	2.3	0.1342
8	Acetochlor	145	33	19.0	16.0	Field matrix	2.2	0.1390
70	Bromoxynil	145	34	19.9	14.4	Field matrix	2.2	0.1401
152	Disulfoton_oxon	145	33	22.8	12.3	Field matrix	2.1	0.1497
73	Deisopropylatrazine	145	33	19.5	14.0	Field matrix	2.1	0.1497
185	Kresoxim-methyl	145	33	19.5	14.4	Field matrix	2.1	0.1537
207	Phorate_sulfone	145	33	22.9	15.7	Field matrix	2.0	0.1550
46	Phorate_oxon	145	33	20.3	13.1	Field matrix	2.0	0.1564
74	Dicamba	144	34	52.3	24.5	Field matrix	2.0	0.1574
191	Metolachlor_ESA	136	34	25.9	18.9	Field matrix	2.0	0.1602
201	O-Ethyl-S-propy_oate	145	33	34.4	16.8	Field matrix	1.9	0.1675
14	Cyanazine	100	33	16.9	14.3	Field matrix	1.9	0.1700
199	O-Ethyl-O-methy_oate	145	33	23.9	13.9	Field matrix	1.9	0.1726
205	Phorate_oxon_su_xide	145	33	20.6	14.3	Field matrix	1.9	0.1751
61	cis-Permethrin	136	32	19.2	14.5	Field matrix	1.8	0.1784
88	Propiconazole	145	33	16.8	13.6	Field matrix	1.8	0.1816
21	Dimethoate	145	33	22.2	14.0	Field matrix	1.8	0.1843
217	Pyriproxyfen	145	33	15.8	12.7	Field matrix	1.7	0.1884
36	Methidathion	145	33	21.4	12.2	Field matrix	1.7	0.1892
20	Dicrotophos	145	33	24.0	13.3	Field matrix	1.7	0.1951
154	Disulfoton_oxon_xide	145	33	22.3	15.1	Field matrix	1.7	0.2004
159	Fenbutatin_oxide	145	32	34.6	23.0	Field matrix	1.7	0.2006
180	Hydroxytebuthurion	145	31	17.6	12.4	Field matrix	1.6	0.2025

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
236	cis-Bifenthrin_acid	144	34	51.8	29.2	Field matrix	1.6	0.2018
171	Hydroxy_didemet_uron	145	33	19.0	15.0	Field matrix	1.6	0.2057
10	Azinphos-methyl	145	33	21.9	14.3	Field matrix	1.6	0.2126
22	Disulfoton	145	33	15.4	11.9	Field matrix	1.6	0.2134
28	Fenamiphos_sulfoxide	145	33	25.8	14.9	Field matrix	1.6	0.2145
99	2-[(2-Ethyl-6-m_anol	145	33	17.4	14.8	Field matrix	1.5	0.2194
169	Hexazinone_Tran_ct_E	145	34	19.2	16.1	Field matrix	1.5	0.2288
200	O-Ethyl-S-methy_oate	145	33	22.7	13.5	Field matrix	1.5	0.2291
40	Myclobutanil	145	33	18.1	15.5	Field matrix	1.5	0.2288
203	Oxamyl_oxime	145	33	26.2	17.5	Field matrix	1.4	0.2321
204	Paraoxon-ethyl	145	33	23.4	14.7	Field matrix	1.4	0.2378
212	Propazine	145	33	12.8	11.1	Field matrix	1.3	0.2588
227	Tebuthiuron_TP_109	145	33	45.2	12.2	Field matrix	1.3	0.2586
92	Terbacil	145	33	24.2	21.1	Field matrix	1.3	0.2615
173	Hydroxyacetochlor	145	33	18.8	16.6	Field matrix	1.2	0.2691
145	Diflufenzopyr	145	34	28.3	23.5	Field matrix	1.2	0.2751
187	Metconazole	145	33	15.0	12.6	Field matrix	1.1	0.2877
6	Tebuthiuron	145	33	9.5	8.3	Field matrix	1.1	0.2880
232	Terbufos_sulfoxide	145	33	21.8	15.0	Field matrix	1.1	0.2888
130	Chlorsulfuron	145	33	15.6	12.6	Field matrix	1.1	0.2988
85	Norflurazon	145	33	22.7	13.1	Field matrix	1.1	0.2981
42	Paraoxon-methyl	145	33	22.9	18.4	Field matrix	1.1	0.3010
124	Bifenthrin	137	32	24.3	20.6	Field matrix	1.1	0.3027
195	Metribuzin_DK	145	34	20.9	17.9	Field matrix	1.1	0.3035
155	Disulfoton_sulfoxide	145	33	24.2	17.5	Field matrix	1.1	0.3051
27	Fenamiphos_sulfone	145	33	23.3	15.9	Field matrix	1.0	0.3110
109	Acephate	141	33	25.7	17.7	Field matrix	1.0	0.3169
49	Prometon	145	33	12.5	10.5	Field matrix	1.0	0.3271
100	3,4-Dichlorophe_urea	145	33	14.1	12.6	Field matrix	1.0	0.3295
12	Chlorpyrifos	145	33	13.6	11.4	Field matrix	0.9	0.3338
97	2-Aminobenzimidazole	145	33	14.6	11.9	Field matrix	0.9	0.3326
208	Phorate_sulfoxide	145	33	23.1	16.7	Field matrix	0.9	0.3450
5	Metalaxyl	145	33	14.7	12.7	Field matrix	0.9	0.3438
65	Aldicarb	145	33	17.2	13.0	Field matrix	0.9	0.3434
112	Acetochlor_OXA	142	34	21.0	17.5	Field matrix	0.9	0.3497
64	3-Hydroxycarbofuran	145	33	18.2	15.0	Field matrix	0.8	0.3642
116	Alachlor_SAA	145	34	21.7	19.0	Field matrix	0.8	0.3676
231	Terbufos_sulfone	145	33	23.9	18.0	Field matrix	0.8	0.3766

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
186	Lactofen	145	33	26.2	22.8	Field matrix	0.8	0.3810
128	Carboxy_molinate	145	33	18.2	16.2	Field matrix	0.7	0.3953
193	Metolachlor_hyd_none	145	33	18.9	16.8	Field matrix	0.6	0.4316
138	Demethyl_fluometuron	145	33	8.9	8.1	Field matrix	0.6	0.4374
161	Fipronil_amide	145	34	19.0	17.0	Field matrix	0.6	0.4471
53	Propyzamide	145	33	17.5	16.1	Field matrix	0.6	0.4509
19	Dichlorvos	145	33	22.4	19.7	Field matrix	0.6	0.4595
29	Fipronil	145	34	13.5	12.3	Field matrix	0.5	0.4616
51	Propanil	145	33	18.6	17.0	Field matrix	0.5	0.4614
83	Methomyl	145	33	20.8	17.8	Field matrix	0.5	0.4693
98	2-Isopropyl-6-m_inol	145	33	43.1	18.1	Field matrix	0.5	0.4778
104	4-Chlorobenzylm_xide	145	33	18.2	16.6	Field matrix	0.5	0.4930
189	Methomyl_oxime	145	33	24.8	21.5	Field matrix	0.5	0.4985
44	Pendimethalin	145	33	15.3	13.9	Field matrix	0.4	0.5129
69	Bromacil	145	33	19.2	16.3	Field matrix	0.4	0.5105
18	Diazoxon	145	33	14.2	11.7	Field matrix	0.4	0.5382
210	Piperonyl_butoxide	137	33	16.3	14.9	Field matrix	0.4	0.5402
60	Tribuphos	145	32	18.5	16.3	Field matrix	0.4	0.5493
66	Aldicarb_sulfone	145	33	19.4	18.1	Field matrix	0.3	0.5635
94	1H-1,2,4-Triazole	115	33	23.9	20.7	Field matrix	0.3	0.5809
38	Metribuzin	145	33	12.1	11.3	Field matrix	0.3	0.5816
103	4-(Hydroxymeth_halin	145	34	28.5	25.3	Field matrix	0.3	0.5936
220	Sulfosulfuron_e_fone	145	33	11.5	10.7	Field matrix	0.3	0.6032
202	Orthosulfamuron	145	33	18.2	17.3	Field matrix	0.2	0.6275
90	Siduron	145	33	11.3	10.5	Field matrix	0.2	0.6325
3	Carbofuran	145	33	14.6	13.6	Field matrix	0.2	0.6403
106	4-Hydroxychloro_onil	142	34	33.9	31.9	Field matrix	0.2	0.6448
55	Tebuconazole	145	33	15.5	14.7	Field matrix	0.2	0.6477
174	Hydroxyalachlor	145	33	16.9	16.1	Field matrix	0.2	0.6589
149	Dimethenamid_OXA	145	34	14.5	13.8	Field matrix	0.2	0.6645
7	2-Chloro-2,6-d_ilide	145	33	16.9	16.2	Field matrix	0.2	0.6748
140	Demethyl_norflurazon	145	33	11.2	10.8	Field matrix	0.1	0.7202
33	Hexazinone	145	33	9.1	8.8	Field matrix	0.1	0.7170
72	Dacthal_monoacid	145	34	61.4	58.0	Field matrix	0.1	0.7317
177	Hydroxymetolachlor	145	33	11.6	11.1	Field matrix	0.1	0.7459
194	Metribuzin-desamino	145	33	10.4	10.0	Field matrix	0.1	0.7396
170	Hexazinone_Tran_ct_G	145	33	11.4	11.0	Field matrix	0.1	0.7654
131	Dechlorofipronil	145	34	13.6	13.0	Field matrix	0.1	0.7803

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
75	Diuron	143	33	9.5	10.1	Field matrix	0.1	0.7782
226	Tebuthiuron_TP_108	145	33	9.7	9.5	Field matrix	0.1	0.7951
115	Alachlor_OXA	145	34	15.2	14.9	Field matrix	0.1	0.8015
168	Hexazinone_Tran_ct_D	145	34	33.8	32.9	Field matrix	0.1	0.8121
102	3-Phenoxybenzoi_acid	145	34	9.9	9.8	Field matrix	0.0	0.8391
110	Acet/Met_sec_amide	145	33	17.7	17.6	Field matrix	0.0	0.8853
113	Acetochlor_SAA	144	34	26.7	26.6	Field matrix	0.0	0.9317
123	Bifenazate_diazene	145	32	10.0	40.6	Laboratory reagent	95.7	**<0.0001**
47	Phosmet	122	33	12.8	35.6	Laboratory reagent	38.2	**<0.0001**
48	Phosmet_oxon	54	10	0.0	71.9	Laboratory reagent	37.6	**<0.0001**
101	3-Ketocarbofuran	54	20	13.9	37.5	Laboratory reagent	27.6	**<0.0001**
158	Famoxadone	122	33	21.5	34.2	Laboratory reagent	19.2	**<0.0001**
120	Asulam	145	33	11.9	22.8	Laboratory reagent	14.2	**0.0002**
198	Novaluron	145	33	19.9	32.5	Laboratory reagent	13.3	**0.0004**
122	Bifenazate	145	31	3.9	373.4	Laboratory reagent	11.7	**0.0008**
80	Imidacloprid	145	33	24.5	8.2	Laboratory reagent	9.6	**0.0023**
165	Formetanate	122	31	10.6	15.9	Laboratory reagent	7.3	**0.0078**
142	Didealkylatrazine	143	33	111.3	15.3	Laboratory reagent	6.4	**0.0122**
117	Ametryn	145	33	13.0	8.6	Laboratory reagent	6.4	**0.0124**
181	Imazamox	145	33	18.3	9.8	Laboratory reagent	6.3	**0.0129**
1	Atrazine	141	33	16.0	9.8	Laboratory reagent	6.3	**0.0133**
31	Fipronil_sulfone	145	34	11.3	14.9	Laboratory reagent	6.1	**0.0147**
175	Hydroxydiazinon	145	33	15.1	7.6	Laboratory reagent	5.3	**0.0226**
197	Naled	145	33	20.5	26.9	Laboratory reagent	5.1	**0.0258**
238	sec-Alachlor_OXA	145	34	12.3	15.6	Laboratory reagent	4.8	**0.0294**
25	Ethoprophos	145	33	16.0	9.2	Laboratory reagent	4.5	**0.0362**
225	Tebuthiuron_TP_104	145	36	16.1	7.6	Laboratory reagent	4.3	**0.0386**
58	Terbuthylazine	145	33	11.3	8.0	Laboratory reagent	4.3	**0.0388**
26	Fenamiphos	145	33	14.7	8.8	Laboratory reagent	4.3	**0.0395**
57	Terbufos_sulfo_nalog	145	33	20.9	9.8	Laboratory reagent	3.8	0.0524
224	Tebupirimfos_oxon	145	33	15.4	9.2	Laboratory reagent	3.6	0.0590
223	Tebupirimfos	145	33	15.1	9.1	Laboratory reagent	3.5	0.0614
56	Terbufos	145	33	14.4	9.6	Laboratory reagent	3.5	0.0623
166	Halosulfuron-methyl	145	33	14.0	9.6	Laboratory reagent	3.5	0.0642
91	Sulfometuron-methyl	145	33	14.2	9.8	Laboratory reagent	2.8	0.0982
37	Metolachlor	137	33	11.2	8.9	Laboratory reagent	2.5	0.1176
95	2-(1-Hydroxyeth_line	145	33	17.2	21.6	Laboratory reagent	2.2	0.1414
179	Hydroxysimazine	145	33	15.8	19.5	Laboratory reagent	2.1	0.1499

Table 8. Comparison of variability of recovery of pesticides in stream-water matrix spikes and laboratory reagent-water spikes analyzed by schedule 2437.—Continued

[Pesticides are sorted by the type of spikes with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than; nc, not calculated]

Index	Pesticide short name	Number of		Standard deviation of recovery (percent)		Type of spike having the larger standard deviation of recovery	Levene's test for equality of variance	
		Field matrix spikes	Laboratory reagent spikes	Field matrix spikes	Laboratory reagent spikes		Test statistic	*p*-value
141	Desamino-diketo_uzin	145	34	21.4	26.3	Laboratory reagent	1.8	0.1775
78	Imazaquin	145	33	11.8	9.8	Laboratory reagent	1.8	0.1870
16	Desulfinylfipronil	145	34	10.9	8.9	Laboratory reagent	1.6	0.2101
41	Oxyfluorfen	145	32	41.0	48.0	Laboratory reagent	1.2	0.2751
219	Sulfosulfuron	145	33	11.7	9.9	Laboratory reagent	1.0	0.3242
50	Prometryn	145	33	10.3	8.6	Laboratory reagent	0.9	0.3356
209	Phthalazinone	145	33	13.6	15.5	Laboratory reagent	0.9	0.3387
221	TCPSA_ethyl_ester	145	34	12.6	14.0	Laboratory reagent	0.6	0.4439
30	Fipronil_sulfide	145	34	11.4	12.7	Laboratory reagent	0.6	0.4503
143	Didemethyl_hexa_ne_F	145	33	8.8	9.8	Laboratory reagent	0.5	0.4957
132	Dechlorometolachlor	145	33	10.1	9.5	Laboratory reagent	0.4	0.5513
237	sec-Acetochlor_OXA	145	34	12.0	13.1	Laboratory reagent	0.3	0.5663
139	Demethyl_hexazi_ne_B	145	33	8.8	9.5	Laboratory reagent	0.3	0.6073
89	Propoxur	145	33	14.4	15.6	Laboratory reagent	0.2	0.6514
144	Diflubenzuron	145	33	10.4	9.9	Laboratory reagent	0.2	0.6911
148	Dimethenamid_ESA	145	34	15.1	15.9	Laboratory reagent	0.1	0.7758
15	Desulfinylfipro_mide	145	34	12.7	13.4	Laboratory reagent	0.1	0.8135
228	Tebuthiuron_Tra_106	145	33	12.9	13.6	Laboratory reagent	0.1	0.8219
81	Linuron	145	33	10.2	10.7	Laboratory reagent	0.1	0.8280
118	Aminopyralid	25	31	59.6	61.5	Laboratory reagent	0.0	0.8904
150	Dimethenamid_SAA	145	34	21.9	22.6	Laboratory reagent	0.0	0.9198
196	N-(3,4-Dichloro_urea	144	33	9.6	9.8	Laboratory reagent	0.0	0.9221
108	7-Hydroxycarbofuran	145	22	40.1	41.3	Laboratory reagent	0.0	0.9448
111	Acetochlor_ESA	0	19	nc	37.4	Laboratory reagent	nc	nc
114	Alachlor_ESA	0	19	nc	60.6	Laboratory reagent	nc	nc
134	Deiodo_flubendiamide	145	33	14.5	14.8	Laboratory reagent	0.0	0.9560
67	Aldicarb_sulfoxide	145	33	14.3	14.4	Laboratory reagent	0.0	0.9838

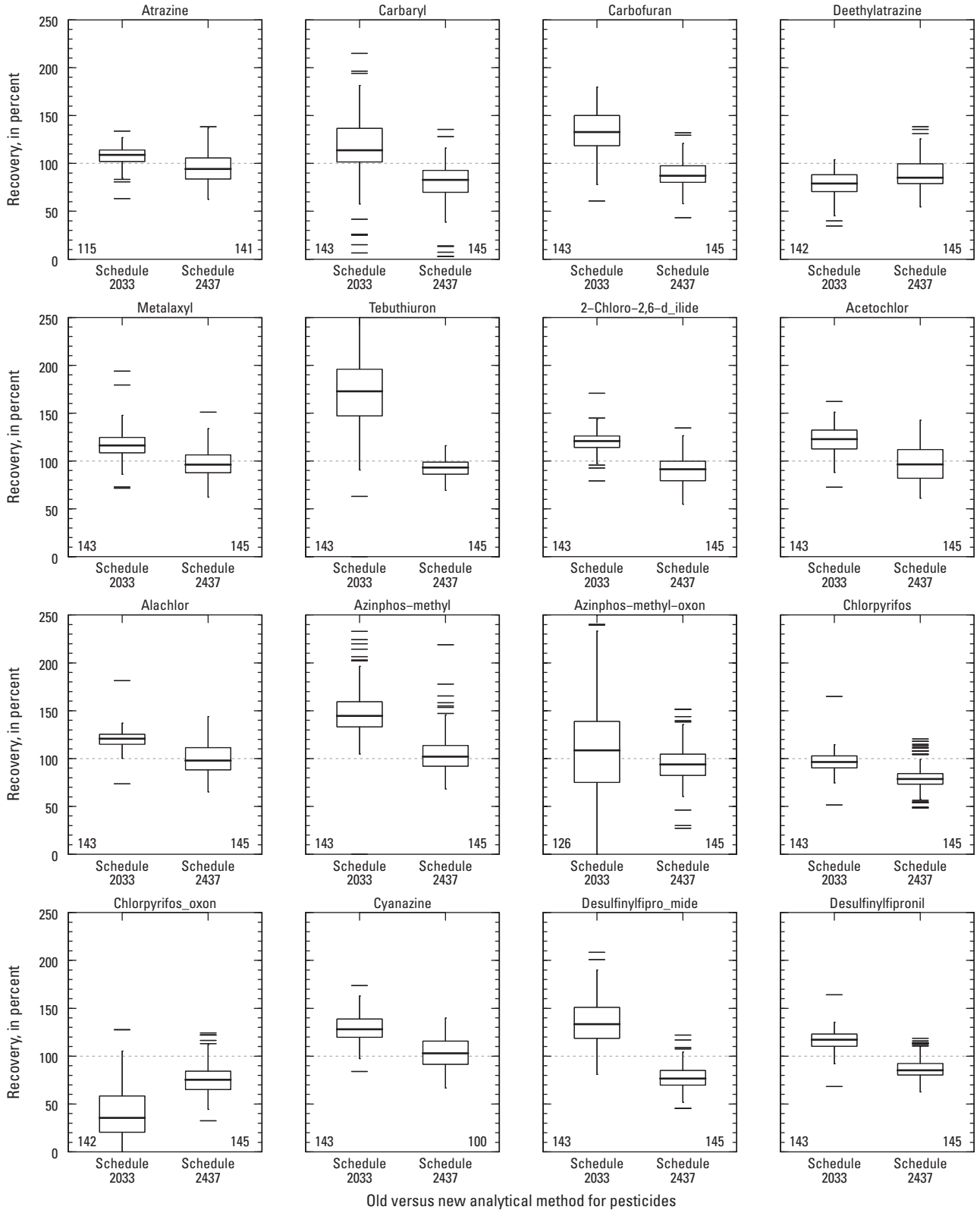


Figure 5. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2033 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.

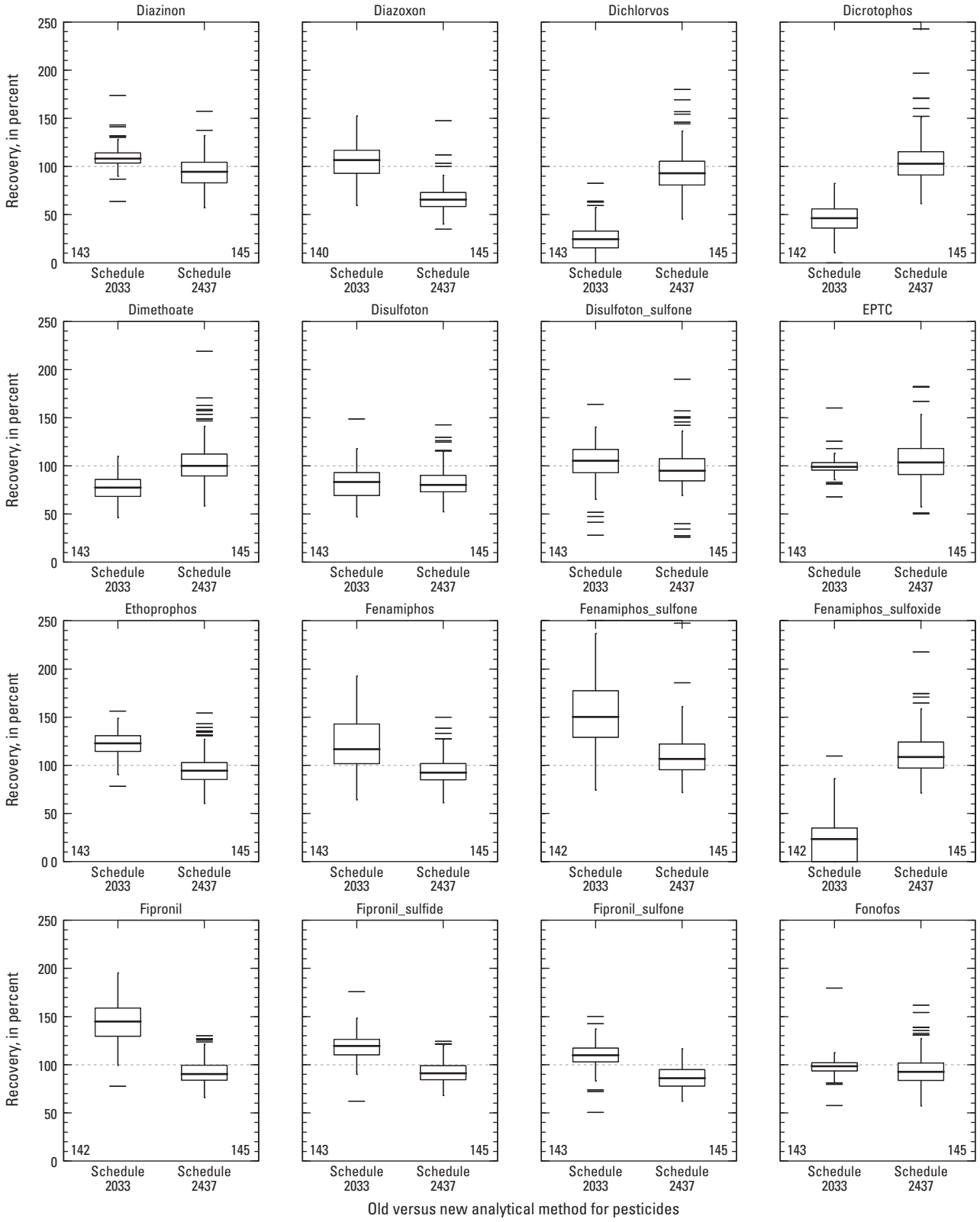


Figure 5. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2033 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.—Continued

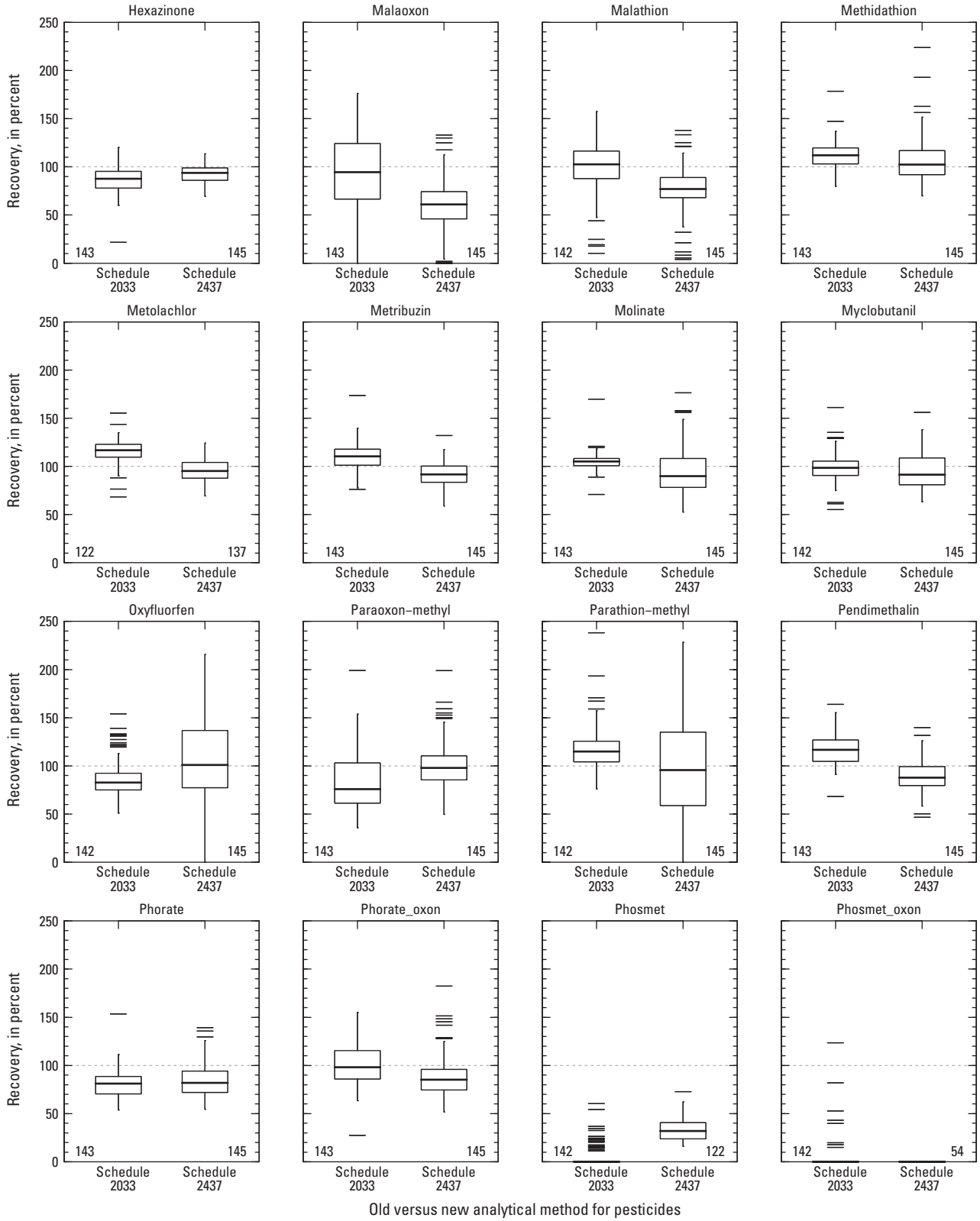


Figure 5. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2033 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.—Continued

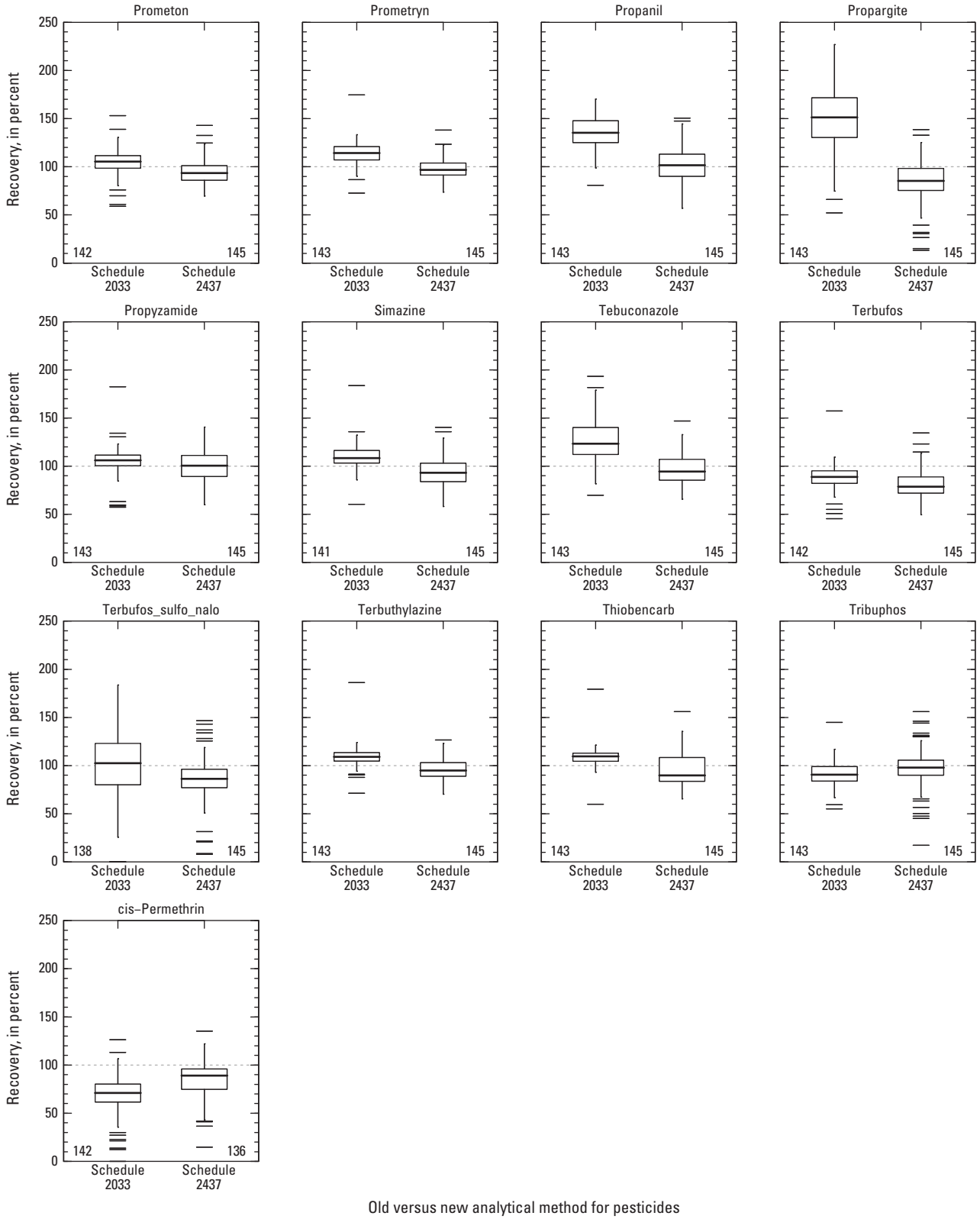


Figure 5. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2033 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.—Continued

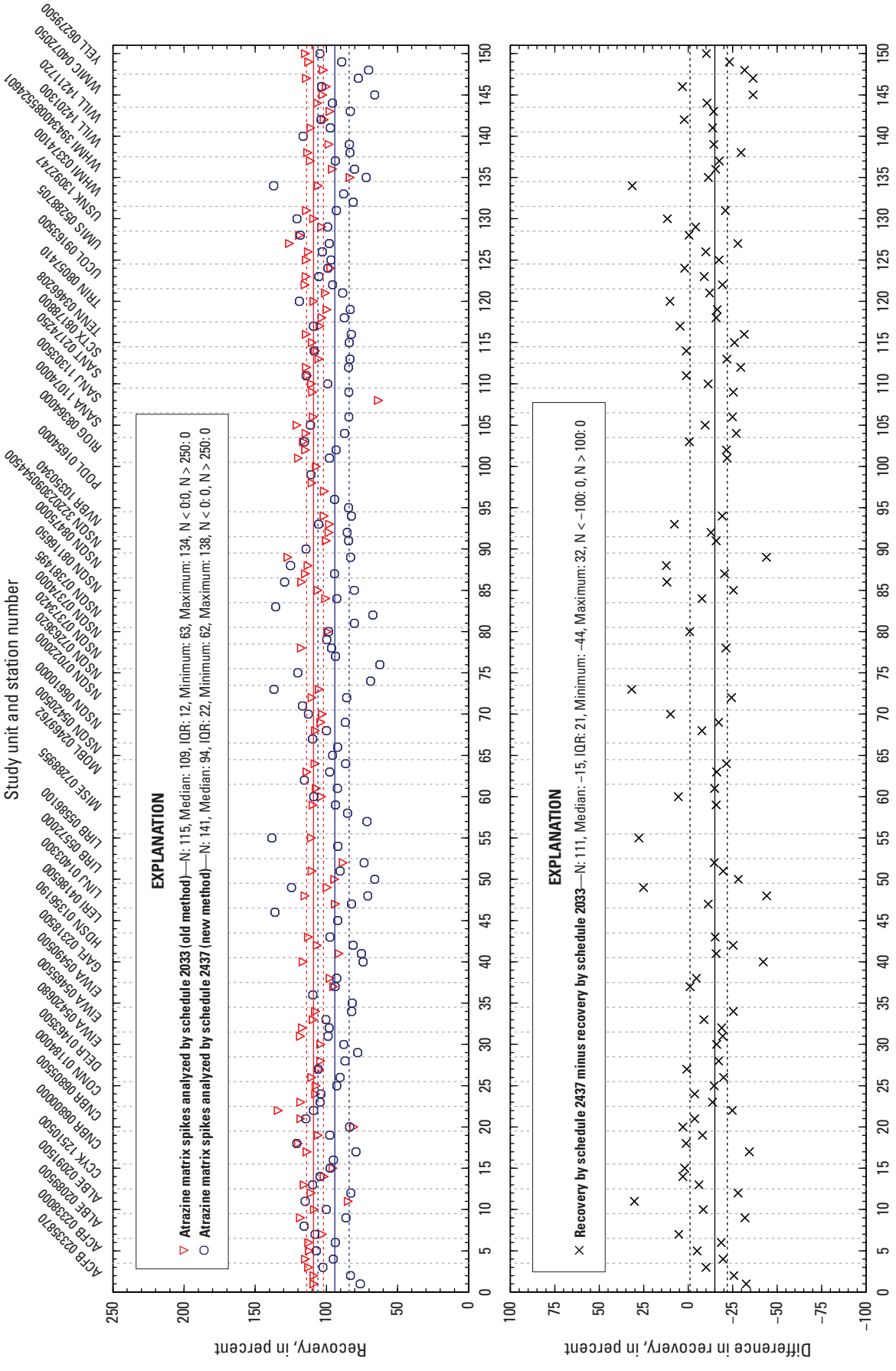


Figure 6. Comparison of recovery of atrazine in stream-water matrix spikes analyzed by schedule 2033 and by schedule 2437 by study unit, station number, and site visit. Solid horizonal lines in the graphs are median values; dashed horizontal lines are the 25th and 75th percentile values. Recoveries greater or less than the y–axis limits are plotted at the axis limits. N, number of values; IQR, interquartile range (75th percentile minus 25th percentile); <, less than; >, greater than.

Table 9. Comparison of median recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2033 and schedule 2437.

[Pesticides are sorted by the method with the largest standard deviation and by the test statistic. Probability values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of paired matrix spikes	Median recovery (percent) in matrix spikes analyzed by		Method closer to 100-percent recovery	Median paired difference in recovery (schedule 2033–schedule 2437) (percent)	Sign test	
			Schedule 2033	Schedule 2437			Test statistic	*p*-value
19	Dichlorvos	139	23.70	93.05	2437	-69.59	-68.5	**<0.0001**
20	Dicrotophos	139	45.71	102.87	2437	-59.41	-68.5	**<0.0001**
28	Fenamiphos_sulfoxide	139	23.09	108.52	2437	-93.15	-68.5	**<0.0001**
21	Dimethoate	139	76.83	99.99	2437	-24.08	-54.5	**<0.0001**
13	Chlorpyrifos_oxon	139	35.33	75.13	2437	-40.37	-53.5	**<0.0001**
47	Phosmet	117	0.00	32.26	2437	-31.47	-53.5	**<0.0001**
42	Paraoxon-methyl	139	75.58	97.62	2437	-20.60	-30.5	**<0.0001**
61	cis-Permethrin	129	71.23	88.63	2437	-14.64	-30.5	**<0.0001**
4	Deethylatrazine	138	78.89	84.98	2437	-9.26	-27.0	**<0.0001**
60	Tribuphos	139	90.23	97.41	2437	-6.37	-26.5	**<0.0001**
41	Oxyfluorfen	138	82.67	100.65	2437	-19.54	-24.0	**<0.0001**
33	Hexazinone	139	87.44	93.62	2437	-6.53	-22.5	**0.0002**
24	EPTC	139	99.08	103.62	2033	-4.62	-10.5	0.0895
22	Disulfoton	139	83.04	80.23	2033	-1.92	-3.5	0.6110
45	Phorate	139	80.90	81.66	2437	-1.89	-3.5	0.6110
48	Phosmet_oxon	50	0.00	0.00	both	0.00	1.0	0.5000
11	Azinphos-methyl-oxon	122	107.90	93.63	2437	11.34	8.0	0.1742
40	Myclobutanil	138	98.78	91.26	2033	6.89	20.0	**0.0008**
23	Disulfoton_sulfone	139	105.14	93.86	2033	9.85	20.5	**0.0006**
36	Methidathion	139	112.09	101.95	2437	8.97	20.5	**0.0006**
43	Parathion-methyl	138	114.93	95.28	2437	23.81	21.0	**0.0004**
32	Fonofos	139	98.72	92.46	2033	5.85	21.5	**0.0003**
57	Terbufos_sulfo_nalog	134	101.53	85.29	2033	14.75	24.0	**<0.0001**
53	Propyzamide	139	106.09	99.74	2437	5.53	24.5	**<0.0001**
39	Molinate	139	104.96	89.72	2033	13.44	28.5	**<0.0001**
56	Terbufos	138	88.94	78.55	2033	9.53	31.0	**<0.0001**
1	Atrazine	111	108.82	94.29	2437	14.63	31.5	**<0.0001**
46	Phorate_oxon	139	97.83	85.32	2033	14.61	34.5	**<0.0001**
49	Prometon	138	105.49	93.05	2033	10.76	36.5	**<0.0001**
59	Thiobencarb	139	109.59	89.22	2033	17.98	37.5	**<0.0001**
14	Cyanazine	94	127.34	102.17	2437	23.97	41.0	**<0.0001**
17	Diazinon	139	108.01	93.91	2437	14.36	41.5	**<0.0001**
26	Fenamiphos	139	116.14	92.20	2437	22.90	41.5	**<0.0001**
54	Simazine	137	108.56	93.27	2437	16.07	43.5	**<0.0001**
34	Malaoxon	139	93.29	60.44	2033	34.76	46.0	**<0.0001**
37	Metolachlor	118	117.00	94.60	2437	21.93	48.0	**<0.0001**
38	Metribuzin	139	110.53	91.01	2437	19.22	48.5	**<0.0001**
58	Terbuthylazine	139	109.37	94.78	2437	15.01	51.5	**<0.0001**

Table 9. Comparison of median recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2033 and schedule 2437.—Continued

[Pesticides are sorted by the method with the largest standard deviation and by the test statistic. Probability values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of paired matrix spikes	Median recovery (percent) in matrix spikes analyzed by		Method closer to 100-percent recovery	Median paired difference in recovery (schedule 2033–schedule 2437) (percent)	Sign test	
			Schedule 2033	Schedule 2437			Test statistic	*p*-value
12	Chlorpyrifos	139	96.43	78.56	2033	18.22	52.5	**<0.0001**
5	Metalaxyl	139	116.51	95.85	2437	20.52	52.5	**<0.0001**
55	Tebuconazole	139	122.82	93.29	2437	27.84	52.5	**<0.0001**
35	Malathion	138	101.89	76.22	2033	26.13	53.0	**<0.0001**
25	Ethoprophos	139	122.76	94.25	2437	28.53	53.5	**<0.0001**
8	Acetochlor	139	123.24	96.40	2437	26.00	53.5	**<0.0001**
9	Alachlor	139	121.02	97.06	2437	21.54	53.5	**<0.0001**
31	Fipronil_sulfone	139	109.53	85.71	2033	24.41	54.5	**<0.0001**
27	Fenamiphos_sulfone	138	149.57	106.60	2437	40.25	56.0	**<0.0001**
44	Pendimethalin	139	116.57	87.34	2437	28.27	56.5	**<0.0001**
10	Azinphos-methyl	139	144.57	101.68	2437	42.52	57.5	**<0.0001**
50	Prometryn	139	114.37	96.29	2437	18.17	58.5	**<0.0001**
2	Carbaryl	139	113.32	81.20	2033	34.37	59.5	**<0.0001**
51	Propanil	139	135.22	100.75	2437	32.42	60.5	**<0.0001**
18	Diazoxon	136	106.76	65.58	2033	44.42	61.0	**<0.0001**
7	2-Chloro-2,6-d_ilide	139	120.86	90.88	2437	30.09	61.5	**<0.0001**
16	Desulfinylfipronil	139	117.60	84.94	2437	30.74	63.5	**<0.0001**
30	Fipronil_sulfide	139	119.45	91.02	2437	26.38	64.5	**<0.0001**
3	Carbofuran	139	132.72	86.21	2437	47.00	65.5	**<0.0001**
6	Tebuthiuron	139	173.81	93.15	2437	81.27	65.5	**<0.0001**
15	Desulfinylfipro_mide	139	133.13	76.01	2437	57.06	66.5	**<0.0001**
29	Fipronil	138	143.85	90.33	2437	51.90	68.0	**<0.0001**
52	Propargite	139	151.06	84.90	2437	64.24	68.5	**<0.0001**

Table 10. Comparison of variability of recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2033 and schedule 2437.

[Pesticides are sorted by the method with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of field matrix spikes analyzed by		Standard deviation of recovery (percent) of field matrix spikes analyzed by		Method having the larger standard deviation of recovery	Levene's test for equality of variance	
		Schedule 2033	Schedule 2437	Schedule 2033	Schedule 2437		Test statistic	*p*-value
11	Azinphos-methyl-oxon	126	145	63.0	20.2	NWQL2033	44.6	**<0.0001**
26	Fenamiphos	143	145	27.6	14.7	NWQL2033	39.0	**<0.0001**
6	Tebuthiuron	143	145	43.9	9.5	NWQL2033	37.7	**<0.0001**
15	Desulfinylfipro_mide	143	145	23.1	12.7	NWQL2033	29.3	**<0.0001**
13	Chlorpyrifos_oxon	142	145	29.3	16.4	NWQL2033	28.9	**<0.0001**
34	Malaoxon	143	145	39.4	26.0	NWQL2033	21.6	**<0.0001**
29	Fipronil	142	145	20.1	13.5	NWQL2033	16.9	**<0.0001**
3	Carbofuran	143	145	21.6	14.6	NWQL2033	16.5	**<0.0001**
27	Fenamiphos_sulfone	142	145	38.8	23.3	NWQL2033	14.3	**0.0002**
57	Terbufos_sulfo_nalog	138	145	32.9	20.9	NWQL2033	13.3	**0.0003**
52	Propargite	143	145	30.4	20.9	NWQL2033	12.6	**0.0005**
33	Hexazinone	143	145	14.4	9.1	NWQL2033	11.9	**0.0006**
55	Tebuconazole	143	145	21.6	15.5	NWQL2033	11.5	**0.0008**
2	Carbaryl	143	145	33.0	21.5	NWQL2033	10.3	**0.0015**
31	Fipronil_sulfone	143	145	14.4	11.3	NWQL2033	4.7	**0.0314**
42	Paraoxon-methyl	143	145	29.0	22.9	NWQL2033	4.6	**0.0322**
18	Diazoxon	140	145	17.9	14.2	NWQL2033	3.5	0.0616
10	Azinphos-methyl	143	145	26.8	21.9	NWQL2033	1.4	0.2400
35	Malathion	142	145	24.4	21.3	NWQL2033	1.2	0.2797
48	Phosmet_oxon	142	54	14.1	0.0	NWQL2033	1.2	0.2850
5	Metalaxyl	143	145	19.4	14.7	NWQL2033	0.9	0.3446
22	Disulfoton	143	145	16.9	15.4	NWQL2033	0.9	0.3461
30	Fipronil_sulfide	143	145	12.8	11.4	NWQL2033	0.9	0.3541
38	Metribuzin	143	145	13.4	12.1	NWQL2033	0.8	0.3657
46	Phorate_oxon	143	145	21.7	20.3	NWQL2033	0.4	0.5357
37	Metolachlor	122	137	12.0	11.2	NWQL2033	0.4	0.5501
50	Prometryn	143	145	10.7	10.3	NWQL2033	0.1	0.8089
49	Prometon	142	145	12.7	12.5	NWQL2033	0.0	0.9063
44	Pendimethalin	143	145	15.4	15.3	NWQL2033	0.0	0.9504
41	Oxyfluorfen	142	145	16.7	41.0	NWQL2437	47.2	**<0.0001**
43	Parathion-methyl	142	145	21.5	64.1	NWQL2437	47.1	**<0.0001**
39	Molinate	143	145	8.8	24.5	NWQL2437	43.5	**<0.0001**
24	EPTC	143	145	8.8	24.7	NWQL2437	38.8	**<0.0001**
7	2-Chloro-2,6-d_ilide	143	145	10.7	16.9	NWQL2437	20.0	**<0.0001**
1	Atrazine	115	141	9.7	16.0	NWQL2437	17.6	**<0.0001**
8	Acetochlor	143	145	13.7	19.0	NWQL2437	16.8	**<0.0001**
9	Alachlor	143	145	9.7	16.0	NWQL2437	15.9	**<0.0001**
59	Thiobencarb	143	145	9.5	16.9	NWQL2437	14.4	**0.0002**

Table 10. Comparison of variability of recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2033 and schedule 2437.—Continued

[Pesticides are sorted by the method with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of field matrix spikes analyzed by		Standard deviation of recovery (percent) of field matrix spikes analyzed by		Method having the larger standard deviation of recovery	Levene's test for equality of variance	
		Schedule 2033	Schedule 2437	Schedule 2033	Schedule 2437		Test statistic	*p*-value
19	Dichlorvos	143	145	13.7	22.4	NWQL2437	14.1	**0.0002**
17	Diazinon	143	145	11.2	17.2	NWQL2437	11.0	**0.0010**
21	Dimethoate	143	145	12.5	22.2	NWQL2437	9.5	**0.0022**
40	Myclobutanil	142	145	13.3	18.1	NWQL2437	9.0	**0.0029**
60	Tribuphos	143	145	11.8	18.5	NWQL2437	8.7	**0.0034**
32	Fonofos	143	145	10.1	17.1	NWQL2437	8.0	**0.0051**
53	Propyzamide	143	145	12.7	17.5	NWQL2437	5.9	**0.0155**
4	Deethylatrazine	142	145	13.0	16.3	NWQL2437	5.8	**0.0165**
20	Dicrotophos	142	145	14.8	24.0	NWQL2437	5.6	**0.0188**
36	Methidathion	143	145	13.6	21.4	NWQL2437	5.3	**0.0226**
14	Cyanazine	143	100	14.0	16.9	NWQL2437	4.8	**0.0287**
45	Phorate	143	145	13.9	17.5	NWQL2437	4.1	**0.0436**
25	Ethoprophos	143	145	13.3	16.0	NWQL2437	3.2	0.0754
12	Chlorpyrifos	143	145	10.4	13.6	NWQL2437	3.0	0.0822
47	Phosmet	142	122	10.1	12.8	NWQL2437	2.6	0.1089
51	Propanil	143	145	16.4	18.6	NWQL2437	2.3	0.1284
54	Simazine	141	145	11.8	14.6	NWQL2437	2.1	0.1525
56	Terbufos	142	145	12.2	14.4	NWQL2437	1.5	0.2240
23	Disulfoton_sulfone	143	145	19.3	22.0	NWQL2437	1.0	0.3222
58	Terbuthylazine	143	145	9.7	11.3	NWQL2437	0.6	0.4527
28	Fenamiphos_sulfoxide	142	145	23.3	25.8	NWQL2437	0.4	0.5136
61	cis-Permethrin	142	136	18.3	19.2	NWQL2437	0.2	0.6988
16	Desulfinylfipronil	143	145	10.8	10.9	NWQL2437	0.0	0.9800

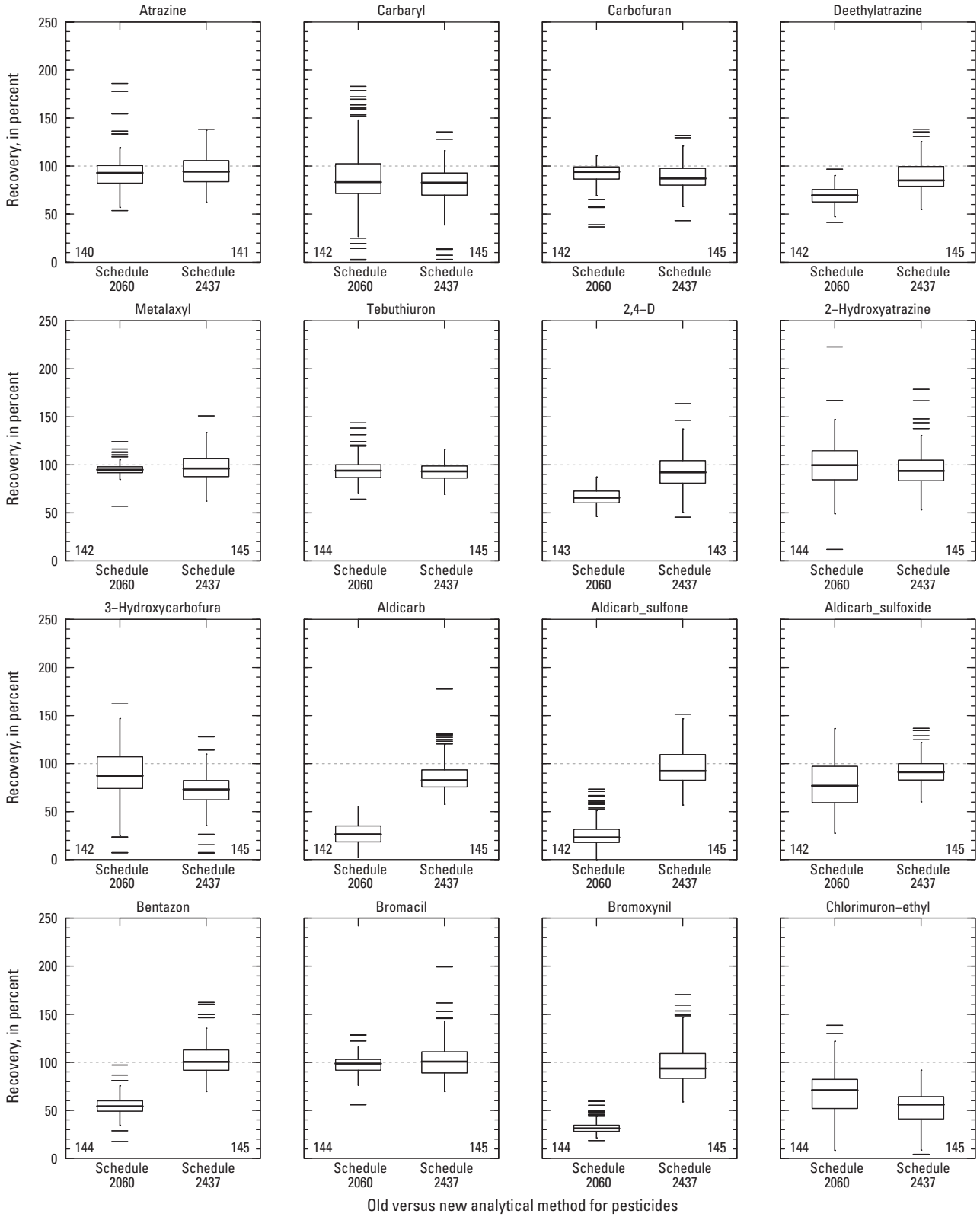


Figure 7. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2060 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.

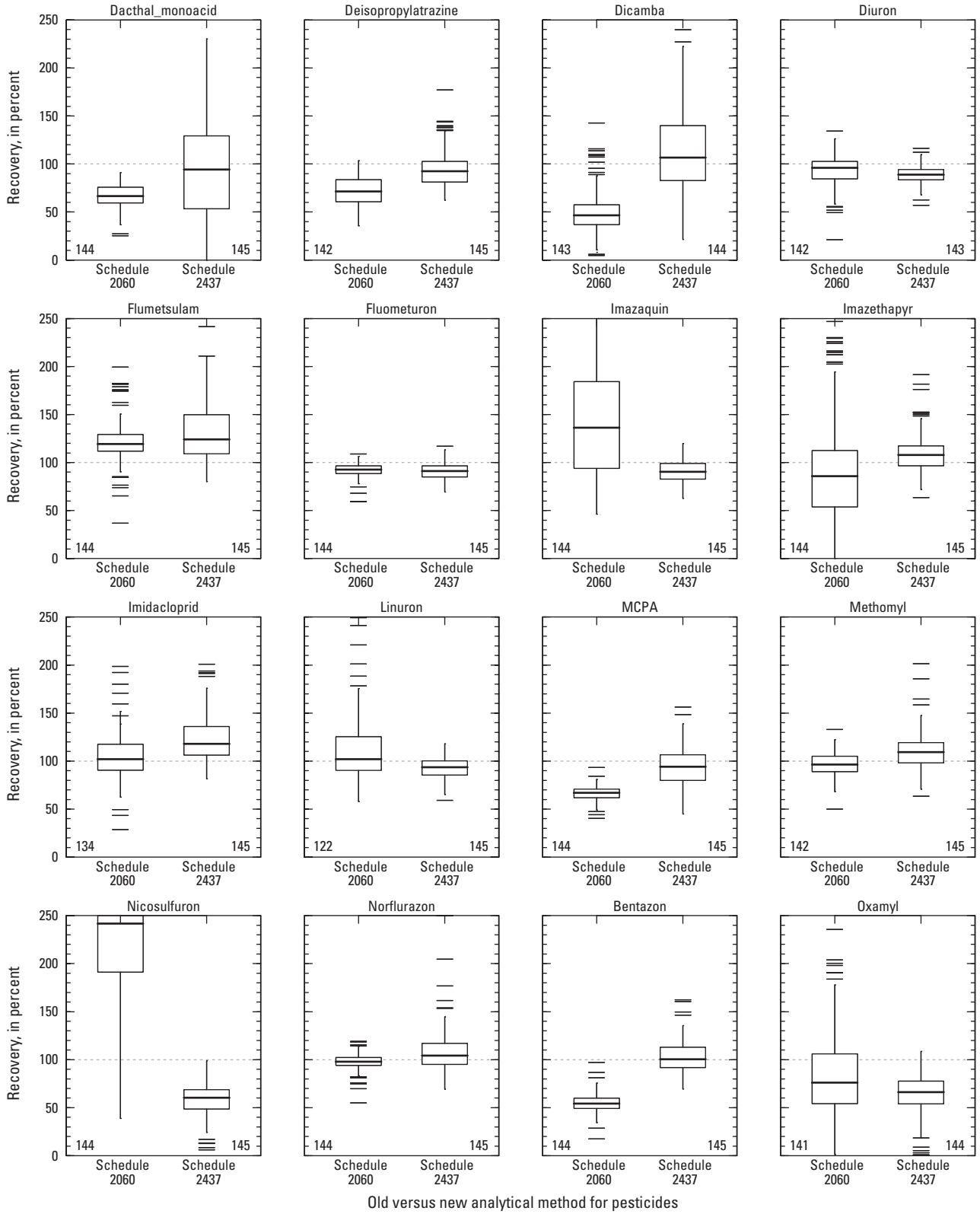


Figure 7. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2060 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.—Continued

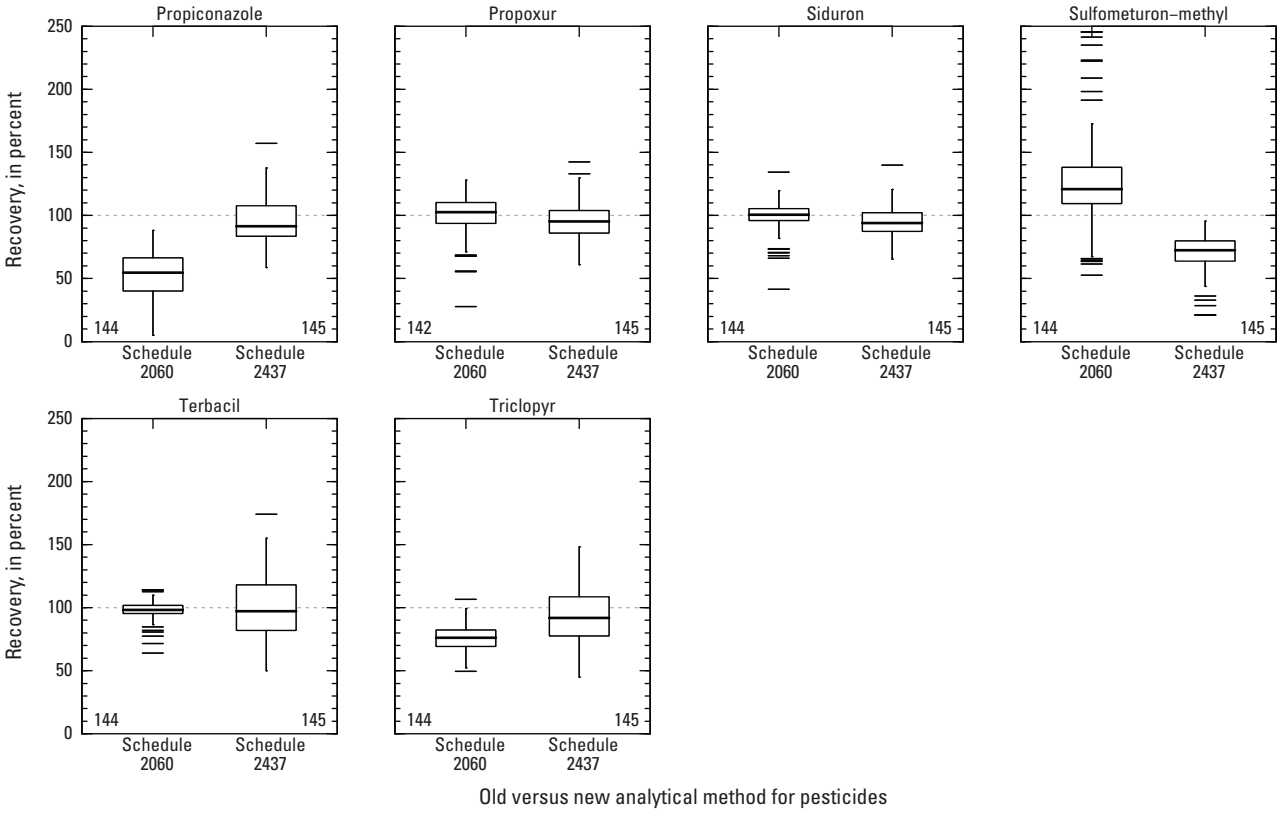


Figure 7. Distribution of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2060 (old method) and by schedule 2437 (new method). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 2. Recoveries greater than 250 percent are not shown.—Continued

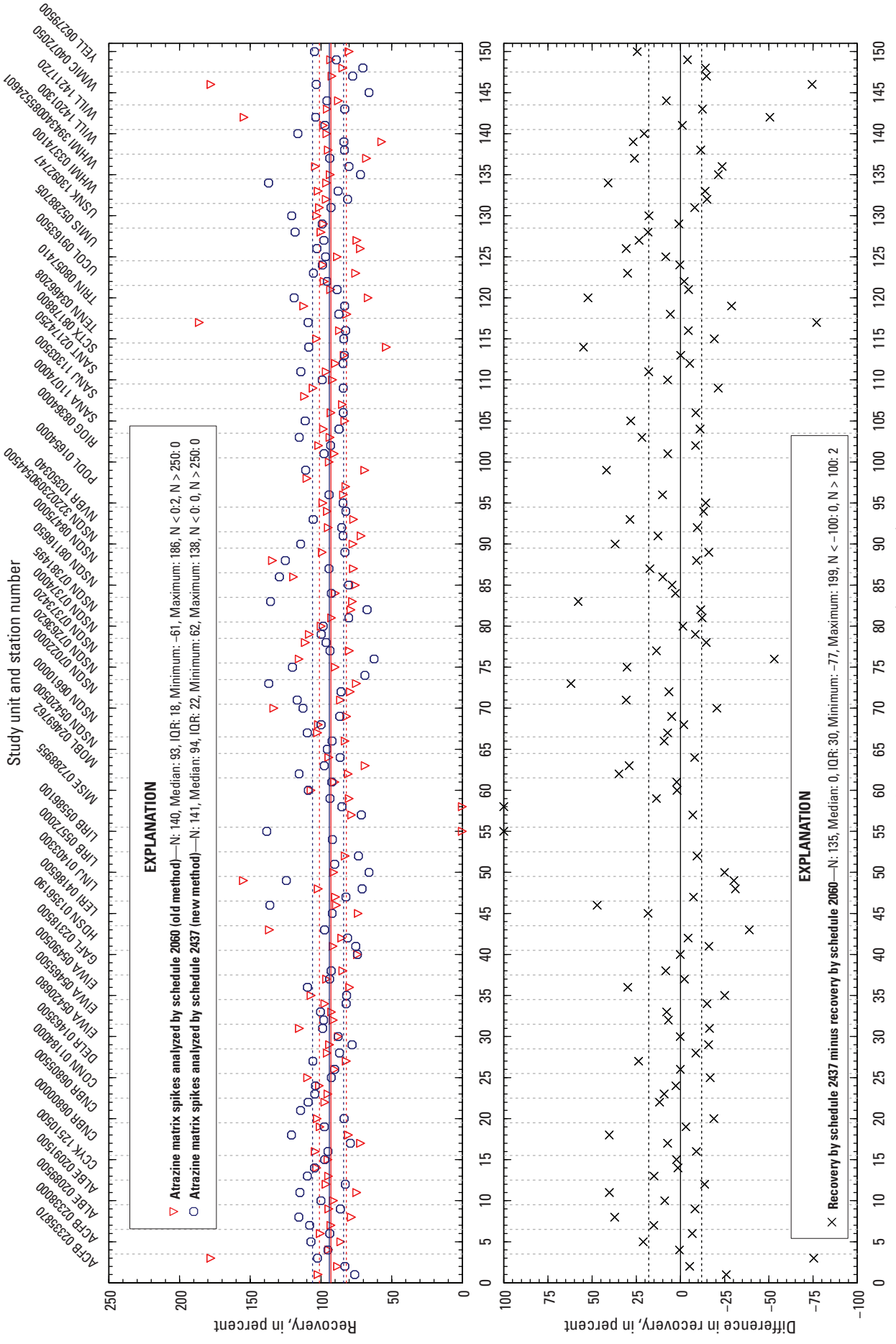


Figure 8. Comparison of recovery of atrazine in stream-water matrix spikes analyzed by schedule 2060 and by schedule 2437 by study unit, station number, and site visit. Solid horizonal lines in the graphs are median values; dashed horizontal lines are the 25th and 75th percentile values. Recoveries greater or less than the y–axis limits are plotted at the axis limits. N, number of values; IQR, interquartile range (75th percentile minus 25th percentile); <, less than; >, greater than.

Table 11. Comparison of median recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2060 and schedule 2437.

[Pesticides are sorted by the sign test statistic. Probablity values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of paired matrix spikes	Median recovery (percent) in matrix spikes analyzed by		Method closer to 100-percent recovery	Median paired difference in recovery (schedule 2060–schedule 2437) (percent)	Sign test	
			sh2060	sh2437			Test statistic	*p*-value
68	Bentazon	139	54.45	100.31	2437	-46.04	-69.5	**<0.0001**
70	Bromoxynil	139	31.22	93.45	2437	-61.68	-69.5	**<0.0001**
86	Oryzalin	139	37.05	105.45	2437	-66.49	-69.5	**<0.0001**
65	Aldicarb	137	26.13	82.83	2437	-55.17	-68.5	**<0.0001**
66	Aldicarb_sulfone	137	22.46	92.61	2437	-66.71	-68.5	**<0.0001**
88	Propiconazole	139	54.94	91.17	2437	-42.24	-65.5	**<0.0001**
62	2,4-D	137	65.65	91.98	2437	-26.13	-56.5	**<0.0001**
74	Dicamba	137	46.33	106.75	2437	-61.16	-54.5	**<0.0001**
4	Deethylatrazine	137	69.29	85.05	2437	-15.50	-53.5	**<0.0001**
82	MCPA	139	66.93	93.43	2437	-25.60	-50.5	**<0.0001**
73	Deisopropylatrazine	137	69.77	92.41	2437	-20.17	-41.5	**<0.0001**
83	Methomyl	137	95.90	110.29	2060	-10.72	-39.5	**<0.0001**
93	Triclopyr	139	76.01	91.10	2437	-14.36	-31.5	**<0.0001**
67	Aldicarb_sulfoxide	137	76.89	91.49	2437	-13.80	-26.5	**<0.0001**
80	Imidacloprid	129	102.09	118.13	2060	-12.77	-25.5	**<0.0001**
72	Dacthal_monoacid	139	66.61	94.18	2437	-25.28	-22.5	**0.0002**
79	Imazethapyr	139	85.66	107.11	2437	-25.35	-22.5	**0.0002**
85	Norflurazon	139	97.87	104.25	2060	-6.19	-18.5	**0.0021**
2	Carbaryl	137	82.97	83.41	2437	-1.47	-7.5	0.2315
76	Flumetsulam	139	119.22	123.81	2060	-3.53	-4.5	0.4976
1	Atrazine	135	92.94	94.29	2437	-0.39	-3.5	0.6057
5	Metalaxyl	137	95.00	96.26	2437	-0.34	-2.5	0.7327
69	Bromacil	139	98.68	100.69	2437	-0.33	-2.5	0.7345
92	Terbacil	139	98.32	97.76	2060	-1.52	-2.5	0.7345
3	Carbofuran	137	94.06	87.34	2060	3.86	10.5	0.0871
6	Tebuthiuron	139	94.42	93.18	2060	2.03	10.5	0.0895
87	Oxamyl	136	75.55	67.64	2060	6.14	12.0	**0.0482**
77	Fluometuron	139	92.58	91.03	2060	2.44	13.5	**0.0271**
89	Propoxur	137	102.40	97.02	2060	5.66	14.5	**0.0164**
63	2-Hydroxyatrazine	139	99.04	94.11	2060	7.41	17.5	**0.0038**
75	Diuron	137	96.18	88.82	2060	6.35	18.5	**0.0020**
81	Linuron	117	102.60	93.83	2060	10.42	23.5	**<0.0001**
90	Siduron	139	100.67	93.99	2060	7.14	23.5	**<0.0001**
64	3-Hydroxycarbofuran	137	86.90	73.22	2060	12.65	25.5	**<0.0001**
71	Chlorimuron-ethyl	139	71.57	56.35	2060	17.20	28.5	**<0.0001**
78	Imazaquin	139	136.20	90.25	2437	42.66	39.5	**<0.0001**
91	Sulfometuron-methyl	139	119.99	72.37	2060	52.38	57.5	**<0.0001**
84	Nicosulfuron	139	241.02	60.23	2437	181.85	68.5	**<0.0001**

Table 12. Comparison of variability of recovery of pesticides in stream-water matrix spikes analyzed by both schedule 2060 and schedule 2437.

[Pesticides are sorted by the method with the largest standard deviation and by the test statistic. Probablity values less than 0.05 are shown in bold. <, less than]

Index	Pesticide short name	Number of field matrix spikes analyzed by		Standard deviation of recovery (percent) of field matrix spikes analyzed by		Method having the larger standard deviation of recovery	Levene's test for equality of variance	
		Schedule 2060	Schedule 2437	Schedule 2060	Schedule 2437		Test statistic	*p*-value
84	Nicosulfuron	144	145	91.1	17.9	NWQL2060	62.9	**<0.0001**
78	Imazaquin	144	145	71.4	11.8	NWQL2060	58.1	**<0.0001**
67	Aldicarb_sulfoxide	142	145	24.7	14.3	NWQL2060	37.1	**<0.0001**
87	Oxamyl	141	144	52.6	22.4	NWQL2060	32.5	**<0.0001**
79	Imazethapyr	144	145	62.8	20.3	NWQL2060	27.1	**<0.0001**
91	Sulfometuron-methyl	144	145	45.8	14.2	NWQL2060	24.9	**<0.0001**
81	Linuron	122	145	36.4	10.2	NWQL2060	20.1	**<0.0001**
2	Carbaryl	142	145	35.4	21.5	NWQL2060	19.5	**<0.0001**
75	Diuron	142	143	15.1	9.5	NWQL2060	17.1	**<0.0001**
64	3-Hydroxycarbofuran	142	145	28.5	18.2	NWQL2060	16.7	**<0.0001**
71	Chlorimuron-ethyl	144	145	23.4	17.7	NWQL2060	8.9	**0.0031**
6	Tebuthiuron	144	145	12.9	9.5	NWQL2060	7.5	**0.0066**
88	Propiconazole	144	145	19.6	16.8	NWQL2060	3.6	0.0591
1	Atrazine	140	141	27.1	16.0	NWQL2060	3.5	0.0626
63	2-Hydroxyatrazine	144	145	29.6	19.1	NWQL2060	2.9	0.0905
80	Imidacloprid	134	145	27.6	24.5	NWQL2060	0.5	0.4785
92	Terbacil	144	145	7.0	24.2	NWQL2437	75.3	**<0.0001**
82	MCPA	144	145	7.6	22.0	NWQL2437	57.0	**<0.0001**
93	Triclopyr	144	145	10.0	20.4	NWQL2437	36.9	**<0.0001**
62	2,4-D	143	143	8.3	19.7	NWQL2437	33.6	**<0.0001**
70	Bromoxynil	144	145	7.0	19.9	NWQL2437	31.1	**<0.0001**
72	Dacthal_monoacid	144	145	12.7	61.4	NWQL2437	30.1	**<0.0001**
5	Metalaxyl	142	145	6.8	14.7	NWQL2437	28.7	**<0.0001**
4	Deethylatrazine	142	145	9.3	16.3	NWQL2437	25.6	**<0.0001**
66	Aldicarb_sulfone	142	145	13.8	19.4	NWQL2437	12.7	**0.0004**
69	Bromacil	144	145	9.8	19.2	NWQL2437	12.0	**0.0006**
83	Methomyl	142	145	12.3	20.8	NWQL2437	11.6	**0.0007**
68	Bentazon	144	145	10.5	16.2	NWQL2437	11.3	**0.0009**
74	Dicamba	143	144	22.8	52.3	NWQL2437	8.9	**0.0030**
85	Norflurazon	144	145	8.8	22.7	NWQL2437	7.6	**0.0063**
65	Aldicarb	142	145	12.3	17.2	NWQL2437	4.7	**0.0316**
77	Fluometuron	144	145	7.5	9.5	NWQL2437	4.7	**0.0317**
73	Deisopropylatrazine	142	145	15.5	19.5	NWQL2437	4.5	**0.0343**
76	Flumetsulam	144	145	25.7	36.9	NWQL2437	4.5	**0.0354**
3	Carbofuran	142	145	11.6	14.6	NWQL2437	3.3	0.0686
86	Oryzalin	144	145	18.4	21.2	NWQL2437	2.9	0.0922
90	Siduron	144	145	11.1	11.3	NWQL2437	0.0	0.8837
89	Propoxur	142	145	14.3	14.4	NWQL2437	0.0	0.9147

Detections in Paired Environmental Stream-Water Samples

Counts and percentages of samples with pesticide detections have been an important metric for water-quality assessments (Gilliom and others, 2006). The sign test was used to identify differences in pesticide detections in paired environmental water samples analyzed by old and new methods. Detected concentrations were assigned a value of 1 and nondetections were assigned a value of 0 for the purposes of the paired sign test. The sign test was applied to (1) all paired samples, regardless of the concentration detected, and (2) paired samples where concentrations detected were less than or equal to the concentration of the largest reporting level for either method.

A little more than one-half of the 61 pesticides common to sh2033 and sh2437 had one or more detections in paired water samples (table 13). For all concentrations, detection frequency was significantly greater by sh2033 for nine pesticides and significantly greater by sh2437 for five pesticides. Sign test results were very similar for concentrations less than or equal to the concentration of the largest reporting level for either method. Only one additional pesticide, tebuconazole, had a significantly different frequency of detection for the low range of concentrations (greater by sh2437, table 13). About 60 percent of the pesticides had six or fewer detections by either method; consequently, difference in detection capability for these pesticides could not be readily assessed. The distributions of pesticide detections in paired environmental water samples analyzed by sh2033 and sh2437 are shown in scatterplots in appendix 5 and for atrazine in figure 9.

Most of the 38 pesticides common to sh2060 and sh2437 had one or more detections in paired water samples (table 14). For all concentrations, detection frequency was significantly greater by sh2060 for 0 pesticides and significantly greater by sh2437 for 22 pesticides. As above, sign test results were very similar for all concentrations and for concentrations less than or equal to the concentration of the largest reporting level for either method. No additional pesticides had a significantly different frequency of detection for the low range of concentrations. About 35 percent of the pesticides had six or fewer detections by either method; consequently, difference in detection capability for these pesticides could not be readily assessed. The distributions of pesticide detections in paired environmental water samples analyzed by sh2060 and sh2437 are shown in scatterplots in appendix 6 and for atrazine in figure 10.

Concentrations in Paired Environmental Stream-Water Samples

The sign test was used to identify differences in pesticide concentrations in paired environmental water samples analyzed by old and new methods. Only pairs where the pesticide was detected by both methods were used in the tests. The sign test was done for the original concentrations as reported by the laboratory and for recovery-adjusted concentrations.

Only 27 of the 61 pesticides common to sh2033 and sh2437 had at least one pair of detections by both methods (table 15). Statistical test results for unadjusted and recovery-adjusted concentrations were similar. Of the 27 pesticides, 17 had significantly higher concentrations measured by sh2033 than by sh2437 (table 15). Based on the magnitude of the mean logical percent difference, and the lowess smooths in appendix 7, recovery adjustment improved the agreement between schedules for 16 of the 17 pesticides with significant differences. Hexazinone was the lone exception (table 15). Statistical significance was a strong function of sample size as all pesticides with 6 or fewer paired samples with detections were not significant and all pesticides (except for deethylatrazine) with 11 or more paired samples with detections were significant (table 15).

Scatterplots of atrazine concentrations measured by both methods in paired environmental water samples showed that measurements by sh2033 were approximately 1.5 to 2.5 times greater than those measured by sh2437 at concentrations less than 10 ng/L (fig. 11). At concentrations greater than 100 ng/L, the measurements by both methods were similar. This pattern of distinctly greater concentrations by sh2033 at the low range of concentrations and more similar concentrations at the high range of concentrations was exhibited by many of the pesticides with detections over a large range of concentrations (appendix 7).

Only 24 of the 38 pesticides common to sh2060 and sh2437 had at least one pair of detections by both methods (table 16). For original, unadjusted concentrations, six pesticides had significantly higher concentrations measured by sh2060 and five had significantly higher concentrations measured by sh2437 (table 16). For recovery-adjusted concentrations, five pesticides had significantly higher concentrations measured by sh2060 and only two had significantly higher concentrations measured by sh2437. Statistical significance generally was a function of sample size, but less so than for the sh2033 method. Pesticides (except imidacloprid) with 17 or more paired samples with detections generally showed significant differences between methods, whereas pesticides with 6 or fewer paired samples with detections were not significantly different (table 16).

Scatterplots of atrazine concentrations measured by both methods in paired environmental water samples showed that measurements by sh2060 generally were slightly greater than those measured by sh2437 at concentrations less than approximately 25 ng/L (fig. 12). At concentrations greater than 25 ng/L, the measurements by both methods were similar, with some exceptions. This pattern of greater concentrations by sh2060 at the low range of concentrations and similar concentrations at the high range of concentrations was exhibited by several of the pesticides with detections over a large range of concentrations (appendix 8).

Table 13. Comparison of pesticide detections in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437.

[Pesticides are sorted by the paired sign test statistic for all concentrations. Probablity values less than 0.05 are shown in bold. ng/L, nanogram per liter; <, less than; NA, not applicable]

Index	Pesticide short name	Method reporting level (ng/L)		Information for all concentrations					
		Schedule 2033	Schedule 2437	Number of paired environmental samples	Number of paired environmental samples with no detections by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2033 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods
33	Hexazinone	12	3	150	90	12	1	47	20.0
6	Tebuthiuron	28	3	150	72	27	3	48	34.6
5	Metalaxyl	14	6	150	85	29	3	33	44.6
20	Dicrotophos	80	4	150	132	2	0	16	11.1
21	Dimethoate	10	3	150	133	6	0	11	35.3
55	Tebuconazole	20	5	150	104	20	8	18	43.5
17	Diazinon	6	3	150	144	2	0	4	33.3
40	Myclobutanil	10	7	150	123	11	6	10	40.7
49	Prometon	12	4	150	22	104	10	14	81.3
25	Ethoprophos	16	5	150	146	1	0	3	25.0
3	Carbofuran	60	4	150	147	0	0	3	0.0
43	Parathion-methyl	8	500	150	148	0	0	2	0.0
58	Terbuthylazine	8	3	150	115	27	3	5	77.1
18	Diazoxon	12	4	150	149	0	0	1	0.0
31	Fipronil_sulfone	24	4	150	115	12	11	12	34.3
35	Malathion	16	6	149	147	1	0	1	50.0
44	Pendimethalin	12	3	150	142	3	2	3	37.5
53	Propyzamide	3.6	4	150	146	3	0	1	75.0
61	cis-Permethrin	10	2	142	139	0	1	2	0.0
10	Azinphos-methyl	120	8	150	150	0	0	0	NA
11	Azinphos-methyl-oxon	42	15	150	150	0	0	0	NA
13	Chlorpyrifos_oxon	80	4	150	150	0	0	0	NA
14	Cyanazine	22	16	150	150	0	0	0	NA
19	Dichlorvos	40	52	150	150	0	0	0	NA
22	Disulfoton	40	13	150	150	0	0	0	NA
23	Disulfoton_sulfone	14	9	150	150	0	0	0	NA
26	Fenamiphos	30	2	150	150	0	0	0	NA
27	Fenamiphos_sulfone	54	5	150	150	0	0	0	NA
28	Fenamiphos_sulfoxide	80	5	150	150	0	0	0	NA
32	Fonofos	4.8	11	150	150	0	0	0	NA
34	Malaoxon	22	3	150	150	0	0	0	NA
36	Methidathion	12	10	150	150	0	0	0	NA
39	Molinate	4	18	150	150	0	0	0	NA
42	Paraoxon-methyl	14	19	150	150	0	0	0	NA

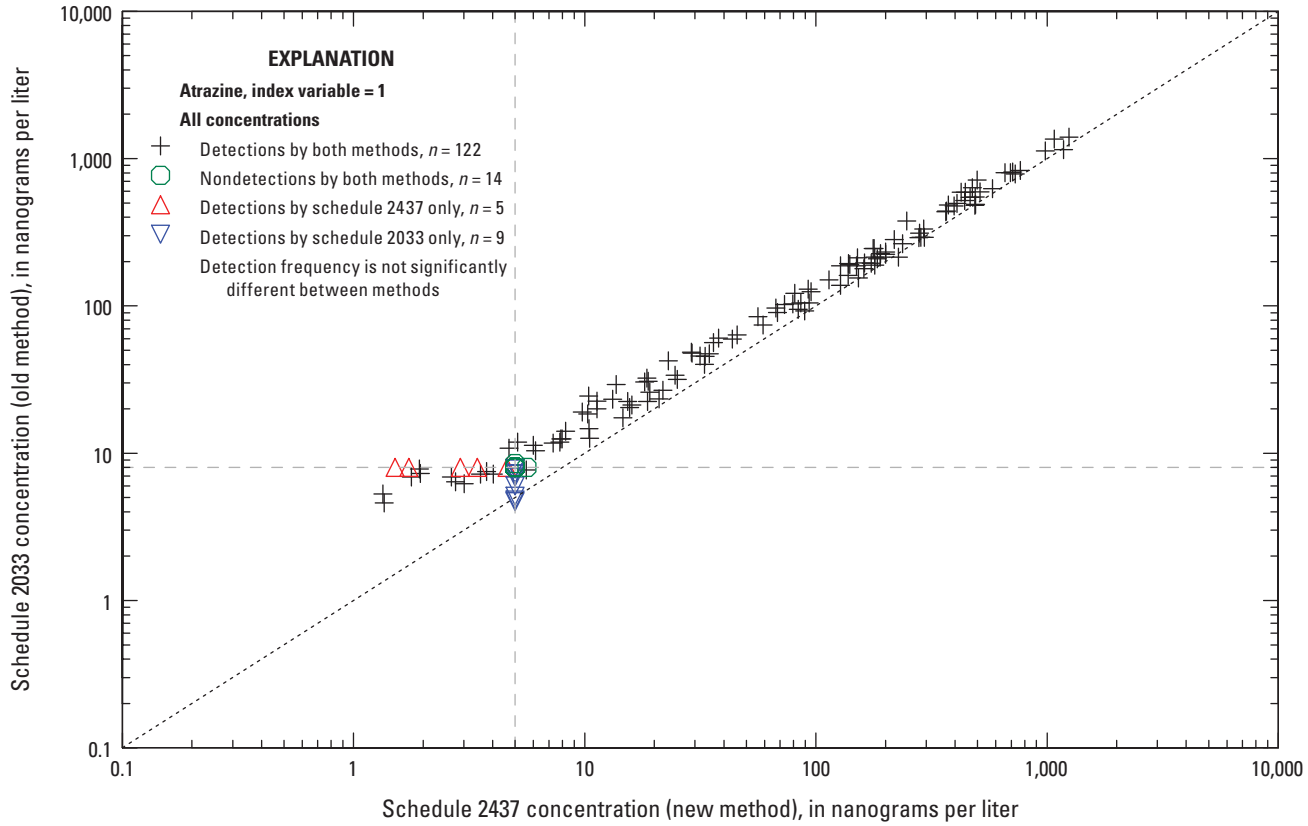
Sign test		Information for concentrations less than the largest reporting level of either method						Sign test	
Test statistic	*p*-value	Number of paired environ-mental samples	Number of paired environ-mental samples with no detec-tions by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2033 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods	Test statistic	*p*-value
-23.0	**<0.0001**	145	90	8	0	47	14.5	-23.5	**<0.0001**
-22.5	**<0.0001**	135	72	13	2	48	20.6	-23.0	**<0.0001**
-15.0	**<0.0001**	138	84	18	3	33	33.3	-15.0	**<0.0001**
-8.0	**<0.0001**	150	132	2	0	16	11.1	-8.0	**<0.0001**
-5.5	**0.0010**	146	133	2	0	11	15.4	-5.5	**0.0010**
-5.0	0.0755	137	104	8	7	18	24.2	-5.5	**0.0433**
-2.0	0.1250	148	144	0	0	4	0.0	-2.0	0.1250
-2.0	0.4545	142	123	5	4	10	26.3	-3.0	0.1796
-2.0	0.5413	114	22	70	10	12	76.1	-1.0	0.8318
-1.5	0.2500	147	146	0	0	1	0.0	-0.5	1.0000
-1.5	0.2500	150	147	0	0	3	0.0	-1.5	0.2500
-1.0	0.5000	150	148	0	0	2	0.0	-1.0	0.5000
-1.0	0.7266	138	115	15	3	5	65.2	-1.0	0.7266
-0.5	1.0000	149	149	0	0	0	NA	NA	NA
-0.5	1.0000	148	115	11	10	12	33.3	-1.0	0.8318
-0.5	1.0000	148	146	1	0	1	50.0	-0.5	1.0000
-0.5	1.0000	146	142	0	2	2	0.0	0.0	1.0000
-0.5	1.0000	147	146	0	0	1	0.0	-0.5	1.0000
-0.5	1.0000	140	139	0	1	0	0.0	0.5	1.0000
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150w	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	101	101	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA

Table 13. Comparison of pesticide detections in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437.—Continued

[Pesticides are sorted by the paired sign test statistic for all concentrations. Probablity values less than 0.05 are shown in bold. ng/L, nanogram per liter; <, less than; NA, not applicable]

Index	Pesticide short name	Method reporting level (ng/L)		Information for all concentrations					
		Schedule 2033	Schedule 2437	Number of paired environmental samples	Number of paired environmental samples with no detections by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2033 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods
45	Phorate	20	6	150	150	0	0	0	NA
46	Phorate_oxon	27	4	150	150	0	0	0	NA
47	Phosmet	80	20	150	150	0	0	0	NA
48	Phosmet_oxon	51.1	21	54	54	0	0	0	NA
51	Propanil	10	11	150	150	0	0	0	NA
56	Terbufos	18	4	150	150	0	0	0	NA
57	Terbufos_sulfo_nalog	45	11	146	146	0	0	0	NA
59	Thiobencarb	16	2	150	150	0	0	0	NA
7	2-Chloro-2,6-d_ilide	10	5	150	150	0	0	0	NA
9	Alachlor	8	9	150	148	0	1	1	0.0
52	Propargite	20	2	150	149	0	1	0	0.0
60	Tribuphos	18	2	150	149	0	1	0	0.0
41	Oxyfluorfen	10	500	149	147	0	2	0	0.0
50	Prometryn	10	2	150	117	26	5	2	78.8
1	Atrazine	8	5	150	14	122	9	5	89.7
24	EPTC	5.6	206	150	145	0	5	0	0.0
37	Metolachlor	20	9	150	24	112	10	4	88.9
2	Carbaryl	60	6	150	129	11	9	1	52.4
38	Metribuzin	12	20	150	136	6	8	0	42.9
29	Fipronil	18	4	150	91	30	19	10	50.8
4	Deethylatrazine	6	11	150	18	112	17	3	84.8
12	Chlorpyrifos	3.6	4	150	133	2	15	0	11.8
8	Acetochlor	10	10	150	92	36	21	1	62.1
15	Desulfinylfipro_mide	29	9	150	128	0	22	0	0.0
30	Fipronil_sulfide	12	4	150	87	23	38	2	36.5
54	Simazine	6	10	150	44	62	42	2	58.5
16	Desulfinylfipronil	12	4	150	63	38	48	1	43.7

Sign test		Information for concentrations less than the largest reporting level of either method						Sign test	
Test statistic	*p*-value	Number of paired environmental samples	Number of paired environmental samples with no detections by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2033 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods	Test statistic	*p*-value
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	149	149	0	0	0	NA	NA	NA
NA	NA	126	126	0	0	0	NA	NA	NA
NA	NA	54	54	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	146	146	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
NA	NA	150	150	0	0	0	NA	NA	NA
0.0	1.0000	150	148	0	1	1	0.0	0.0	1.0000
0.5	1.0000	149	149	0	0	0	NA	NA	NA
0.5	1.0000	149	148	0	1	0	0.0	0.5	1.0000
1.0	0.5000	149	147	0	2	0	0.0	1.0	0.5000
1.5	0.4531	137	117	13	5	2	65.0	1.5	0.4531
2.0	0.4240	39	13	12	9	5	46.2	2.0	0.4240
2.5	0.0625	150	145	0	5	0	0.0	2.5	0.0625
3.0	0.1796	73	24	35	10	4	71.4	3.0	0.1796
4.0	**0.0215**	149	129	10	9	1	50.0	4.0	**0.0215**
4.0	**0.0078**	145	136	3	6	0	33.3	3.0	**0.0313**
4.5	0.1360	141	91	21	19	10	42.0	4.5	0.1360
7.0	**0.0026**	53	18	16	17	2	45.7	7.5	**0.0007**
7.5	**<0.0001**	138	132	0	6	0	0.0	3.0	**0.0313**
10.0	**<0.0001**	102	92	0	10	0	0.0	5.0	**0.0020**
11.0	**<0.0001**	150	128	0	22	0	0.0	11.0	**<0.0001**
18.0	**<0.0001**	147	87	22	36	2	36.7	17.0	**<0.0001**
20.0	**<0.0001**	84	44	4	34	2	10.0	16.0	**<0.0001**
23.5	**<0.0001**	150	63	38	48	1	43.7	23.5	**<0.0001**



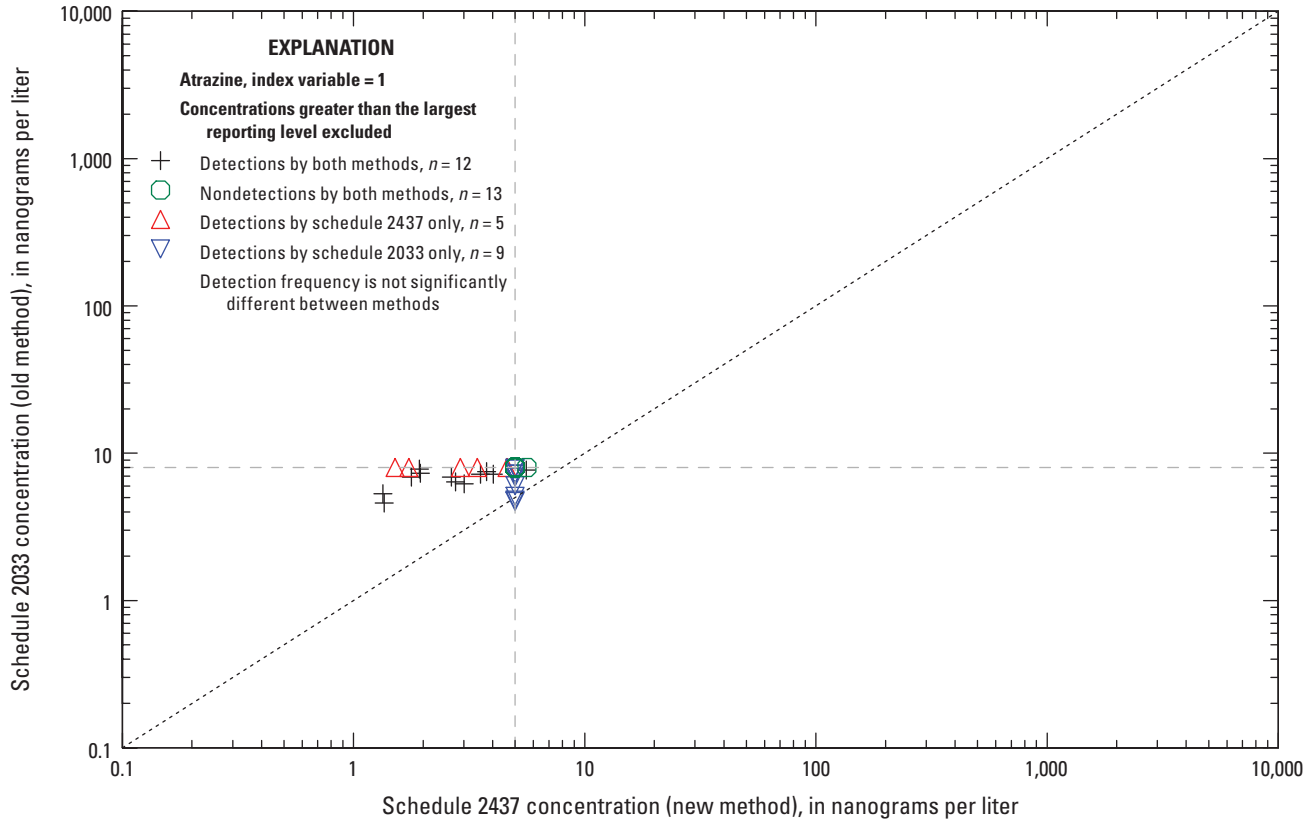


Figure 9. Comparison of atrazine detections in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437. The horizontal dashed line is the reporting level for schedule 2033 and the vertical dashed line is the reporting level for schedule 2437. See table 13 for information on statistical differences between methods.

Recovery adjustment generally improved agreement between methods; atrazine and metalaxyl, however, had mean logical percent differences closer to zero for unadjusted concentrations than for recovery-adjusted concentrations (table 16). The distributions of unadjusted and recovery-adjusted concentrations in paired environmental water samples analyzed by sh2060 and sh2437 are shown in scatterplots in appendix 8.

Contamination in Field Blank Water Samples

Three field blank water samples were collected during the same site visit from almost every stream-water site. Each of the blank samples was analyzed by one of the three methods/schedules. Only 16 of 283 pesticides were detected in field blank samples (table 17). The vast majority of pesticide detections were at concentrations less than the reporting level. Only tebuconazole, diuron, and 2-isopropyl-6-methyl-4-pyrimidinol were detected in blanks at concentrations greater than the reporting level (table 18).

Diuron was the most frequently detected pesticide and was detected in 3 of 44 (6.8 percent) blanks analyzed by sh2060 and by 1 of 43 (2.3 percent) blanks analyzed by sh2437. The frequency of detection of diuron, however, was not significantly different (alpha = 0.05) from pesticides with no detections. A statistically significant difference would require 7 versus 0 detections in 44 field blanks and indicates insufficient evidence to identify a difference in contamination among pesticides or among analytical methods.

Variability of Pesticides Analyzed by Schedule 2437

Knowledge of the variability of pesticide detections or concentrations is critical for interpreting water-quality conditions, particularly when only one sample is used to characterize a particular condition. Variability of pesticide detections and concentrations typically is a function of concentration (Martin, 2002, p. 1) and is assessed as a function of concentration in the next two sections. Analytical data for duplicate environmental water samples analyzed by sh2437 are provided in Martin and Baker (2017, dataset 7).

Variability of Detection

"Inconsistent detection" is the term used to describe the condition where a pesticide is detected in one duplicate water sample but is not detected in the paired duplicate water sample. The rate of inconsistent detection of pesticides in duplicate environmental water samples was assessed as a function of concentration class. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting level. Median concentrations less than the reporting level were assigned to class 1Low. Median concentrations greater than or equal to the reporting level but less than 10 times the reporting level were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting level were assigned to class 3High. Nondetections were set to 0 ng/L for calculating the median concentration of duplicate sets.

Of the 239 pesticides analyzed by sh2437, 114 were detected at least once in at least one of the 52 sets of duplicate environmental water samples (table 19). The most pesticide detections in a concentration class were 28 for hydroxysimazine and for diuron in the class 2Med. Inconsistent detection was 3.6 percent for hydroxysimazine and was 0.0 percent for diuron. The upper 90-percent confidence bound for inconsistent detection in this concentration class was 13.2 percent for hydroxysimazine and was 7.9 percent for diuron (table 19).

The frequency of inconsistent detection for pesticides analyzed by sh2437 is much less than that observed for older GC–MS and high-performance liquid chromatograph (HPLC) pesticide methods summarized in Martin (2002). Martin (2002, p. 32–33) used the thresholds of less than 25 percent inconsistent duplicate sets to indicate low variability of detection and more than 50 percent inconsistent duplicate sets to indicate high variability of detection. For the low range of concentration, older methods had only 3 of 50 pesticides that exhibited low detection variability and 45 of 50 pesticides that exhibited high detection variability. For sh2437 in the low range of concentration, 65 of 91 pesticides have low detection variability and only 8 of 91 pesticides have high detection variability (table 19).

Martin (2002) summed the numbers of replicate sets, by concentration class, for all pesticides measured by old GC–MS and HPLC pesticide methods. The overall frequency of inconsistent replicate sets was 60.0 percent in the low range, 13.7 percent in the medium range, and 1.1 percent in the high range of concentration (Martin, 2002, p. 33). For sh2437, the overall frequency of inconsistent replicate sets was 14.3 percent in the low range, 0.8 percent in the medium range, and 0.6 percent in the high range of concentration.

Variability of Concentrations

The variability of pesticide concentrations in duplicate environmental water samples was assessed as a function of 11 overlapping, "order of magnitude" concentration classes (for example, <1 ng/L (CR01), 0.5 to <5 ng/L (CR02), 1 to <10 ng/L (CR03), and so forth). Duplicate sets typically were assigned to two concentration classes on the basis of the median concentration of the duplicate set. Nondetections were set to 0 ng/L for calculating the median concentration of duplicate sets. The most duplicates in a concentration class were 29 for prometon in CR03 (1 to less than 10 ng/L) (table 20).

Variability estimates presented in table 20 are summarized by concentration class in table 21. Most duplicate sets with detections were in concentration classes CR02 to CR07 (0.5 to <1,000 ng/L). In these classes, median pooled standard deviation ranged from 0.47 to 13 ng/L and median pooled

Table 14. Comparison of pesticide detections in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437.

[Pesticides are sorted by the paired sign test statistic for all concentrations. Probablity values less than 0.05 are shown in bold. ng/L, nanogram per liter; <, less than; NA, not applicable]

Index	Pesticide short name	Method reporting level (ng/L)		Information for all concentrations					
		Schedule 2060	Schedule 2437	Number of paired environmental samples	Number of paired environmental samples with no detections by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2060 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods
69	Bromacil	60	6	147	79	3	0	65	4.4
6	Tebuthiuron	60	3	147	73	11	1	62	14.9
73	Deisopropylatrazine	80	20	147	53	33	0	61	35.1
88	Propiconazole	38	6	147	86	7	0	54	11.5
80	Imidacloprid	80	11	146	70	20	6	50	26.3
5	Metalaxyl	40	6	147	86	19	0	42	31.1
4	Deethylatrazine	60	11	147	34	73	0	40	64.6
68	Bentazon	60	10	147	96	19	0	32	37.3
75	Diuron	40	5	147	21	86	4	36	68.3
76	Flumetsulam	80	17	147	119	1	0	27	3.6
1	Atrazine	80	5	147	22	98	1	26	78.4
91	Sulfometuron-methyl	60	4	147	102	18	1	26	40.0
62	2,4-D	60	62	147	69	41	7	30	52.6
85	Norflurazon	40	4	147	126	6	0	15	28.6
93	Triclopyr	80	88	147	128	3	1	15	15.8
89	Propoxur	60	4	147	131	3	0	13	18.8
2	Carbaryl	40	6	147	136	0	0	11	0.0
63	2-Hydroxyatrazine	60	8	147	19	113	2	13	88.3
79	Imazethapyr	80	20	147	117	12	4	14	40.0
71	Chlorimuron-ethyl	80	8	147	139	1	0	7	12.5
77	Fluometuron	40	3	147	116	17	4	10	54.8
84	Nicosulfuron	320	14	147	140	1	0	6	14.3
87	Oxamyl	120	2	147	140	1	0	6	14.3
67	Aldicarb_sulfoxide	80	3	147	142	0	0	5	0.0
83	Methomyl	120	3	147	142	0	0	5	0.0
81	Linuron	40	6	144	140	0	0	4	0.0
3	Carbofuran	40	4	147	144	0	0	3	0.0
86	Oryzalin	40	11	147	144	0	0	3	0.0
92	Terbacil	46	21	147	143	2	0	2	50.0
70	Bromoxynil	120	79	147	146	0	0	1	0.0
64	3-Hydroxycarbofuran	60	16	147	147	0	0	0	NA
65	Aldicarb	120	8	147	147	0	0	0	NA
66	Aldicarb_sulfone	80	20	147	147	0	0	0	NA
72	Dacthal_monoacid	40	500	147	147	0	0	0	NA
74	Dicamba	60	500	147	147	0	0	0	NA
82	MCPA	40	95	147	145	2	0	0	100.0
90	Siduron	40	5	147	147	0	0	0	NA
78	Imazaquin	100	19	147	142	0	4	1	0.0

Sign test		Information for concentrations less than the largest reporting level of either method						Sign test	
Test statistic	*p*-value	Number of paired environmental samples	Number of paired environmental samples with no detections by either method	Number of paired environmental samples with detections by both methods	Number of paired environmental samples with detections by schedule 2060 only	Number of paired environmental samples with detections by schedule 2437 only	When detected by at least one method, the percentage of samples with detections by both methods	Test statistic	*p*-value
-32.5	**<0.0001**	144	79	0	0	65	0.0	-32.5	**<0.0001**
-30.5	**<0.0001**	147	73	11	1	62	14.9	-30.5	**<0.0001**
-30.5	**<0.0001**	133	53	21	0	59	26.3	-29.5	**<0.0001**
-27.0	**<0.0001**	141	86	3	0	52	5.5	-26.0	**<0.0001**
-22.0	**<0.0001**	123	68	5	2	48	9.1	-23.0	**<0.0001**
-21.0	**<0.0001**	145	86	18	0	41	30.5	-20.5	**<0.0001**
-20.0	**<0.0001**	107	34	34	0	39	46.6	-19.5	**<0.0001**
-16.0	**<0.0001**	142	96	14	0	32	30.4	-16.0	**<0.0001**
-16.0	**<0.0001**	114	21	53	4	36	57.0	-16.0	**<0.0001**
-13.5	**<0.0001**	146	119	1	0	26	3.7	-13.0	**<0.0001**
-12.5	**<0.0001**	85	22	36	1	26	57.1	-12.5	**<0.0001**
-12.5	**<0.0001**	145	102	16	1	26	37.2	-12.5	**<0.0001**
-11.5	**0.0002**	112	69	11	4	28	25.6	-12.0	**<0.0001**
-7.5	**<0.0001**	147	126	6	0	15	28.6	-7.5	**<0.0001**
-7.0	**0.0005**	125	110	1	1	13	6.7	-6.0	**0.0018**
-6.5	**0.0002**	147	131	3	0	13	18.8	-6.5	**0.0002**
-5.5	**0.0010**	147	136	0	0	11	0.0	-5.5	**0.0010**
-5.5	**0.0074**	78	19	45	2	12	76.3	-5.0	**0.0129**
-5.0	**0.0309**	146	117	11	4	14	37.9	-5.0	**0.0309**
-3.5	**0.0156**	147	139	1	0	7	12.5	-3.5	**0.0156**
-3.0	0.1796	137	116	7	4	10	33.3	-3.0	0.1796
-3.0	**0.0313**	147	140	1	0	6	14.3	-3.0	**0.0313**
-3.0	**0.0313**	146	140	0	0	6	0.0	-3.0	**0.0313**
-2.5	0.0625	147	142	0	0	5	0.0	-2.5	0.0625
-2.5	0.0625	147	142	0	0	5	0.0	-2.5	0.0625
-2.0	0.1250	144	140	0	0	4	0.0	-2.0	0.1250
-1.5	0.2500	147	144	0	0	3	0.0	-1.5	0.2500
-1.5	0.2500	147	144	0	0	3	0.0	-1.5	0.2500
-1.0	0.5000	147	143	2	0	2	50.0	-1.0	0.5000
-0.5	1.0000	147	146	0	0	1	0.0	-0.5	1.0000
NA	NA	147	147	0	0	0	NA	NA	NA
NA	NA	147	147	0	0	0	NA	NA	NA
NA	NA	147	147	0	0	0	NA	NA	NA
NA	NA	147	147	0	0	0	NA	NA	NA
NA	NA	146	146	0	0	0	NA	NA	NA
NA	NA	145	145	0	0	0	NA	NA	NA
NA	NA	147	147	0	0	0	NA	NA	NA
1.5	0.3750	147	142	0	4	1	0.0	1.5	0.3750

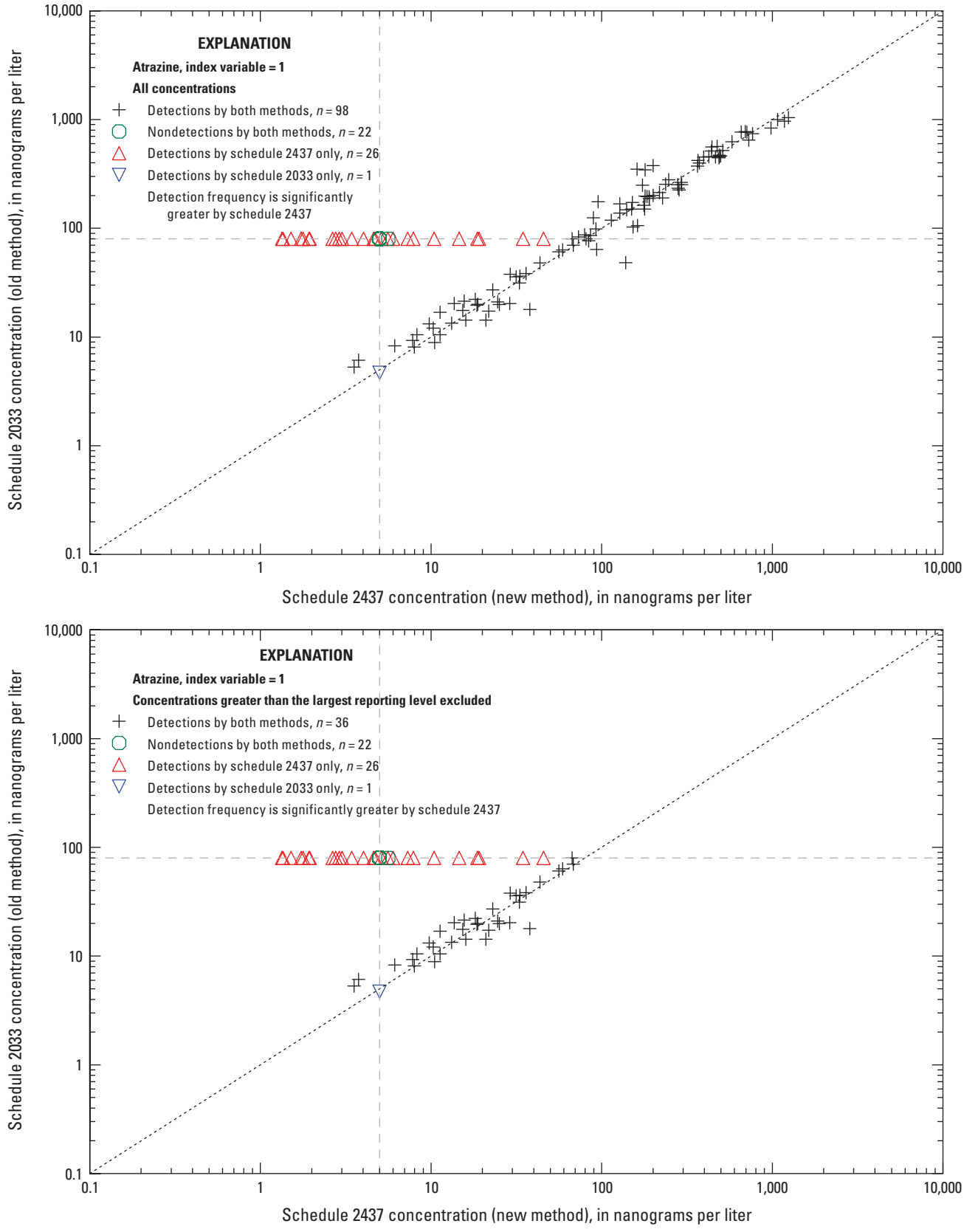
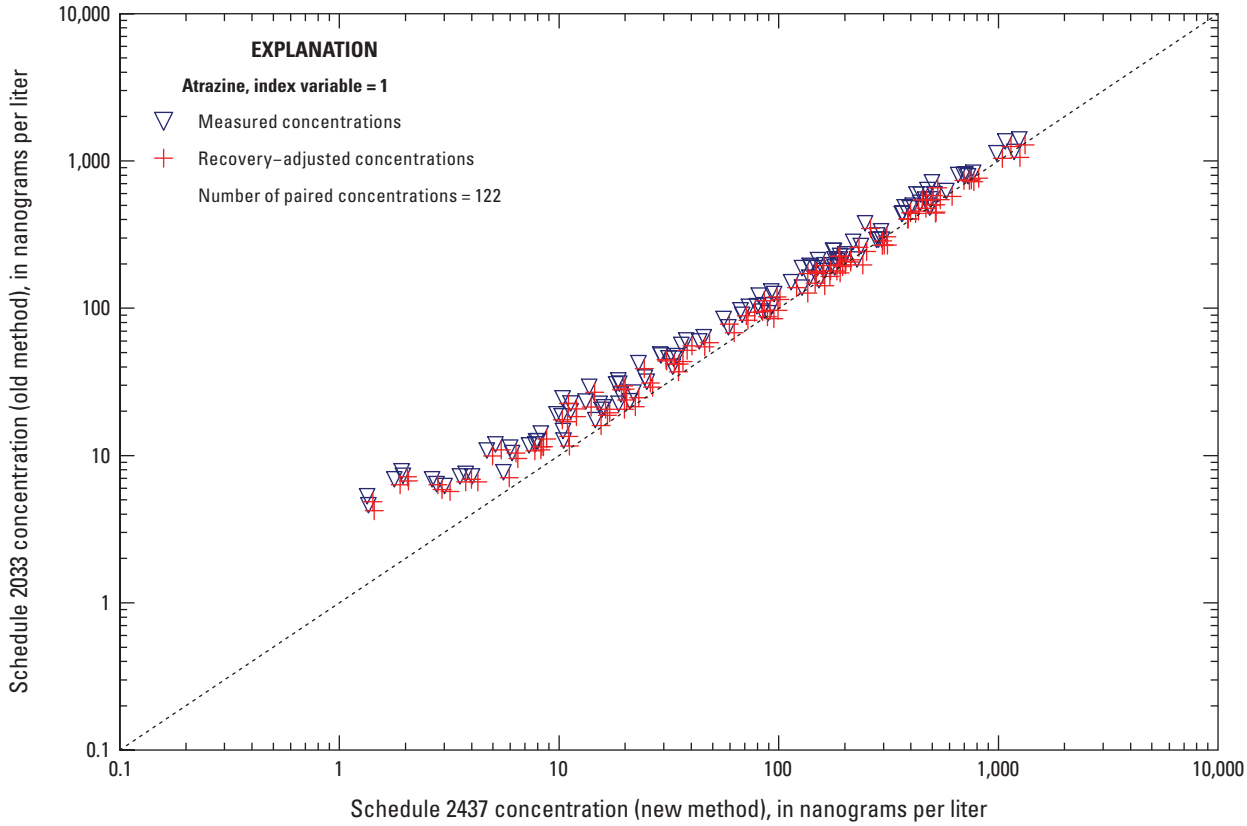


Figure 10. Comparison of atrazine detections in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437. The horizontal dashed line is the reporting level for schedule 2060 and the vertical dashed line is the reporting level for schedule 2437. See table 14 for information on statistical differences between methods.

Table 15. Comparison of pesticide concentrations in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437.

[Pesticides are sorted by the paired sign test statistic for unadjusted concentrations. Probability values less than 0.05 are shown in bold. LPD; Logical percent difference (the natural logrithm of the ratio of the concentration measured by schedule 2033 divided by the concentration measured by schedule 2437, times 100 percent). LPDs greater than zero indicate concentrations measured by schedule 2033 are greater than those measured by schedule 2437. LPDs less than zero indicate concentrations measured by schedule 2437 are greater than those measured by schedule 2033. Recovery-adjusted concentrations are measured concentrations divided by the median recovery in matrix spikes. Median recovery in matrix spikes is shown in the figures in appendix 3. <, less than]

Index	Pesticide short name	Number of paired environmental samples with detections by both methods	Unadjusted concentrations			Recovery-adjusted concentrations			Difference in mean LPD, unadjusted minus recovery-adjusted (percent)	Does unadjusted or recovery-adjusted concentrations provide better agreement between methods?
				Sign test			Sign test			
			Mean LPD (percent)	Test statistic	*p*-value	Mean LPD (percent)	Test statistic	*p*-value		
4	Deethylatrazine	112	-0.9	-5.0	0.3952	6.3	6.0	0.2986	-7.2	Unadjusted
20	Dicrotophos	2	-58.2	-1.0	0.5000	21.9	0.0	1.0000	-80.1	Recovery
17	Diazinon	2	26.3	0.0	1.0000	12.6	0.0	1.0000	13.7	Recovery
21	Dimethoate	6	3.8	0.0	1.0000	29.3	2.0	0.2188	-25.5	Unadjusted
25	Ethoprophos	1	77.9	0.5	1.0000	51.5	0.5	1.0000	26.4	Recovery
35	Malathion	1	31.5	0.5	1.0000	2.5	0.5	1.0000	29.0	Recovery
12	Chlorpyrifos	2	132.4	1.0	0.5000	112.1	1.0	0.5000	20.3	Recovery
44	Pendimethalin	3	212.0	1.5	0.2500	183.6	1.5	0.2500	28.4	Recovery
53	Propyzamide	3	75.3	1.5	0.2500	70.0	1.5	0.2500	5.3	Recovery
38	Metribuzin	6	21.1	2.0	0.2188	2.6	0.0	1.0000	18.6	Recovery
2	Carbaryl	11	117.4	5.5	**0.0010**	85.9	5.5	**0.0010**	31.5	Recovery
40	Myclobutanil	11	76.5	5.5	**0.0010**	68.9	5.5	**0.0010**	7.7	Recovery
31	Fipronil_sulfone	12	112.1	6.0	**0.0005**	87.7	6.0	**0.0005**	24.3	Recovery
33	Hexazinone	12	67.4	6.0	**0.0005**	74.1	6.0	**0.0005**	-6.8	Unadjusted
55	Tebuconazole	20	97.1	10.0	**<0.0001**	70.4	9.0	**<0.0001**	26.7	Recovery
30	Fipronil_sulfide	23	191.9	11.5	**<0.0001**	164.7	11.5	**<0.0001**	27.2	Recovery
50	Prometryn	26	75.3	13.0	**<0.0001**	58.5	13.0	**<0.0001**	16.7	Recovery
6	Tebuthiuron	27	164.3	13.5	**<0.0001**	102.6	13.5	**<0.0001**	61.7	Recovery
58	Terbuthylazine	27	57.5	13.5	**<0.0001**	43.6	12.5	**<0.0001**	14.0	Recovery
5	Metalaxyl	29	75.5	14.5	**<0.0001**	56.7	13.5	**<0.0001**	18.8	Recovery
29	Fipronil	30	134.6	15.0	**<0.0001**	87.4	15.0	**<0.0001**	47.2	Recovery
8	Acetochlor	36	55.8	17.0	**<0.0001**	31.5	17.0	**<0.0001**	24.3	Recovery
16	Desulfinylfipronil	38	120.8	19.0	**<0.0001**	89.0	19.0	**<0.0001**	31.9	Recovery
54	Simazine	62	35.6	26.0	**<0.0001**	20.4	17.0	**<0.0001**	15.2	Recovery
49	Prometon	104	62.6	46.0	**<0.0001**	50.7	43.0	**<0.0001**	12.0	Recovery
1	Atrazine	122	35.1	56.0	**<0.0001**	20.7	31.0	**<0.0001**	14.4	Recovery
37	Metolachlor	112	64.6	56.0	**<0.0001**	44.2	48.0	**<0.0001**	20.4	Recovery



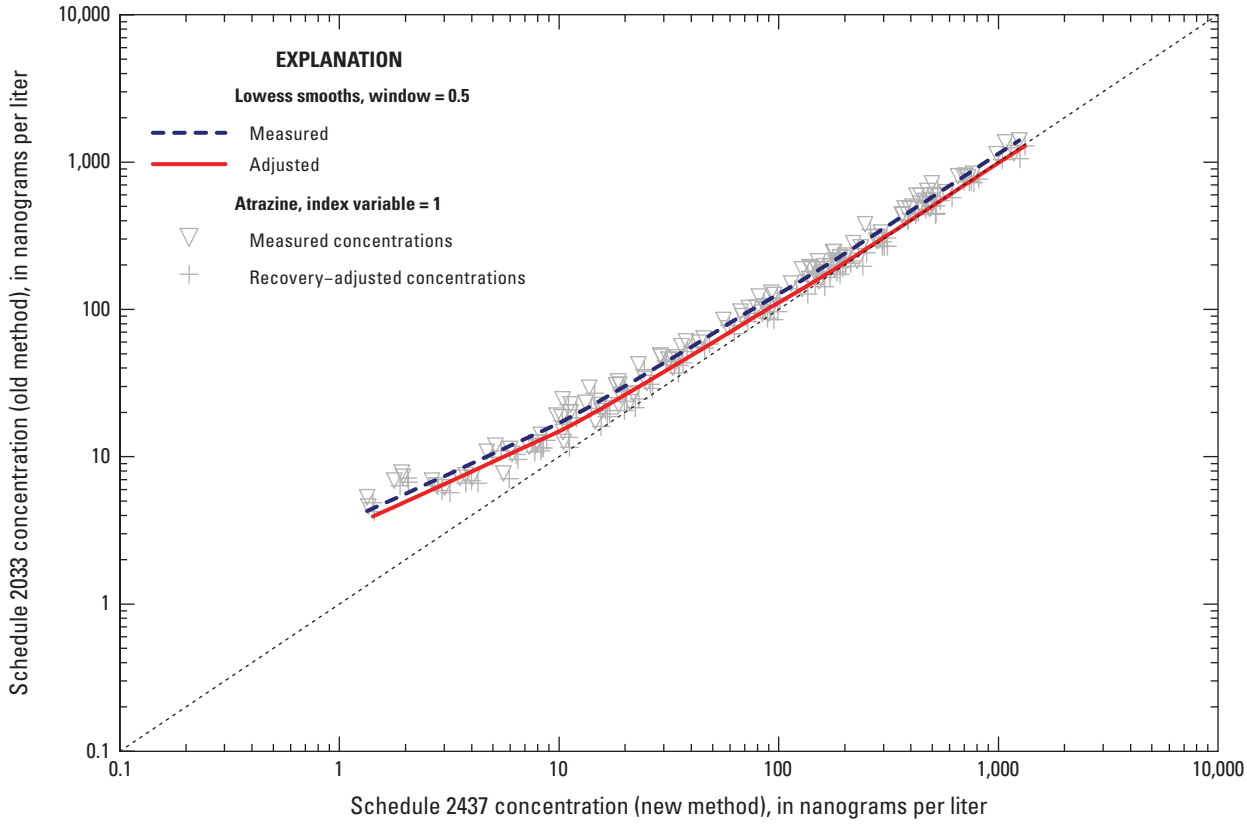


Figure 11. Comparison of atrazine concentrations in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437. Recovery-adjusted concentrations are measured concentrations divided by the median recovery in field matrix spikes. Lowess smooths were not done for three or fewer measurements.

Table 16. Comparison of pesticide concentrations in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437.

[Pesticides are sorted by the paired sign test statistic for unadjusted concentrations. Probability values less than 0.05 are shown in bold. LPD, logical percent difference (the natural logrithm of the ratio of the concentration measured by schedule 2060 divided by the concentration measured by schedule 2437, times 100 percent). LPDs greater than zero indicate concentrations measured by schedule 2060 are greater than those measured by schedule 2437. LPDs less than zero indicate concentrations measured by schedule 2437 are greater than those measured by schedule 2060. Recovery-adjusted concentrations are measured concentrations divided by the median recovery in matrix spikes. Median recovery in matrix spikes is shown in the figures in appendix 4. <, less than]

Index	Pesticide short name	Number of paired environmental samples with detections by both methods	Unadjusted concentrations			Recovery-adjusted concentrations			Difference in mean LPD, unadjusted minus recovery-adjusted (percent)	Does unadjusted or recovery-adjusted concentrations provide better agreement between methods?
				Sign test			Sign test			
			Mean LPD (percent)	Test statistic	*p*-value	Mean LPD (percent)	Test statistic	*p*-value		
4	Deethylatrazine	73	-34.4	-33.5	**<0.0001**	-14.6	-23.5	**<0.0001**	-19.8	Recovery
62	2,4-D	41	-57.4	-17.5	**<0.0001**	-23.6	-11.5	**0.0004**	-33.9	Recovery
73	Deisopropylatrazine	33	-29.1	-11.5	**<0.0001**	-3.1	-4.5	0.1628	-25.9	Recovery
68	Bentazon	19	-54.4	-9.5	**<0.0001**	6.9	3.5	0.1671	-61.3	Recovery
88	Propiconazole	7	-32.1	-3.5	**0.0156**	19.1	2.5	0.1250	-51.2	Recovery
79	Imazethapyr	12	-29.7	-1.0	0.7744	-6.8	1.0	0.7744	-22.9	Recovery
82	MCPA	2	-79.9	-1.0	0.5000	-45.8	-1.0	0.5000	-34.1	Recovery
71	Chlorimuron-ethyl	1	-60.1	-0.5	1.0000	-84.0	-0.5	1.0000	23.9	Unadjusted
76	Flumetsulam	1	-83.1	-0.5	1.0000	-79.2	-0.5	1.0000	-3.9	Recovery
93	Triclopyr	3	-17.5	-0.5	1.0000	1.4	-0.5	1.0000	-18.9	Recovery
6	Tebuthiuron	11	7.8	0.5	1.0000	6.9	0.5	1.0000	0.9	Recovery
84	Nicosulfuron	1	117.5	0.5	1.0000	-21.5	-0.5	1.0000	139.0	Recovery
87	Oxamyl	1	6.9	0.5	1.0000	-6.9	-0.5	1.0000	13.8	Unadjusted
89	Propoxur	3	8.6	0.5	1.0000	1.2	-0.5	1.0000	7.4	Recovery
85	Norflurazon	6	6.4	1.0	0.6875	12.7	2.0	0.2188	-6.4	Unadjusted
92	Terbacil	2	60.8	1.0	0.5000	59.8	1.0	0.5000	1.0	Recovery
69	Bromacil	3	91.7	1.5	0.2500	93.7	1.5	0.2500	-2.0	Unadjusted
80	Imidacloprid	20	72.8	2.0	0.5034	87.3	2.0	0.5034	-14.6	Unadjusted
77	Fluometuron	17	3.8	4.5	**0.0490**	2.2	0.5	1.0000	1.6	Recovery
5	Metalaxyl	19	28.9	8.5	**<0.0001**	30.2	9.5	**<0.0001**	-1.4	Unadjusted
91	Sulfometuron-methyl	18	78.9	9.0	**<0.0001**	27.6	5.0	**0.0309**	51.3	Recovery
1	Atrazine	98	3.7	11.0	**0.0334**	5.0	12.0	**0.0197**	-1.3	Unadjusted
75	Diuron	86	38.0	32.0	**<0.0001**	30.3	29.0	**<0.0001**	7.7	Recovery
63	2-Hydroxyatrazine	113	40.1	38.5	**<0.0001**	33.9	33.5	**<0.0001**	6.2	Recovery

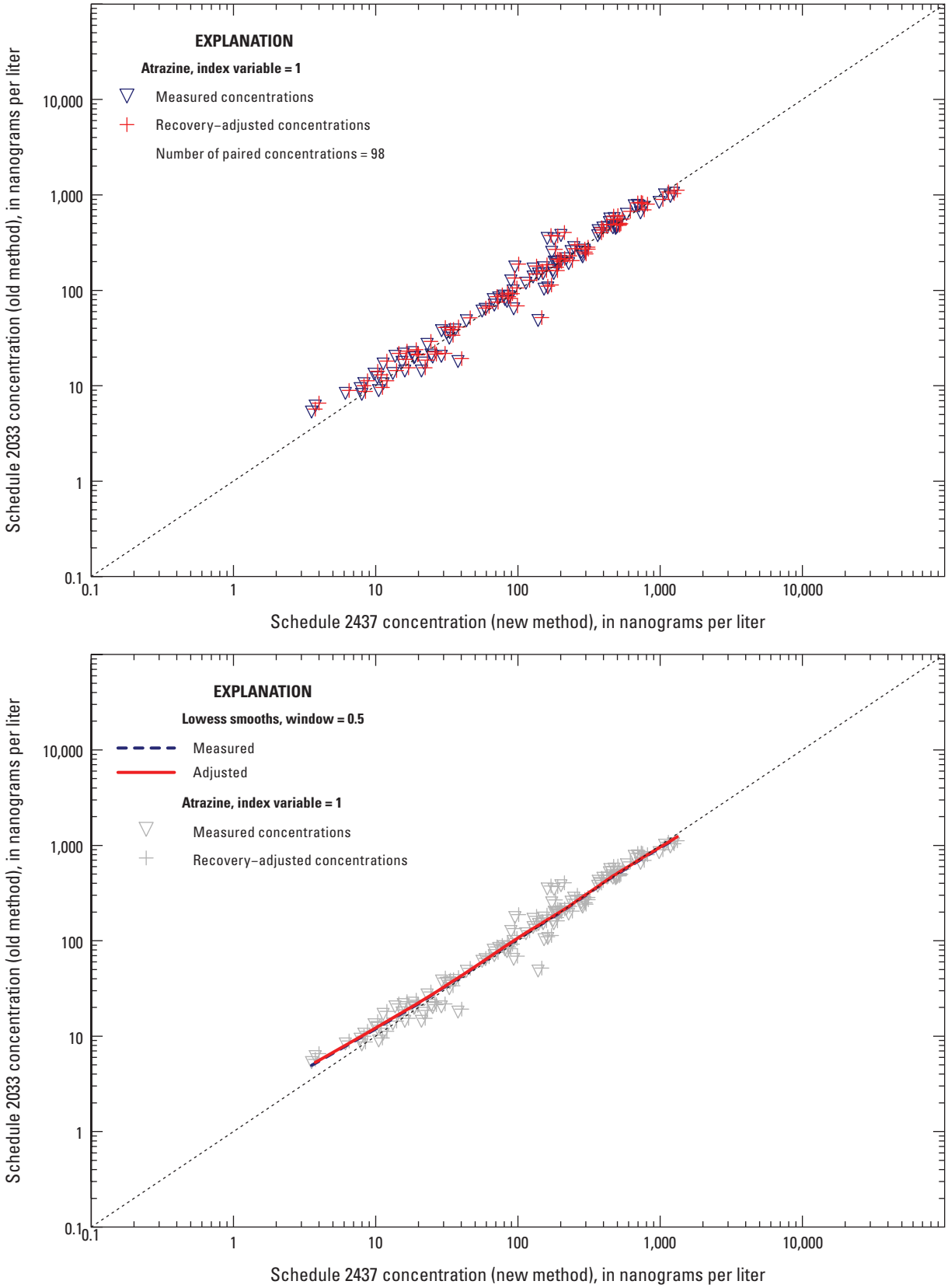


Figure 12. Comparison of atrazine concentrations in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437. Recovery-adjusted concentrations are measured concentrations divided by the median recovery in field matrix spikes. Lowess smooths were not done for three or fewer measurements.

Table 17. Summary of pesticide detections in field blank water samples analyzed by schedule 2033, schedule 2060, and schedule 2437.

[Pesticides not detected by a method are not shown in the table. Pesticides are sorted by index and analytical method. Index, A numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules. ng/L, nanogram per liter]

Index	Pesticide short name	Analytical method	Number of field blank water samples	Number of detections	Percentage of detections	Maximum concentration detected (ng/L)	Reporting level (ng/L)
37	Metolachlor	NWQL2033	45	1	2.22	5.30	20
37	Metolachlor	NWQL2437	43	2	4.65	3.47	9
55	Tebuconazole	NWQL2437	43	1	2.33	7.90	5
62	2,4-D	NWQL2437	44	1	2.27	19.80	62
63	2-Hydroxyatrazine	NWQL2060	44	1	2.27	10.20	60
63	2-Hydroxyatrazine	NWQL2437	43	1	2.33	1.74	8
67	Aldicarb_sulfoxide	NWQL2437	43	1	2.33	1.70	3
75	Diuron	NWQL2060	44	3	6.82	9.30	40
75	Diuron	NWQL2437	43	1	2.33	5.19	5
79	Imazethapyr	NWQL2060	44	1	2.27	16.70	80
84	Nicosulfuron	NWQL2060	44	1	2.27	20.40	320
84	Nicosulfuron	NWQL2437	43	1	2.33	8.09	14
98	2-Isopropyl-6-m_inol	NWQL2437	43	2	4.65	112.57	20
121	Azoxystrobin	NWQL2437	43	1	2.33	0.54	3
133	Deethylhydroxy_azine	NWQL2437	43	1	2.33	2.57	4
163	Flubendiamide	NWQL2437	44	1	2.27	1.90	5
190	Methoxyfenozide	NWQL2437	43	2	4.65	1.14	2
249	Dacthal	NWQL2033	45	1	2.22	1.50	7.6
257	Trifluralin	NWQL2033	45	1	2.22	1.70	18
270	Caffeine	NWQL2060	44	1	2.27	38.80	80

relative standard deviation ranged from 6.1 to 21 percent (table 21). The estimates of variability of pesticide concentrations analyzed by sh2437 are comparable to those for similar concentration ranges analyzed by older GC–MS and HPLC pesticide methods summarized in Martin (2002, p. 56).

In general, pooled estimates of RSD rather than pooled estimates of SD should be used to characterize variability of concentrations because RSD is a more robust estimate of variability (less affected by heteroscedasticity) than SD (Martin, 2002, p. 45). Examples of the use of estimates of variability of concentration measurements are given in Martin (2002, p. 49–55).

Table 18. Concentrations of pesticides detected in field blank water samples analyzed by schedule 2033, schedule 2060, and schedule 2437.

[Pesticides sorted by station number, date, index, and method. Index, A numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schdeules. See table 17 for a summary of detections by all three methods. ng/L, nanogram per liter]

Station number (table 2)	Study unit abbreviation (table 1)	Sampling date	Index	Pesticide short name	Analytical method	Concentration detected (ng/L)	Reporting limit (ng/L)
01403300	LINJ	8/22/2012	55	Tebuconazole	NWQL2437	7.900	5
01403300	LINJ	8/22/2012	79	Imazethapyr	NWQL2060	0.017	80
01403300	LINJ	8/22/2012	249	Dacthal	NWQL2033	0.002	7.6
02089500	ALBE	7/10/2012	163	Flubendiamide	NWQL2437	1.899	5
02174250	SANT	8/6/2012	75	Diuron	NWQL2437	5.193	5
04186500	LERI	8/21/2012	75	Diuron	NWQL2060	0.009	40
05420500	NSQN	6/26/2012	98	2-Isopropyl-6-m_inol	NWQL2437	112.570	20
05465500	EIWA	9/5/2012	98	2-Isopropyl-6-m_inol	NWQL2437	68.848	20
05572000	LIRB	8/6/2012	84	Nicosulfuron	NWQL2437	8.087	14
05572000	LIRB	8/6/2012	190	Methoxyfenozide	NWQL2437	1.143	2
05586100	LIRB	8/21/2012	63	2-Hydroxyatrazine	NWQL2437	1.743	8
05586100	LIRB	8/21/2012	67	Aldicarb_sulfoxide	NWQL2437	1.696	3
05586100	LIRB	8/21/2012	75	Diuron	NWQL2060	0.008	40
05586100	LIRB	8/21/2012	133	Deethylhydroxy_azine	NWQL2437	2.573	4
05586100	LIRB	8/21/2012	190	Methoxyfenozide	NWQL2437	0.514	2
06279500	YELL	7/9/2012	37	Metolachlor	NWQL2437	3.468	9
06800000	CNBR	8/21/2012	37	Metolachlor	NWQL2437	0.707	9
07022000	NSQN	6/25/2012	62	2,4-D	NWQL2437	19.801	62
07022000	NSQN	6/25/2012	270	Caffeine	NWQL2060	0.039	80
07288955	MISE	8/23/2012	257	Trifluralin	NWQL2033	0.002	18
07374000	NSQN	6/11/2012	63	2-Hydroxyatrazine	NWQL2060	0.010	60
07381495	NSQN	6/12/2012	37	Metolachlor	NWQL2033	0.005	20
08364000	RIOG	7/12/2012	84	Nicosulfuron	NWQL2060	0.020	320
08364000	RIOG	7/12/2012	121	Azoxystrobin	NWQL2437	0.536	3
14211720	WILL	8/21/2012	75	Diuron	NWQL2060	0.008	40

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
1	Atrazine	1Low	5	6	5	1	2.0	16.7	51.0
1	Atrazine	2Med	5	13	13	0	14.6	0.0	16.2
1	Atrazine	3High	5	26	26	0	212.9	0.0	8.5
2	Carbaryl	1Low	6	5	3	2	1.8	40.0	75.3
2	Carbaryl	2Med	6	3	3	0	11.2	0.0	53.6
3	Carbofuran	1Low	4	1	1	0	1.7	0.0	90.0
4	Deethylatrazine	1Low	11	10	9	1	6.6	10.0	33.7
4	Deethylatrazine	2Med	11	25	25	0	57.1	0.0	8.8
4	Deethylatrazine	3High	11	6	6	0	145.6	0.0	31.9
5	Metalaxyl	1Low	6	18	15	3	1.5	16.7	33.4
5	Metalaxyl	2Med	6	5	5	0	14.3	0.0	36.9
5	Metalaxyl	3High	6	1	1	0	114.5	0.0	90.0
6	Tebuthiuron	1Low	3	25	21	4	1.3	16.0	29.5
6	Tebuthiuron	2Med	3	9	9	0	5.2	0.0	22.6
8	Acetochlor	1Low	10	4	4	0	6.4	0.0	43.8
8	Acetochlor	2Med	10	6	6	0	31.1	0.0	31.9
8	Acetochlor	3High	10	1	1	0	153.6	0.0	90.0
9	Alachlor	1Low	9	1	0	1	2.9	100.0	100.0
16	Desulfinylfipronil	1Low	4	18	15	3	1.3	16.7	33.4
17	Diazinon	3High	3	1	1	0	104.5	0.0	90.0
18	Diazoxon	2Med	4	1	1	0	15.3	0.0	90.0
20	Dicrotophos	1Low	4	3	2	1	1.6	33.3	80.4
20	Dicrotophos	2Med	4	2	2	0	12.6	0.0	68.4
20	Dicrotophos	3High	4	1	1	0	46.1	0.0	90.0
21	Dimethoate	1Low	3	3	3	0	0.6	0.0	53.6
21	Dimethoate	2Med	3	2	2	0	3.7	0.0	68.4
25	Ethoprophos	2Med	5	2	2	0	18.0	0.0	68.4
29	Fipronil	1Low	4	8	6	2	1.2	25.0	53.8
29	Fipronil	2Med	4	8	8	0	5.6	0.0	25.0
30	Fipronil_sulfide	1Low	4	13	11	2	1.0	15.4	36.0
31	Fipronil_sulfone	1Low	4	11	7	4	2.5	36.4	59.9
31	Fipronil_sulfone	2Med	4	1	1	0	6.1	0.0	90.0
33	Hexazinone	1Low	3	18	16	2	1.4	11.1	26.9
33	Hexazinone	2Med	3	2	2	0	4.8	0.0	68.4
33	Hexazinone	3High	3	1	1	0	34.1	0.0	90.0

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
35	Malathion	2Med	6	2	2	0	6.4	0.0	68.4
37	Metolachlor	1Low	9	15	14	1	3.2	6.7	23.6
37	Metolachlor	2Med	9	13	13	0	37.5	0.0	16.2
37	Metolachlor	3High	9	12	12	0	287.8	0.0	17.5
38	Metribuzin	1Low	20	1	1	0	17.4	0.0	90.0
40	Myclobutanil	1Low	7	6	6	0	1.5	0.0	31.9
40	Myclobutanil	2Med	7	2	2	0	7.7	0.0	68.4
40	Myclobutanil	3High	7	1	1	0	526.3	0.0	90.0
44	Pendimethalin	1Low	3	1	1	0	0.9	0.0	90.0
44	Pendimethalin	2Med	3	1	1	0	4.8	0.0	90.0
49	Prometon	1Low	4	18	18	0	2.4	0.0	12.0
49	Prometon	2Med	4	20	19	1	7.1	5.0	18.1
49	Prometon	3High	4	3	3	0	45.2	0.0	53.6
50	Prometryn	1Low	2	1	1	0	1.8	0.0	90.0
50	Prometryn	2Med	2	6	6	0	4.3	0.0	31.9
50	Prometryn	3High	2	1	1	0	31.5	0.0	90.0
53	Propyzamide	2Med	4	1	1	0	10.0	0.0	90.0
54	Simazine	1Low	10	4	4	0	6.6	0.0	43.8
54	Simazine	2Med	10	16	16	0	23.0	0.0	13.4
54	Simazine	3High	10	2	2	0	154.2	0.0	68.4
55	Tebuconazole	1Low	5	9	9	0	3.1	0.0	22.6
55	Tebuconazole	2Med	5	5	5	0	7.1	0.0	36.9
58	Terbuthylazine	1Low	3	4	4	0	1.6	0.0	43.8
58	Terbuthylazine	2Med	3	5	5	0	11.6	0.0	36.9
58	Terbuthylazine	3High	3	2	2	0	42.8	0.0	68.4
62	2,4-D	1Low	62	19	12	7	27.6	36.8	54.1
62	2,4-D	2Med	62	14	14	0	108.4	0.0	15.2
62	2,4-D	3High	62	1	1	0	850.1	0.0	90.0
63	2-Hydroxyatrazine	1Low	8	12	10	2	4.2	16.7	38.6
63	2-Hydroxyatrazine	2Med	8	16	16	0	52.6	0.0	13.4
63	2-Hydroxyatrazine	3High	8	17	17	0	124.5	0.0	12.7
67	Aldicarb_sulfoxide	1Low	3	1	0	1	0.5	100.0	100.0
68	Bentazon	1Low	10	15	13	2	5.9	13.3	31.7
68	Bentazon	2Med	10	6	6	0	12.0	0.0	31.9
68	Bentazon	3High	10	1	1	0	141.4	0.0	90.0

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
69	Bromacil	1Low	6	8	5	3	4.9	37.5	65.5
69	Bromacil	2Med	6	18	18	0	11.2	0.0	12.0
71	Chlorimuron-ethyl	2Med	8	1	1	0	37.1	0.0	90.0
73	Deisopropylatrazine	1Low	20	11	10	1	10.4	9.1	31.0
73	Deisopropylatrazine	2Med	20	22	22	0	42.8	0.0	9.9
73	Deisopropylatrazine	3High	20	1	1	0	291.6	0.0	90.0
75	Diuron	1Low	5	8	8	0	2.1	0.0	25.0
75	Diuron	2Med	5	28	28	0	14.0	0.0	7.9
75	Diuron	3High	5	10	10	0	118.8	0.0	20.6
76	Flumetsulam	1Low	17	3	3	0	10.0	0.0	53.6
76	Flumetsulam	2Med	17	4	4	0	29.7	0.0	43.8
77	Fluometuron	1Low	3	1	1	0	2.3	0.0	90.0
77	Fluometuron	2Med	3	4	4	0	5.0	0.0	43.8
77	Fluometuron	3High	3	3	3	0	130.1	0.0	53.6
79	Imazethapyr	1Low	20	6	4	2	5.6	33.3	66.7
79	Imazethapyr	2Med	20	3	3	0	60.7	0.0	53.6
80	Imidacloprid	1Low	11	5	5	0	7.8	0.0	36.9
80	Imidacloprid	2Med	11	18	18	0	29.5	0.0	12.0
80	Imidacloprid	3High	11	4	4	0	161.8	0.0	43.8
81	Linuron	1Low	6	1	0	1	1.1	100.0	100.0
81	Linuron	2Med	6	1	1	0	6.2	0.0	90.0
82	MCPA	2Med	95	2	2	0	184.5	0.0	68.4
83	Methomyl	1Low	3	2	2	0	1.7	0.0	68.4
83	Methomyl	2Med	3	1	1	0	26.0	0.0	90.0
84	Nicosulfuron	1Low	14	2	1	1	2.0	50.0	94.9
85	Norflurazon	1Low	4	1	1	0	3.0	0.0	90.0
85	Norflurazon	2Med	4	3	3	0	6.1	0.0	53.6
86	Oryzalin	2Med	11	1	1	0	16.8	0.0	90.0
87	Oxamyl	1Low	2	1	0	1	0.5	100.0	100.0
87	Oxamyl	3High	2	1	1	0	80.4	0.0	90.0
88	Propiconazole	1Low	6	5	5	0	3.3	0.0	36.9
88	Propiconazole	2Med	6	17	17	0	12.6	0.0	12.7
89	Propoxur	1Low	4	4	4	0	2.2	0.0	43.8
89	Propoxur	2Med	4	4	4	0	13.4	0.0	43.8
91	Sulfometuron-methyl	1Low	4	9	8	1	2.6	11.1	36.8

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
91	Sulfometuron-methyl	2Med	4	10	10	0	6.3	0.0	20.6
91	Sulfometuron-methyl	3High	4	1	1	0	44.9	0.0	90.0
92	Terbacil	2Med	21	1	1	0	22.6	0.0	90.0
93	Triclopyr	1Low	88	11	7	4	28.8	36.4	59.9
93	Triclopyr	2Med	88	1	1	0	107.5	0.0	90.0
94	1H-1,2,4-Triazole	2Med	22	3	3	0	89.9	0.0	53.6
94	1H-1,2,4-Triazole	3High	22	3	3	0	512.3	0.0	53.6
97	2-Aminobenzimidazole	1Low	9	5	4	1	7.5	20.0	58.4
97	2-Aminobenzimidazole	2Med	9	1	0	1	10.8	100.0	100.0
98	2-Isopropyl-6-m_inol	1Low	20	3	3	0	10.9	0.0	53.6
98	2-Isopropyl-6-m_inol	2Med	20	3	3	0	28.2	0.0	53.6
100	3,4-Dichlorophe_urea	1Low	144	1	1	0	31.0	0.0	90.0
100	3,4-Dichlorophe_urea	2Med	144	1	1	0	144.2	0.0	90.0
106	4-Hydroxychloro_onil	2Med	98	4	4	0	215.9	0.0	43.8
106	4-Hydroxychloro_onil	3High	98	1	0	1	1,032.8	100.0	100.0
109	Acephate	1Low	10	4	3	1	5.5	25.0	68.0
109	Acephate	2Med	10	10	10	0	24.6	0.0	20.6
109	Acephate	3High	10	4	4	0	272.8	0.0	43.8
110	Acet/Met_sec_amide	2Med	5	1	1	0	5.5	0.0	90.0
112	Acetochlor_OXA	1Low	90	5	5	0	71.0	0.0	36.9
112	Acetochlor_OXA	2Med	90	13	13	0	179.3	0.0	16.2
112	Acetochlor_OXA	3High	90	1	1	0	1,401.3	0.0	90.0
113	Acetochlor_SAA	1Low	176	10	9	1	55.8	10.0	33.7
115	Alachlor_OXA	1Low	84	9	8	1	33.3	11.1	36.8
117	Ametryn	1Low	3	13	13	0	2.2	0.0	16.2
117	Ametryn	2Med	3	11	11	0	4.3	0.0	18.9
119	Ammelide	1Low	75	1	1	0	6.0	0.0	90.0
121	Azoxystrobin	1Low	3	22	20	2	1.4	9.1	22.4
121	Azoxystrobin	2Med	3	12	12	0	10.7	0.0	17.5
121	Azoxystrobin	3High	3	5	5	0	54.0	0.0	36.9
127	Carbendazim	1Low	3	9	9	0	1.4	0.0	22.6
127	Carbendazim	2Med	3	27	27	0	8.8	0.0	8.2
127	Carbendazim	3High	3	3	3	0	47.3	0.0	53.6
129	Chlorosulfonami_acid	2Med	75	1	1	0	111.1	0.0	90.0
130	Chlorsulfuron	1Low	50	1	1	0	19.8	0.0	90.0

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
132	Dechlorometolachlor	1Low	2	5	5	0	1.3	0.0	36.9
132	Dechlorometolachlor	2Med	2	20	20	0	11.1	0.0	10.9
132	Dechlorometolachlor	3High	2	5	5	0	123.6	0.0	36.9
133	Deethylhydroxy_azine	1Low	4	6	6	0	3.8	0.0	31.9
133	Deethylhydroxy_azine	2Med	4	27	27	0	12.5	0.0	8.2
133	Deethylhydroxy_azine	3High	4	1	1	0	81.7	0.0	90.0
134	Deiodo_flubendiamide	2Med	4	1	1	0	7.0	0.0	90.0
135	Deisopropyl_pr_etryn	1Low	3	8	8	0	1.3	0.0	25.0
136	Deisopropylhyd_azine	2Med	6	2	2	0	35.1	0.0	68.4
138	Demethyl_fluometuron	1Low	2	1	1	0	1.3	0.0	90.0
138	Demethyl_fluometuron	3High	2	3	3	0	40.8	0.0	53.6
139	Demethyl_hexazi_ne_B	1Low	3	1	1	0	1.1	0.0	90.0
139	Demethyl_hexazi_ne_B	2Med	3	1	1	0	5.7	0.0	90.0
140	Demethyl_norflurazon	2Med	4	3	3	0	18.6	0.0	53.6
141	Desamino-diketo_uzin	1Low	200	4	4	0	63.1	0.0	43.8
142	Didealkylatrazine	1Low	24	2	2	0	18.9	0.0	68.4
142	Didealkylatrazine	2Med	24	20	19	1	123.7	5.0	18.1
142	Didealkylatrazine	3High	24	8	8	0	303.4	0.0	25.0
146	Diketonitrile-i_tole	1Low	62	7	7	0	9.1	0.0	28.0
146	Diketonitrile-i_tole	2Med	62	1	1	0	88.8	0.0	90.0
147	Dimethenamid	1Low	3	8	8	0	1.7	0.0	25.0
147	Dimethenamid	2Med	3	15	14	1	5.4	6.7	23.6
147	Dimethenamid	3High	3	1	1	0	3,694.3	0.0	90.0
148	Dimethenamid_ESA	1Low	79	11	7	4	10.7	36.4	59.9
148	Dimethenamid_ESA	2Med	79	1	1	0	204.4	0.0	90.0
149	Dimethenamid_OXA	1Low	85	1	1	0	30.3	0.0	90.0
149	Dimethenamid_OXA	2Med	85	1	1	0	198.0	0.0	90.0
150	Dimethenamid_SAA	1Low	189	1	1	0	88.8	0.0	90.0
161	Fipronil_amide	1Low	9	6	4	2	5.5	33.3	66.7
163	Flubendiamide	1Low	5	1	1	0	1.0	0.0	90.0
163	Flubendiamide	2Med	5	4	4	0	9.5	0.0	43.8
166	Halosulfuron-methyl	1Low	22	1	0	1	14.4	100.0	100.0
173	Hydroxyacetochlor	1Low	9	1	1	0	7.1	0.0	90.0
173	Hydroxyacetochlor	2Med	9	14	14	0	20.6	0.0	15.2
173	Hydroxyacetochlor	3High	9	1	1	0	156.0	0.0	90.0

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
174	Hydroxyalachlor	1Low	8	7	7	0	4.2	0.0	28.0
174	Hydroxyalachlor	2Med	8	1	1	0	9.4	0.0	90.0
177	Hydroxymetolachlor	2Med	2	21	21	0	12.8	0.0	10.4
177	Hydroxymetolachlor	3High	2	5	5	0	106.6	0.0	36.9
179	Hydroxysimazine	1Low	3	6	5	1	2.8	16.7	51.0
179	Hydroxysimazine	2Med	3	28	27	1	8.0	3.6	13.2
179	Hydroxysimazine	3High	3	5	5	0	72.7	0.0	36.9
184	Isoxaflutole_ac_3328	1Low	9	3	2	1	5.3	33.3	80.4
184	Isoxaflutole_ac_3328	2Med	9	1	1	0	62.0	0.0	90.0
187	Metconazole	2Med	5	2	2	0	16.0	0.0	68.4
188	Methamidophos	2Med	3	4	4	0	13.1	0.0	43.8
188	Methamidophos	3High	3	4	4	0	40.9	0.0	43.8
190	Methoxyfenozide	1Low	2	8	7	1	0.6	12.5	40.6
190	Methoxyfenozide	2Med	2	3	3	0	12.8	0.0	53.6
191	Metolachlor_ESA	1Low	68	9	6	3	20.1	33.3	59.9
191	Metolachlor_ESA	2Med	68	22	22	0	191.3	0.0	9.9
191	Metolachlor_ESA	3High	68	4	4	0	840.9	0.0	43.8
192	Metolachlor_OXA	1Low	149	17	17	0	73.8	0.0	12.7
192	Metolachlor_OXA	2Med	149	7	7	0	557.7	0.0	28.0
193	Metolachlor_hyd_none	1Low	7	1	0	1	3.1	100.0	100.0
194	Metribuzin-desamino	1Low	9	7	7	0	7.6	0.0	28.0
194	Metribuzin-desamino	2Med	9	6	6	0	13.9	0.0	31.9
194	Metribuzin-desamino	3High	9	1	1	0	110.5	0.0	90.0
195	Metribuzin_DK	1Low	200	1	0	1	29.1	100.0	100.0
196	N-(3,4-Dichloro_urea	1Low	5	8	8	0	3.6	0.0	25.0
196	N-(3,4-Dichloro_urea	2Med	5	19	19	0	13.1	0.0	11.4
196	N-(3,4-Dichloro_urea	3High	5	2	2	0	583.6	0.0	68.4
203	Oxamyl_oxime	2Med	2	1	1	0	2.4	0.0	90.0
203	Oxamyl_oxime	3High	2	1	1	0	57.4	0.0	90.0
210	Piperonyl_butoxide	1Low	4	1	1	0	2.1	0.0	90.0
210	Piperonyl_butoxide	2Med	4	4	4	0	5.7	0.0	43.8
212	Propazine	1Low	4	11	11	0	3.2	0.0	18.9
212	Propazine	2Med	4	6	6	0	5.9	0.0	31.9
215	Pyraclostrobin	1Low	3	3	2	1	1.8	33.3	80.4
215	Pyraclostrobin	2Med	3	2	2	0	6.7	0.0	68.4

Table 19. Variability of pesticide detections in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Consistent detection is the case where a pesticide is detected in both duplicates. Inconsistent detection is the case where a pesticide is detected in only one of the duplicates. Duplicate sets where both measurements were nondetections were deleted from the analysis. Nondetections were set to 0 nanogram per liter for the purpose of calculating the median concentration of duplicate sets. Duplicate sets were assigned to a concentration class on the basis of the median concentration of the duplicate set. Concentration classes are a function of the reporting limit. Median concentrations less than the reporting limit were assigned to class 1Low. Median concentrations greater than or equal to the reporting limit but less than 10 times the reporting limit were assigned to class 2Med. Median concentrations greater than or equal to 10 times the reporting limit were assigned to class 3High. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules]

Index	Pesticide short name	Concentration class	Reporting limit (ng/L)	Number of duplicate sets where duplicates in the set have			Median concentration of all duplicate sets in the class (ng/L)	Duplicate sets with inconsistent detection (percent)	
				At least one detection	Consistent detection	Inconsistent detection		Measured	90-percent upper confidence bound
218	Sulfentrazone	1Low	11	3	2	1	7.1	33.3	80.4
218	Sulfentrazone	2Med	11	5	5	0	17.9	0.0	36.9
218	Sulfentrazone	3High	11	1	1	0	340.1	0.0	90.0
219	Sulfosulfuron	2Med	9	2	2	0	19.6	0.0	68.4
222	Tebufenozide	1Low	2	1	1	0	1.3	0.0	90.0
225	Tebuthiuron_TP_104	1Low	6	3	0	3	0.9	100.0	100.0
226	Tebuthiuron_TP_108	1Low	10	5	3	2	1.4	40.0	75.3
226	Tebuthiuron_TP_108	2Med	10	5	5	0	46.5	0.0	36.9
226	Tebuthiuron_TP_108	3High	10	1	1	0	111.9	0.0	90.0
232	Terbufos_sulfoxide	2Med	3	1	1	0	3.2	0.0	90.0
233	Tetraconazole	2Med	6	2	2	0	11.5	0.0	68.4
235	Trifloxystrobin	1Low	2	3	2	1	0.7	33.3	80.4
237	sec-Acetochlor_OXA	1Low	52	3	3	0	39.2	0.0	53.6
237	sec-Acetochlor_OXA	2Med	52	1	1	0	72.7	0.0	90.0

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
1	Atrazine	5	CR02	0.5 to <5	5	0.704	1.24	26.0	45.7	1.665	2.120	3.313
1	Atrazine	5	CR03	1 to <10	9	3.28	4.82	42.0	61.7	1.66	3.31	8.87
1	Atrazine	5	CR04	5 to <50	13	3.40	4.61	32.8	44.5	5.54	14.63	36.17
1	Atrazine	5	CR05	10 to <100	13	4.13	5.61	11.8	16.0	10.97	31.33	96.12
1	Atrazine	5	CR06	50 to <500	24	13.9	17.2	6.54	8.10	59.3	192.4	483.8
1	Atrazine	5	CR07	100 to <1,000	21	14.6	18.4	5.75	7.24	116.6	229.8	983.8
1	Atrazine	5	CR08	500 to <5,000	2	6.44	19.8	0.604	1.86	983.81	1,026.03	1,068.25
1	Atrazine	5	CR09	1,000 to <10,000	1	8.97	71.4	0.840	6.68	nc	1,068.25	nc
2	Carbaryl	6	CR01	<1	1	0.202	1.60	22.2	177	nc	0.909	nc
2	Carbaryl	6	CR02	0.5 to <5	3	0.615	1.39	20.8	47.1	0.909	1.830	3.735
2	Carbaryl	6	CR03	1 to <10	3	1.02	2.32	18.3	41.5	1.83	3.73	10.00
2	Carbaryl	6	CR04	5 to <50	3	2.37	5.36	21.4	48.5	10.00	11.19	11.48
2	Carbaryl	6	CR05	10 to <100	2	2.72	8.36	24.2	74.5	11.19	11.33	11.48
3	Carbofuran	4	CR02	0.5 to <5	1	0.178	1.42	10.2	81.1	nc	1.749	nc
3	Carbofuran	4	CR03	1 to <10	1	0.178	1.42	10.2	81.1	nc	1.749	nc
4	Deethylatrazine	11	CR02	0.5 to <5	1	0.951	7.57	25.8	205	nc	3.693	nc
4	Deethylatrazine	11	CR03	1 to <10	8	2.93	4.43	35.5	53.7	3.69	6.62	9.67
4	Deethylatrazine	11	CR04	5 to <50	19	4.19	5.35	26.6	34.0	5.41	13.22	49.01
4	Deethylatrazine	11	CR05	10 to <100	25	5.00	6.16	13.8	17.0	10.39	51.99	98.71
4	Deethylatrazine	11	CR06	50 to <500	19	5.90	7.54	6.52	8.32	51.99	74.02	193.06
4	Deethylatrazine	11	CR07	100 to <1,000	7	20.8	32.7	5.23	8.23	103.4	125.7	718.1
4	Deethylatrazine	11	CR08	500 to <5,000	1	52.2	416	7.27	57.9	nc	718.1	nc
5	Metalaxyl	6	CR02	0.5 to <5	14	0.536	0.718	25.1	33.6	1.091	1.618	4.510
5	Metalaxyl	6	CR03	1 to <10	17	0.606	0.787	23.2	30.1	1.091	1.871	8.499
5	Metalaxyl	6	CR04	5 to <50	6	1.68	2.77	12.3	20.3	5.24	11.38	31.67
5	Metalaxyl	6	CR05	10 to <100	3	2.22	5.02	13.7	31.1	14.25	14.85	31.67
5	Metalaxyl	6	CR06	50 to <500	1	7.77	61.8	6.79	54.0	nc	114.47	nc
5	Metalaxyl	6	CR07	100 to <1,000	1	7.77	61.8	6.79	54.0	nc	114.47	nc
6	Tebuthiuron	3	CR01	<1	5	0.205	0.362	35.0	61.7	0.187	0.573	0.939
6	Tebuthiuron	3	CR02	0.5 to <5	23	0.504	0.627	27.5	34.3	0.573	1.559	4.207
6	Tebuthiuron	3	CR03	1 to <10	23	0.590	0.734	26.3	32.7	1.047	1.970	6.847
6	Tebuthiuron	3	CR04	5 to <50	5	0.810	1.43	13.5	23.8	5.169	6.847	15.444
6	Tebuthiuron	3	CR05	10 to <100	2	0.684	2.11	4.43	13.7	13.259	14.352	15.444
8	Acetochlor	10	CR02	0.5 to <5	1	1.45	11.5	33.5	266	nc	4.34	nc
8	Acetochlor	10	CR03	1 to <10	4	1.43	2.78	24.1	46.8	4.34	6.36	8.95
8	Acetochlor	10	CR04	5 to <50	9	1.38	2.03	12.1	17.8	6.14	19.66	48.63
8	Acetochlor	10	CR05	10 to <100	6	1.36	2.24	4.32	7.13	16.05	31.11	48.63
8	Acetochlor	10	CR06	50 to <500	1	15.9	127	10.4	82.6	nc	153.6	nc
8	Acetochlor	10	CR07	100 to <1,000	1	15.9	127	10.4	82.6	nc	153.6	nc

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
16	Desulfinylfipronil	4	CR01	<1	2	0.0964	0.297	12.6	38.9	0.7574	0.7816	0.8058
16	Desulfinylfipronil	4	CR02	0.5 to <5	15	0.344	0.456	21.4	28.4	0.757	1.547	3.478
16	Desulfinylfipronil	4	CR03	1 to <10	13	0.368	0.499	22.5	30.5	1.055	1.577	3.478
17	Diazinon	3	CR06	50 to <500	1	2.03	16.1	1.94	15.4	nc	104.51	nc
17	Diazinon	3	CR07	100 to <1,000	1	2.03	16.1	1.94	15.4	nc	104.51	nc
18	Diazoxon	4	CR04	5 to <50	1	0.459	3.65	3.01	23.9	nc	15.252	nc
18	Diazoxon	4	CR05	10 to <100	1	0.459	3.65	3.01	23.9	nc	15.252	nc
20	Dicrotophos	4	CR02	0.5 to <5	3	0.281	0.636	15.2	34.3	1.626	2.301	4.360
20	Dicrotophos	4	CR03	1 to <10	3	0.281	0.636	15.2	34.3	1.626	2.301	4.360
20	Dicrotophos	4	CR04	5 to <50	2	1.44	4.43	4.21	13.0	20.75	33.45	46.14
20	Dicrotophos	4	CR05	10 to <100	2	1.44	4.43	4.21	13.0	20.75	33.45	46.14
21	Dimethoate	3	CR01	<1	2	0.0774	0.238	13.3	41.0	0.4875	0.5418	0.5962
21	Dimethoate	3	CR02	0.5 to <5	4	0.294	0.569	12.4	24.1	0.596	2.389	4.141
21	Dimethoate	3	CR03	1 to <10	3	0.334	0.756	10.2	23.2	1.430	3.349	4.141
25	Ethoprophos	5	CR04	5 to <50	2	2.24	6.89	12.1	37.2	13.99	17.95	21.91
25	Ethoprophos	5	CR05	10 to <100	2	2.24	6.89	12.1	37.2	13.99	17.95	21.91
29	Fipronil	4	CR01	<1	1	0.464	3.69	50.7	404	nc	0.914	nc
29	Fipronil	4	CR02	0.5 to <5	7	0.372	0.584	24.4	38.3	0.914	1.237	4.443
29	Fipronil	4	CR03	1 to <10	13	0.693	0.941	14.8	20.1	1.108	5.246	7.908
29	Fipronil	4	CR04	5 to <50	7	0.885	1.39	13.5	21.3	5.246	5.673	7.908
30	Fipronil_sulfide	4	CR01	<1	6	0.181	0.298	27.7	45.7	0.383	0.900	0.992
30	Fipronil_sulfide	4	CR02	0.5 to <5	10	0.304	0.436	20.5	29.4	0.732	1.136	2.930
30	Fipronil_sulfide	4	CR03	1 to <10	5	0.392	0.691	22.1	38.9	1.279	1.593	2.930
31	Fipronil_sulfone	4	CR02	0.5 to <5	7	0.720	1.13	25.7	40.4	2.020	2.907	3.230
31	Fipronil_sulfone	4	CR03	1 to <10	8	0.673	1.02	24.0	36.4	2.020	2.988	6.116
31	Fipronil_sulfone	4	CR04	5 to <50	1	0.0130	0.104	0.213	1.69	nc	6.1156	nc
33	Hexazinone	3	CR01	<1	2	0.102	0.314	12.2	37.5	0.833	0.862	0.891
33	Hexazinone	3	CR02	0.5 to <5	17	0.358	0.464	22.5	29.2	0.833	1.569	3.373
33	Hexazinone	3	CR03	1 to <10	16	0.375	0.491	22.8	29.9	1.001	1.627	6.284
33	Hexazinone	3	CR04	5 to <50	2	0.358	1.10	3.56	11.0	6.284	20.185	34.086
33	Hexazinone	3	CR05	10 to <100	1	0.402	3.20	1.18	9.39	nc	34.086	nc
35	Malathion	6	CR03	1 to <10	2	0.546	1.68	8.29	25.5	6.219	6.409	6.599
35	Malathion	6	CR04	5 to <50	2	0.546	1.68	8.29	25.5	6.219	6.409	6.599
37	Metolachlor	9	CR02	0.5 to <5	10	0.868	1.24	27.7	39.7	1.103	2.877	4.286
37	Metolachlor	9	CR03	1 to <10	14	0.759	1.02	23.6	31.6	1.103	3.379	8.759
37	Metolachlor	9	CR04	5 to <50	13	1.92	2.61	6.08	8.27	5.70	23.02	48.45
37	Metolachlor	9	CR05	10 to <100	14	3.05	4.09	5.84	7.84	13.84	39.08	95.82
37	Metolachlor	9	CR06	50 to <500	12	6.60	9.10	3.91	5.40	63.98	107.55	390.19

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
37	Metolachlor	9	CR07	100 to <1,000	7	7.93	12.5	3.12	4.91	100.64	264.00	390.19
37	Metolachlor	9	CR08	500 to <5,000	4	70.9	138	3.18	6.17	1,144.6	2,144.8	3,221.7
37	Metolachlor	9	CR09	1,000 to <10,000	4	70.9	138	3.18	6.17	1,144.6	2,144.8	3,221.7
38	Metribuzin	20	CR04	5 to <50	1	5.17	41.2	29.8	237	nc	17.37	nc
38	Metribuzin	20	CR05	10 to <100	1	5.17	41.2	29.8	237	nc	17.37	nc
40	Myclobutanil	7	CR01	<1	1	0.0653	0.519	11.2	89.0	nc	0.5836	nc
40	Myclobutanil	7	CR02	0.5 to <5	6	0.985	1.63	35.7	58.9	0.584	1.469	4.827
40	Myclobutanil	7	CR03	1 to <10	7	1.14	1.80	34.0	53.4	1.06	3.29	7.82
40	Myclobutanil	7	CR04	5 to <50	2	1.29	3.98	16.8	51.8	7.67	7.74	7.82
40	Myclobutanil	7	CR07	100 to <1,000	1	5.37	42.8	1.02	8.13	nc	526.27	nc
40	Myclobutanil	7	CR08	500 to <5,000	1	5.37	42.8	1.02	8.13	nc	526.27	nc
44	Pendimethalin	3	CR01	<1	1	0.379	3.02	42.0	334	nc	0.904	nc
44	Pendimethalin	3	CR02	0.5 to <5	2	0.798	2.46	33.5	103	0.904	2.859	4.814
44	Pendimethalin	3	CR03	1 to <10	1	1.06	8.46	22.1	176	nc	4.81	nc
49	Prometon	4	CR02	0.5 to <5	19	0.425	0.543	16.0	20.4	1.064	2.372	4.509
49	Prometon	4	CR03	1 to <10	29	0.596	0.722	15.2	18.4	1.064	3.173	7.812
49	Prometon	4	CR04	5 to <50	20	4.27	5.42	14.3	18.1	5.29	9.10	45.20
49	Prometon	4	CR05	10 to <100	10	5.99	8.59	15.0	21.5	10.38	20.57	45.20
49	Prometon	4	CR06	50 to <500	1	13.5	107	4.54	36.1	nc	296.4	nc
49	Prometon	4	CR07	100 to <1,000	1	13.5	107	4.54	36.1	nc	296.4	nc
50	Prometryn	2	CR02	0.5 to <5	5	0.365	0.643	11.5	20.2	1.840	2.237	4.792
50	Prometryn	2	CR03	1 to <10	6	0.461	0.761	11.0	18.2	1.840	3.049	9.301
50	Prometryn	2	CR04	5 to <50	3	1.16	2.63	6.22	14.1	9.30	11.55	31.46
50	Prometryn	2	CR05	10 to <100	2	1.31	4.04	4.76	14.7	11.55	21.51	31.46
53	Propyzamide	4	CR03	1 to <10	1	1.35	10.7	13.5	108	nc	9.95	nc
53	Propyzamide	4	CR04	5 to <50	1	1.35	10.7	13.5	108	nc	9.95	nc
54	Simazine	10	CR03	1 to <10	4	4.00	7.75	61.9	120	5.29	6.59	8.71
54	Simazine	10	CR04	5 to <50	17	3.52	4.58	35.1	45.5	5.29	13.86	44.55
54	Simazine	10	CR05	10 to <100	16	4.05	5.31	18.9	24.8	10.06	23.01	86.29
54	Simazine	10	CR06	50 to <500	5	6.66	11.7	6.43	11.3	65.55	86.29	155.10
54	Simazine	10	CR07	100 to <1,000	2	7.31	22.5	4.71	14.5	153.23	154.17	155.10
55	Tebuconazole	5	CR01	<1	1	0.291	2.32	35.7	284	nc	0.815	nc
55	Tebuconazole	5	CR02	0.5 to <5	9	0.364	0.535	15.6	22.9	0.815	3.108	4.894
55	Tebuconazole	5	CR03	1 to <10	13	0.835	1.13	13.6	18.5	2.373	4.344	9.448
55	Tebuconazole	5	CR04	5 to <50	5	1.26	2.22	17.3	30.6	5.08	7.06	9.45
58	Terbuthylazine	3	CR02	0.5 to <5	5	0.175	0.309	8.50	15.0	1.183	1.611	4.737
58	Terbuthylazine	3	CR03	1 to <10	6	0.341	0.563	8.76	14.5	1.183	1.749	7.418
58	Terbuthylazine	3	CR04	5 to <50	6	2.24	3.70	10.8	17.9	7.42	16.93	47.86

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

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Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
58	Terbuthylazine	3	CR05	10 to <100	5	2.43	4.29	11.0	19.4	11.60	20.89	47.86
62	2,4-D	62	CR04	5 to <50	9	4.79	7.04	17.0	25.0	18.77	27.58	36.53
62	2,4-D	62	CR05	10 to <100	18	15.2	19.5	21.5	27.7	18.8	45.2	98.8
62	2,4-D	62	CR06	50 to <500	17	24.6	32.0	20.5	26.6	53.8	98.8	374.6
62	2,4-D	62	CR07	100 to <1,000	9	27.6	40.6	12.7	18.6	101.8	161.2	850.1
62	2,4-D	62	CR08	500 to <5,000	1	22.2	177	2.62	20.8	nc	850.1	nc
63	2-Hydroxyatrazine	8	CR02	0.5 to <5	6	0.449	0.741	11.4	18.9	1.712	3.633	4.768
63	2-Hydroxyatrazine	8	CR03	1 to <10	10	0.892	1.28	15.8	22.7	1.712	4.676	7.751
63	2-Hydroxyatrazine	8	CR04	5 to <50	12	2.58	3.56	14.0	19.3	5.92	15.32	48.28
63	2-Hydroxyatrazine	8	CR05	10 to <100	19	6.13	7.82	9.72	12.4	12.21	60.51	95.14
63	2-Hydroxyatrazine	8	CR06	50 to <500	25	10.9	13.4	8.55	10.5	56.9	109.0	451.2
63	2-Hydroxyatrazine	8	CR07	100 to <1,000	14	12.8	17.2	6.85	9.18	102.4	151.1	451.2
68	Bentazon	10	CR02	0.5 to <5	3	0.758	1.72	30.2	68.4	1.323	4.377	4.803
68	Bentazon	10	CR03	1 to <10	13	1.56	2.12	25.1	34.2	1.32	6.30	8.99
68	Bentazon	10	CR04	5 to <50	16	2.67	3.49	21.7	28.4	5.14	8.70	27.26
68	Bentazon	10	CR05	10 to <100	6	3.74	6.17	18.4	30.3	10.74	12.02	27.26
68	Bentazon	10	CR06	50 to <500	1	6.40	50.9	4.52	36.0	nc	141.39	nc
68	Bentazon	10	CR07	100 to <1,000	1	6.40	50.9	4.52	36.0	nc	141.39	nc
69	Bromacil	6	CR02	0.5 to <5	2	0.457	1.41	15.2	46.9	2.465	3.642	4.818
69	Bromacil	6	CR03	1 to <10	12	1.30	1.80	19.2	26.4	2.47	7.02	8.92
69	Bromacil	6	CR04	5 to <50	21	1.96	2.47	17.5	22.1	5.08	10.34	41.90
69	Bromacil	6	CR05	10 to <100	11	2.35	3.30	15.1	21.2	10.34	18.38	41.90
71	Chlorimuron-ethyl	8	CR04	5 to <50	1	5.02	39.9	13.5	108	nc	37.11	nc
71	Chlorimuron-ethyl	8	CR05	10 to <100	1	5.02	39.9	13.5	108	nc	37.11	nc
73	Deisopropylatrazine	20	CR03	1 to <10	4	3.01	5.84	42.1	81.6	6.16	7.48	8.81
73	Deisopropylatrazine	20	CR04	5 to <50	23	5.82	7.24	30.5	38.0	6.16	25.48	44.99
73	Deisopropylatrazine	20	CR05	10 to <100	27	7.91	9.65	24.8	30.3	10.39	34.17	94.70
73	Deisopropylatrazine	20	CR06	50 to <500	10	9.97	14.3	15.0	21.5	50.05	84.78	291.64
73	Deisopropylatrazine	20	CR07	100 to <1,000	2	4.92	15.1	2.01	6.19	119.47	205.56	291.64
75	Diuron	5	CR01	<1	1	0.302	2.40	34.0	271	nc	0.888	nc
75	Diuron	5	CR02	0.5 to <5	8	0.559	0.846	23.3	35.3	0.888	2.115	3.551
75	Diuron	5	CR03	1 to <10	14	0.799	1.07	16.8	22.5	1.457	4.546	9.947
75	Diuron	5	CR04	5 to <50	28	3.45	4.19	17.4	21.1	5.54	14.04	42.64
75	Diuron	5	CR05	10 to <100	25	3.81	4.70	17.6	21.7	10.26	20.73	89.73
75	Diuron	5	CR06	50 to <500	9	82.3	121	40.9	60.2	57.2	115.1	363.4
75	Diuron	5	CR07	100 to <1,000	5	110	195	54.8	96.5	115	202	363
75	Diuron	5	CR10	5,000 to <50,000	1	1,160	9,228	6.20	49.3	nc	18,719	nc
75	Diuron	5	CR11	10,000 to <100,000	1	1,160	9,228	6.20	49.3	nc	18,719	nc

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

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										Minimum	Median	Maximum
76	Flumetsulam	17	CR03	1 to <10	1	0.130	1.03	1.62	12.9	nc	7.989	nc
76	Flumetsulam	17	CR04	5 to <50	7	6.00	9.44	15.5	24.4	7.99	23.38	49.94
76	Flumetsulam	17	CR05	10 to <100	6	6.48	10.7	16.7	27.6	10.03	25.80	49.94
77	Fluometuron	3	CR02	0.5 to <5	4	0.415	0.805	12.8	24.9	2.342	4.152	4.986
77	Fluometuron	3	CR03	1 to <10	5	0.468	0.824	12.6	22.2	2.342	4.944	5.500
77	Fluometuron	3	CR04	5 to <50	1	0.636	5.06	11.6	92.0	nc	5.500	nc
77	Fluometuron	3	CR05	10 to <100	1	1.18	9.39	2.34	18.6	nc	50.38	nc
77	Fluometuron	3	CR06	50 to <500	3	11.6	26.3	3.71	8.42	50.4	130.1	344.3
77	Fluometuron	3	CR07	100 to <1,000	2	14.2	43.7	4.24	13.1	130.1	237.2	344.3
79	Imazethapyr	20	CR03	1 to <10	3	2.45	5.54	40.5	91.8	5.11	6.10	6.93
79	Imazethapyr	20	CR04	5 to <50	5	5.33	9.40	37.5	66.0	5.11	6.93	46.27
79	Imazethapyr	20	CR05	10 to <100	4	7.51	14.6	24.3	47.2	16.53	53.50	65.68
79	Imazethapyr	20	CR06	50 to <500	2	7.12	21.9	11.7	36.1	60.73	63.21	65.68
80	Imidacloprid	11	CR02	0.5 to <5	1	0.514	4.09	14.5	116	nc	3.539	nc
80	Imidacloprid	11	CR03	1 to <10	3	0.784	1.78	12.6	28.5	3.539	7.336	7.750
80	Imidacloprid	11	CR04	5 to <50	18	7.82	10.1	30.3	39.1	7.34	22.44	49.08
80	Imidacloprid	11	CR05	10 to <100	20	7.52	9.54	28.6	36.3	10.41	25.51	63.58
80	Imidacloprid	11	CR06	50 to <500	8	33.2	50.3	10.5	15.9	54.8	91.7	490.6
80	Imidacloprid	11	CR07	100 to <1,000	4	46.8	90.9	14.0	27.2	119.9	161.8	490.6
81	Linuron	6	CR03	1 to <10	1	0.655	5.21	10.6	84.2	nc	6.185	nc
81	Linuron	6	CR04	5 to <50	1	0.655	5.21	10.6	84.2	nc	6.185	nc
82	MCPA	95	CR06	50 to <500	2	23.6	72.8	11.4	35.2	137.2	184.5	231.9
82	MCPA	95	CR07	100 to <1,000	2	23.6	72.8	11.4	35.2	137.2	184.5	231.9
83	Methomyl	3	CR02	0.5 to <5	2	0.640	1.97	35.2	108	1.326	1.676	2.026
83	Methomyl	3	CR03	1 to <10	2	0.640	1.97	35.2	108	1.326	1.676	2.026
83	Methomyl	3	CR04	5 to <50	1	0.196	1.56	0.751	5.98	nc	26.032	nc
83	Methomyl	3	CR05	10 to <100	1	0.196	1.56	0.751	5.98	nc	26.032	nc
84	Nicosulfuron	14	CR02	0.5 to <5	1	0.472	3.76	16.7	133	nc	2.818	nc
84	Nicosulfuron	14	CR03	1 to <10	1	0.472	3.76	16.7	133	nc	2.818	nc
85	Norflurazon	4	CR02	0.5 to <5	2	0.247	0.761	8.10	25.0	3.034	3.849	4.665
85	Norflurazon	4	CR03	1 to <10	3	0.237	0.538	6.93	15.7	3.034	4.665	6.101
85	Norflurazon	4	CR04	5 to <50	2	0.570	1.76	5.04	15.5	6.101	9.323	12.545
85	Norflurazon	4	CR05	10 to <100	1	0.777	6.18	6.19	49.3	nc	12.545	nc
86	Oryzalin	11	CR04	5 to <50	1	1.22	9.71	7.28	57.9	nc	16.77	nc
86	Oryzalin	11	CR05	10 to <100	1	1.22	9.71	7.28	57.9	nc	16.77	nc
87	Oxamyl	2	CR05	10 to <100	1	21.9	174	27.2	216	nc	80.4	nc
87	Oxamyl	2	CR06	50 to <500	1	21.9	174	27.2	216	nc	80.4	nc
88	Propiconazole	6	CR02	0.5 to <5	4	0.891	1.73	26.1	50.6	2.114	2.978	4.058

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										Minimum	Median	Maximum
88	Propiconazole	6	CR03	1 to <10	10	1.89	2.71	30.2	43.4	2.11	6.33	8.63
88	Propiconazole	6	CR04	5 to <50	17	2.86	3.72	24.2	31.4	5.90	12.09	47.60
88	Propiconazole	6	CR05	10 to <100	12	3.01	4.16	17.1	23.6	10.20	20.66	57.60
88	Propiconazole	6	CR06	50 to <500	1	1.42	11.3	2.47	19.6	nc	57.60	nc
89	Propoxur	4	CR01	<1	1	0.0116	0.0923	1.55	12.3	nc	0.7478	nc
89	Propoxur	4	CR02	0.5 to <5	5	0.619	1.09	31.4	55.3	0.748	2.696	4.400
89	Propoxur	4	CR03	1 to <10	5	0.619	1.09	31.4	55.3	1.782	3.222	5.642
89	Propoxur	4	CR04	5 to <50	3	0.471	1.07	2.24	5.07	5.642	21.087	22.529
89	Propoxur	4	CR05	10 to <100	2	0.576	1.78	2.72	8.37	21.087	21.808	22.529
91	Sulfometuron-methyl	4	CR01	<1	2	0.457	1.41	49.8	154	0.916	0.918	0.920
91	Sulfometuron-methyl	4	CR02	0.5 to <5	12	0.624	0.862	26.1	35.9	0.916	2.973	4.712
91	Sulfometuron-methyl	4	CR03	1 to <10	13	0.586	0.796	15.7	21.4	2.450	4.007	9.143
91	Sulfometuron-methyl	4	CR04	5 to <50	7	11.1	17.5	45.9	72.2	5.9	13.9	44.9
91	Sulfometuron-methyl	4	CR05	10 to <100	4	14.7	28.5	60.7	118	13.9	27.8	44.9
92	Terbacil	21	CR04	5 to <50	1	9.34	74.4	41.3	329	nc	22.61	nc
92	Terbacil	21	CR05	10 to <100	1	9.34	74.4	41.3	329	nc	22.61	nc
93	Triclopyr	88	CR04	5 to <50	5	19.2	33.9	43.9	77.3	15.8	28.8	49.3
93	Triclopyr	88	CR05	10 to <100	7	22.6	35.6	44.5	70.0	15.8	34.6	81.1
93	Triclopyr	88	CR06	50 to <500	3	24.2	54.7	37.8	85.6	58.6	81.1	107.5
93	Triclopyr	88	CR07	100 to <1,000	1	3.87	30.8	3.60	28.6	nc	107.52	nc
94	1H-1,2,4-Triazole	22	CR05	10 to <100	3	5.07	11.5	5.42	12.3	88.35	89.90	94.90
94	1H-1,2,4-Triazole	22	CR06	50 to <500	4	5.62	10.9	4.81	9.32	88.35	92.40	331.69
94	1H-1,2,4-Triazole	22	CR07	100 to <1,000	2	12.7	39.0	2.72	8.39	331.7	422.0	512.3
94	1H-1,2,4-Triazole	22	CR08	500 to <5,000	1	16.5	131	3.22	25.6	nc	512.3	nc
94	1H-1,2,4-Triazole	22	CR10	5,000 to <50,000	1	829	6,595	4.99	39.7	nc	16,614	nc
94	1H-1,2,4-Triazole	22	CR11	10,000 to <100,000	1	829	6,595	4.99	39.7	nc	16,614	nc
97	2-Aminobenzimidazole	9	CR02	0.5 to <5	1	0.0531	0.423	1.43	11.3	nc	3.7249	nc
97	2-Aminobenzimidazole	9	CR03	1 to <10	4	0.637	1.23	8.48	16.4	3.725	7.638	7.782
97	2-Aminobenzimidazole	9	CR04	5 to <50	3	0.735	1.66	9.76	22.1	7.504	7.772	7.782
98	2-Isopropyl-6-m_inol	20	CR04	5 to <50	5	2.47	4.35	14.2	25.1	10.83	17.25	28.19
98	2-Isopropyl-6-m_inol	20	CR05	10 to <100	5	2.47	4.35	14.2	25.1	10.83	17.25	28.19
98	2-Isopropyl-6-m_inol	20	CR06	50 to <500	1	149	1,186	96.5	768	nc	154	nc
98	2-Isopropyl-6-m_inol	20	CR07	100 to <1,000	1	149	1,186	96.5	768	nc	154	nc
100	3,4-Dichlorophe_urea	144	CR04	5 to <50	1	8.96	71.3	28.9	230	nc	30.97	nc
100	3,4-Dichlorophe_urea	144	CR05	10 to <100	1	8.96	71.3	28.9	230	nc	30.97	nc
100	3,4-Dichlorophe_urea	144	CR06	50 to <500	1	6.56	52.2	4.55	36.2	nc	144.18	nc
100	3,4-Dichlorophe_urea	144	CR07	100 to <1,000	1	6.56	52.2	4.55	36.2	nc	144.18	nc
106	4-Hydroxychloro_onil	98	CR06	50 to <500	3	82.8	188	35.8	81.1	112.8	151.0	280.8

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
106	4-Hydroxychloro_onil	98	CR07	100 to <1,000	4	71.8	139	31.0	60.1	112.8	215.9	904.0
106	4-Hydroxychloro_onil	98	CR08	500 to <5,000	1	5.21	41.5	0.577	4.59	nc	904.03	nc
109	Acephate	10	CR03	1 to <10	3	1.10	2.50	15.1	34.2	5.04	5.92	8.44
109	Acephate	10	CR04	5 to <50	9	1.26	1.85	11.2	16.5	5.04	12.54	31.54
109	Acephate	10	CR05	10 to <100	10	2.94	4.21	7.45	10.7	10.29	24.64	93.06
109	Acephate	10	CR06	50 to <500	7	5.46	8.58	5.61	8.82	64.05	93.06	434.49
109	Acephate	10	CR07	100 to <1,000	3	6.66	15.1	6.11	13.8	101.33	111.03	434.49
109	Acephate	10	CR08	500 to <5,000	1	268	2,135	10.9	86.5	nc	2,469	nc
109	Acephate	10	CR09	1,000 to <10,000	1	268	2,135	10.9	86.5	nc	2,469	nc
110	Acet/Met_sec_amide	5	CR03	1 to <10	1	2.87	22.8	51.9	413	nc	5.52	nc
110	Acet/Met_sec_amide	5	CR04	5 to <50	1	2.87	22.8	51.9	413	nc	5.52	nc
112	Acetochlor_OXA	90	CR05	10 to <100	6	17.4	28.7	27.4	45.3	55.7	75.4	92.1
112	Acetochlor_OXA	90	CR06	50 to <500	15	27.2	36.1	22.1	29.3	55.7	110.7	333.0
112	Acetochlor_OXA	90	CR07	100 to <1,000	12	52.3	72.2	17.5	24.2	102.9	210.1	564.1
112	Acetochlor_OXA	90	CR08	500 to <5,000	4	77.4	150	14.6	28.4	520.2	549.2	1,401.3
112	Acetochlor_OXA	90	CR09	1,000 to <10,000	1	20.3	161	1.45	11.5	nc	1,401.3	nc
113	Acetochlor_SAA	176	CR04	5 to <50	3	16.8	38.1	54.9	124	28.3	28.6	32.5
113	Acetochlor_SAA	176	CR05	10 to <100	8	27.7	42.0	54.2	82.1	28.3	55.8	94.5
113	Acetochlor_SAA	176	CR06	50 to <500	6	30.6	50.5	49.6	81.8	55.1	75.2	109.6
113	Acetochlor_SAA	176	CR07	100 to <1,000	1	17.7	141	16.2	129	nc	109.6	nc
115	Alachlor_OXA	84	CR04	5 to <50	5	4.32	7.61	12.7	22.4	18.11	31.51	35.85
115	Alachlor_OXA	84	CR05	10 to <100	8	7.26	11.0	14.1	21.3	18.11	34.56	73.16
115	Alachlor_OXA	84	CR06	50 to <500	3	10.5	23.7	16.1	36.5	51.0	67.5	73.2
117	Ametryn	3	CR01	<1	1	0.237	1.89	24.6	196	nc	0.962	nc
117	Ametryn	3	CR02	0.5 to <5	20	0.425	0.538	15.9	20.1	0.962	2.724	4.545
117	Ametryn	3	CR03	1 to <10	23	0.469	0.584	14.3	17.8	1.155	2.916	9.337
117	Ametryn	3	CR04	5 to <50	4	0.615	1.19	8.19	15.9	6.463	8.901	9.337
119	Ammelide	75	CR03	1 to <10	1	0.468	3.73	7.82	62.2	nc	5.987	nc
119	Ammelide	75	CR04	5 to <50	1	0.468	3.73	7.82	62.2	nc	5.987	nc
121	Azoxystrobin	3	CR01	<1	2	0.0620	0.191	10.5	32.3	0.5568	0.6064	0.6560
121	Azoxystrobin	3	CR02	0.5 to <5	23	0.292	0.363	14.6	18.2	0.557	1.628	4.403
121	Azoxystrobin	3	CR03	1 to <10	23	0.351	0.437	14.5	18.0	1.071	1.682	9.284
121	Azoxystrobin	3	CR04	5 to <50	10	2.25	3.23	12.6	18.0	6.42	17.31	46.69
121	Azoxystrobin	3	CR05	10 to <100	10	2.92	4.18	12.6	18.1	10.08	18.94	53.97
121	Azoxystrobin	3	CR06	50 to <500	4	3.45	6.69	5.66	11.0	52.58	93.20	163.69
121	Azoxystrobin	3	CR07	100 to <1,000	2	2.49	7.68	1.88	5.80	132.42	148.05	163.69
127	Carbendazim	3	CR01	<1	3	0.227	0.515	34.6	78.3	0.615	0.895	0.925
127	Carbendazim	3	CR02	0.5 to <5	16	0.463	0.607	23.8	31.2	0.615	2.565	4.527

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

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										Minimum	Median	Maximum
127	Carbendazim	3	CR03	1 to <10	21	1.71	2.15	27.8	35.0	1.15	3.85	8.95
127	Carbendazim	3	CR04	5 to <50	22	8.24	10.3	36.3	45.4	5.11	18.32	47.35
127	Carbendazim	3	CR05	10 to <100	14	10.1	13.6	36.1	48.4	10.2	21.7	47.3
127	Carbendazim	3	CR06	50 to <500	1	1.60	12.7	1.53	12.2	nc	104.21	nc
127	Carbendazim	3	CR07	100 to <1,000	1	1.60	12.7	1.53	12.2	nc	104.21	nc
129	Chlorosulfonami_acid	75	CR06	50 to <500	1	18.3	146	16.5	131	nc	111.1	nc
129	Chlorosulfonami_acid	75	CR07	100 to <1,000	1	18.3	146	16.5	131	nc	111.1	nc
130	Chlorsulfuron	50	CR04	5 to <50	1	5.89	46.9	29.8	237	nc	19.78	nc
130	Chlorsulfuron	50	CR05	10 to <100	1	5.89	46.9	29.8	237	nc	19.78	nc
132	Dechlorometolachlor	2	CR02	0.5 to <5	6	0.120	0.199	8.58	14.2	1.005	1.466	4.299
132	Dechlorometolachlor	2	CR03	1 to <10	13	0.420	0.570	7.92	10.8	1.005	6.844	9.647
132	Dechlorometolachlor	2	CR04	5 to <50	21	1.28	1.62	9.74	12.3	6.84	12.22	47.12
132	Dechlorometolachlor	2	CR05	10 to <100	14	1.52	2.04	10.7	14.4	10.40	13.67	47.12
132	Dechlorometolachlor	2	CR06	50 to <500	3	4.71	10.7	2.15	4.87	123.59	156.37	278.74
132	Dechlorometolachlor	2	CR07	100 to <1,000	3	4.71	10.7	2.15	4.87	123.59	156.37	278.74
133	Deethylhydroxy_azine	4	CR02	0.5 to <5	8	0.665	1.01	18.9	28.6	2.000	3.865	4.979
133	Deethylhydroxy_azine	4	CR03	1 to <10	15	0.679	0.900	15.0	19.8	2.000	4.979	9.903
133	Deethylhydroxy_azine	4	CR04	5 to <50	25	1.65	2.03	11.7	14.4	5.50	12.53	33.87
133	Deethylhydroxy_azine	4	CR05	10 to <100	19	1.86	2.38	12.4	15.8	10.33	15.55	81.66
133	Deethylhydroxy_azine	4	CR06	50 to <500	1	1.17	9.30	1.43	11.4	nc	81.66	nc
134	Deiodo_flubendiamide	4	CR03	1 to <10	1	0.354	2.82	5.09	40.5	nc	6.958	nc
134	Deiodo_flubendiamide	4	CR04	5 to <50	1	0.354	2.82	5.09	40.5	nc	6.958	nc
135	Deisopropyl_pr_etryn	3	CR01	<1	3	0.190	0.431	31.3	70.9	0.275	0.761	0.863
135	Deisopropyl_pr_etryn	3	CR02	0.5 to <5	7	0.281	0.442	22.5	35.3	0.761	1.357	2.447
135	Deisopropyl_pr_etryn	3	CR03	1 to <10	5	0.301	0.531	19.2	33.8	1.211	1.760	2.447
136	Deisopropylhyd_azine	6	CR04	5 to <50	2	1.80	5.54	5.23	16.1	32.19	35.11	38.02
136	Deisopropylhyd_azine	6	CR05	10 to <100	2	1.80	5.54	5.23	16.1	32.19	35.11	38.02
138	Demethyl_fluometuron	2	CR02	0.5 to <5	1	0.669	5.32	53.4	425	nc	1.253	nc
138	Demethyl_fluometuron	2	CR03	1 to <10	1	0.669	5.32	53.4	425	nc	1.253	nc
138	Demethyl_fluometuron	2	CR04	5 to <50	2	2.03	6.25	7.87	24.3	20.96	30.88	40.79
138	Demethyl_fluometuron	2	CR05	10 to <100	3	4.77	10.8	8.42	19.1	20.96	40.79	82.33
138	Demethyl_fluometuron	2	CR06	50 to <500	1	7.76	61.7	9.42	75.0	nc	82.33	nc
139	Demethyl_hexazi_ne_B	3	CR02	0.5 to <5	1	0.00841	0.0670	0.747	5.94	nc	1.12655	nc
139	Demethyl_hexazi_ne_B	3	CR03	1 to <10	2	0.292	0.898	5.12	15.8	1.127	3.426	5.724
139	Demethyl_hexazi_ne_B	3	CR04	5 to <50	1	0.412	3.28	7.20	57.3	nc	5.724	nc
140	Demethyl_norflurazon	4	CR04	5 to <50	3	1.79	4.05	8.17	18.5	11.21	18.62	26.81
140	Demethyl_norflurazon	4	CR05	10 to <100	3	1.79	4.05	8.17	18.5	11.21	18.62	26.81
141	Desamino-diketo_uzin	200	CR04	5 to <50	1	1.01	8.01	4.95	39.4	nc	20.33	nc

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

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										Minimum	Median	Maximum
141	Desamino-diketo_uzin	200	CR05	10 to <100	4	17.1	33.1	25.2	49.0	20.3	63.1	73.7
141	Desamino-diketo_uzin	200	CR06	50 to <500	3	19.7	44.6	29.0	65.7	58.5	67.7	73.7
142	Didealkylatrazine	24	CR04	5 to <50	4	6.41	12.4	18.3	35.6	18.78	27.98	43.84
142	Didealkylatrazine	24	CR05	10 to <100	9	7.87	11.6	14.2	20.8	18.78	60.21	99.47
142	Didealkylatrazine	24	CR06	50 to <500	24	27.7	34.3	12.9	15.9	60.2	163.8	480.3
142	Didealkylatrazine	24	CR07	100 to <1,000	20	30.2	38.3	13.2	16.8	108.1	204.8	522.3
142	Didealkylatrazine	24	CR08	500 to <5,000	1	12.3	97.7	2.35	18.7	nc	522.3	nc
146	Diketonitrile-i_tole	62	CR03	1 to <10	4	3.89	7.54	50.8	98.6	5.29	5.91	9.11
146	Diketonitrile-i_tole	62	CR04	5 to <50	6	3.26	5.38	41.8	68.9	5.29	7.73	17.23
146	Diketonitrile-i_tole	62	CR05	10 to <100	4	9.60	18.6	18.0	34.8	15.42	35.14	88.84
146	Diketonitrile-i_tole	62	CR06	50 to <500	2	13.5	41.7	24.0	74.0	53.1	70.9	88.8
147	Dimethenamid	3	CR01	<1	1	0.190	1.51	24.1	192	nc	0.790	nc
147	Dimethenamid	3	CR02	0.5 to <5	14	0.453	0.607	18.8	25.1	0.790	2.290	4.995
147	Dimethenamid	3	CR03	1 to <10	16	0.485	0.635	16.8	22.0	1.236	3.268	9.882
147	Dimethenamid	3	CR04	5 to <50	8	1.09	1.65	6.96	10.5	5.38	13.87	21.77
147	Dimethenamid	3	CR05	10 to <100	5	1.31	2.31	6.66	11.7	13.02	19.49	21.77
147	Dimethenamid	3	CR08	500 to <5,000	1	172	1,366	4.65	37.0	nc	3,694	nc
147	Dimethenamid	3	CR09	1,000 to <10,000	1	172	1,366	4.65	37.0	nc	3,694	nc
148	Dimethenamid_ESA	79	CR03	1 to <10	2	6.06	18.7	65.6	202	8.95	9.15	9.36
148	Dimethenamid_ESA	79	CR04	5 to <50	6	4.91	8.10	40.3	66.4	8.95	12.62	37.29
148	Dimethenamid_ESA	79	CR05	10 to <100	5	9.18	16.2	18.7	32.9	10.75	28.77	74.85
148	Dimethenamid_ESA	79	CR06	50 to <500	2	18.9	58.3	18.9	58.1	74.8	139.6	204.4
148	Dimethenamid_ESA	79	CR07	100 to <1,000	1	19.1	152	9.35	74.4	nc	204.4	nc
149	Dimethenamid_OXA	85	CR04	5 to <50	1	1.27	10.1	4.18	33.3	nc	30.27	nc
149	Dimethenamid_OXA	85	CR05	10 to <100	1	1.27	10.1	4.18	33.3	nc	30.27	nc
149	Dimethenamid_OXA	85	CR06	50 to <500	1	33.2	264	16.8	133	nc	198.0	nc
149	Dimethenamid_OXA	85	CR07	100 to <1,000	1	33.2	264	16.8	133	nc	198.0	nc
150	Dimethenamid_SAA	189	CR05	10 to <100	1	34.8	277	39.2	312	nc	88.8	nc
150	Dimethenamid_SAA	189	CR06	50 to <500	1	34.8	277	39.2	312	nc	88.8	nc
161	Fipronil_amide	9	CR02	0.5 to <5	1	2.66	21.2	71.7	570	nc	3.71	nc
161	Fipronil_amide	9	CR03	1 to <10	4	2.14	4.16	44.8	86.8	3.71	5.89	6.42
161	Fipronil_amide	9	CR04	5 to <50	3	1.94	4.40	31.0	70.2	5.57	6.21	6.42
163	Flubendiamide	5	CR02	0.5 to <5	1	0.603	4.80	57.6	458	nc	1.046	nc
163	Flubendiamide	5	CR03	1 to <10	3	0.461	1.04	33.7	76.5	1.046	5.186	5.473
163	Flubendiamide	5	CR04	5 to <50	4	2.65	5.14	12.7	24.6	5.19	9.51	23.51
163	Flubendiamide	5	CR05	10 to <100	2	3.73	11.5	16.6	51.0	13.55	18.53	23.51
173	Hydroxyacetochlor	9	CR03	1 to <10	1	0.292	2.32	4.11	32.7	nc	7.104	nc
173	Hydroxyacetochlor	9	CR04	5 to <50	14	5.29	7.09	22.5	30.2	7.10	18.03	46.49

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

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										Minimum	Median	Maximum
173	Hydroxyacetochlor	9	CR05	10 to <100	14	5.75	7.71	22.8	30.5	10.56	20.62	63.68
173	Hydroxyacetochlor	9	CR06	50 to <500	2	6.11	18.8	9.45	29.1	63.68	109.84	156.01
173	Hydroxyacetochlor	9	CR07	100 to <1,000	1	1.63	13.0	1.05	8.32	nc	156.01	nc
174	Hydroxyalachlor	8	CR02	0.5 to <5	7	1.27	1.99	36.1	56.7	2.75	4.24	4.98
174	Hydroxyalachlor	8	CR03	1 to <10	8	1.19	1.80	33.7	51.1	2.75	4.34	9.36
174	Hydroxyalachlor	8	CR04	5 to <50	1	0.241	1.92	2.57	20.5	nc	9.358	nc
177	Hydroxymetolachlor	2	CR02	0.5 to <5	2	1.00	3.08	22.8	70.1	3.30	3.87	4.43
177	Hydroxymetolachlor	2	CR03	1 to <10	8	0.907	1.37	14.8	22.4	3.302	7.893	9.678
177	Hydroxymetolachlor	2	CR04	5 to <50	20	1.87	2.37	11.6	14.7	6.28	13.47	41.01
177	Hydroxymetolachlor	2	CR05	10 to <100	15	2.50	3.31	11.6	15.4	11.66	15.85	66.00
177	Hydroxymetolachlor	2	CR06	50 to <500	4	5.97	11.6	4.80	9.30	66.00	141.50	370.86
177	Hydroxymetolachlor	2	CR07	100 to <1,000	3	6.16	14.0	2.99	6.79	106.55	176.44	370.86
179	Hydroxysimazine	3	CR02	0.5 to <5	14	0.515	0.690	15.4	20.7	2.402	3.431	4.926
179	Hydroxysimazine	3	CR03	1 to <10	22	0.667	0.834	14.5	18.2	2.402	4.712	9.717
179	Hydroxysimazine	3	CR04	5 to <50	20	2.14	2.72	11.5	14.6	6.14	11.22	41.03
179	Hydroxysimazine	3	CR05	10 to <100	13	2.93	3.98	10.4	14.1	10.84	19.16	72.72
179	Hydroxysimazine	3	CR06	50 to <500	3	10.7	24.2	6.47	14.7	72.7	141.2	207.6
179	Hydroxysimazine	3	CR07	100 to <1,000	2	12.6	38.7	6.18	19.0	141.2	174.4	207.6
184	Isoxaflutole_ac_3328	9	CR03	1 to <10	2	0.392	1.21	5.61	17.3	5.287	6.202	7.117
184	Isoxaflutole_ac_3328	9	CR04	5 to <50	2	0.392	1.21	5.61	17.3	5.287	6.202	7.117
184	Isoxaflutole_ac_3328	9	CR05	10 to <100	1	6.38	50.7	10.3	81.9	nc	61.99	nc
184	Isoxaflutole_ac_3328	9	CR06	50 to <500	1	6.38	50.7	10.3	81.9	nc	61.99	nc
187	Metconazole	5	CR03	1 to <10	1	1.74	13.8	30.7	244	nc	5.66	nc
187	Metconazole	5	CR04	5 to <50	2	1.34	4.14	21.8	67.2	5.66	16.02	26.38
187	Metconazole	5	CR05	10 to <100	1	0.772	6.14	2.93	23.3	nc	26.376	nc
188	Methamidophos	3	CR03	1 to <10	2	1.19	3.66	16.1	49.5	7.39	8.37	9.34
188	Methamidophos	3	CR04	5 to <50	7	2.33	3.66	11.5	18.1	7.39	21.08	41.66
188	Methamidophos	3	CR05	10 to <100	5	2.65	4.67	9.03	15.9	16.91	38.81	41.66
188	Methamidophos	3	CR06	50 to <500	1	32.6	260	11.2	89.5	nc	290.2	nc
188	Methamidophos	3	CR07	100 to <1,000	1	32.6	260	11.2	89.5	nc	290.2	nc
190	Methoxyfenozide	2	CR01	<1	6	0.0789	0.130	12.6	20.8	0.4274	0.5554	0.9802
190	Methoxyfenozide	2	CR02	0.5 to <5	6	0.313	0.516	26.0	42.9	0.516	0.682	1.331
190	Methoxyfenozide	2	CR03	1 to <10	2	2.54	7.83	51.8	159	1.33	4.37	7.41
190	Methoxyfenozide	2	CR04	5 to <50	3	2.23	5.06	28.3	64.2	7.41	12.83	15.43
190	Methoxyfenozide	2	CR05	10 to <100	2	1.13	3.49	8.78	27.0	12.83	14.13	15.43
191	Metolachlor_ESA	68	CR04	5 to <50	4	6.85	13.3	34.0	65.9	18.12	23.90	44.00
191	Metolachlor_ESA	68	CR05	10 to <100	10	17.7	25.4	35.3	50.5	18.1	54.6	92.6
191	Metolachlor_ESA	68	CR06	50 to <500	20	29.1	36.9	23.2	29.5	50.8	186.0	482.2

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
191	Metolachlor_ESA	68	CR07	100 to <1,000	21	52.5	66.1	13.4	16.9	102.0	353.8	874.1
191	Metolachlor_ESA	68	CR08	500 to <5,000	8	84.7	128	10.8	16.3	576.5	707.8	1,002.9
191	Metolachlor_ESA	68	CR09	1,000 to <10,000	1	116	923	11.6	92.0	nc	1,003	nc
192	Metolachlor_OXA	149	CR04	5 to <50	1	6.39	50.9	30.0	239	nc	21.32	nc
192	Metolachlor_OXA	149	CR05	10 to <100	11	14.1	19.8	21.5	30.2	21.3	62.0	88.5
192	Metolachlor_OXA	149	CR06	50 to <500	19	22.3	28.5	18.1	23.1	54.4	88.5	283.4
192	Metolachlor_OXA	149	CR07	100 to <1,000	11	26.8	37.6	13.7	19.3	110.1	133.2	587.4
192	Metolachlor_OXA	149	CR08	500 to <5,000	4	87.4	169	7.84	15.2	557.7	867.3	1,313.1
192	Metolachlor_OXA	149	CR09	1,000 to <10,000	2	122	377	10.7	32.8	1,147	1,230	1,313
194	Metribuzin-desamino	9	CR03	1 to <10	7	2.43	3.81	31.4	49.3	6.31	7.57	8.88
194	Metribuzin-desamino	9	CR04	5 to <50	12	2.48	3.42	26.7	36.9	6.31	8.41	25.95
194	Metribuzin-desamino	9	CR05	10 to <100	6	3.27	5.39	17.1	28.3	10.92	13.93	66.38
194	Metribuzin-desamino	9	CR06	50 to <500	2	4.25	13.1	6.13	18.9	66.38	88.47	110.55
194	Metribuzin-desamino	9	CR07	100 to <1,000	1	2.18	17.3	1.97	15.7	nc	110.55	nc
196	N-(3,4-Dichloro_urea	5	CR02	0.5 to <5	8	1.65	2.50	41.8	63.3	1.65	3.62	4.33
196	N-(3,4-Dichloro_urea	5	CR03	1 to <10	16	1.47	1.93	33.0	43.3	1.65	4.75	7.68
196	N-(3,4-Dichloro_urea	5	CR04	5 to <50	19	2.40	3.06	19.0	24.2	5.16	13.10	45.93
196	N-(3,4-Dichloro_urea	5	CR05	10 to <100	12	23.4	32.3	38.8	53.6	10.5	17.1	66.6
196	N-(3,4-Dichloro_urea	5	CR06	50 to <500	1	80.6	641	121	964	nc	66.6	nc
196	N-(3,4-Dichloro_urea	5	CR08	500 to <5,000	1	43.8	349	3.98	31.7	nc	1,100.6	nc
196	N-(3,4-Dichloro_urea	5	CR09	1,000 to <10,000	1	43.8	349	3.98	31.7	nc	1,100.6	nc
203	Oxamyl_oxime	2	CR02	0.5 to <5	1	0.126	1.00	5.22	41.5	nc	2.413	nc
203	Oxamyl_oxime	2	CR03	1 to <10	1	0.126	1.00	5.22	41.5	nc	2.413	nc
203	Oxamyl_oxime	2	CR05	10 to <100	1	2.24	17.8	3.90	31.1	nc	57.43	nc
203	Oxamyl_oxime	2	CR06	50 to <500	1	2.24	17.8	3.90	31.1	nc	57.43	nc
210	Piperonyl_butoxide	4	CR02	0.5 to <5	1	0.123	0.977	5.85	46.5	nc	2.101	nc
210	Piperonyl_butoxide	4	CR03	1 to <10	4	0.354	0.687	6.99	13.6	2.101	5.165	6.089
210	Piperonyl_butoxide	4	CR04	5 to <50	4	0.403	0.782	6.45	12.5	5.088	5.666	18.500
210	Piperonyl_butoxide	4	CR05	10 to <100	1	0.405	3.22	2.19	17.4	nc	18.500	nc
212	Propazine	4	CR02	0.5 to <5	13	0.489	0.664	14.0	19.1	2.249	3.253	4.778
212	Propazine	4	CR03	1 to <10	16	0.572	0.750	13.3	17.4	2.249	3.499	9.515
212	Propazine	4	CR04	5 to <50	4	1.20	2.32	10.7	20.8	5.29	7.97	13.37
212	Propazine	4	CR05	10 to <100	1	1.90	15.1	14.2	113	nc	13.37	nc
215	Pyraclostrobin	3	CR02	0.5 to <5	3	1.81	4.10	39.6	89.7	1.81	1.97	4.61
215	Pyraclostrobin	3	CR03	1 to <10	4	1.60	3.09	34.5	66.8	1.81	3.29	8.70
215	Pyraclostrobin	3	CR04	5 to <50	1	0.591	4.70	6.79	54.1	nc	8.697	nc
218	Sulfentrazone	11	CR03	1 to <10	2	3.00	9.23	39.9	123	7.13	7.62	8.10
218	Sulfentrazone	11	CR04	5 to <50	7	5.32	8.36	33.1	52.1	7.13	17.41	25.03

Table 20. Variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.—Continued

[Duplicate sets where one or both measurements were nondetections were deleted from the analysis. Eleven overlapping concentration classes were used to characterize variability. Duplicate sets were assigned to a concentration classes on the basis of the median concentration of the duplicate set. ng/L, nanogram per liter; Index, a numerical code assigned by the authors to facilitate identification of the same pesticide in different analytical schedules; nc, not calculated; <, less than]

Index	Pesticide short name	Reporting limit (ng/L)	Concentration class	Range of concentrations in class (ng/L)	Number of duplicate sets	Pooled standard deviation (ng/L)	90-percent upper confidence bound for pooled standard deviation (ng/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound for pooled relative standard deviation (percent)	Concentration of replicate sets in class (ng/L)		
										Minimum	Median	Maximum
218	Sulfentrazone	11	CR05	10 to <100	5	6.00	10.6	30.0	52.8	11.79	17.93	25.03
218	Sulfentrazone	11	CR06	50 to <500	1	16.7	133	4.92	39.2	nc	340.1	nc
218	Sulfentrazone	11	CR07	100 to <1,000	1	16.7	133	4.92	39.2	nc	340.1	nc
219	Sulfosulfuron	9	CR04	5 to <50	2	6.39	19.7	27.5	84.8	15.07	19.62	24.17
219	Sulfosulfuron	9	CR05	10 to <100	2	6.39	19.7	27.5	84.8	15.07	19.62	24.17
222	Tebufenozide	2	CR02	0.5 to <5	1	0.0331	0.263	2.46	19.6	nc	1.3461	nc
222	Tebufenozide	2	CR03	1 to <10	1	0.0331	0.263	2.46	19.6	nc	1.3461	nc
226	Tebuthiuron_TP_108	10	CR02	0.5 to <5	2	1.00	3.09	25.6	79.0	1.36	2.97	4.58
226	Tebuthiuron_TP_108	10	CR03	1 to <10	3	2.58	5.86	43.3	98.2	1.36	4.58	6.46
226	Tebuthiuron_TP_108	10	CR04	5 to <50	4	2.78	5.39	33.2	64.4	6.46	21.18	46.47
226	Tebuthiuron_TP_108	10	CR05	10 to <100	5	3.95	6.96	6.53	11.5	12.37	46.47	73.48
226	Tebuthiuron_TP_108	10	CR06	50 to <500	3	6.11	13.9	7.27	16.5	73.22	73.48	111.86
226	Tebuthiuron_TP_108	10	CR07	100 to <1,000	1	6.84	54.5	6.12	48.7	nc	111.86	nc
232	Terbufos_sulfoxide	3	CR02	0.5 to <5	1	0.0199	0.159	0.628	5.00	nc	3.1767	nc
232	Terbufos_sulfoxide	3	CR03	1 to <10	1	0.0199	0.159	0.628	5.00	nc	3.1767	nc
233	Tetraconazole	6	CR03	1 to <10	1	0.0469	0.373	0.493	3.93	nc	9.5033	nc
233	Tetraconazole	6	CR04	5 to <50	2	0.749	2.31	5.53	17.0	9.503	11.531	13.560
233	Tetraconazole	6	CR05	10 to <100	1	1.06	8.42	7.80	62.1	nc	13.56	nc
235	Trifloxystrobin	2	CR01	<1	1	0.0242	0.192	3.67	29.2	nc	0.6583	nc
235	Trifloxystrobin	2	CR02	0.5 to <5	2	0.0499	0.154	4.17	12.9	0.6583	1.0467	1.4351
235	Trifloxystrobin	2	CR03	1 to <10	1	0.0663	0.527	4.62	36.7	nc	1.4351	nc
237	sec-Acetochlor_OXA	52	CR04	5 to <50	3	7.30	16.6	16.8	38.0	27.91	39.24	46.67
237	sec-Acetochlor_OXA	52	CR05	10 to <100	4	6.97	13.5	15.1	29.2	27.91	42.95	72.71
237	sec-Acetochlor_OXA	52	CR06	50 to <500	1	5.87	46.7	8.07	64.2	nc	72.71	nc

Table 21. Typical variability of pesticide concentrations in field duplicate environmental water samples analyzed by schedule 2437.

[Data in this table are the median values of the statistics presented in table 19. ng/L, nanogram per liter; <, less than]

Concentration class	Range of concentrations in class (ng/L)	Number of pesticides with at least one duplicate set in concentration class	Minimum number of duplicate sets in concentration class	Median number of duplicate sets in concentration class	Maximum number of duplicate sets in concentration class	Total number of duplicate sets in concentration class	Median pooled standard deviation (ng/L)	Median 90-percent upper confidence bound for pooled standard deviation (ng/L)	Median pooled relative standard deviation (percent)	Median 90-percent upper confidence bound for pooled relative standard deviation (percent)	Median concentration of replicate sets in concentration class (ng/L)
CR01	<1	20	1	1.5	6	43	0.19	0.47	24	75	0.80
CR02	0.5 to <5	58	1	5	23	377	0.47	0.83	21	36	2.40
CR03	1 to <10	78	1	4	29	554	0.66	1.3	17	34	4.67
CR04	5 to <50	89	1	4	28	604	2.1	4.4	14	30	13.9
CR05	10 to <100	78	1	4.5	27	521	3.8	8.4	14	28	25.1
CR06	50 to <500	53	1	2	25	289	11	36	9.5	31	104
CR07	100 to <1,000	41	1	2	21	177	13	43	6.1	19	161
CR08	500 to <5,000	14	1	1	8	31	48	140	3.6	20	859
CR09	1,000 to <10,000	8	1	1	4	12	93	360	4.3	32	1,316
CR10	5,000 to <50,000	2	1	1	1	2	990	7,900	5.6	44	17,670
CR11	10,000 to <100,000	2	1	1	1	2	990	7,900	5.6	44	17,670

Considerations for Analysis and Interpretation of Data Analyzed by Old and New Analytical Methods

The results of the field study identified several challenges for the analysis and interpretation of data analyzed by both old and new methods, particularly when data span the change in methods and are combined for analysis of temporal trends in water quality. The main challenges identified are large (greater than 30 percent), statistically significant differences in analytical recovery; detection capability; and (or) measured concentrations for selected pesticides. These challenges are documented and discussed, but specific guidance or statistical methods to resolve these differences in methods are beyond the scope of the report.

Analytical recovery in paired stream-water matrix spikes typically was significantly different for most pesticides analyzed by both old and new methods (tables 9 and 11). In addition to statistical significance, the median difference in paired measurements of recovery often was large, frequently greater than 30 percent. Such differences are expected between different analytical methods. Adjusting measured concentrations for analytical recovery (as was done in Martin and others, 2009) may reduce or eliminate this bias for some pesticides.

Detection capability in paired environmental water samples differed significantly for several pesticides analyzed by old and new methods, particularly for pesticides analyzed by sh2060 (tables 13 and 14). Difference in detection capability was large, often greater than 30 percent. In addition, detection capability could not be confidently assessed for many pesticides because paired environmental water samples had few or no detections of these pesticides. Analysis of pooled datasets for selected pesticides with large differences in detection capability will introduce a bias in detection frequency where new measurements (typically) may more readily detect a pesticide. When comparing detection frequencies among old and new methods, care must be taken to select detection thresholds that are equally achievable by both methods.

Before adjustment for analytical recovery, concentrations measured in paired environmental water samples differed significantly for most pesticides with sufficient detections by both old and new methods (11 for sh2033 and 17 for sh2060, tables 15 and 16). When significantly different, the old methods typically reported higher concentrations, especially at low concentrations (appendix 7, 8). Recovery adjustment generally improved agreement between methods (reduced the mean logical percent difference between paired concentrations, and moved the lowess smooths closer to the line of equality between methods), but most of the pesticides that had statistically different concentrations also had statistically different recovery-adjusted concentrations, and the difference in concentrations was often greater than 30 percent. Analysis of pooled datasets for selected pesticides with large differences in concentrations or recovery-adjusted concentrations will introduce a bias where new measurements are typically smaller (or larger) than old measurements. The information on recovery-adjusted concentrations in paired environmental water samples provided in Martin and Baker (2017, dataset 6) could be used to construct empirical models (such as the lowess models in appendix 7 and 8) to adjust old method concentrations to new method concentrations (or vice versa) for selected pesticides with sufficient observed concentrations. For pesticides without sufficient paired concentrations to construct an empirical model, it is possible that a generalized model could be developed based on empirical models for other pesticides.

The results of the field study show that the implications of the change in analytical methods must be assessed individually for each pesticide and method. In addition, temporal changes in analytical recovery for a single method are common. Modeled temporal changes in recovery for 52 pesticides analyzed by GC–MS during 1992–2006 ranged from 17 to 139 percent (Martin and others, 2009, p. 12). The implications of potential temporal changes in analytical recovery are that the recoveries measured in samples collected for this field study in summer and fall 2012 might be different than those measured in samples collected in previous or future years. The potential for temporal changes in recovery emphasizes the need for the routine collection of field and laboratory quality-control samples to assess data quality.

Understanding the possible causes of the systematic differences in concentrations between methods that remain after recovery adjustment might be necessary to determine how to account for the systematic differences during data analysis. Because recoveries for each method are independently determined from separate calibration standards and spiking solutions, the differences could have been caused by an error in one of the calibration standards or spike solutions or some other basic aspect of standard procedure in the analytical process. The standards and solutions for one method, however, were checked by analysis by the other method and all were measured within acceptable limits of error (within 20 percent of the expected value). The calibration models in the new method used weighted regression curves (1/x) for calibration, whereas the instrument software for the old methods did not offer this option. Weighted regression curves significantly improve the fit of the data at lower calibration levels. Unweighted regression curves will tend to fit points better at upper calibration levels than those points at lower calibration levels, and use of an unweighted regression curve tends to give less accurate results at lower calibration levels (U.S. Environmental Protection Agency, 2014). Differences in weighted versus unweighted calibration curves could be part of the cause of the systematic biases between methods for some pesticides, especially at low concentrations.

The systematic pattern of differences in recovery-adjusted concentrations across a wide range of water types, pesticides, and concentrations as was demonstrated in this field study is not what one would expect from differing recovery problems from various water matrices or sample processing in the field.

Further investigation of the possible causes is needed, which will lead to specific decisions on how to compensate for these differences in concentrations in data analysis. Possible additional studies that could be performed include (1) a multiple regression analysis of the stream-water matrix characteristics measured in the field study and their effect on pesticide recovery (these data are provided in Martin and Baker, 2017, dataset 4), (2) a bench-scale spike study in reagent water for old and new analytical methods to characterize recovery across a range of concentrations near the reporting level, (3) a similar bench-scale spike study in stream-water samples to characterize matrix effects on recovery at concentrations near the reporting level (perhaps matrix-enhanced recovery in the old method is more pronounced at very low concentrations), and (4) a comparison of weighted versus unweighted calibration curves.

In the event that further investigations do not provide insight into the causes of systematic differences in concentrations between methods, the authors recommend continuing to collect and analyze paired environmental water samples by both old and new methods. This effort should be targeted to seasons, sites, and expected concentrations to supplement those concentrations already assessed and to compare the ongoing analytical recovery of old and new methods to those observed in the summer and fall of 2012.

Summary

U.S. Geological Survey (USGS) monitoring programs have extensively used two analytical methods, gas chromatography/mass spectrometry (GC–MS) and liquid chromatography/mass spectrometry (LC–MS), to measure pesticides in filtered water samples from 1992 to 2012. In October 2012, monitoring programs began using a new analytical method for pesticides, direct aqueous-injection liquid chromatography tandem mass spectrometry (DAI LC–MS/MS). Changes in analytical methods may introduce changes in data quality. In this report the GC–MS method is referred to as schedule 2033 (sh2033), the LC–MS method is referred to as schedule 2060 (sh2060), and the DAI LC–MS/MS method is referred to as schedule 2437 (sh2437) (the analytical schedule numbers).

A field study was designed to document performance of the new method in a variety of stream-water matrices and to quantify any potential changes in measurement bias or variability that could be attributed to changes in analytical methods. The goals of the field study were to (1) summarize performance (bias and variability of pesticide recovery) of the new method in a variety of stream-water matrices; (2) compare performance of the new method in laboratory blank water (laboratory reagent spikes) to that in a variety of stream-water matrices; (3) compare performance (analytical recovery) of the new method to that of the old methods in a variety of stream-water matrices; (4) compare pesticide detections and concentrations measured by the new method to those of the old methods in a variety of stream-water matrices; (5) compare contamination measured by field blank water samples in old and new methods; (6) summarize the variability of pesticide detections and concentrations measured by the new method in field duplicate water samples; and (7) identify matrix characteristics of environmental water samples that adversely influence the performance of the new method. Stream-water samples and a variety of field quality-control samples were collected at 48 sites in the USGS monitoring networks during June–September 2012. Stream sites were located across the United States and included sites in agricultural and urban land-use settings, as well as sites on major rivers.

Recovery is the ratio of a measured concentration divided by a theoretical or "expected" concentration and is the principal measure of analytical method performance. The three analytical schedules used in the field study provided data for 283 pesticides. Analytical data stored in the National Water Information System are primarily managed by a 5-digit numerical parameter code. Parameter codes for the common pesticides measured by sh2437 are different than those for sh2033 and sh2060 because the units of measurement are different (nanograms per liter for sh2437 but micrograms per liter for sh2033 and sh2060). A variable (index) was created to facilitate management of data for pesticides with different parameter codes. Indexes 1–6 are pesticides common to all three schedules. Indexes 7–61 are pesticides common to sh2437 and sh2033 (61 common pesticides). Indexes 62–93 are pesticides common to sh2437 and sh2060 (38 common pesticides). Indexes 94–283 are pesticides analyzed only by sh2437, sh2033, or sh2060.

The median recovery of pesticides in stream-water matrix spikes analyzed by sh2437 ranged from 0 percent for 3-ketocarbofuran,[5] ammelide,[5] and phosmet_oxon[5] to 209.6 percent for didealkylatrazine. The median recovery for all 237 pesticides was 91.3 percent. Relative standard deviation of pesticide recovery in stream-water matrix spikes analyzed by sh2437 ranged from 9.8 percent for hexazinone to 369.5 percent for ammelide.

Pesticide recovery in stream-water matrix spikes was compared to recovery in laboratory reagent spikes in order to determine if recovery in laboratory reagent spikes would suitably characterize recovery in stream-water. The Wilcoxon rank-sum test was used to compare the median recovery of pesticides in field matrix spikes and laboratory reagent spikes. Of the 237 pesticides tested, median recovery was significantly (probability less than 5 percent) greater in field matrix spikes for 50 pesticides and in laboratory reagent spikes for 58 pesticides. Large differences in recovery reinforces the need for field matrix spikes to accurately describe the performance of sh2437 in stream-water samples for many of the pesticides measured.

Pesticide recovery in paired stream-water matrix spikes analyzed by old and new methods was compared using the sign test to determine if recovery of old and new methods was

[5]These compounds were subsequently deleted from the method.

statistically different. Of the 61 pesticides common to schedules 2033 (old method) and 2437 (new method), recovery was significantly greater in samples analyzed by sh2033 for 44 pesticides and was significantly greater in samples analyzed by sh2437 for 12 pesticides. Of the 38 pesticides common to schedules 2060 (old method) and 2437 (new method), recovery was significantly greater in samples analyzed by sh2060 for 12 pesticides and was significantly greater in samples analyzed by sh2437 for 18 pesticides.

The sign test was used to identify differences in pesticide detections in paired environmental water samples analyzed by old and new methods. Many of the pesticides had few or no detections by either the old or new methods; consequently, difference in detection capability for these pesticides and methods could not be readily assessed. A little more than one-half of the 61 pesticides common to sh2033 and sh2437 had one or more detections in paired water samples. Detection frequency was significantly greater by sh2033 for 9 pesticides and significantly greater by sh2437 for 5 pesticides. Most of the 38 pesticides common to sh2060 and sh2437 had one or more detections in paired water samples. Detection frequency was significantly greater by sh2060 for 0 pesticides and significantly greater by sh2437 for 22 pesticides.

The sign test was used to identify differences in pesticide concentrations in paired environmental water samples analyzed by old and new methods. The sign test was done for the original concentrations as reported by the laboratory and for recovery-adjusted concentrations. Statistical significance generally was a function of sample size; the larger the sample size, the more likely the test was significant. Only 27 of the 61 pesticides common to sh2033 and sh2437 had at least one pair of detections by both methods. Statistical test results for unadjusted and recovery-adjusted concentrations were similar. Of the 27 pesticides, 17 had significantly higher concentrations measured by sh2033 than by sh2437. Only 24 of the 38 pesticides common to sh2060 and sh2437 had at least one pair of detections by both methods. For original, unadjusted concentrations, six pesticides had significantly higher concentrations measured by sh2060 and five had significantly higher concentrations measured by sh2437. For recovery-adjusted concentrations, five pesticides had significantly higher concentrations measured by sh2060 and only two had significantly higher concentrations measured by sh2437. Recovery adjustment generally improved the agreement between concentrations measured by both old and new methods/schedules.

The results of the field study identified several challenges for the analysis and interpretation of data analyzed by both old and new methods, particularly when data span the change in methods and are combined for analysis of temporal trends in water quality. The main challenges identified are large, statistically significant differences in analytical recovery, detection capability, and (or) measured concentrations for selected pesticides (large is greater than 30 percent). These challenges are documented and discussed, but specific guidance or statistical methods to resolve these differences in methods are beyond the scope of the report. The results of the field study show that the implications of the change in analytical methods must be assessed individually for each pesticide and method.

Understanding the possible causes of the systematic differences in concentrations between methods that remain after recovery adjustment might be necessary to determine how to account for the differences in data analysis. Because recoveries for each method are independently determined from separate calibration standards and spiking solutions, the differences could have been caused by an error in one of the calibration standards or spike solutions or some other basic aspect of standard procedure in the analytical process. The standards and solutions for one method, however, were checked by analysis by the other method and all were measured within acceptable limits of error (within 20 percent of the expected value).

The systematic pattern of differences in recovery-adjusted concentrations across a wide range of water types, pesticides, and concentrations as was demonstrated in this field study is not what one would expect from differing recovery problems from various water matrices or sample processing in the field. Further investigation of the possible causes is needed, which will lead to specific decisions on how to compensate for these differences in concentrations in data analysis. Possible additional studies that could be performed include (1) a multiple regression analysis of the stream-water matrix characteristics measured in the field study and their effect on pesticide recovery, (2) bench-scale spike study in reagent water for old and new analytical methods to characterize recovery across a range of concentrations near the reporting level, (3) a similar bench-scale spike study in stream-water samples to characterize matrix effects on recovery at concentrations near the reporting level (perhaps matrix-enhanced recovery in the old method is more pronounced at very low concentrations), and (4) a comparison of weighted versus unweighted calibration curves.

In the event that further investigations do not provide insight into the causes of systematic differences in concentrations between methods, the authors recommend continuing to collect and analyze paired environmental water samples by both old and new methods. This effort should be targeted to seasons, sites, and expected concentrations to supplement those concentrations already assessed and to compare the ongoing analytical recovery of old and new methods to those observed in the summer and fall of 2012.

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Appendixes

Two types of appendixes are provided: regular text (appendix 1) and figures of 15 or more pages (appendixes 2–8). Appendixes 2–8 are available online and can be downloaded from https://doi.org/10.3133/sir20175049.

Appendix 1. Instructions for the collection and processing of the field-study samples.

Appendix 2. Distribution of recovery of pesticides in field matrix spikes and laboratory reagent spikes analyzed by the new analytical method (schedule 2437) (15 pages of figures).

Appendix 3. Comparison of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2033 and by schedule 2437 by study unit, station number, and site visit (61 pages of figures).

Appendix 4. Comparison of recovery of pesticides in stream-water matrix spikes analyzed by schedule 2060 and by schedule 2437 by study unit, station number, and site visit (38 pages of figures).

Appendix 5. Comparison of pesticide detections in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437 (61 pages of figures).

Appendix 6. Comparison of pesticide detections in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437 (38 pages of figures).

Appendix 7. Comparison of pesticide concentrations in paired environmental stream-water samples analyzed by both schedule 2033 and schedule 2437 (27 pages of figures).

Appendix 8. Comparison of pesticide concentrations in paired environmental stream-water samples analyzed by both schedule 2060 and schedule 2437 (24 pages of figures).

Appendix 1. Instructions for the Collection and Processing of the Field-Study Samples.

Pesticide Method Schedule 2437 Evaluation and Comparison Study Field and Processing Protocol for selected National Stream Quality Accounting Network (NASQAN), National Water Quality Assessment (NAWQA), and National Monitoring Network (NMN) Sites

Background

The National Water Quality Laboratory (NWQL) has developed a new method for pesticide analysis, which requires a low volume sample. The new pesticide method will be requested as NWQL Schedule 2437 (S2437). Before S2437 can be accepted, an evaluation and comparison study must be performed to compare S2437 to the current 2033 and 2060 pesticide schedules (S2033 and S2060). This comparison study will ensure any bias and variability will be documented so that the data from the new and old methods can be merged for long-term analysis. S2437 differs from S2033 and S2060 in both analytical and field methods. This comparison study will require S2033, S2060, and S2437 samples to be collected concurrently.

This new method incorporates a pesticide filtering method designed to save time during sample processing, and should also reduce other preparation time by eliminating the amount of equipment used; thereby cleaning time should also be reduced. The FMI pump, corrugated Teflon tubing, aluminum filter plate, and 142-mm GF/Fused for S2033 and S2060 will be replaced with a graduated 30-ml syringe, a large bore needle, and 25-mm 0.7 um GF/F disposable disk syringe filter. Once the new method is approved, it will only require a 20-ml sample to be shipped to the laboratory for analysis. However, for this evaluation study, (3)20-ml samples in 40-ml GCV vials (USGS One Stop product code N1560), must be collected.

This comparison study will require the help of the experienced NAWQA/NASQAN field crews. Although complicated, the rewards of this new method outweigh the task.

Your site has been chosen to help field validate S2437 because of its past pesticide detections (concentration and variation of pesticide compounds) as well as its unique water matrix. Field crews are requested to collect samples for S2033 and S2060 analyses, and for the new method (S2437) at the listed site(s). Field crews are requested to perform this comparison sampling on 3 trips per site by the end of September 2012 (see sampling schedule).

This evaluation requires multiple spikes, and one S2033 blank at each site. These QA samples will be collected in conjunction with spike and blank samples for S2060 and S2437. If you have already collected your S2033 spike and blank samples, you will need to collect them again. If it fits your schedule, the additional S2033 QA samples required by this evaluation can take the place of your routine S2033 spike and blank.

Instructions for the collection and processing of these new samples are provided below. If you have questions, please contact either Mike Manning (mmanning@usgs.gov) or Claire Rose (cerose@usgs.gov).

The additional equipment and NWQL laboratory work should be charged to your usual/current NASQAN, NAWQA, or NMN account. Additional funds will be transferred to your account to cover these new supply and sampling expenses. New proposal numbers will need to be used on the analytical services request form (ASR). (Refer to account information in the ASR section).

Field Procedures

(Please take these instructions to the field for reference)

Collection

1. Collect your samples as you usually would, as described in the standard methods. The additional pesticide samples for this evaluation will require about 5 liters of water. Be sure that your compositing container for the pesticide sample can accommodate the additional water.

Processing

As per the NFM (Chapter 5.2.2) **"**CH/DH techniques and associated QA procedures for inorganic analytes with parts-per- billion concentrations are not required for organic analytes **but are recommended** as good field practices to maintain the integrity of sample chemistry. Field personnel must wear disposable, powder-less gloves.

1. At the field site, cover the field bench or work area with a clean sheet of aluminum foil to **prepare a clean work surface**. Place plastic bag containing syringe, large bore needle, and disposable filter near the clean work surface. Change gloves.

2. Remove syringe, large bore needle, and syringe disk filter from the bag and its wrappings, and place on the clean foil. **Attach needle to** Luer-Lock fitting on **syringe** (The open female end of the syringe is twisted onto the male Luer-Lock fitting on the syringe to provide a secure fit).

3. **Homogenize** the composited pesticide **sample** in your standard manner.

   A. If you usually use a glass carboy for your pesticide sample, you'll have to pump (using the FMI pump and tubing only) a raw, unfiltered subsample into a suitable container for pesticide analysis (such as a 125-ml glass baked amber bottle) for syringe filtering. The bore needle will not reach the bottom of this bottle, and refilling will be necessary throughout the process.

   B. If you usually use the Teflon churn as your pesticide compositing device, you can withdraw the sample directly from the churn using the syringe and bore needle.

4. **Rinse syringe, bore, and filter.** Submerse the bore needle into the subsample or the churn and withdraw 10-mL of sample through the needle into syringe. Invert syringe, pull stopper to the 30-mL mark on the syringe and shake, ensuring full rinse of the syringe. Depress plunger, expelling water into a waste container. Again, submerse the attached bore needle into the subsample or churn, and withdraw 5-mL of sample into the syringe. Invert syringe and carefully remove needle. Place needle on clean piece of aluminum foil. Attach the filter to the syringe by pushing straight down and twisting until the filter is firmly in place on the syringe mechanism.

   Invert syringe and slowly depress the plunger to force the sample water out of the syringe, through the filter to rinse the filter with sample water and expel the rinse water into a waste container. This completes the cleaning and conditioning steps.

5. Remove the filter and place on clean aluminum foil. Carefully reattach the needle to the syringe, and withdraw sample from the subsample as stated above, filling to the 30-ml mark.
   Invert syringe, while tapping and depressing plunger to expel air, push the plunger to about the 25-mL mark. Remove needle and attach rinsed filter. Invert syringe downward, and **Filter 20-ml into a 40-ml glass vial** by depressing the plunger slowly.

   To collect as closely to 20 ml as possible, it is suggested to move the plunger from the 25-ml mark to the 5-ml mark. (expel the remaining 5-ml to waste).

   Note: In the event that samples have extremely high suspended sediment, organic blank water (OBW) may be used to rinse and condition the filter instead of the 5 ml sample. If OBW is used for rinsate, the OBW rinse must be followed with at least 2mL of sample water (before collecting sample) to remove any remaining OBW. Pre-tests have shown that most high sediment sites can filter at least a 30-ml sample using this filter. If the syringe filter medium becomes clogged before a sufficient amount of sample has been filtered, re-filter with a new, conditioned filter by repeating steps 4 and 5 as necessary until at least 20-mL have been collected. These additional steps must be documented on the field sheets.

6. **Repeat steps 4, 5, and 6 two times.** Use a new filter for each vial. Repeat steps 5 and 6 two times on trips without a scheduled blank sample. This will result in three 40-ml glass vials with 20-ml of filtered sample in each vial. If a blank is scheduled, only repeat steps 5 and 6 one additional time, resulting in two 40-ml glass vials with 20-ml of filtered sample in each vial.

   The 1st of the 3 vials is the environmental sample for the S2437.

7. **The 2nd of the 3 vials is always a spike sample. Spike thi**s sample using the new S2437 spike mixture. Use the same micropipette and glass bores as used for the S2033 and S2060 spikes. Instructions for spiking samples accompany each spike kit; also refer to NFM Chapter A4. (4.3.3) and Chapter A5 (5.3.2).

Note: When spiking samples remember to (1) use a new glass bore for each spiked sample, (2) rinse the micro-pipetor's Teflon tip before and after each use with pesticide-grade methanol, and (3) release the spike into the sample (by depressing the plunger) once the glass bore is under the surface. The plunger should remain depressed as the glass bore is withdrawn from the sample. Always dispose of used spike kits and used glass bores in proper hazardous waste containers.

8. **The last of the 3 vials** will be processed according to the quality assurance schedule for the additional QA/QC scheduled for 2437.This vial will either be an environmental replicate, a spike replicate or a field blank. (See sample schedule).

9. **Label the vials** with the appropriate station ID, date**, time offset**, (see table, and figure below***),* **medium code,** schedule number, and sample type. Ensure caps are on firmly. Do not freeze. Chill and maintain the sample at or below 4°C without freezing during storage and shipment.

10. Discard the needle, syringe and filter. The syringes can be put into a plastic recycling bin. On field forms and in the field notes, document the number of filters used for each vial and any problems you encountered.

11. Collect a blank sample for both S2033 and S2060 only if a S2437 blank is scheduled This blank is done only once per site for this study, and at the same time as the blank for the S2437. The S2033 and 2060 blank will be in addition to the samples in step 12 below. On the blank sample date there will be a total of 3-S2033, and 3-S2060 bottles (one environmental, one spike, and one blank for both S2033, and S2060).

12. **Filter the S2033 and S2060 samples** using standard field methods and equipment. Filter four 1L baked glass amber bottles, changing filters between each bottle, or more often if needed. (See NFM 5.2.2A and NAWQA SW QC OFR 97-223, p. 5).

13. **The first two 1-L baked glass amber bottles are environmental samples for S2033 and S2060**. No further processing or treatment is required.

14. **The third and fourth 1-L baked glass amber bottles are spiked samples for S2033 and S2060**. Spike one bottle using the S2033 spike kit. Spike the other bottle using the S2060 spike kit. Instructions for spiking samples accompany each spike kit; also refer to NFM Chapter A4. (4.3.3) and Chapter A5 (5.3.2).

Note: The 2060 spike kits have two vials of spike solution containing different pesticides. Be sure to use both for the 2060 spike. (See instructions included with the spike kits).

15. **Label the 1L bottles** with the appropriate station ID, date**, time offsets**,(refer to table, and figure below)**, medium code,** schedule number, and sample type. Ensure caps are on firmly. Do not freeze. Chill and maintain the sample at or below 4°C without freezing during storage and shipment.

16. Ship all pesticide samples overnight to NWQL along with your other samples.

17. **Due to the limited number of samples collected for this evaluation, it is of high importance that these samples are protected from breakage. Place each 40-ml vial in a foam sleeve purchased from USGS One Stop # Q358FLD, or use the sleeve the new vials are shipped with. Seal all three foam sleeves in a zip-lock bag. Package each 1L amber glass bottle in a 32 oz. styrofoam bottle shippers and secure with fiber tape. The 32 oz. styrofoam shippers are available from Label Master: http://www.labelmaster.com, item number: UNIP32F.** ***Note: The styrofoam bottle shippers are designed for horizontal shipment, i.e. the bottle will be lying on its side in the cooler.***

Table 1–1. Sample overview.

[ASR, analytical service request form; NAWQA, National Water-Quality Assessment; NASQAN, National Stream Quality Accounting Network; 1-L, one-liter; WS, environmental surface water; SUID, study unit identification; WSQ, quality-control surface water; OAQ, quality-control artificial; OBW, organic blank water; min., minute; QA, quality assurance; 40-ml, 40-milliliter]

Schedule	Analysis type	Bottle	Time offset	Time example	Med code	S-type	Treatment	ASR	Project account number	Program/project	If NAWQA site: Proposal number	If NASQAN site: Proposal number
2033	Environmental	1-L glass	None	1200	WS	9	Sample	Routine	No change	No change	[3]CL12 SUID	CL12001
	Spike	1-L glass	None	1200	WSQ	1	2033 Spike kit	Separate	No change	No change	[3]CL12 SUID	[3]CL12 SUID
	[1]Blank	1-L glass	None	1200	QAQ	2	OBW	Separate	No change	No change	[3]CL12 SUID	[3]CL12 SUID
2060	Environmental	1-L glass	1 min. after 2033	1201	WS	9	Sample	Separate	No change	No change	[3]CL12 SUID	[3]CL12 SUID
	Spike	1-L glass	1 min. after 2033	1201	WSQ	1	2033 Spike kit	Separate	No change	No change	[3]CL12 SUID	[3]CL12 SUID
	Blank[1]	1-L glass	1 min. after 2033	1201	QAQ	2	OBW	Separate	No change	No change	[3]CL12 SUID	[3]CL12 SUID
2437	Vial #1: Environmental	40-ml glass	3 min. after 2033	1202	WSQ	B	Sample	Separate	No change	No change	CL12023	CL12023
	Vial #2: Spike	40-ml glass	3 min. after 2033	1202	WSQ	1	2437 Spike kit	Separate	No change	No change	CL12023	CL12023
	[2]Vial #3 QA: Blank[1]	40-ml glass	3 min. after 2033	1202	QAQ WSQ WSQ	2 7 1	OBW Sample 2437 Spike kit	Separate	No change	No change	CL12023	CL12023

[1]This 2437 vial will alternate between either a blank, an environmental sample, or a spike replicate.

[2]One blank per site. Blanks should be done on all 3 schedules on the same date. (See sample schedule.)

[3]SUID is your study unit's 4-letter ID.

ASR Forms

No changes will be necessary on the primary ASR for the environmental S2033 sample. Continue to use the same ASR you normally use for your site(s).Due to the overlap of parameters, and complexity for this evaluation, **all other pesticide samples** will require their own unique and separate ASR due to either medium codes, and/or time differences. This will result in as many as 9 ASRs.

The first time recorded (main sample) should be to the nearest 10 min. (example: sch.2033 = 1200, or 1210, or 1220….)

The new ASR's will use the usual (pesticide) NASQAN/NAWQA/ or NMN project account code (GX12DD009CE0000) or the NMN project account code (GX12DD009U2LA00), or in some cases your NAWQA S&T account. Refer to the table above for ASR project account numbers and proposal numbers to use for your site. Note that NASQAN stations will have to use a NAWQA proposal code for some of their sample types.

In the Analytical Work Requests section of the ASR enter: ***"SCH 2437"***

In the Field Comments section of the ASR enter: **"S2437 vial #1 environmental / S2437 vial #2 spike / S2437 vial#3 blank, or spike replicate, or environmental replicate" depending on the sample type. (See schedule).**

Also, in the field comments section of the ASR, note the type of sample (environmental, spike, or blank) for the S2033 and S2060 as well. Record the blank water and spike lot numbers here.

In the "shipping information" section of the S2437 ASRs, enter "1 PEST" for the number of vials and bottle type for S2437 samples only. All S2033 and S2060 bottle types will still be "GCC". "PEST" is the new bottle type assigned to the new schedule.

Medium Codes, Time Offsets, and Sample Types

Round the sample time for the primary environmental sample to the nearest 10 minutes, for example 0940, 1200, or 1320. This sample time will be used for the environmental S2033 and your non-pesticide samples (nutrients, sediment, etc).

All S2060 and S2437 samples **MUST** use a time offset. Additionally, all S2033 spike, replicate, and blank samples **MUST** use a time offset. The time offset is required to prevent overwriting data in QWDATA due to identical parameter codes and multiple samples. Time offsets will be used in conjunction with medium codes to differentiate the samples. **Sample times and medium codes are critical**. Do not deviate from the coding in this guidance, even if your Water Science Center would not normally code samples in this manner.

Refer to the table above for the proper coding for each bottle and ASR.

Blank Processing

Field blanks should be processed using standard methods as stated in the National Field Manual (NFM) Chapter A4 (4.3.1). Blanks for S2437 should mirror those guidelines. Follow the procedures outlined in this document (steps 1-9), substituting OBW for environmental water. These blanks should be done in the field, but prior to collecting and processing the environmental samples. Only one field blank will be done per site. For each site, the field blanks for S2033, S2060, and S2437 should be collected on the same date.

Spike Kits

Use the appropriate spike mixture kit for each schedule (2033 spike kit for S2033 samples, 2060 spike kit for S2060 samples, and the new 2437 spike kit for S2437 samples).Please record lot number for each spike kit within the field notes. 2060 has two lot numbers.

Sample Login

When logging in samples, it is imperative that within the sample header under "field remarks"(Line 19) be filled out to indicate whether the 2437 schedule is an environmental replicate, spike replicate, or a blank. For example: Field Remarks: "New 2437 method- environmental sample"

The following parameter codes should be added when logging the samples into NWIS:

Environmental Sample Coding

(in addition to normal codes)

Pcode 99105 = Replicate type =30 (split)

Pcode 99112 = Purpose of topical QC = 200 (variability due to laboratory)

Pcode 99111= QC Data Associated with Sample = 100 = more than one type of QC

Environmental Replicates

(in addition to normal codes)

Pcode 71999 = Sample Purpose = NAWQA = 15/NASQAN = 20, or NMN = 25

Pcode 50280 = Purpose of Visit =1098 (QA/QC, surface water)

Pcode 99105 = Replicate type = 30 (split)

Pcode 99112 = Purpose of topical QC = 200 (variability due to laboratory)

Spikes and Spike Replicates

Pcode 71999 = Sample Purpose = either NAWQA = 15/NASQAN = 20, or NMN = 25

Pcode 50280 = Purpose of Visit =1098 (QA/QC, surface water)

Pcode 99105 = Replicate type = 30 (split) [Only use this Pcode if it is a replicate spike]

Pcode 99107 = Source of Spike Solution = 10 NWQL

Pcode 99106 = Type of Spike Sample = 10 Field

Pcode 82075 = Amount of Rinse = in L, (20-ml = 0.02-L)

Pcode 99108 = Spike Volume = (ml) 100 u/L = .1 ml

Pcode 99104 = Spike Lot number = See Spike Kit for NWIS Lot number

Pcode 99112 = (purpose of topical QC) = 200 (variability due to laboratory)

Blank Coding

Pcode 71999 = Sample Purpose = either NAWQA = 15/NASQAN = 20, or NMN = 25

Pcode 50280 = Purpose of Visit =1098 (QA/QC, surface water)

Pcode 99100 = Type of Blank Solution = 40 Organic-Free water

Pcode 99101 = Source of Blank Solution = 10 NWQL

Pcode 99102 = Type of Blank Sample = 100 Field

Pcode 82075 = Amount of Rinse = in L, (20-ml = 0.02-L)

Pcode 99202 = Organic Blank Lot = (see container for NWIS Lot or NWQL web page)

Pcode 99112 = Purpose of Topical QC = 200 Variability due to Laboratory

Equipment for Schedule 2437 Method Comparison Evaluation

Contact Milton Marshall (memarsha@usgs.gov) with your name, shipping address, phone number, site number(s) chosen for this evaluation study, and account to charge. Tell him you are involved in the S2437 Comparison Evaluation. For every *one site* you are scheduled to sample for this evaluation study, you will need to order the following:

- **1** bag (of 50) Plastic syringes (Order from Milton Marshall)
- **1** bag (of 50) Large-bore needles (Order from Milton Marshall)
- **1** bag (of 20) 25 mm 0.7 um glass-fiber syringe disk filters (Order from Milton Marshall)
- **3** S2437 spike mixtures (Order from Milton Marshall)

Note: The orders can be made in no fewer amounts than 50 for syringes and needles, and 20 for filters. The actual amount of syringes, needles, and filters needed for one site are 9 of each (or 1 syringe, needle, and filter per S2437 vial). Keep this in mind when ordering supplies for more than one site- you may not have to order more than one bag of syringes or needles. *Also, when vial#3 is scheduled to be a spike replicate, take the spike and the spike replicate out of the same spike mixture, so that you only have to order 3 spike mixtures, rather than 4.*

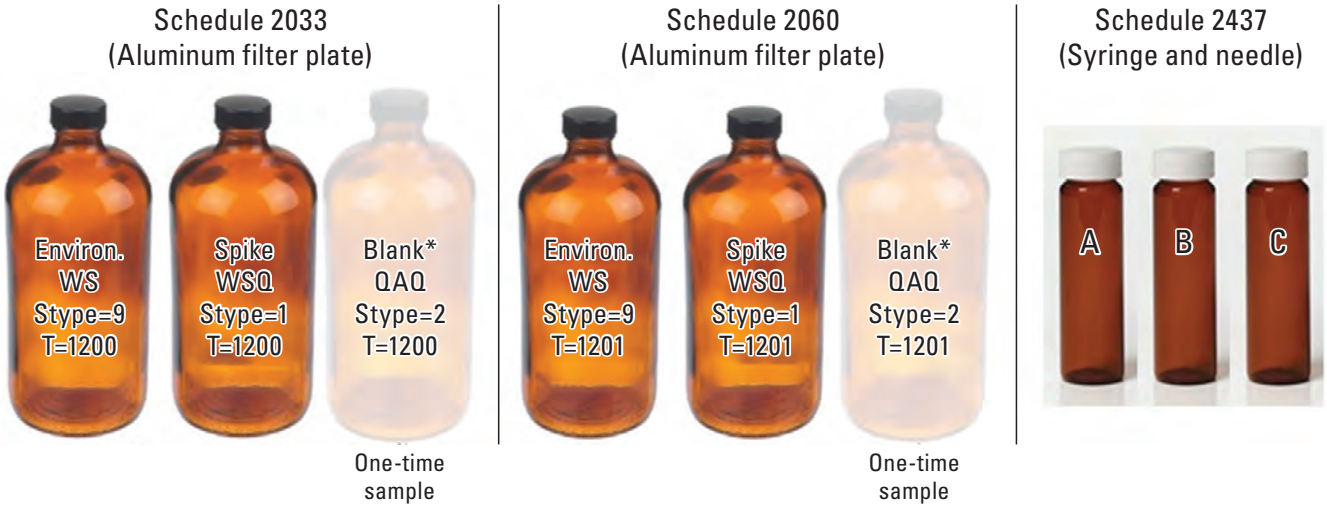
From USGS OneStop, Order: (for every one site scheduled to be sampled in this evaluation study)

- **3** S2033 spike mixtures (Order from USGS 1Stop, N1420)
- **3** S2060 spike mixtures (Order from USGS 1Stop, N1490)

You may also need to order the following from USGS OneStop if you are running low on supplies in your office:

- **10** 142-mm 0.7 um glass-fiber filters (Order from USGS 1Stop, Q375FLD)
- **27** 40-ml glass vials, GCV (Order from USGS 1Stop, N1560)
- **10** 1-L baked glass amber bottles (Order from USGS 1Stop, Q27FLD)
- **4L** Pesticide-grade blank water (Order from USGS 1Stop, N1590)
- Foam sleeves or shippers for glass bottles (Order from laboratory supplier such as Label Master http://www.labelmaster.com item number: "UNIP32F")

Schedule 2437 Evaluation Procedure



*Note 2033 and 2060 Blanks are *only* collected when Schedule 2437 vial "C" is scheduled to be a blank. If Schedule 2437 vial "C" is scheduled to be a replicate or spike replicate, do not collect the 3rd 1-liter 2033 or 2060.

A. Environmental: WSQ–B (T=1202)
B. Spike: WSQ–1 (T=1203)

C. Either: (See Schedule)
Replicate: WSQ–7 (T=1204)
Spike Replicate: WSQ–1 (T=1204)
Blank: QAQ–2 (T=1204)

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