NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Variability of Pesticide Detections and Concentrations in Field Replicate Water Samples Collected for the National Water-Quality Assessment Program, 1992-97

Water-Resources Investigations Report 01-4178

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By Jeffrey D. Martin

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Indianapolis, Indiana
2002

U.S. Department of the Interior

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Foreword

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

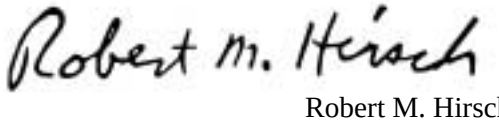
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Chief Hydrologist

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WATER-QUALITY UNITS AND ABBREVIATIONS

Water-quality units used in this report: Chemical concentration is given in micrograms per liter (µg/L). Micrograms per liter is a unit expressing the concentration of chemical constituents in solution as weight (micrograms) of solute per unit volume (liter) of water. For pesticide concentrations in the range commonly found in environmental water samples, the numerical value is the same as for concentrations in parts per billion.

The following abbreviations are used in this report:

Abbreviation	Description
α	Probability of a Type I error
CV	Coefficient of variation
E	Remark indicating that concentration is estimated
g'	Factor for calculating a one-sided tolerance bound
GCMS	Gas chromatography/mass spectrometry
HPLC	High-performance liquid chromatography
IRS	Inconsistent replicate sets
LOWESS	Locally weighted scatterplot smooths
LT-MDL	Long-term method detection limit
MDL	Method detection limit
MRL	Minimum reporting level
µ	Population mean
µg/L	Microgram per liter
n	Sample size
NAWQA	National Water-Quality Assessment
NWQL	National Water Quality Laboratory
OBSP	Organic Blind Sample Program
p	Probability of obtaining the result by chance
p	Proportion of the normal population
QC	Quality control
RSD	Relative standard deviation
SD	Standard deviation
Tp	Upper tolerance bound
t	Value of the t-distribution
USGS	U.S. Geological Survey
$\overline{X}$	Sample mean or a single measurement

Variability of Pesticide Detections and Concentrations in Field Replicate Water Samples Collected for the National Water-Quality Assessment Program, 1992–97

By Jeffrey D. Martin

Abstract

Field replicate water samples ("field replicates") collected for the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program during 1992 to 1997 were used to assess the variability of pesticide detections and concentrations in environmental water samples collected from the surface- and ground-water-quality networks of the NAWQA Program. Field replicates are two or more identically collected, processed, and analyzed environmental water samples that are used to assess the overall variability of field and laboratory procedures. Variability is the degree of random error in independent measurements of the same quantity and is the opposite of precision—the degree of mutual agreement. Information on variability can be used to estimate the reproducibility of individual measurements, the concentration needed to be assured of exceeding a water-quality standard, and the likelihood that two measurements of water quality are different.

Variability of pesticide detections was assessed by calculating the mean percentage detection of a pesticide and the percentage of inconsistent replicate sets. Variability of pesticide concentrations was assessed by pooling estimates of the standard deviation and relative standard deviation in replicate sets. Variability of pesticide detections and concentrations was a function of concentration, and estimates of variability were developed for discrete ranges of concentration. Reliability of estimates of variability was assessed by calculating 90-percent upper confidence bounds for the percentage of inconsistent replicate sets and for the pooled estimates.

The variability of detection for most pesticides is high at concentrations less than the minimum reporting level, but the variability of detection decreases dramatically at higher concentrations. In view of the highly diverse sources of water submitted as field replicates for the NAWQA Program and the generally low concentrations (concentrations in 79 percent of replicate sets were less than 0.1 microgram per liter) of pesticides in most replicates, inconsistent detections in replicate sets likely were caused by variability in the analytical method and by water-matrix interferences (or other loss processes) that result in false-negative errors. Consequently, estimates of the frequency of detection of pesticides in environmental water samples collected for the NAWQA Program probably are biased low because of false-negative errors at concentrations near the minimum reporting level.

Correlation analysis indicates that for most pesticides and concentrations, pooled estimates of relative standard deviation rather than pooled estimates of standard deviation should be used to estimate variability because pooled estimates of relative standard deviation are less affected by heteroscedasticity. The

median pooled relative standard deviation was calculated for all pesticides to summarize the typical variability for pesticide data collected for the NAWQA Program. The median pooled relative standard deviation was 15 percent at concentrations less than 0.01 micrograms per liter (µg/L), 13 percent at concentrations near 0.01 µg/L, 12 percent at concentrations near 0.1 µg/L, 7.9 percent at concentrations near 1 µg/L, and 2.7 percent at concentrations greater than 5 µg/L. Pooled estimates of standard deviation or relative standard deviation presented in this report are larger than estimates based on averages, medians, smooths, or regression of the individual measurements of standard deviation or relative standard deviation from field replicates. Pooled estimates, however, are the preferred method for characterizing variability because they provide unbiased estimates of the variability of the population. Assessments of variability based on standard deviation (rather than variance) underestimate the true variability of the population. Because pooled estimates of variability are larger than estimates based on other approaches, users of estimates of variability must be cognizant of the approach used to obtain the estimate and must use caution in the comparison of estimates based on different approaches.

INTRODUCTION

The U.S. Geological Survey (USGS) began implementing the National Water-Quality Assessment (NAWQA) Program in 1991. The goals of the NAWQA Program are to describe current water-quality conditions and trends in the Nation's streams and ground water and to understand the natural characteristics and human influences that affect water quality (Hirsch and others, 1988, p. 1).

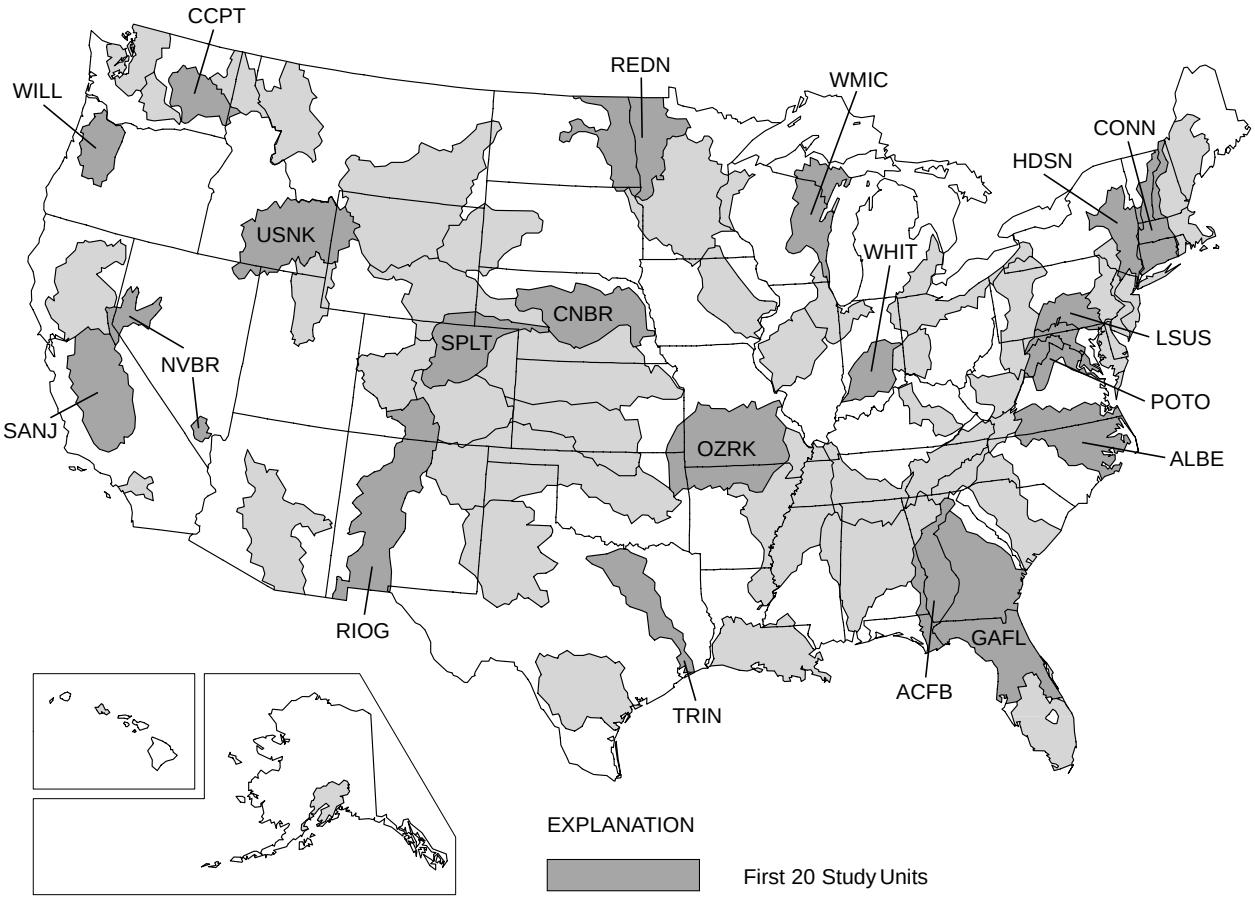
The NAWQA Program is assessing the water quality in more than 50 of the Nation's largest river basins and aquifers. These river basins and aquifers, known as NAWQA Study Units, account for about half the land area of the conterminous United States and approximately 60 to 70 percent of the Nation's water use and population served by public water supplies (Leahy and Wilber, 1991, p. 1). The Study-Unit investigations are divided into three groups that assess water quality on a rotational schedule. Investigations of water quality in 20 Study Units began in 1991 (fig. 1). Study-Unit investigations and national synthesis are the major design features of the NAWQA Program that allow water-quality information collected and interpreted locally to be integrated into a national description of water quality (Gilliom and others, 1995, p. 2–3).

One of the major tasks of the NAWQA Program is to assess the occurrence and distribution of pesticides in surface and ground water. The goal for Study-Unit investigations is to identify pesticides in the water resources of the Study Unit and to characterize and explain the geographic and seasonal distributions of pesticides (Gilliom and others, 1995, p. 4–6). The goal for national synthesis is to characterize, compare, and explain the geographic and seasonal distributions of pesticides among the broad range of land-use and hydrologic settings in the United States.

Purpose and Scope

The purpose of this report is to assess the variability of pesticide detections and concentrations in field replicate water samples and, from the data for the field replicate samples, estimate the variability of pesticide detections and concentrations in environmental water samples collected from the surface- and ground-water-quality networks of the NAWQA Program. This report summarizes concentrations of 86 pesticides and pesticide degradates (hereafter referred to as "pesticides") in field replicate water samples collected by the first 20 Study Units of the NAWQA Program during 1992 to 1997 and provides examples of the use of estimates of variability in water-quality assessments.

Field replicate water samples (hereafter referred to as "field replicates") were collected in sets—either duplicates (sets consisting of two replicates) or triplicates (sets consisting of three replicates) routinely throughout the period of collection of environmental water samples. Analytical data for 241 sets of surface-water field replicates and 95 sets of ground-water field replicates for pesticides analyzed by gas chromatography/mass



EXPLANATION

First 20 Study Units

Other Study Units

Map Acronym	NAWQA Study Units
ALBE	Albemarle-Pamlico Drainage
ACFB	Apalachicola-Chattahoochee-Flint River Basin
CCPT	Central Columbia Plateau
CNBR	Central Nebraska Basin
CONN	Connecticut, Housatonic, and Thames River Basins
GAFL	Georgia-Florida Coastal Plain
HDSN	Hudson River Basin
LSUS	Lower Susquehanna River Basin
NVBR	Nevada Basin and Range
OZRK	Ozark Plateaus
POTO	Potomac River Basin
REDN	Red River of the North
RIOG	Rio Grande Valley
SANJ	San Joaquin-Tulare Basins
SPLT	South Platte River Basin
TRIN	Trinity River Basin
USNK	Upper Snake River Basin
WMIC	Western Lake Michigan Drainage
WHIT	White River Basin
WILL	Willamette Basin

Figure 1. Locations of U.S. Geological Survey National Water-Quality Assessment Program Study Units, 1991.

spectrometry (GCMS) and data for 161 sets of surface-water field replicates and 92 sets of groundwater field replicates for pesticides analyzed by high-performance liquid chromatography (HPLC) were pooled for analysis and are presented in tables and selected figures that provide national summaries of the variability of pesticide detections and concentrations.

The variability of pesticide detections was assessed by calculating the mean percentage detection of a pesticide and the percentage of inconsistent field replicates. The mean percentage detection and the percentage of inconsistent replicate sets were calculated separately for three ranges of concentration that are a function of the minimum reporting level (MRL): (1) less than the MRL, (2) the MRL to 10 times the MRL, and (3) greater than 10 times the MRL. The reliability of the estimates of variability of detection was assessed by calculation of the 90-percent upper confidence bound for the percentage of inconsistent field replicates.

The variability of pesticide concentrations was assessed by calculating standard deviation and relative standard deviation of replicates in a set and examining these statistics as a function of the mean concentration of the replicate set. Replicate sets consisting of all nondetections were excluded from the analysis of variability of pesticide concentrations. Pooled estimates of the standard deviation and relative standard deviation are reported for eight overlapping ranges of concentration. The reliability of the pooled estimates of variability was assessed by calculation of the 90-percent upper confidence bound.

Acknowledgments

I thank the NAWQA field teams that collected, reviewed, compiled, and answered questions about the analytical data for the field replicates summarized in this report. I thank the following U.S. Geological Survey employees: David K. Mueller, Charles G. Crawford, Jonathon C. Scott, Mark E. Brigham, Timothy C. Willoughby, and Robert J. Gilliom for invaluable discussions on analytical approaches; Jonathon C. Scott for assistance in data compilation and programming; Charles G. Crawford, Robert J. Gilliom, David K. Mueller, and Peter F. Rogerson for technical review of early drafts of the report; Michael Eberle for editorial review; and Barbara A. Korzendorfer, Patricia H. Long, and Ann Marie Squillacci for assistance in production of the text.

OBJECTIVES AND METHODS FOR COLLECTION AND ANALYSIS OF FIELD REPLICATES

Replicates are environmental water samples that are used to assess variability. Replicates are two or more environmental water samples that are collected or processed such that they are thought to be identical in composition (Mueller and others, 1997, p. 2) and are analyzed by identical laboratory methods. Variability is the degree of random error in independent measurements of the same quantity (Mueller, 1998, p. vii) and is the opposite of precision—the degree of mutual agreement in independent measurements of the same quantity (Taylor, 1987, p. 7). High-quality data are characterized by low variability (high precision), whereas low-quality data are characterized by high variability (low precision). Replicates measure different sources of variability depending on the point in the sampling process that replication is done and the specific procedures, equipment, and personnel used to collect, process, or analyze the replicates.

Objectives and Use

Field replicates are a particular type of replicate that allow assessment of all or nearly all of the sources of variability that affect environmental water samples. Field replicates are identically collected, processed, and analyzed environmental water samples that provide information on the overall variability of field and laboratory procedures (termed “sampling variability” by Mueller, 1998, p. vii). Because field replicates are collected, processed, and analyzed identically to environmental water samples (or as much so as practicable), the variability of pesticide detections or concentrations in field replicates is used to estimate the variability of pesticide detections or concentrations in environmental water samples.

Information on variability is used to (1) document the quality of the environmental data; (2) decide whether data quality is sufficient to meet the study objectives or whether changes to the data program or objectives are needed; and (3) qualify, where needed, interpretation of water-quality data. Data-quality goals for the NAWQA Program are (1) use of documented data-collection methods, (2) measurement and assessment of the quality of the data, and (3) water-quality assessments done with data of appropriate quality. Specifically, information on variability can be used to estimate the precision or reproducibility of individual measurements, the concentration needed to be assured of exceeding a water-quality standard, and the likelihood that two measurements of water quality are different.

Types of Field Replicates

The terminology concerning replicates is confusing. Field replicates are collected in sets—either duplicates (sets consisting of two replicates) or triplicates (sets consisting of three replicates). The term "replicates" refers to all similarly collected and analyzed samples in a replicate set. For the purposes of providing instructions for collecting and processing field replicates and for data management, the terms "primary environmental sample," "duplicate environmental sample," and "triplicate environmental sample" are used to refer to particular samples in the replicate set (Mueller and others, 1997, p. 2).

Several types of field replicates were collected or processed to assess variability. The types of field replicates differ in the sources of variability assessed. **Split replicates** are processed by dividing a single sample of water into multiple samples. Split replicates are used to assess variability associated with sample processing in the field (division into subsamples, filtration of subsamples, field extraction, and transport) and laboratory analysis. Split replicates cannot be used to assess variability associated with sample collection. **Concurrent replicates** are multiple samples collected from an environmental matrix as closely as possible to the same location and at the same time. Concurrent replicates are used to assess variability associated with sample collection, processing, and analysis. Depending on the specific sampling procedures, concurrent replicates also may include an unknown amount of temporal or spatial environmental variability (true differences in concentrations over short time intervals or small distances). **Sequential replicates** are multiple samples collected from an environmental matrix as closely as possible to the same location but at different times (usually one right after the other). Sequential replicates are used to assess the same sources of variability as concurrent replicates but include a larger amount of temporal environmental variability because the time between collection of the replicates is longer.

Field replicates were collected or processed by use of similar procedures as for environmental water samples. Field procedures were similar—but not exactly the same—because the collection and processing of field replicates might have required larger volumes of water, larger or more numerous containers, or longer holding times for sample processing. Procedures for the collection and processing of environmental water samples for the NAWQA Program are described by Shelton (1994) for surface water and by Koterba and others (1995) for ground water.

Collection Guidelines

Guidelines for the collection of quality-control (QC) samples for the 20 NAWQA Study-Unit investigations that began in 1991 recommended that approximately 15 percent of the Study-Unit analytical budget be allocated for the analysis of QC samples collected by NAWQA field teams. Field blanks (for estimating bias), field replicates (for estimating variability), and replicate field matrix spikes (for estimating bias and variability) were the recommended types of QC samples, but NAWQA field teams had the flexibility to collect the types of QC samples that addressed individual Study-Unit conditions and the concerns of field teams (P.P. Leahy, U.S. Geological Survey, written commun., December 21, 1992, and June 9, 1993).

The guidelines recommended that field replicates be (1) collected routinely during the collection period of environmental water samples; (2) collected during periods when concentrations are expected to be greater than the MRL; and (3) distributed among sites and times to assess a

broad range of locations, hydrologic conditions, concentrations, water types, field personnel, and field equipment. Field replicates for pesticides in ground water were not emphasized to the same degree as field replicates for surface water because pesticide concentrations were expected to be less than the MRL at many ground-water sites. Guidelines for the collection of QC samples for NAWQA Study-Unit investigations that began in 1994 or 1997 have been revised and published (Koterba and others, 1995; Mueller and others, 1997).

Analytical Methods for Pesticides

Environmental water samples and field replicates were analyzed for pesticides at the National Water Quality Laboratory (NWQL) of the USGS in Arvada, Colo. The NWQL developed two analytical methods for identification and quantitation of various pesticides at concentrations as low as 0.001 µg/L. NAWQA field teams select these analytical methods by requesting NWQL laboratory schedules, which are specific lists of pesticides that are analyzed by particular types of laboratory instrumentation and procedures (Timme, 1995, p. 22). NWQL schedules are identified for the benefit of USGS readers of this report. Chemical Abstract Service registry numbers, analytical methods, and USGS National Water Information System and U.S. Environmental Protection Agency Data Storage and Retrieval System parameter codes are presented in appendix 1.

NWQL schedules 2001 and 2010 (Timme, 1995, pp. 60, 80) request analyses for 47 pesticides that are isolated from filtered water by C-18 solid-phase extraction and identified and quantitated by capillary column GCMS with selected-ion monitoring (Zaugg and others, 1995). The pesticide acetochlor was added to the GCMS method in June 1994 (Lindley and others, 1996). NWQL schedules 2050 and 2051 (Timme, 1995, pp. 61, 80) request analyses for 39 pesticides that are isolated from filtered water by Carbopak-B solid-phase extraction and identified and quantitated by HPLC with a photodiode-array detector (Werner and others, 1996). The pesticides carbaryl, carbofuran, and linuron are analyzed by both analytical methods. Both methods have optional procedures for the onsite extraction of water samples by field personnel. Schedules 2010 and 2051 request analyses for pesticides that were extracted from filtered water samples onsite, whereas schedules 2001 and 2050 request analyses for pesticides that were extracted from filtered water samples at the NWQL. For the purposes of this report, the location of sample extraction is not considered in the analysis of field replicates (that is, a valid replicate set may consist of field-extracted and laboratory-extracted samples).

The NWQL has historically used the minimum reporting level (MRL) for reporting analytical data (Oblinger Childress and others, 1999, p. 2). The MRL is the "less-than" concentration used for reporting nondetections of an analyte. The MRL is defined as

> the smallest measured concentration of a constituent that may be reliably reported using a given analytical method (Timme, 1995, p. 92).

The definition of the MRL is not quantitatively specific, and various approaches have been used by NWQL to set the concentration of the MRL. For the analytical methods used in this report, the MRL initially was set equal to the method detection limit (MDL) but was subsequently revised for 14 pesticides on the basis of laboratory QC information. An in-depth discussion of the various reporting levels used by the NWQL and considerations for their use and interpretation is presented in Oblinger Childress and others (1999).

Statistically determined method detection limits were calculated for all pesticides in both methods. The MDL is defined as

> the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing [the] analyte (Wershaw and others, 1987, p. 4)

and was determined by the procedure described by the U.S. Environmental Protection Agency (1992). The calculated MDL controls the rate of false-positive errors (determining that a pesticide is present in a sample when, in truth, it is absent) primarily on the basis of quantitation variability at concentrations near the MDL. The MDLs determined in a matrix of pesticide-grade water ranged from 0.001 to 0.032 µg/L (Zaugg and others, 1995, pp. 32–33; Werner and others, 1996, p. 18).

The MDL does not control the rate of false-negative errors (determining that a pesticide is absent in a sample when, in truth, it is present). If a pesticide is present in a sample at the concentration of the MDL, the probability is 50 percent that the measured concentration will be less than the MDL (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 94–12, 1994). If detections are censored at the MDL, then 50 percent of the samples with pesticides present at the concentration of the MDL will be reported as nondetections. In the above discussion, no bias in the analytical method is assumed. If the analytical method is negatively biased (recovery is less than 100 percent), the frequency of false-negative errors may be increased (P.F. Rogerson, U.S. Geological Survey, written commun., March 2, 2001).

Low-level detections of pesticides, however, are not censored at the MRL/MDL for the analytical methods used in this report.

With clean environmental samples, analysts are able to detect analytes in concentrations less than the MDL; while conversely, with complex samples, analysts may be unable to detect analytes in concentrations greater than the MDL (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 94–12, 1994).

All detections (pesticides conclusively identified by retention time and spectral characteristics) are quantitated, and concentrations less than the MRL/MDL are reported by the NWQL with an "E" remark (for example, E0.004 µg/L) to indicate that the concentration (but not the presence) of the pesticide is estimated. Although detections of pesticides by the analytical methods used for this report are not censored at the MRL, the probability of detection decreases as concentration decreases. The word "minimum" in MRL, in conjunction with analytical methods that report detections at estimated concentrations that are less than the MRL, has created confusion for some users and is one of the reasons why new data-reporting conventions and terminology developed by NWQL were needed (Oblinger Childress and others, 1999, pp. 6–10).

Any detections of five pesticides analyzed by GCMS (azinphos-methyl, carbaryl, carbofuran, desethylatrazine, and terbacil) and six pesticides analyzed by HPLC (aldicarb, aldicarb sulfone, aldicarb sulfoxide, chlorothalonil, dichlobenil, and DNOC) also are reported by the NWQL with an "E" remark, regardless of concentration. These pesticides have lower or more variable recovery in laboratory QC spikes than the other pesticides analyzed by the method (Zaugg and others, 1995, p. 35; Werner and others, 1996, pp. 27, 34; U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 98–03A, 1998).

Nondetections (pesticides that could not be conclusively identified by retention time and spectral characteristics) are reported by the NWQL as less than the MRL. Before December 15, 1997, the MRL was set equal to the MDL. On December 15, 1997, the MRLs for 14 of the 39 pesticides analyzed by HPLC were raised (U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 98–03A, 1998). Justification of an MRL that was greater than the MDL was based on internal NWQL spiking programs, which showed that the rate of false-negative errors was unacceptably high at concentrations near the MDL. Detections of these 14 pesticides before December 15, 1997, are valid; only the numerical threshold used to indicate nondetections increased.

Data Compilation and Characteristics

Water-quality data for field replicates and other types of QC samples were reviewed by NAWQA field teams and submitted for aggregation into a national QC data base for the NAWQA Program consistent with guidance provided by the NAWQA Data and Software Integration Group (written commun., October 23, 1997). Most teams submitted QC data in December 1997 or January 1998.

The data set of field replicates used for this report is a subset of the NAWQA national QC data base obtained by retrieving samples that were (1) analyzed for pesticides by GCMS or HPLC (2) coded as environmental samples or QC-replicate environmental samples, (3) collected at the same field site and on the same date, and (4) collected by the first 20 Study Units. Replicate sets having replicates with times of sample collection more than 2 hours apart (seven sets) were examined carefully to ensure that the samples were truly field replicates. Four sets of replicates were deleted from the data set as a result of this check. The frequency of inconsistently detected pesticide

in replicates was calculated for all replicate sets and pesticides. Replicate sets with an unusually large number (more than five or six) of inconsistently detected pesticides were examined carefully, and seven of these replicate sets were referred to Study-Unit teams for further review. Errors in two replicate sets were caused by the switching of duplicate environmental samples among sites. Errors in five replicate sets were caused by inclusion of field spiked environmental samples as replicates, either because of miscoding or by inadvertent switching of sample bottles. Either the errors were resolved or the samples were deleted from the data set.

The data set used for this report consisted of 241 sets of surface-water field replicates and 95 sets of ground-water field replicates for pesticides analyzed by GCMS and 161 sets of surface-water field replicates and 92 sets of ground-water field replicates for pesticides analyzed by HPLC. Field replicates were fairly well distributed among the first 20 Study Units (table 1). Differences in the number of replicates among Study Units can partly be explained by differences in the number of environmental water samples collected. Of 402 sets of surface-water replicates, 63 (16 percent) were triplicates (45 sets analyzed by GCMS and 18 sets analyzed by HPLC). Of 187 sets of ground-water replicates, 7 (4 percent) were triplicates (7 sets analyzed by GCMS). Of the surface-water replicates, 49 percent were split replicates, 45 percent were sequential replicates, and 6 percent were concurrent replicates. Of the ground-water replicates, 96 percent were sequential replicates and 4 percent were concurrent replicates. Approximately 3 percent of the replicate sets consisted of both field-extracted and laboratory-extracted samples.

Most of the surface-water replicates (93 percent) and all of the ground-water replicates used for this report were collected during 1993–95 (fig. 2), the 3-year intensive data-collection phase for the first 20 Study Units (Gilliom and others, 1995, pp. 2–4). A much smaller number of replicates were collected during 1992 (a prototype study of surface-water sampling by three Study Units) and during 1996–97 (low-intensity monitoring at selected sites). Most replicates (74 percent) were collected during April-August (fig. 2), a period that corresponds to the pesticide-application season in much of the United States and to the period of high-frequency pesticide sampling at surface-water sites for most Study Units.

Table 1. Distribution of field replicates among type of site, analytical method, and Study Units of the National Water-Quality Assessment Program

[Study-Unit abbreviations are explained in figure 1. GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography]

Study unit	Number of replicate sets			
	Surface-water sites		Ground-water sites	
	GCMS	HPLC	GCMS	HPLC
ACFB	18	19	6	7
ALBE	3	1	7	4
CCPT	8	8	5	3
CNBR	5	3	0	0
CONN	3	2	3	3
GAFL	13	10	8	9
HDSN	17	10	5	6
LSUS	15	7	0	6
NVBR	10	10	4	5
OZRK	4	2	8	9
POTO	24	7	10	3
REDN	13	10	11	10
RIOG	8	7	0	0
SANJ	25	11	3	2
SPLT	9	7	3	3
TRIN	19	12	11	11
USNK	12	7	0	0
WHIT	20	14	6	6
WILL	5	4	3	3
WMIC	10	10	2	2
Total	241	161	95	92

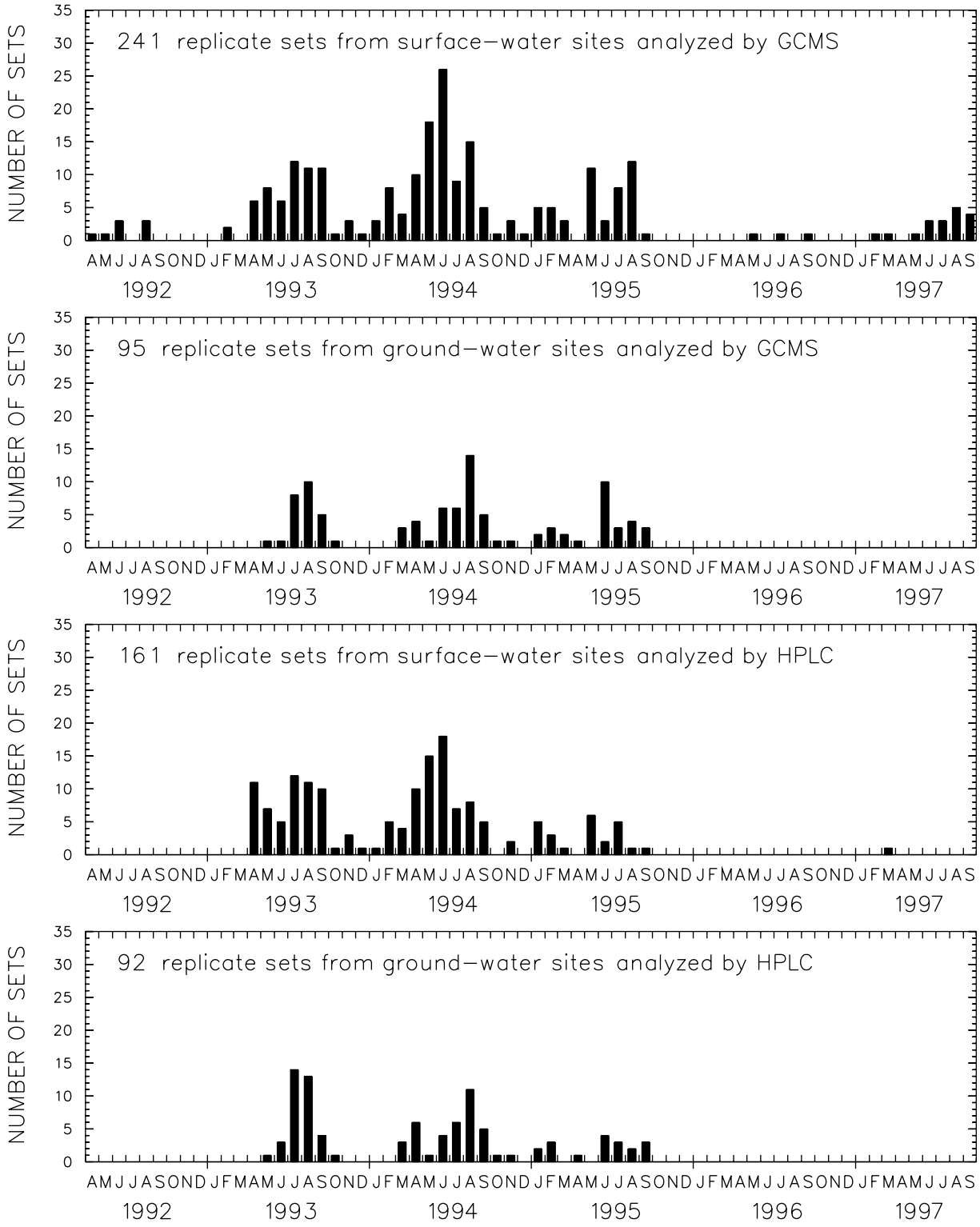


Figure 2. Temporal distribution of field replicates (GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography).

Statistical Methods, Calculations, and Analytical Approach

The UNIVARIATE procedure of SAS (SAS Institute, Inc., 1990, pp. 617–634) was used to calculate mean concentration, variance of concentration, standard deviation of concentration (*SD*), range of concentration, number of replicates, detection rate, and other common statistics for the replicates in each replicate set. The coefficient of variation (CV) of replicates in a set was calculated as the standard deviation divided by the mean (CV is expressed as a proportion), and the relative standard deviation (*RSD*) was calculated as CV multiplied by 100 percent (*RSD* is expressed as a percentage, Taylor, 1987, p. 20). Kendall's tau, a nonparametric measure of the correlation between two variables (Conover, 1980, p. 256), and the approximate significance probability of the correlation were calculated using the KENDALL option of the CORR procedure (SAS Institute, Inc., 1990, pp. 209–224) and were used to test *SD* and *RSD* of replicate sets for heteroscedasticity (increasing or decreasing variability) over selected ranges of concentration. An approximate significance probability of less than 0.05 for Kendall's tau was used to indicate heteroscedasticity. Tests for heteroscedasticity were done only for pesticides with three or more replicate sets in a concentration range. Locally weighted scatterplot smooths, termed LOWESS smooths (Cleveland, 1979), were used to show the relation of variability and concentration. A smoothing factor of 0.25 was used for all smooths.

The UNIVARIATE procedure also was used to calculate statistics that summarized variability of detection and concentration over the appropriate number of replicate sets. Other than for counts of the number of replicates sets collected (table 2), replicate sets that contained only nondetections of a pesticide were excluded from statistical analysis because they provide little information on the variability of detections or concentrations. The mean detection rate of a pesticide is a measure of the consistency of detection and was calculated as the average of the percentage detections in each replicate set. The percentage detections in a replicate set was 100 or 50 percent for duplicates or was 100, 66.7, or 33.3 percent for triplicates (replicate sets with all nondetections were excluded from analysis). Mean detection rate was weighted by the number of replicates in the set (either 2 or 3). Confidence limits were not calculated for the mean detection rate because, for most pesticides, sample size was insufficient (less than 30) and the distribution of percent detection in replicate sets was too highly skewed to assume a normal distribution of means using the central limit theorem (Helsel and Hirsch, 1992, p. 74).

Replicate sets with inconsistent detections are those where a pesticide was detected in at least one, but not all, replicates in the set (table 2). The percentage of replicate sets with inconsistent detections (replicate sets that contain both detections and nondetections of a pesticide) is a measure of the variability of detection and was calculated as the number of replicate sets with inconsistent detections divided by the sum of the number of replicate sets with consistent detections plus the number of replicate sets with inconsistent detections. Replicate sets with consistent nondetections were excluded from the calculation because the objective of the analysis was to evaluate the variability of detection rather than the variability of nondetection. For brevity, "replicate sets with inconsistent detections" is sometimes referred to as "inconsistent replicate sets" (IRS) in the text.

One-sided, 90-percent upper confidence bounds were calculated for the percentage of nonconforming units following the method of Hahn and Meeker (1991, pp. 104–105). Nonconforming units in the context of this report are replicate sets with inconsistent detection. Conforming units are replicate sets that contain only detections of a pesticide (consistent detection). One-sided, upper confidence bounds were calculated to estimate an upper limit of uncertainty in the measured rate of inconsistency of detection. An upper confidence bound was used because the objective of the analysis was to obtain a pessimistic estimate of detection variability; in other words, "how bad might things be?" (Hahn and Meeker, 1991, p. 30). A 90-percent confidence level was selected for calculation of the upper confidence bound, primarily because higher levels of confidence have extremely wide confidence limits (large confidence bounds). The 90-percent confidence level is a compromise between a reasonable level of confidence and the size of the confidence interval. The 90-percent confidence bound is conservative because calculated confidence bounds typically are greater than 90 percent (Hahn and Meeker, 1991, p. 101).

Table 2. Number of replicate sets and consistency of pesticide detection or nondetection

[Pesticides are sorted by the percentage of sets that have consistent detections or nondetections, the percentage of sets that have at least one detection, and pesticide name; parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; µg/L, microgram per liter; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; nc, not calculated]

Table 2. Number of replicate sets and consistency of pesticide detection or nondetection

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets	Number of replicate sets where replicates in the set have			Percentage of replicate sets where replicates in the set have		Median detected concentration[4] (µg/L)
					Consistent nondetections[1]	Consistent detections[2]	Inconsistent detections[3]	Consistent detections or consistent nondetections	At least one detection	
82671	Molinate	GCMS	0.004	336	325	11	0	100.0	3.3	0.140
82665	Terbacil	GCMS	.007	330	324	6	0	100.0	1.8	.017
82672	Ethoprop	GCMS	.003	336	332	4	0	100.0	1.2	.009
49293	Norflurazon	HPLC	.024	253	250	3	0	100.0	1.2	.090
04024	Propachlor	GCMS	.007	336	332	4	0	100.0	1.2	.031
49299	DNOC	HPLC	.420	248	247	1	0	100.0	.4	.505
49297	Fenuron	HPLC	.013	252	251	1	0	100.0	.4	.140
49292	Oryzalin	HPLC	.310	253	252	1	0	100.0	.4	.515
49291	Picloram	HPLC	.050	245	244	1	0	100.0	.4	.110
49312	Aldicarb	HPLC	.550	253	253	0	0	100.0	.0	nc
49313	Aldicarb sulfone	HPLC	.100	250	250	0	0	100.0	.0	nc
49307	Chloramben	HPLC	.420	253	253	0	0	100.0	.0	nc
49306	Chlorothalonil	HPLC	.480	248	248	0	0	100.0	.0	nc
49305	Clopyralid	HPLC	.230	246	246	0	0	100.0	.0	nc
49304	Dacthal monoacid	HPLC	.017	248	248	0	0	100.0	.0	nc
38746	2,4-DB	HPLC	.240	249	249	0	0	100.0	.0	nc
38442	Dicamba	HPLC	.035	248	248	0	0	100.0	.0	nc
49302	Dichlorprop	HPLC	.032	249	249	0	0	100.0	.0	nc
49308	3-Hydroxycarbofuran	HPLC	.014	252	252	0	0	100.0	.0	nc
38487	MCPB	HPLC	.140	249	249	0	0	100.0	.0	nc
38501	Methiocarb	HPLC	.026	253	253	0	0	100.0	.0	nc
49294	Neburon	HPLC	.015	253	253	0	0	100.0	.0	nc
38866	Oxamyl	HPLC	.018	249	249	0	0	100.0	.0	nc
39542	Parathion	GCMS	.004	336	336	0	0	100.0	.0	nc
82664	Phorate	GCMS	.002	336	336	0	0	100.0	.0	nc
49236	Propham	HPLC	.035	253	253	0	0	100.0	.0	nc
39762	Silvex	HPLC	.021	248	248	0	0	100.0	.0	nc
39742	2,4,5-T	HPLC	.035	248	248	0	0	100.0	.0	nc
82684	Napropamide	GCMS	.003	336	320	15	1	99.7	4.8	.012
82666	Linuron	GCMS	.002	336	326	9	1	99.7	3.0	.022

Table 2. Number of replicate sets and consistency of pesticide detection or nondetection—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets	Number of replicate sets where replicates in the set have			Percentage of replicate sets where replicates in the set have		Median detected concentration[4] (µg/L)
					Consistent non-detections[1]	Consistent detections[2]	Inconsistent detections[3]	Consistent detections or consistent nondetections	At least one detection	
82681	Thiobencarb	GCMS	0.002	336	330	5	1	99.7	1.8	0.011
82667	Methyl parathion	GCMS	.006	336	331	4	1	99.7	1.5	.018
82669	Pebulate	GCMS	.004	336	331	4	1	99.7	1.5	.024
34253	*alpha*-HCH	GCMS	.002	336	334	1	1	99.7	.6	.019
82677	Disulfoton	GCMS	.017	336	335	0	1	99.7	.3	.003
82675	Terbufos	GCMS	.013	336	335	0	1	99.7	.3	.005
38811	Fluometuron	HPLC	.035	253	246	6	1	99.6	2.8	.115
38478	Linuron	HPLC	.018	253	250	2	1	99.6	1.2	.057
49311	Bromoxynil	HPLC	.035	248	246	1	1	99.6	.8	.093
49235	Triclopyr	HPLC	.250	249	247	1	1	99.6	.8	.141
49314	Aldicarb sulfoxide	HPLC	.021	250	249	0	1	99.6	.4	.900
49303	Dichlobenil	HPLC	1.200	253	252	0	1	99.6	.4	.020
49301	Dinoseb	HPLC	.035	249	248	0	1	99.6	.4	.025
49296	Methomyl	HPLC	.017	250	249	0	1	99.6	.4	.050
04095	Fonofos	GCMS	.003	336	313	21	2	99.4	6.8	.005
04028	Butylate	GCMS	.002	336	320	14	2	99.4	4.8	.006
82686	Azinphos-methyl	GCMS	.001	333	320	11	2	99.4	3.9	.074
82685	Propargite	GCMS	.013	336	324	10	2	99.4	3.6	.033
82663	Ethalfluralin	GCMS	.004	336	329	5	2	99.4	2.1	.023
82676	Pronamide	GCMS	.003	336	329	5	2	99.4	2.1	.009
82679	Propanil	GCMS	.004	336	332	2	2	99.4	1.2	.007
82687	*cis*-Permethrin	GCMS	.005	336	334	0	2	99.4	.6	.002
49260	Acetochlor	GCMS	.002	122	110	11	1	99.2	9.8	.045
04029	Bromacil	HPLC	.035	252	246	4	2	99.2	2.4	.100
49310	Carbaryl	HPLC	.008	253	247	4	2	99.2	2.4	.060
49315	Acifluorfen	HPLC	.035	249	245	2	2	99.2	1.6	.105
49309	Carbofuran	HPLC	.120	253	250	1	2	99.2	1.2	.080
38482	MCPA	HPLC	.170	248	245	1	2	99.2	1.2	.005
38538	Propoxur	HPLC	.035	242	240	0	2	99.2	.8	.075
82678	Triallate	GCMS	.001	336	320	13	3	99.1	4.8	.005
39341	*gamma*-HCH	GCMS	.004	336	327	6	3	99.1	2.7	.010
82673	Benfluralin	GCMS	.002	336	332	1	3	99.1	1.2	.004
82668	EPTC	GCMS	.002	336	286	46	4	98.8	14.9	.016
82660	2,6-Diethylaniline	GCMS	.003	336	323	8	5	98.5	3.9	.001
38711	Bentazon	HPLC	.014	248	236	8	4	98.4	4.8	.153

Table 2. Number of replicate sets and consistency of pesticide detection or nondetection—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets	Number of replicate sets where replicates in the set have			Percentage of replicate sets where replicates in the set have		Median detected concentration[4] (µg/L)
					Consistent nondetections[1]	Consistent detections[2]	Inconsistent detections[3]	Consistent detections or consistent nondetections	At least one detection	
39532	Malathion	GCMS	0.005	336	313	17	6	98.2	6.8	0.010
39381	Dieldrin	GCMS	.001	336	318	12	6	98.2	5.4	.008
49300	Diuron	HPLC	.020	252	227	20	5	98.0	9.9	.110
82683	Pendimethalin	GCMS	.004	336	310	18	8	97.6	7.7	.010
82674	Carbofuran	GCMS	.003	336	314	14	8	97.6	6.5	.018
04041	Cyanazine	GCMS	.004	336	258	69	9	97.3	23.2	.045
46342	Alachlor	GCMS	.002	336	261	65	10	97.0	22.3	.015
82682	Dacthal	GCMS	.002	336	274	50	12	96.4	18.5	.003
82680	Carbaryl	GCMS	.003	336	279	45	12	96.4	17.0	.019
82661	Trifluralin	GCMS	.002	336	294	30	12	96.4	12.5	.007
39732	2,4-D	HPLC	.150	247	228	10	9	96.4	7.7	.105
04037	Prometon	GCMS	.018	336	192	131	13	96.1	42.9	.020
39632	Atrazine	GCMS	.001	336	116	206	14	95.8	65.5	.039
39415	Metolachlor	GCMS	.002	336	168	154	14	95.8	50.0	.027
82630	Metribuzin	GCMS	.004	336	298	24	14	95.8	11.3	.012
38933	Chlorpyrifos	GCMS	.004	336	264	57	15	95.5	21.4	.010
39572	Diazinon	GCMS	.002	334	216	102	16	95.2	35.3	.018
04040	Desethylatrazine	GCMS	.002	336	161	158	17	94.9	52.1	.016
04035	Simazine	GCMS	.005	336	149	168	19	94.3	55.7	.028
82670	Tebuthiuron	GCMS	.010	336	263	54	19	94.3	21.7	.010
34653	*p,p'*-DDE	GCMS	.006	336	302	12	22	93.5	10.1	.001

[1]Replicate sets that have consistent nondetections are those where the pesticide was not detected in any replicate in the set.
[2]Replicate sets that have consistent detections are those where the pesticide was detected in all replicates in the set.
[3]Replicate sets that have inconsistent detections are those where the pesticide was detected in at least one, but not all, replicates in the set.
[4]Median detected concentration of all replicates where the pesticide was detected.

The variances of individual replicate sets were pooled by use of the procedure given in Anderson (1987, pp. 44–45). Pooling the variances provides a better estimate of variability than do individual estimates because the pooled estimate is based on a larger number of degrees of freedom (Taylor, 1987, p. 24). The variance is a squared term. The positive square root of the pooled variance yields the pooled standard deviation (a statistic more commonly used to describe variability because the units of measurement are the same as those for individual measurements). Pooled estimates were weighted by the number of replicates in the set. Pooled estimates of the *RSD* were computed by use of the same procedure (Anderson, 1987, pp. 44–45).

Pooled estimates of variance were tested for equality of variance between surface-water and ground-water field replicates by use of a two-tailed *F*-test, as shown in Sokal and Rohlf (1969, pp. 185–186). The PROBF function of SAS (SAS Institute, Inc., 1982, p. 178) was used to calculate probabilities and significance levels of the *F*-distribution for tests of equality of variance.

Analysis of the variability of pesticide detections and concentrations was complicated by (1) nondetections of pesticides in many replicate sets, (2) collection of different types of field replicates, (3) different numbers of replicates in replicate sets, (4) variability that is a strong function of concentration, (5) excessively rounded analytical data for pesticide concentrations, and (6) inconsistent detection of pesticides in a single replicate set. These difficulties were addressed by the following analytical approaches.

Replicate sets that contain only nondetections provide information on the variability of nondetection but provided little useful information on the variability of detection or concentration. Replicate sets that contained only nondetections of a pesticide were excluded from statistical analysis. Of 86 pesticides analyzed for in this report, 19 were not detected in any field replicate (table 2). Laboratory QC samples provide information on some aspects of variability for these pesticides. Some of the most useful information is obtained from laboratory control (analytical set) spikes done by NWQL and summarized by Martin (1999, table 4), blind spikes done by the Organic Blind Sample Program (OBSP) (http://btdqs.usgs.gov/OBSP/index.html), and low-concentration long-term method detection limit (LT-MDL) spikes done by NWQL (http://wwwnwql.cr.usgs.gov/Public/ltmdl/ltmdlsplash.html).

Split, concurrent, and sequential field replicates measure different sources of variability but were combined for analysis. Different types of replicates were combined because (1) laboratory processing and analysis are expected to be the main sources of variability, (2) the low number of replicates with detections for most pesticides requires combining the replicates to increase sample size and improve reliability of the estimated variability, and (3) the lack of a nested experimental design (split replicates nested within concurrent or sequential replicates) prevented a rigorous evaluation of the importance of variability contributed by sample collection. If sample collection adds an important component of variability, then estimates of variability given in this report could be biased low because split replicates do not measure the variability of sample collection. Mueller (1998, pp. 11–12) assessed the standard deviation of concentrations of nitrogen and phosphorus among split and other types of field replicates. His evaluation did not find differences in variability that could be attributed to the type of replicate and, subsequently, the various types of field replicates were combined for further analysis. The use of pessimistic estimates of uncertainty (upper confidence bounds) for the estimated variability of pesticide detections and concentrations provided in this report may compensate for a potentially low bias in variability caused by the use of split replicates. The NAWQA Study Units that began investigations in 1994 were directed to collect a limited number of surface-water field replicates by use of a nested experimental design so that the importance of variability of sample collection could be evaluated (T.L. Miller, U.S. Geological Survey, written commun., July 17, 1996).

Surface-water and ground-water field replicates also were combined for analysis. Replicates from these two sources were combined because (1) laboratory processing and analysis (rather than water matrix or sampling procedures) are expected to be the main sources of variability, (2) the low number of replicates with detections (particularly for ground water) for most pesticides requires combining surface-water and ground-water field

replicates to increase sample size and improve reliability of the estimated variability, and (3) statistically significant differences in variability are either generally lacking or inconsistent between surface-water and ground-water field replicates. Variability of surface-water and ground-water replicates was compared by use of an *F*-test of the pooled variances of replicates sets with consistent detections in eight ranges of concentration. Taylor (1987, p. 38) recommends that the *F*-test be based on at least 14 degrees of freedom. Although none of the pesticides met this criterion, the *F*-test was performed for six pesticides that had at least 3 degrees of freedom for ground-water field replicates (table 3). No statistically significant ($p >= 0.05$) differences in variability between surface-water and ground-water replicates were identified for alachlor, desethylatrazine, or metolachlor. Statistically significant differences in variability were identified for atrazine, simazine, or prometon in some ranges of concentration (table 3). In other ranges of concentration, however, differences in variability were not statistically significant or, in the case of prometon, were inconsistent as to which type of replicate (surface water or ground water) was more variable. Comparison of variability between surface- and ground-water replicates where nondetections were set to zero for inconsistent replicate sets yielded similar results to those discussed here. In view of the few ground-water replicates with detections of pesticides, the lack of a consistent pattern of variability between surface- and ground-water replicates indicates that differences in variability are not a major function of differences in the source of the water, sampling protocols, or sampling equipment, and that surface- and ground-water replicates may be combined for analysis.

Replicate sets of duplicates and triplicates were combined for analysis. Different numbers of replicates in a replicate set complicated analysis of variability by restricting analytical approaches, requiring multiple analytical approaches for the variability of detection, and introducing bias in some measures of variability. Triplicates prevented the calculation of percent difference or the use of log percent difference (Tornqvist and others, 1985), a simple but useful, intuitive, and nonparametric measure of variability of concentration. Mean detection rate was calculated solely to account for differences in the number of replicates in a set. The percentage of inconsistent replicates is the preferred measure of variability of detection because estimates of uncertainty can be made. Combined analysis of duplicates and triplicates required that measures of variability be weighted by the number of replicates in a set; however, not all measures could be weighted. LOWESS smooths, the percentage of inconsistent replicate sets, and correlations (Kendall's tau) were not weighted; thus, inferences based on these measures may be biased.

Variability of pesticide detections and concentrations usually is a strong function of concentration (for purposes of this report, "strong" means that the measure of variability increases or decreases markedly as concentration increases). Not only is the magnitude of the variability a function of concentration (particularly the standard deviation), but the variance or scatter of the individual measurements of variability also may be a function of concentration. This condition is known as "heteroscedasticity" or nonconstant variance. For example, even though the general relation (as shown by the smooth) of the magnitude of the *RSD* and concentration is relatively constant over the range of concentration (fig. 3), the scatter of the individual measurements of *RSD* is much greater at low concentrations than at high concentrations. Pooling the individual measurements of *RSD* for the entire range of concentration would serve to overestimate variability at high concentrations and underestimate variability at low concentrations. Consequently, estimates of the variability of pesticide detections or concentrations were pooled separately for selected ranges of concentration where the magnitude of the variability (and the scatter of the individual measurements) is constant or relatively constant over the range of concentration.

Regression equations were not used to model variability of concentrations because regression models did not adequately describe the relation between variability and concentration. Even the nonlinear least-squares regression model used by Mueller (1998, p. 6) provided poor fit, perhaps because standard deviation increased with concentration over the entire range of concentration and did not exhibit regions of constant standard deviation at very high or very low concentrations as did replicates for nutrients. In addition, estimates of uncertainty (confidence limits) for variability were desired but could not be calculated because the

Table 3. Comparison of variability of pesticide concentrations in surface-water and ground-water field replicates

[Replicate sets with no detections or inconsistent detections were excluded from analysis. µg/L, microgram per liter; p, the probability of obtaining an *F* ratio greater than or equal to that shown by chance; parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; GW, ground water; SW, surface water; ns, not significant at p <= 0.05; *, significant at p <= 0.05; **, significant at p <= 0.01; ***, significant at p <= 0.001]

Concentration range (µg/L)	Surface-water replicates		Field replicates with greater variance	Ground-water replicates		*F* ratio	p	Statistical significance
	Degrees of freedom	Pooled standard deviation (µg/L)		Degrees of freedom	Pooled standard deviation (µg/L)			
Alachlor, parameter code 46342, analysis by GCMS, MRL 0.002 µg/L								
< 0.01	18	0.00081	SW	3	0.00041	3.9	0.2928	ns
Atrazine, parameter code 39632, analysis by GCMS, MRL 0.001 µg/L								
< 0.01	50	.0012	SW	8	.00068	3.3	.0786	ns
0.005 to < 0.05	99	.0014	GW	6	.0021	2.2	.0898	ns
0.01 to < 0.1	86	.0039	GW	6	.0043	1.3	.5736	ns
0.05 to < 0.5	78	.0130	SW	12	.0120	1.2	.8278	ns
0.1 to < 1	64	.0271	SW	9	.0135	4.0	.0298	*
Desethylatrazine, parameter code 04040, analysis by GCMS, MRL 0.002 µg/L								
< 0.01	47	.0010	SW	9	.00064	2.4	.1516	ns
0.005 to < 0.05	78	.0045	GW	8	.0057	1.6	.2521	ns
0.01 to < 0.1	83	.0061	GW	9	.0065	1.2	.6606	ns
0.05 to < 0.5	42	.0150	GW	9	.0155	1.1	.8098	ns
0.1 to < 1	24	.0273	SW	6	.0184	2.2	.3308	ns
Metolachlor, parameter code 39415, analysis by GCMS, MRL 0.002 µg/L								
0.005 to < 0.05	73	.0014	SW	4	.0010	2.0	.5320	ns
0.01 to < 0.1	74	.0023	SW	3	.0010	5.1	.2004	ns
Prometon, parameter code 04037, analysis by GCMS, MRL 0.018 µg/L								
0.005 to < 0.05	102	.0034	SW	7	.0011	9.8	.0038	**
0.01 to < 0.1	100	.0052	SW	8	.0016	10.5	.0014	**
0.05 to < 0.5	37	.0085	GW	3	.0187	4.9	.0118	*
Simazine, parameter code 04035, analysis by GCMS, MRL 0.005 µg/L								
< 0.01	33	.0011	SW	4	.00041	7.1	.0689	ns
0.005 to < 0.05	102	.0018	GW	9	.0038	4.5	.0001	***
0.01 to < 0.1	103	.0025	GW	8	.0049	3.8	.0011	**
0.05 to < 0.5	59	.0139	SW	3	.0061	5.3	.1941	ns

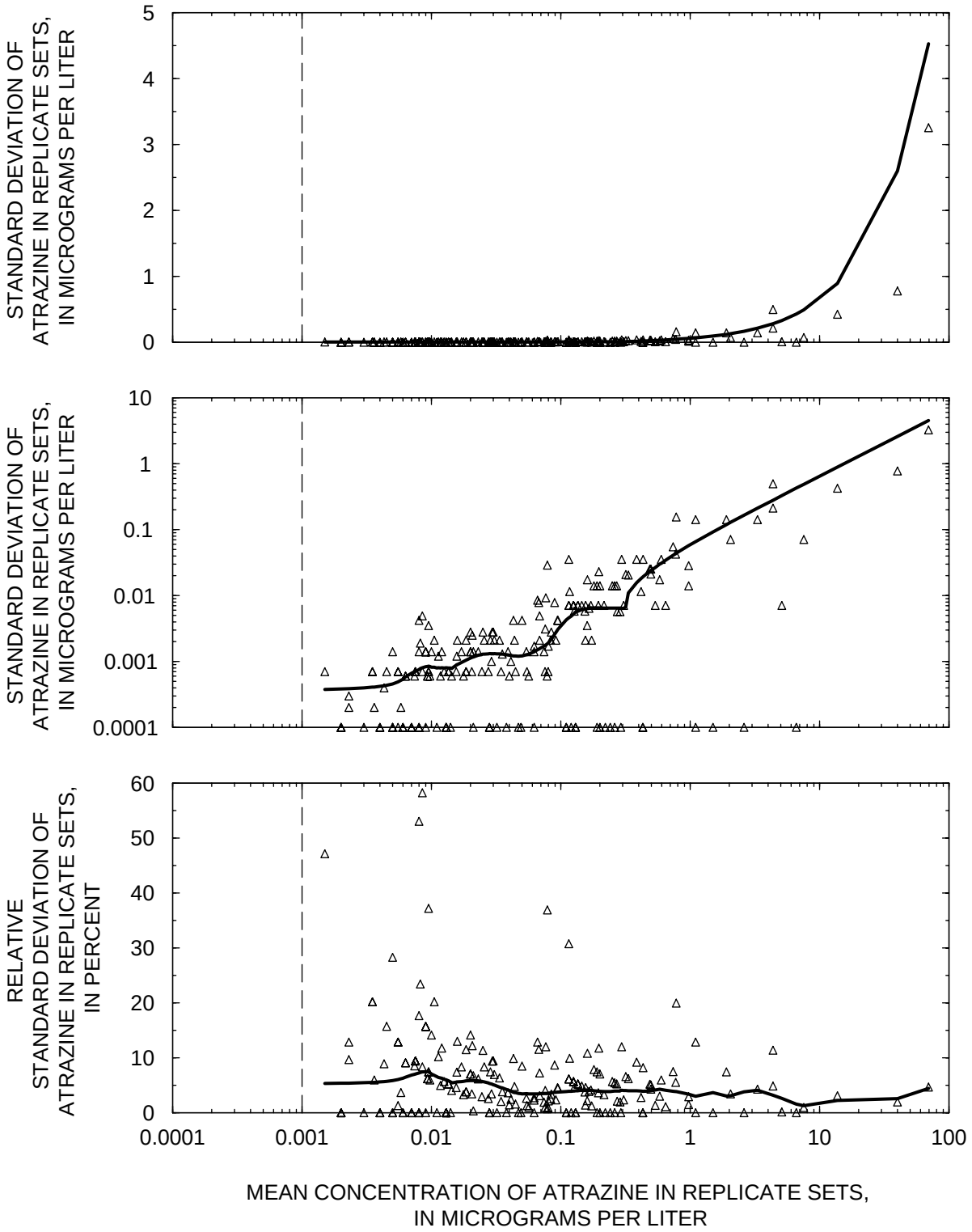


Figure 3. Variability of atrazine in field replicates. Standard deviation of 0 µg/L is plotted as 0.0001 µg/L. The solid line in the scatterplot is a smooth that shows the general relation of variability and concentration. The vertical dashed line is the minimum reporting level.

residuals from regression models were not normally distributed nor were they of constant variance over the entire range of concentration (Helsel and Hirsch, 1992, pp. 224–225). Logarithmic transformations of the concentrations only marginally improved problems of heteroscedasticity and lack of normality. Rounding of analytical data resulted in many replicate sets where the concentrations of all replicates in the set were the same and, therefore, the estimated variability was zero. Estimates of zero variability contributed greatly to lack of normality and to heteroscedasticity (fig. 3).

Replicate sets with inconsistent detections (replicate sets that contain both detections and nondetections of a pesticide) typically are deleted from assessments of the variability of concentrations because of the difficulty in assigning a concentration to a nondetection. Three approaches were used in this report for the analysis of variability of concentrations for replicate sets with inconsistent detections: (1) nondetections were deleted as is typically done, (2) nondetections were set to zero concentration, and (3) nondetections were set to the concentration of the MRL (fig. 4). The intent of setting nondetections to zero and to the MRL is an attempt to bound the probable concentration of the nondetections. For most pesticides, setting nondetections to zero probably provides a worst-case estimate of variability (estimated variability is largest), whereas deleting nondetections provides a much better case estimate of variability (estimated variability is much smaller) (fig. 4). A best-case estimate of variability could have been obtained by setting the nondetections equal to the concentration of the other replicate(s) in the set (estimated variability is the smallest). This approach, however, was not pursued because an optimistic estimate of data quality was not desired.

Estimates of the variability of concentrations using approach 1 generally are the most useful (a) for assessments of variability, (b) for comparison with other studies, (c) when assumptions about nondetections are not desired, or (d) for estimating variability in water samples where matrix interference is low. Estimates of the variability of concentrations using approaches 2 or 3 usually provide different, higher estimates of variability (generally at low concentrations) that may be appropriate for some special types of assessments including (e) estimating variability in water samples where matrix interference is high, or (f) estimating a detection limit that is more conservative (higher) than the MDL (by use of estimates of variability that incorporate the variability of detecting pesticides at low concentrations in a wide variety of natural water matrices). In essence, approach 1 estimates variability of concentration in the quantitation step of the analysis, whereas approaches 2 and 3 estimate variability of concentration in the detection and quantitation steps combined.

VARIABILITY OF PESTICIDE DETECTIONS

Variability of pesticide detections was estimated for each pesticide by calculating the mean detection rate of a pesticide in replicate sets and the percentage of replicate sets with inconsistent pesticide detections (the percentage of inconsistent replicate sets). These measures provide information on the consistency of detection. Given that a pesticide was detected in at least one replicate of a set, these measures indicate the likelihood that the pesticide also would be detected in other replicates of the set. Uncertainty in the estimates of the variability of detection was evaluated by calculating the 90-percent upper confidence bound for the percentage of inconsistent replicate sets.

The mean detection rate and the percentage of inconsistent replicate sets are closely related measures of the variability of detection. Mean detection rates that are high correspond to percentages of inconsistent replicate sets that are low, and the converse also is true. Both measures are provided because both have limitations related to either the goal of the analysis or to the characteristics of the data set. The mean detection rate is used as a measure of the variability of detection because the replicate sets in this report are a combination of duplicates and triplicates and the mean detection rate can be weighted by the number of replicates in the set, thus giving more emphasis to sets with triplicates. The major shortcoming of the mean detection rate is that an estimate of uncertainty (confidence limits) cannot be calculated for this measure of variability. The percentage of inconsistent replicate sets is the preferred measure of the variability of detection for this assessment because uncertainty in this measure of variability can be

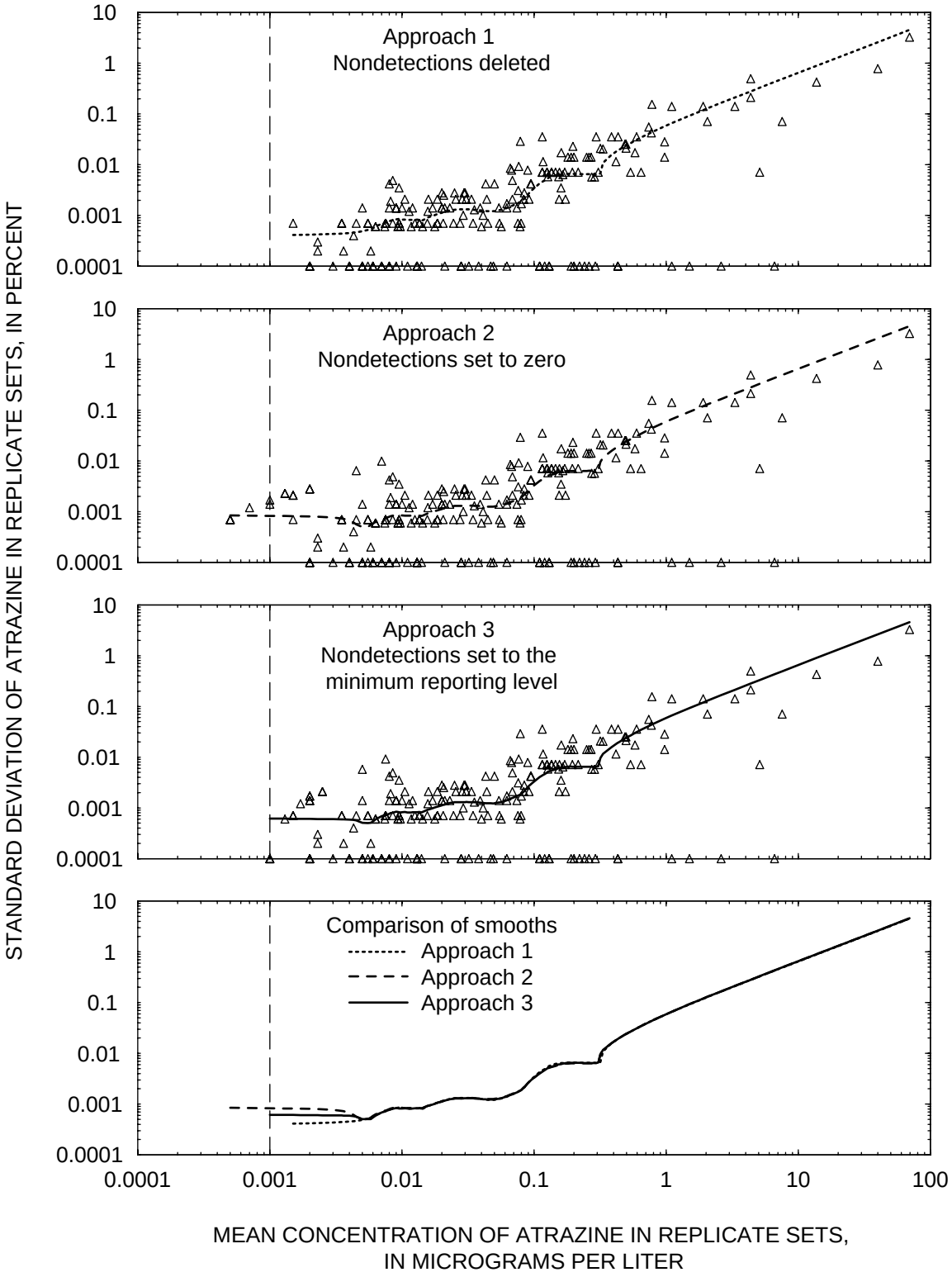


Figure 4. Three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections. Standard deviation of 0 µg/L is plotted as 0.0001 µg/L. The vertical dashed line is the minimum reporting level.

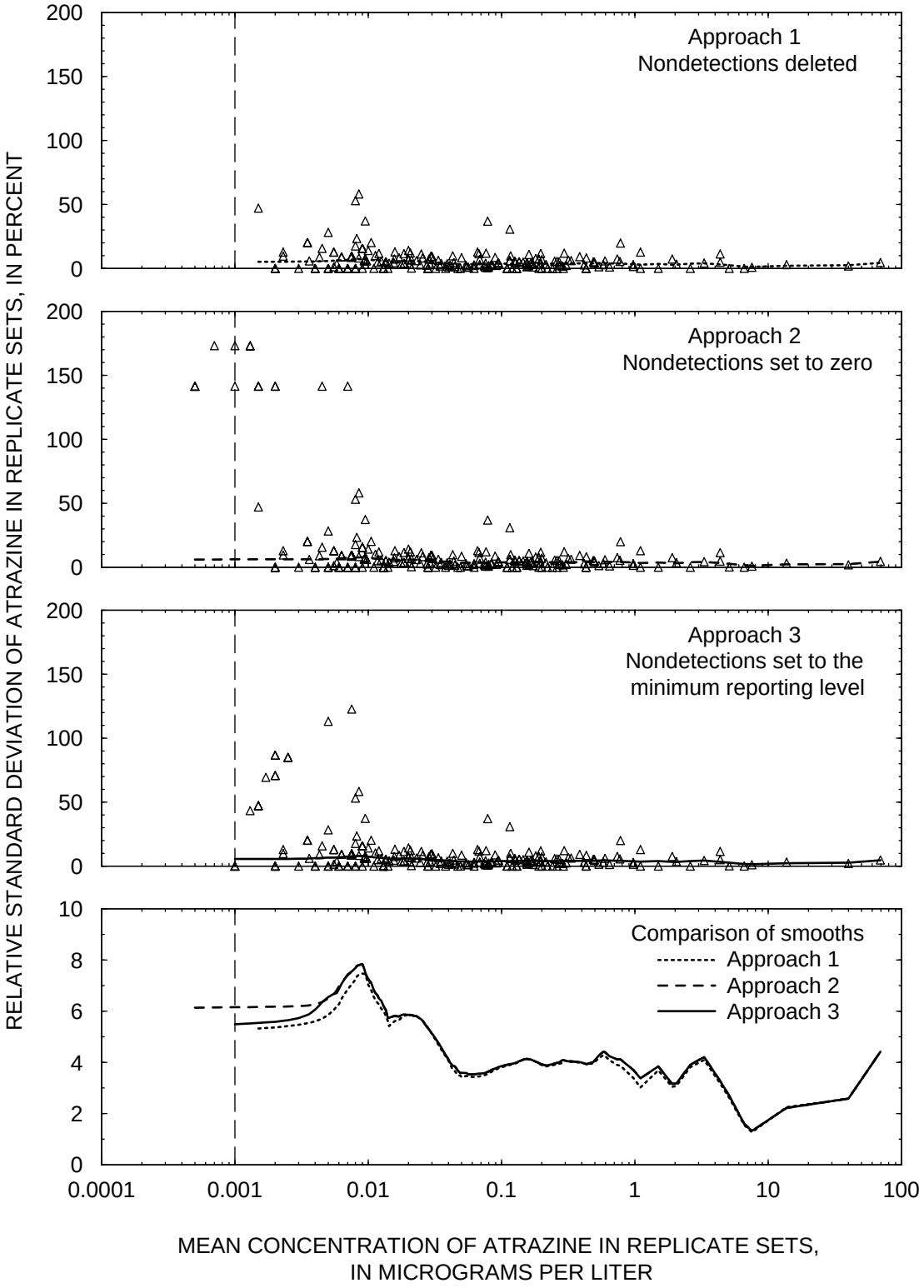


Figure 4. Three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections—Continued.

estimated by calculating confidence limits. The percentage of inconsistent replicate sets could not be weighted by the number of replicates in a set, and the shortcoming of this measure is that duplicates and triplicates are given equal weight. Detections in a single replicate set either are consistent or inconsistent (only two possible outcomes) regardless of the number of replicates in the set. Measures that have only two possible outcomes (and the percentages of these outcomes) are suitable for the calculation of confidence limits by use of the binomial distribution (Hahn and Meeker, 1991, pp. 100–108).

Although the percentage of inconsistent replicate sets is not weighted by the number of replicates in a set, this measure of variability is sensitive to the number of replicates. The likelihood of an inconsistent detection increases with the number of replicates in the set; therefore, inconsistent replicate sets are more likely for triplicates than for duplicates. The inclusion of triplicates in the analysis probably increases the percentage of inconsistent replicate sets for some pesticides over that which could be calculated on the basis of duplicates alone. Triplicates were included in the analysis because (1) sometimes they are the only replicate sets with detections; (2) a larger number of replicate sets increases the precision of the estimate of uncertainty; and (3) inclusion of triplicates increases the variability of detection, consistent with the objective of obtaining a pessimistic estimate of data quality (in estimating how high variability might be).

Variability of pesticide detection is a strong function of concentration, and mean concentrations of replicate sets for some pesticides span five orders of magnitude. Therefore, mean detection rates and the percentages of replicate sets with inconsistent detections were calculated separately for three ranges of mean concentration in replicate sets: less than the MRL (table 4), the MRL to 10 times the MRL (table 5), and more than 10 times the MRL (table 6). For convenience in the text and for relative comparisons, the three ranges of concentration are referred to as “low,” “medium,” and “high,” respectively. In an absolute sense, however, nearly all of the concentrations of the replicates are very low (less than a few tenths of a microgram per liter).

Nondetections in a replicate set were set to zero for calculating the mean concentration of the replicate set. Although replicate sets were assigned to the low, medium, and high ranges of concentration on the basis of the mean concentration of the replicate set, the median of the individual means is reported in the tables to characterize the typical concentration in the range. Data on the variability of pesticide detections presented in tables 4–6 are sorted by the mean detection rate, the percentage of sets with inconsistent detections, the number of sets with at least one detection, and pesticide name. In this presentation, pesticides with low variability and estimates based on large sample sizes are ranked above pesticides with high variability and estimates based on small sample sizes.

Twenty-two percent (19 of 86) of the pesticides analyzed for were not detected in any field replicates: aldicarb, aldicarb sulfone, chloramben, chlorothalonil, clopyralid, dacthal monoacid, 2,4-DB, dicamba, dichlorprop, 3-hydroxycarbofuran, MCPB, methiocarb, neburon, oxamyl, parathion, phorate, propham, silvex, and 2,4,5-T. Evaluation of variability of detection or concentration cannot be done for these pesticides. The number of pesticides with no detections in field replicates was 36 of 86 (42 percent) in the low range of concentration (table 4), 30 of 86 (35 percent) in the medium range of concentration (table 5), and 40 of 86 (47 percent) in the high range of concentration (table 6).

Table 4. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was less than the minimum reporting level

[Pesticides are sorted by the mean detection rate, the percentage of sets with inconsistent detections, the number of sets with at least one detection, and pesticide name. Concentration of nondetections was set to zero for calculations. Replicate sets with no detections were excluded from analysis. Median concentration may not be less than the MRL because of rounding. Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; µg/L, microgram per liter; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; nc, not calculated]

Table 4. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was less than the minimum reporting level

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
04024	Propachlor	GCMS	0.007	1	1	0	100.0	0.006	0.0	90.0
82665	Terbacil	GCMS	.007	1	1	0	100.0	.007	.0	90.0
04037	Prometon	GCMS	.018	69	58	11	92.1	.009	15.9	23.1
82685	Propargite	GCMS	.013	5	3	2	81.8	.010	40.0	75.3
04029	Bromacil	HPLC	.035	2	1	1	80.0	.013	50.0	94.9
49235	Triclopyr	HPLC	.250	2	1	1	80.0	.141	50.0	94.9
38811	Fluometuron	HPLC	.035	2	1	1	75.0	.006	50.0	94.9
04095	Fonofos	GCMS	.003	2	1	1	75.0	.002	50.0	94.9
82684	Napropamide	GCMS	.003	2	1	1	75.0	.003	50.0	94.9
82670	Tebuthiuron	GCMS	.010	35	17	18	72.2	.005	51.4	63.4
82660	2,6-Diethylaniline	GCMS	.003	11	6	5	70.8	.001	45.5	68.2
39732	2,4-D	HPLC	.150	13	5	8	69.2	.045	61.5	79.9
82682	Dacthal	GCMS	.002	18	7	11	68.4	.001	61.1	76.9
38482	MCPA	HPLC	.170	3	1	2	66.7	.005	66.7	96.5
82677	Disulfoton	GCMS	.017	1	0	1	66.7	.003	100.0	100.0
04035	Simazine	GCMS	.005	24	6	18	63.2	.003	75.0	86.3
04040	Desethylatrazine	GCMS	.002	13	3	10	61.3	.001	76.9	91.2
04028	Butylate	GCMS	.002	2	0	2	60.0	.001	100.0	100.0
82663	Ethalfluralin	GCMS	.004	2	0	2	60.0	.003	100.0	100.0
82687	*cis*-Permethrin	GCMS	.005	2	0	2	60.0	.002	100.0	100.0
34653	*p,p'*-DDE	GCMS	.006	28	7	21	59.7	.001	75.0	85.5
39415	Metolachlor	GCMS	.002	9	1	8	57.9	.002	88.9	98.8
38933	Chlorpyrifos	GCMS	.004	10	2	8	56.5	.003	80.0	94.5
39532	Malathion	GCMS	.005	6	1	5	50.0	.003	83.3	98.3
39572	Diazinon	GCMS	.002	4	0	4	50.0	.002	100.0	100.0
82683	Pendimethalin	GCMS	.004	4	0	4	50.0	.003	100.0	100.0
82668	EPTC	GCMS	.002	3	0	3	50.0	.001	100.0	100.0
49309	Carbofuran	HPLC	.120	2	0	2	50.0	.063	100.0	100.0
49315	Acifluorfen	HPLC	.035	1	0	1	50.0	.010	100.0	100.0
82674	Carbofuran	GCMS	.003	1	0	1	50.0	.003	100.0	100.0

Table 4. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was less than the minimum reporting level—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
04041	Cyanazine	GCMS	0.004	1	0	1	50.0	0.003	100.0	100.0
49303	Dichlobenil	HPLC	1.200	1	0	1	50.0	.020	100.0	100.0
49301	Dinoseb	HPLC	.035	1	0	1	50.0	.025	100.0	100.0
34253	*alpha*-HCH	GCMS	.002	1	0	1	50.0	.001	100.0	100.0
39341	*gamma*-HCH	GCMS	.004	1	0	1	50.0	.001	100.0	100.0
38478	Linuron	HPLC	.018	1	0	1	50.0	.009	100.0	100.0
82669	Pebulate	GCMS	.004	1	0	1	50.0	.003	100.0	100.0
82676	Pronamide	GCMS	.003	1	0	1	50.0	.002	100.0	100.0
38538	Propoxur	HPLC	.035	1	0	1	50.0	.020	100.0	100.0
82675	Terbufos	GCMS	.013	1	0	1	50.0	.005	100.0	100.0
39632	Atrazine	GCMS	.001	4	0	4	44.4	.001	100.0	100.0
46342	Alachlor	GCMS	.002	3	0	3	42.9	.001	100.0	100.0
82630	Metribuzin	GCMS	.004	3	0	3	42.9	.004	100.0	100.0
82661	Trifluralin	GCMS	.002	6	0	6	40.0	.001	100.0	100.0
38711	Bentazon	HPLC	.014	1	0	1	33.3	.013	100.0	100.0
82680	Carbaryl	GCMS	.003	1	0	1	33.3	.002	100.0	100.0
49300	Diuron	HPLC	.020	1	0	1	33.3	.010	100.0	100.0
82667	Methyl parathion	GCMS	.006	1	0	1	33.3	.003	100.0	100.0
82679	Propanil	GCMS	.004	1	0	1	33.3	.002	100.0	100.0
82678	Triallate	GCMS	.001	1	0	1	33.3	.001	100.0	100.0
49260	Acetochlor	GCMS	.002	0	0	0	nc	nc	nc	nc
49312	Aldicarb	HPLC	.550	0	0	0	nc	nc	nc	nc
49313	Aldicarb sulfone	HPLC	.100	0	0	0	nc	nc	nc	nc
49314	Aldicarb sulfoxide	HPLC	.021	0	0	0	nc	nc	nc	nc
82686	Azinphos-methyl	GCMS	.001	0	0	0	nc	nc	nc	nc
82673	Benfluralin	GCMS	.002	0	0	0	nc	nc	nc	nc
49311	Bromoxynil	HPLC	.035	0	0	0	nc	nc	nc	nc
49310	Carbaryl	HPLC	.008	0	0	0	nc	nc	nc	nc
49307	Chloramben	HPLC	.420	0	0	0	nc	nc	nc	nc
49306	Chlorothalonil	HPLC	.480	0	0	0	nc	nc	nc	nc
49305	Clopyralid	HPLC	.230	0	0	0	nc	nc	nc	nc
49304	Dacthal monoacid	HPLC	.017	0	0	0	nc	nc	nc	nc
38746	2,4-DB	HPLC	.240	0	0	0	nc	nc	nc	nc
38442	Dicamba	HPLC	.035	0	0	0	nc	nc	nc	nc
49302	Dichlorprop	HPLC	.032	0	0	0	nc	nc	nc	nc

Table 4. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was less than the minimum reporting level—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
39381	Dieldrin	GCMS	0.001	0	0	0	nc	nc	nc	nc
49299	DNOC	HPLC	.420	0	0	0	nc	nc	nc	nc
82672	Ethoprop	GCMS	.003	0	0	0	nc	nc	nc	nc
49297	Fenuron	HPLC	.013	0	0	0	nc	nc	nc	nc
49308	3-Hydroxycarbofuran	HPLC	.014	0	0	0	nc	nc	nc	nc
82666	Linuron	GCMS	.002	0	0	0	nc	nc	nc	nc
38487	MCPB	HPLC	.140	0	0	0	nc	nc	nc	nc
38501	Methiocarb	HPLC	.026	0	0	0	nc	nc	nc	nc
49296	Methomyl	HPLC	.017	0	0	0	nc	nc	nc	nc
82671	Molinate	GCMS	.004	0	0	0	nc	nc	nc	nc
49294	Neburon	HPLC	.015	0	0	0	nc	nc	nc	nc
49293	Norflurazon	HPLC	.024	0	0	0	nc	nc	nc	nc
49292	Oryzalin	HPLC	.310	0	0	0	nc	nc	nc	nc
38866	Oxamyl	HPLC	.018	0	0	0	nc	nc	nc	nc
39542	Parathion	GCMS	.004	0	0	0	nc	nc	nc	nc
82664	Phorate	GCMS	.002	0	0	0	nc	nc	nc	nc
49291	Picloram	HPLC	.050	0	0	0	nc	nc	nc	nc
49236	Propham	HPLC	.035	0	0	0	nc	nc	nc	nc
39762	Silvex	HPLC	.021	0	0	0	nc	nc	nc	nc
39742	2,4,5-T	HPLC	.035	0	0	0	nc	nc	nc	nc
82681	Thiobencarb	GCMS	.002	0	0	0	nc	nc	nc	nc
	Total			310	124	186	nc	nc	60.0	nc

Table 5. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was greater than or equal to the minimum reporting level and was less than or equal to 10 times the minimum reporting level

[Pesticides are sorted by the mean detection rate, the percentage of sets with inconsistent detections, the number of sets with at least one detection, and pesticide name. Concentration of nondetections was set to zero for calculations. Replicate sets with no detections were excluded from analysis. Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; µg/L, microgram per liter; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; nc, not calculated]

Table 5. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was greater than or equal to the minimum reporting level and was less than or equal to 10 times the minimum reporting level

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
04028	Butylate	GCMS	0.002	12	12	0	100.0	0.006	0.0	17.5
82684	Napropamide	GCMS	.003	10	10	0	100.0	.010	.0	20.6
82667	Methyl parathion	GCMS	.006	4	4	0	100.0	.020	.0	43.8
82685	Propargite	GCMS	.013	4	4	0	100.0	.065	.0	43.8
82665	Terbacil	GCMS	.007	4	4	0	100.0	.017	.0	43.8
82663	Ethalfluralin	GCMS	.004	3	3	0	100.0	.023	.0	53.6
82672	Ethoprop	GCMS	.003	3	3	0	100.0	.004	.0	53.6
38811	Fluometuron	HPLC	.035	3	3	0	100.0	.115	.0	53.6
82671	Molinate	GCMS	.004	3	3	0	100.0	.011	.0	53.6
82669	Pebulate	GCMS	.004	3	3	0	100.0	.024	.0	53.6
82660	2,6-Diethylaniline	GCMS	.003	2	2	0	100.0	.007	.0	68.4
38478	Linuron	HPLC	.018	2	2	0	100.0	.071	.0	68.4
49293	Norflurazon	HPLC	.024	2	2	0	100.0	.088	.0	68.4
04024	Propachlor	GCMS	.007	2	2	0	100.0	.031	.0	68.4
82686	Azinphos-methyl	GCMS	.001	1	1	0	100.0	.006	.0	90.0
49309	Carbofuran	HPLC	.120	1	1	0	100.0	.790	.0	90.0
49299	DNOC	HPLC	.420	1	1	0	100.0	.505	.0	90.0
49292	Oryzalin	HPLC	.310	1	1	0	100.0	.515	.0	90.0
49291	Picloram	HPLC	.050	1	1	0	100.0	.110	.0	90.0
04035	Simazine	GCMS	.005	99	98	1	99.5	.017	1.0	3.9
04037	Prometon	GCMS	.018	73	71	2	98.8	.043	2.7	7.1
82682	Dacthal	GCMS	.002	36	35	1	98.7	.004	2.8	10.4
82670	Tebuthiuron	GCMS	.010	34	33	1	98.6	.020	2.9	11.0
82668	EPTC	GCMS	.002	28	27	1	98.3	.007	3.6	13.2
04095	Fonofos	GCMS	.003	18	17	1	97.4	.005	5.6	19.9
39532	Malathion	GCMS	.005	12	11	1	96.2	.010	8.3	28.7
39415	Metolachlor	GCMS	.002	70	64	6	96.0	.007	8.6	14.6
04040	Desethylatrazine	GCMS	.002	80	73	7	95.9	.005	8.8	14.3
38933	Chlorpyrifos	GCMS	.004	52	45	7	92.8	.010	13.5	21.6
39732	2,4-D	HPLC	.150	6	5	1	92.3	.397	16.7	51.0

Table 5. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was greater than or equal to the minimum reporting level and was less than or equal to 10 times the minimum reporting level —Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
34653	*p,p'*-DDE	GCMS	0.006	6	5	1	92.3	0.011	16.7	51.0
82676	Pronamide	GCMS	.003	6	5	1	91.7	.010	16.7	51.0
46342	Alachlor	GCMS	.002	44	37	7	91.5	.007	15.9	25.3
82678	Triallate	GCMS	.001	11	9	2	91.3	.004	18.2	41.5
39572	Diazinon	GCMS	.002	59	48	11	91.1	.008	18.6	26.8
82666	Linuron	GCMS	.002	5	4	1	90.9	.016	20.0	58.4
39632	Atrazine	GCMS	.001	60	50	10	90.2	.006	16.7	24.5
82661	Trifluralin	GCMS	.002	29	23	6	90.2	.007	20.7	33.5
49300	Diuron	HPLC	.020	14	11	3	89.7	.067	21.4	41.7
04041	Cyanazine	GCMS	.004	35	27	8	89.2	.012	22.9	34.5
82681	Thiobencarb	GCMS	.002	4	3	1	87.5	.009	25.0	68.0
82683	Pendimethalin	GCMS	.004	15	11	4	86.7	.010	26.7	46.4
82680	Carbaryl	GCMS	.003	34	24	10	86.3	.011	29.4	41.6
49310	Carbaryl	HPLC	.008	3	2	1	83.3	.033	33.3	80.4
82630	Metribuzin	GCMS	.004	26	16	10	81.5	.008	38.5	52.9
49260	Acetochlor	GCMS	.002	4	3	1	80.0	.006	25.0	68.0
39341	*gamma*-HCH	GCMS	.004	5	3	2	80.0	.009	40.0	75.3
82674	Carbofuran	GCMS	.003	13	6	7	75.9	.011	53.8	73.6
49315	Acifluorfen	HPLC	.035	2	1	1	75.0	.105	50.0	94.9
04029	Bromacil	HPLC	.035	2	1	1	75.0	.100	50.0	94.9
49311	Bromoxynil	HPLC	.035	2	1	1	75.0	.093	50.0	94.9
39381	Dieldrin	GCMS	.001	12	6	6	74.1	.004	50.0	71.2
38711	Bentazon	HPLC	.014	5	2	3	70.0	.110	60.0	88.8
82673	Benfluralin	GCMS	.002	4	1	3	70.0	.004	75.0	97.4
82679	Propanil	GCMS	.004	2	1	1	66.7	.007	50.0	94.9
49296	Methomyl	HPLC	.017	1	0	1	50.0	.050	100.0	100.0
38538	Propoxur	HPLC	.035	1	0	1	50.0	.130	100.0	100.0
49312	Aldicarb	HPLC	.550	0	0	0	nc	nc	nc	nc
49313	Aldicarb sulfone	HPLC	.100	0	0	0	nc	nc	nc	nc
49314	Aldicarb sulfoxide	HPLC	.021	0	0	0	nc	nc	nc	nc
49307	Chloramben	HPLC	.420	0	0	0	nc	nc	nc	nc
49306	Chlorothalonil	HPLC	.480	0	0	0	nc	nc	nc	nc
49305	Clopyralid	HPLC	.230	0	0	0	nc	nc	nc	nc
49304	Dacthal monoacid	HPLC	.017	0	0	0	nc	nc	nc	nc
38746	2,4-DB	HPLC	.240	0	0	0	nc	nc	nc	nc

Table 5. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was greater than or equal to the minimum reporting level and was less than or equal to 10 times the minimum reporting level —Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
38442	Dicamba	HPLC	0.035	0	0	0	nc	nc	nc	nc
49303	Dichlobenil	HPLC	1.200	0	0	0	nc	nc	nc	nc
49302	Dichlorprop	HPLC	.032	0	0	0	nc	nc	nc	nc
49301	Dinoseb	HPLC	.035	0	0	0	nc	nc	nc	nc
82677	Disulfoton	GCMS	.017	0	0	0	nc	nc	nc	nc
49297	Fenuron	HPLC	.013	0	0	0	nc	nc	nc	nc
34253	*alpha*-HCH	GCMS	.002	0	0	0	nc	nc	nc	nc
49308	3-Hydroxycarbofuran	HPLC	.014	0	0	0	nc	nc	nc	nc
38482	MCPA	HPLC	.170	0	0	0	nc	nc	nc	nc
38487	MCPB	HPLC	.140	0	0	0	nc	nc	nc	nc
38501	Methiocarb	HPLC	.026	0	0	0	nc	nc	nc	nc
49294	Neburon	HPLC	.015	0	0	0	nc	nc	nc	nc
38866	Oxamyl	HPLC	.018	0	0	0	nc	nc	nc	nc
39542	Parathion	GCMS	.004	0	0	0	nc	nc	nc	nc
82687	*cis*-Permethrin	GCMS	.005	0	0	0	nc	nc	nc	nc
82664	Phorate	GCMS	.002	0	0	0	nc	nc	nc	nc
49236	Propham	HPLC	.035	0	0	0	nc	nc	nc	nc
39762	Silvex	HPLC	.021	0	0	0	nc	nc	nc	nc
39742	2,4,5-T	HPLC	.035	0	0	0	nc	nc	nc	nc
82675	Terbufos	GCMS	.013	0	0	0	nc	nc	nc	nc
49235	Triclopyr	HPLC	.250	0	0	0	nc	nc	nc	nc
	Total			940	841	133	nc	nc	13.7	nc

Table 6. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was more than 10 times the minimum reporting level

[Pesticides are sorted by the mean detection rate, the percentage of sets with inconsistent detections, the number of sets with at least one detection, and pesticide name. Concentration of nondetections was set to zero for calculations. Replicate sets with no detections were excluded from analysis. Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; µg/L, microgram per liter; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; nc, not calculated]

Table 6. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was more than 10 times the minimum reporting level

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
39632	Atrazine	GCMS	0.001	156	156	0	100.0	0.095	0.0	1.5
39415	Metolachlor	GCMS	.002	89	89	0	100.0	.113	.0	2.6
04040	Desethylatrazine	GCMS	.002	82	82	0	100.0	.052	.0	2.8
04035	Simazine	GCMS	.005	64	64	0	100.0	.145	.0	3.5
04041	Cyanazine	GCMS	.004	42	42	0	100.0	.178	.0	5.3
46342	Alachlor	GCMS	.002	28	28	0	100.0	.065	.0	7.9
82668	EPTC	GCMS	.002	19	19	0	100.0	.058	.0	11.4
38933	Chlorpyrifos	GCMS	.004	10	10	0	100.0	.128	.0	20.6
49260	Acetochlor	GCMS	.002	8	8	0	100.0	.196	.0	25.0
82674	Carbofuran	GCMS	.003	8	8	0	100.0	.120	.0	25.0
82682	Dacthal	GCMS	.002	8	8	0	100.0	.051	.0	25.0
82671	Molinate	GCMS	.004	8	8	0	100.0	1.975	.0	25.0
82683	Pendimethalin	GCMS	.004	7	7	0	100.0	.060	.0	28.0
82661	Trifluralin	GCMS	.002	7	7	0	100.0	.062	.0	28.0
38711	Bentazon	HPLC	.014	6	6	0	100.0	.193	.0	31.9
39381	Dieldrin	GCMS	.001	6	6	0	100.0	.015	.0	31.9
82666	Linuron	GCMS	.002	5	5	0	100.0	.125	.0	36.9
39532	Malathion	GCMS	.005	5	5	0	100.0	.063	.0	36.9
82684	Napropamide	GCMS	.003	4	4	0	100.0	.064	.0	43.8
82670	Tebuthiuron	GCMS	.010	4	4	0	100.0	.203	.0	43.8
82678	Triallate	GCMS	.001	4	4	0	100.0	.054	.0	43.8
04095	Fonofos	GCMS	.003	3	3	0	100.0	.059	.0	53.6
39341	*gamma*-HCH	GCMS	.004	3	3	0	100.0	.086	.0	53.6
82685	Propargite	GCMS	.013	3	3	0	100.0	.460	.0	53.6
04029	Bromacil	HPLC	.035	2	2	0	100.0	.722	.0	68.4
04028	Butylate	GCMS	.002	2	2	0	100.0	.028	.0	68.4
82663	Ethalfluralin	GCMS	.004	2	2	0	100.0	.076	.0	68.4
38811	Fluometuron	HPLC	.035	2	2	0	100.0	3.323	.0	68.4
04037	Prometon	GCMS	.018	2	2	0	100.0	.628	.0	68.4
82681	Thiobencarb	GCMS	.002	2	2	0	100.0	.027	.0	68.4

Table 6. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was more than 10 times the minimum reporting level—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
49315	Acifluorfen	HPLC	0.035	1	1	0	100.0	0.745	0.0	90.0
82672	Ethoprop	GCMS	.003	1	1	0	100.0	.043	.0	90.0
49297	Fenuron	HPLC	.013	1	1	0	100.0	.140	.0	90.0
34253	*alpha*-HCH	GCMS	.002	1	1	0	100.0	.038	.0	90.0
49293	Norflurazon	HPLC	.024	1	1	0	100.0	.575	.0	90.0
82669	Pebulate	GCMS	.004	1	1	0	100.0	.195	.0	90.0
04024	Propachlor	GCMS	.007	1	1	0	100.0	.085	.0	90.0
82679	Propanil	GCMS	.004	1	1	0	100.0	.051	.0	90.0
82665	Terbacil	GCMS	.007	1	1	0	100.0	.540	.0	90.0
39572	Diazinon	GCMS	.002	55	54	1	99.2	.051	1.8	6.9
82680	Carbaryl	GCMS	.003	22	21	1	98.0	.092	4.5	16.6
49300	Diuron	HPLC	.020	10	9	1	95.2	.795	10.0	33.7
82630	Metribuzin	GCMS	.004	9	8	1	94.7	.090	11.1	36.8
82686	Azinphos-methyl	GCMS	.001	12	10	2	92.6	.078	16.7	38.6
49310	Carbaryl	HPLC	.008	3	2	1	85.7	.495	33.3	80.4
49314	Aldicarb sulfoxide	HPLC	.021	1	0	1	50.0	.900	100.0	100.0
49312	Aldicarb	HPLC	.550	0	0	0	nc	nc	nc	nc
49313	Aldicarb sulfone	HPLC	.100	0	0	0	nc	nc	nc	nc
82673	Benfluralin	GCMS	.002	0	0	0	nc	nc	nc	nc
49311	Bromoxynil	HPLC	.035	0	0	0	nc	nc	nc	nc
49309	Carbofuran	HPLC	.120	0	0	0	nc	nc	nc	nc
49307	Chloramben	HPLC	.420	0	0	0	nc	nc	nc	nc
49306	Chlorothalonil	HPLC	.480	0	0	0	nc	nc	nc	nc
49305	Clopyralid	HPLC	.230	0	0	0	nc	nc	nc	nc
39732	2,4-D	HPLC	.150	0	0	0	nc	nc	nc	nc
49304	Dacthal monoacid	HPLC	.017	0	0	0	nc	nc	nc	nc
38746	2,4-DB	HPLC	.240	0	0	0	nc	nc	nc	nc
34653	*p,p'*-DDE	GCMS	.006	0	0	0	nc	nc	nc	nc
38442	Dicamba	HPLC	.035	0	0	0	nc	nc	nc	nc
49303	Dichlobenil	HPLC	1.200	0	0	0	nc	nc	nc	nc
49302	Dichlorprop	HPLC	.032	0	0	0	nc	nc	nc	nc
82660	2,6-Diethylaniline	GCMS	.003	0	0	0	nc	nc	nc	nc
49301	Dinoseb	HPLC	.035	0	0	0	nc	nc	nc	nc
82677	Disulfoton	GCMS	.017	0	0	0	nc	nc	nc	nc

Table 6. Variability of pesticide detections in field replicates where mean concentration of the replicate sets was more than 10 times the minimum reporting level—Continued

Parameter code	Pesticide	Analytical method	MRL (µg/L)	Number of replicate sets where replicates in the set have			Mean detection rate (percent)	Median concentration (µg/L)	Replicate sets with inconsistent detections (percent)	
				At least one detection	Consistent detections	Inconsistent detections			Measured	90-percent upper confidence bound
49299	DNOC	HPLC	0.420	0	0	0	nc	nc	nc	nc
49308	3-Hydroxycarbofuran	HPLC	.014	0	0	0	nc	nc	nc	nc
38478	Linuron	HPLC	.018	0	0	0	nc	nc	nc	nc
38482	MCPA	HPLC	.170	0	0	0	nc	nc	nc	nc
38487	MCPB	HPLC	.140	0	0	0	nc	nc	nc	nc
38501	Methiocarb	HPLC	.026	0	0	0	nc	nc	nc	nc
49296	Methomyl	HPLC	.017	0	0	0	nc	nc	nc	nc
82667	Methyl parathion	GCMS	.006	0	0	0	nc	nc	nc	nc
49294	Neburon	HPLC	.015	0	0	0	nc	nc	nc	nc
49292	Oryzalin	HPLC	.310	0	0	0	nc	nc	nc	nc
38866	Oxamyl	HPLC	.018	0	0	0	nc	nc	nc	nc
39542	Parathion	GCMS	.004	0	0	0	nc	nc	nc	nc
82687	*cis*-Permethrin	GCMS	.005	0	0	0	nc	nc	nc	nc
82664	Phorate	GCMS	.002	0	0	0	nc	nc	nc	nc
49291	Picloram	HPLC	.050	0	0	0	nc	nc	nc	nc
82676	Pronamide	GCMS	.003	0	0	0	nc	nc	nc	nc
49236	Propham	HPLC	.035	0	0	0	nc	nc	nc	nc
38538	Propoxur	HPLC	.035	0	0	0	nc	nc	nc	nc
39762	Silvex	HPLC	.021	0	0	0	nc	nc	nc	nc
39742	2,4,5-T	HPLC	.035	0	0	0	nc	nc	nc	nc
82675	Terbufos	GCMS	.013	0	0	0	nc	nc	nc	nc
49235	Triclopyr	HPLC	.250	0	0	0	nc	nc	nc	nc
	Total			712	704	8	nc	nc	1.1	nc

Mean Detection Rate

The mean detection rate is a measure of the variability of pesticide detection and shows the overall rate of detection of a pesticide in field replicates for a given range of concentration. For example, in the medium range of concentration, simazine was detected in 99 replicate sets that had mean concentrations greater than or equal to 0.005 µg/L (the MRL for simazine) and less than or equal to 0.050 µg/L (10 times the MRL for simazine). Simazine was detected in all replicates in 98 of the 99 sets, but in 1 of the 99 replicate sets simazine was inconsistently detected (table 5). The mean detection rate for simazine is 99.5 percent, which indicates very low variability in the detection of simazine in the medium range of concentration. On the basis of the high mean detection rate and the large number of replicate sets with at least one detection, data users are assured that detections of simazine at concentrations between 0.005 µg/L and 0.050 µg/L are reproducible.

In the low range of concentration (less than 0.005 µg/L, the MRL for simazine), simazine was detected in 24 replicates (table 4). Simazine was detected in all replicates in 6 of the 24 sets but was inconsistently detected in 18 of the 24 replicate sets. The mean detection rate for simazine is 63.2 percent, which indicates high variability in the detection of simazine at concentrations less than the MRL. On the basis of the low mean detection rate and the relatively large number of replicate sets with at least one detection, data users are assured that detections of simazine at concentrations less than 0.005 µg/L are not reproducible.

The variability of detection for most pesticides is high at concentrations less than the MRL but the variability of detection decreases dramatically at higher concentrations (fig. 5). A mean detection rate of 75 percent or less is used in this assessment to indicate high variability of detection, whereas a mean detection rate of 90 percent or more is used to indicate low variability of detection. The number of pesticides where the mean detection rate indicates high variability of detection is 44 of 50 (88 percent) in the low range, 9 of 57 (16 percent) in the medium range, and 1 of 46 (2 percent) in the high range. The number of pesticides where the mean detection rate indicates low variability of detection is 3 of 50 (6 percent) in the low range, 38 of 57 (67 percent) in the medium range, and 44 of 46 (96 percent) in the high range. Prometon is a notable counterexample—a pesticide with low variability of detection at concentrations less than the MRL (table 4).

Replicate Sets with Inconsistent Detections

The percentage of replicate sets with inconsistent detections also is a measure of the variability of detection. The percentage of replicate sets with inconsistent detections measures the frequency that a pesticide was detected in at least one, but not all, replicates in a set. In the context of the variability of detection in environmental samples, this measure estimates the likelihood that a pesticide that is detected in an environmental sample would not have been detected in a duplicate sample. Alternately, the likelihood that a pesticide would have been detected in a duplicate sample (an estimate of the consistency of detection) is 100 percent minus the percentage of replicate sets with inconsistent detections. Although duplicates and triplicates were included in this assessment, most replicate sets were duplicates (88 percent), and restricting the inference to the likelihood of not detecting (or detecting) a pesticide in a duplicate sample helps clarify the application of this measure of data quality.

For example, diazinon was detected in 59 replicate sets that had mean concentrations greater than or equal to 0.002 µg/L (the MRL for diazinon) and less than or equal to 0.020 µg/L (10 times the MRL for diazinon). Diazinon was detected in all replicates in 48 of the 59 sets but was inconsistently detected in 11 of the 59 replicate sets (table 5). The percentage of replicate sets with inconsistent detections for diazinon, 18.6 percent, indicates low variability in the detection of diazinon in the medium concentration range. Alternately stated, the percentage of replicate sets with consistent detections for diazinon is 81.4 percent (100 percent minus 18.6 percent). On the basis of the low percentage of replicate sets with inconsistent detections and the large number of replicate sets with at least one detection, data users are assured that detections of diazinon at concentrations between 0.002 and 0.020 µg/L are reproducible.

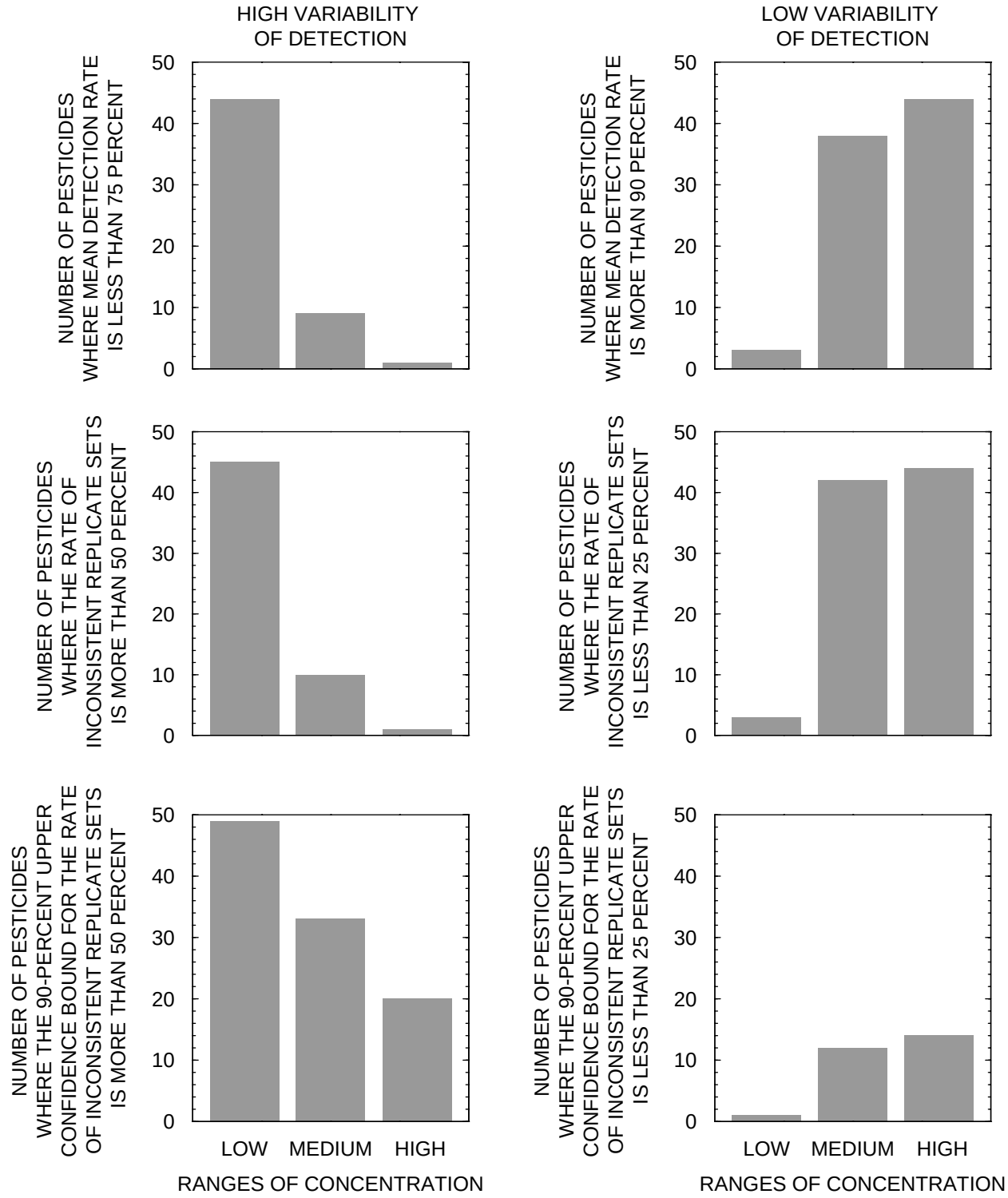


Figure 5. Variability of detection of pesticides in field replicates. Ranges of concentration are a function of the minimum reporting level (MRL) for a pesticide (Low, less than the MRL; Medium, the MRL to 10 times the MRL; High, more than 10 times the MRL).

As with the mean detection rate, variability of detection measured by the percentage of inconsistent replicate sets is high at concentrations less than the MRL but decreases with increasing concentrations (fig. 5). A percentage of inconsistent replicate sets of 25 percent or less is used in this assessment to indicate that variability of detection is low, whereas a percentage of 50 percent or more is used to indicate that variability of detection is high. The number of pesticides where the percentage of inconsistent replicate sets indicates low variability of detection is 3 of 50 (6 percent) in the low range (table 4), 42 of 57 (74 percent) in the medium range (table 5), and 44 of 46 (96 percent) in the high range (table 6). The number of pesticides where the percentage of inconsistent replicate sets indicate high variability of detection is 45 of 50 (90 percent) in the low range, 10 of 57 (18 percent) in the medium range, and 1 of 46 (2 percent) in the high range. The numbers of replicate sets were summed within concentration range for all pesticides (tables 4–6). The overall rate of inconsistent replicate sets is 60.0 percent in the low range, 13.7 percent in the medium range, and 1.1 percent in the high range.

Inconsistent detections are caused by either false-positive or false-negative errors. (See section "Analytical Methods for Pesticides.") Because field replicates, rather than reference materials of known composition, were used to assess inconsistent detections, one cannot determine with certainty the cause of an inconsistent detection for a particular replicate set. False-positive errors usually are caused by sample contamination, whereas false-negative errors usually are caused by water-matrix interference, pesticide degradation, or other chemical-loss processes. Both types of errors may be caused by variability inherent in the analytical method but, as discussed previously, calculation and use of MDLs are intended to protect against false-positive errors.

In an assessment of sample contamination for the NAWQA Program, 63 of the pesticides analyzed for were not detected in any field blank (Martin and others, 1999, p. 24). Of those pesticides that were detected in field blanks, only atrazine, simazine, metolachlor, and *p,p'*-DDE were detected in more than 3 percent of the field blanks (Martin and others, 1999, tables 1–4). On the basis of the low frequency of detection in field blanks, sample contamination is an unlikely cause of inconsistent detections in replicate sets. In view of the highly diverse sources of water submitted as field replicates for the NAWQA Program and the generally low concentrations (concentrations in 79 percent of replicate sets were less than 0.1 μg/L) of pesticides in most replicates, inconsistent detections in replicate sets likely were caused by variability in the analytical method and by water-matrix interferences (or other loss processes) that result in false-negative errors. Additional support for this hypothesis is found in histograms of the distribution of pesticide concentrations in environmental surface-water samples of the NAWQA Program. Most pesticides are detected much more frequently at low concentrations than at high concentrations, and many histograms of pesticide concentrations show a gradual increase in the frequency of detection as concentration decreases. At concentrations at and near the MRL, however, the frequency of detection for many pesticides changes and decreases markedly (S.J. Larson, U.S. Geological Survey, written commun., July, 14, 1997). The decreased frequency of pesticide detections at concentrations near and below the MRL probably can be attributed to false-negative errors rather than a true decrease in environmental concentrations. Both lines of evidence indicate that estimates of the frequency of detection of pesticides in environmental water samples collected for the NAWQA Program probably are biased low because of false-negative errors at concentrations near the MRL.

The measured percentage of inconsistent replicate sets in tables 4–6 only is an estimate of the unknown, true percentage of inconsistent replicate sets in the population of all possible replicate sets that could have been collected for the NAWQA Program. Confidence limits quantify knowledge about the true percentage of inconsistent replicate sets in the population by providing a probability-based estimate of the uncertainty in the measured percentage. A one-sided, upper confidence limit (termed an upper confidence "bound") was calculated to estimate an upper limit of the percentage of inconsistent replicate sets in the population of all possible replicates sets at the 90-percent confidence level. An upper confidence bound is used because the objective of the analysis is to make a pessimistic estimate of detection variability; that is, how high might the variability of

detection truly be? The precision of the estimate of uncertainty in the measured rate of detection variability (the length of the upper confidence bound) primarily is a function of sample size (Hahn, 1979, pp. 294–295), which is the number of replicate sets with at least one detection.

The upper confidence bound for the percentage of replicate sets with inconsistent detections is an estimate of the uncertainty in the measured rate of detection variability and provides an upper limit of the likelihood that a pesticide detected in an environmental sample would fail to be detected in a duplicate sample. Alternatively, a lower limit of the likelihood that a pesticide detected in an environmental sample also would be detected in a duplicate sample (also a pessimistic estimate of detection variability) can be approximated as 100 percent minus the upper confidence bound.

For example, diazinon was detected in 55 replicate sets that had mean concentrations greater than 0.020 µg/L (10 times the MRL for diazinon). The median concentration of diazinon in the 55 replicate sets is 0.051 µg/L (table 6). Diazinon was detected in all replicates in 54 of the 55 sets but was inconsistently detected in 1 of the 55 replicate sets. The percentage of replicate sets with inconsistent detections for diazinon, 1.8 percent (1 divided by 55 multiplied by 100 percent), indicates very low variability in the detection of diazinon in the high range of concentration. The 90-percent upper confidence bound for the measured percentage of replicate sets with inconsistent detections of diazinon is 6.9 percent (table 6). Therefore, the probability is less than 10 percent that the true percentage of inconsistent replicate sets for diazinon is greater than 6.9 percent. Data users are 90 percent confident that the true percentage of inconsistent replicate sets for diazinon is less than or equal to 6.9 percent. In the context of variability of detection of diazinon in environmental samples, data users are 90 percent confident that, when detected in environmental samples, diazinon would fail to be detected in only 6.9 percent or less of duplicate samples.

Alternatively, the percentage of replicate sets with consistent detections of diazinon is 98.2 percent (100 percent minus 1.6 percent). The approximate 90-percent lower confidence bound for the measured percentage of replicate sets with consistent detections of diazinon is 93.1 percent (100 percent minus 6.9 percent). Therefore, the probability is less than 10 percent that the true percentage of consistent replicate sets is less than 93.1 percent. Data users are 90 percent confident that the true percentage of consistent replicate sets in the high range of concentration is more than or equal to 93.1 percent. In the context of variability of detection of diazinon in environmental samples, data users are 90 percent confident that, when detected in environmental samples, diazinon also would be detected in 93.1 percent or more of duplicate samples. Data users have a high degree of confidence that detections of diazinon at concentrations greater than 0.020 µg/L are reproducible.

As expected, the pessimistic estimate of detection variability for all three ranges of concentration indicates many pesticides where detection variability is or might be high and fewer pesticides where data users are confident that detection variability is low (fig. 5). The number of pesticides where the upper confidence bound for the percentage of inconsistent replicate sets indicates high variability of detection is 49 of 50 (98 percent) in the low range, 33 of 57 (58 percent) in the medium range, and 20 of 46 (43 percent) in the high range. The number of pesticides where the upper confidence bound for the percentage of inconsistent replicate sets indicates low variability of detection is 1 of 50 (2 percent) in the low range, 12 of 57 (21 percent) in the medium range, and 14 of 46 (30 percent) in the high range. For many pesticides in the medium or high ranges of concentration (propachlor, for example), the measured percentage of inconsistent replicate sets is very low or zero, yet the upper confidence bound indicates that the variability of detection could be high. Data users lack confidence that variability of detection for these pesticides truly is low because the measured percentage is based only on a small number of replicate sets with at least one detection. Future compilations of field replicates for the NAWQA Program will increase the number of replicate sets with at least one detection and will thus improve the reliability of the estimates of variability of detection.

VARIABILITY OF PESTICIDE CONCENTRATIONS

Variability of pesticide concentrations was estimated for each pesticide by calculating the pooled *SD* and pooled *RSD* of pesticide concentrations in replicate sets. Uncertainty in the estimates of variability of concentrations was evaluated by calculating the 90-percent upper confidence bounds for the pooled estimates of variability. Because variability is a strong function of concentration, variability of pesticide concentrations was estimated separately for eight overlapping ranges of concentration: less than 0.01 µg/L, 0.005 to less than 0.05 µg/L, 0.01 to less than 0.1 µg/L, 0.05 to less than 0.5 µg/L, 0.1 to less than 1 µg/L, 0.5 to less than 5 µg/L, 1 to less than 10 µg/L, and greater than or equal to 5 µg/L (table 7). Overlapping concentration ranges were used to improve estimates for concentrations that otherwise would be at the extremes of a range. In addition to the pooled estimates of variability and upper confidence bounds, selected summary statistics for replicate sets (including the median *SD* and the median *RSD*) also are provided. The median *SD* and *RSD* are useful statistics for comparisons of variability in studies where variability was modeled by regression or smoothing or determined by methods other than pooling.

Some ranges of concentration had no detections for some pesticides; consequently, estimates and statistics for these ranges of concentration are not shown in table 7. Only estimates of variability on the basis of analytical approach 1 (nondetections in inconsistent replicate sets deleted—see section "Statistical Methods, Calculations, and Analytical Approach") are provided in table 7 because they are the most generally useful and to simplify the table. Estimates of variability using all three approaches are provided in appendix 2. Ranges of concentration with no inconsistent replicates sets are shown by a single entry (no IRS) and indicate that analyses by all three approaches are identical.

General Patterns of Variability

Median values of selected statistics presented in appendix 2 were calculated for each range of concentration for all pesticides combined (table 8). The medians are based solely on the statistics published in appendix 2 and are not weighted by the number of replicate sets for each combination of pesticide and concentration range. The purpose of the medians in table 8 is to summarize the typical variability of pesticide concentrations so that (1) the variability for an individual pesticide could be compared to a benchmark for typical variability and (2) general patterns of variability among concentration ranges and analytical approaches could be investigated.

The median pooled *SD* increases markedly with increasing concentration (0.00083 µg/L to 0.42 µg/L, table 8). Scatterplots and smooths of the *SD* of replicate sets for most pesticides are similar to those for atrazine (figs. 3 and 4) and show that the *SD* increases by several orders of magnitude as mean concentration increases by several orders of magnitude. The pooled *RSD*, however, is much less a function of concentration than the pooled *SD* (particularly when nondetections in IRS are deleted) and decreases over the range of concentration (100 percent to 2.7 percent, table 8).

The three analytical approaches for IRS produced different estimates of variability, particularly at low concentrations where the frequency of IRS is most common (table 8). The lowest estimates of variability for every range of concentration are obtained by deleting nondetections in IRS (approach 1). The highest estimates of variability at ranges of concentrations less than 0.1 µg/L are obtained by setting nondetections in IRS to zero (approach 3). Estimates of variability obtained by deleting nondetections in IRS probably are most useful for water-quality assessments because this approach is widely used in assessments of variability and requires no assumptions about nondetections in IRS.

Pooled Estimates of Variability

Pooling individual measurements of variability is appropriate if the individual measurements estimate the same variance. Both *SD* and *RSD* are functions of concentration over the entire range of concentration (several orders of magnitude). The validity of pooling individual estimates of variability over limited ranges of concentration depends upon on the distribution of the individual measurements of variability in the concentration range. If the individual measurements show

Table 7. Variability of pesticide concentrations in field replicates

[All estimates of variability use analytical approach 1: Nondetections in inconsistent replicate sets deleted. Estimates based on measurements that showed increasing or decreasing variability in the range of concentration are shown in ***bold italic*** type. µg/L, microgram per liter; N, number of replicate sets; df, degrees of freedom; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; <, less than; >=, greater than or equal to; parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; MRL, minimum reporting level; nc, not calculated]

Table 7. Variability of pesticide concentrations in field replicates

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Acetochlor, parameter code 49260, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	3	4	0.00079	0.0015	0.00071	12.4	24.0	7.4	0.003	0.006	0.010
0.005 to < 0.05	5	5	.0016	.0029	.0014	***11.7***	***20.6***	***6.7***	.006	.031	.048
0.01 to < 0.1	4	4	.0018	.0035	.0014	4.3	8.3	3.2	.031	.045	.087
0.05 to < 0.5	2	2	.0051	.0157	.0042	2.0	6.2	2.0	.087	.196	.305
0.1 to < 1	1	1	.0071	.0563	.0071	2.3	18.4	2.3	nc	.305	nc
0.5 to < 5	2	2	.0583	.1796	.0566	2.5	7.8	2.5	1.43	2.47	3.51
1 to < 10	3	3	.0981	.2222	.0707	2.6	5.9	2.7	1.43	3.51	5.40
>= 5	1	1	.1485	1.182	.1485	2.7	21.9	2.7	nc	5.40	nc
Acifluorfen, parameter code 49315, analysis by HPLC, MRL 0.035 µg/L											
0.05 to < 0.5	1	1	.0778	.6190	.0778	67.6	538.2	67.6	nc	.115	nc
0.1 to < 1	2	2	.0930	.2865	.0919	48.9	150.6	40.9	.115	.430	.745
0.5 to < 5	1	1	.1061	.8441	.1061	14.2	113.3	14.2	nc	.745	nc
Alachlor, parameter code 46342, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	20	21	.00076	.00095	.00046	18.3	23.0	7.4	.003	.005	.010
0.005 to < 0.05	39	44	***.0018***	***.0021***	***.00071***	9.7	11.3	5.7	.005	.016	.036
0.01 to < 0.1	33	38	.0041	.0048	.00071	10.0	11.8	4.6	.010	.020	.073
0.05 to < 0.5	10	10	.0174	.0249	.0106	11.0	15.8	4.8	.059	.203	.460
0.1 to < 1	10	10	.0300	.0430	.0141	6.6	9.5	4.8	.155	.383	.863
0.5 to < 5	6	6	.0445	.0735	.0177	***6.4***	***10.5***	***2.1***	.515	.766	3.75
1 to < 10	2	2	.0522	.1608	.0460	2.0	6.1	2.0	1.04	2.39	3.75
Atrazine, parameter code 39632, analysis by GCMS, MRL 0.001 µg/L											
< 0.01	49	58	***.0012***	***.0013***	***.00058***	16.3	18.5	8.5	.002	.006	.010
0.005 to < 0.05	90	105	***.0014***	***.0016***	***.00071***	***11.8***	***13.0***	***6.1***	.005	.013	.049
0.01 to < 0.1	80	92	***.0039***	***.0043***	***.0014***	7.6	8.4	3.8	.010	.030	.095
0.05 to < 0.5	78	90	***.0128***	***.0142***	***.0058***	7.5	8.3	4.0	.050	.135	.497
0.1 to < 1	62	73	***.0258***	***.0289***	***.0071***	6.9	7.8	4.4	.110	.208	.970
0.5 to < 5	18	20	.1396	.1770	.0389	7.1	9.0	3.9	.535	1.04	4.35
1 to < 10	12	12	.1732	.2390	.0707	5.8	8.0	2.2	1.10	2.95	7.55
>= 5	6	6	***1.377***	***2.271***	***.2475***	***2.5***	***4.1***	***1.4***	5.10	10.6	69.4
Azinphos-methyl, parameter code 82686, analysis by GCMS, MRL 0.001 µg/L											
< 0.01	1	1	.0014	.0113	.0014	23.6	187.6	23.6	nc	.006	nc
0.005 to < 0.05	4	5	.0030	.0053	.0025	19.9	35.1	20.1	.006	.020	.027
0.01 to < 0.1	6	9	.0116	.0171	.0039	20.0	29.4	12.7	.015	.050	.085
0.05 to < 0.5	7	9	.0431	.0633	.0141	21.7	31.9	8.7	.073	.125	.465
0.1 to < 1	4	4	.0623	.1209	.0389	22.8	44.2	14.4	.125	.203	.465

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Benfluralin, parameter code 82673, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	1	1	0.0	nc	0.0	0.0	nc	0.0	nc	0.003	nc
Bentazon, parameter code 38711, analysis by HPLC, MRL 0.014 µg/L											
0.05 to < 0.5	7	7	***.0440***	***0.0692***	***.0283***	***19.5***	***30.6***	***15.7***	0.120	.165	0.380
0.1 to < 1	8	8	***.0610***	***.0923***	***.0318***	***19.7***	***29.8***	***17.2***	.120	.173	.600
0.5 to < 5	1	1	.1273	1.013	.1273	21.2	168.8	21.2	nc	.600	nc
Bromacil, parameter code 04029, analysis by HPLC, MRL 0.035 µg/L											
< 0.01	1	2	.0035	.0107	.0035	43.3	133.4	43.3	nc	.008	nc
0.005 to < 0.05	1	2	.0035	.0107	.0035	43.3	133.4	43.3	nc	.008	nc
0.01 to < 0.1	1	1	.0	nc	.0	.0	nc	.0	nc	.090	nc
0.05 to < 0.5	1	1	.0	nc	.0	.0	nc	.0	nc	.090	nc
0.1 to < 1	2	2	.0814	.2508	.0813	11.6	35.7	11.5	.640	.722	.805
0.5 to < 5	2	2	.0814	.2508	.0813	11.6	35.7	11.5	.640	.722	.805
Bromoxynil, parameter code 49311, analysis by HPLC, MRL 0.035 µg/L											
0.05 to < 0.5	1	1	.0071	.0563	.0071	5.2	41.7	5.2	nc	.135	nc
0.1 to < 1	1	1	.0071	.0563	.0071	5.2	41.7	5.2	nc	.135	nc
Butylate, parameter code 04028, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	9	10	.00087	.0012	.00071	26.5	38.0	20.2	.002	.004	.009
0.005 to < 0.05	9	10	.0011	.0016	.00064	9.7	14.0	2.0	.005	.012	.031
0.01 to < 0.1	5	5	.0013	.0024	.00064	5.4	9.5	2.0	.012	.020	.031
Carbaryl, parameter code 82680, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	8	9	.00088	.0013	.00071	12.3	18.1	8.3	.005	.007	.010
0.005 to < 0.05	28	33	***.0034***	***.0040***	***.0014***	14.3	17.1	8.8	.005	.017	.050
0.01 to < 0.1	26	32	***.0067***	***.0080***	***.0017***	16.0	19.2	9.9	.010	.025	.073
0.05 to < 0.5	13	17	***.0268***	***.0347***	***.0199***	16.2	21.0	12.3	.051	.123	.460
0.1 to < 1	11	14	.0775	.1040	.0212	16.3	21.8	12.3	.110	.385	.810
0.5 to < 5	3	4	.1352	.2621	.1838	21.0	40.8	22.7	.503	.560	.810
Carbaryl, parameter code 49310, analysis by HPLC, MRL 0.008 µg/L											
0.005 to < 0.05	2	2	.0280	.0861	.0230	85.8	264.4	69.9	.033	.034	.035
0.01 to < 0.1	3	3	.0306	.0694	.0354	74.1	167.8	41.6	.033	.035	.085
0.05 to < 0.5	2	2	.0354	.1089	.0354	29.8	91.9	24.4	.085	.290	.495
0.1 to < 1	1	1	.0354	.2814	.0354	7.1	56.8	7.1	nc	.495	nc
Carbofuran, parameter code 82674, analysis by GCMS, MRL 0.003 µg/L											
0.005 to < 0.05	7	8	.0032	.0049	.0021	16.4	24.8	9.4	.011	.023	.035
0.01 to < 0.1	8	9	.0140	.0206	.0021	28.9	42.4	14.8	.011	.024	.056
0.05 to < 0.5	6	6	.0249	.0411	.0039	34.3	56.6	1.2	.056	.120	.336
0.1 to < 1	6	6	.0189	.0312	.0039	16.8	27.7	.5	.109	.155	.975
0.5 to < 5	1	1	.0099	.0788	.0099	1.0	8.1	1.0	nc	.975	nc

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Carbofuran, parameter code 49309, analysis by HPLC, MRL 0.120 µg/L											
0.1 to < 1	1	1	0.0	nc	0.0	0.0	nc	0.0	nc	0.790	nc
0.5 to < 5	1	1	.0	nc	.0	.0	nc	.0	nc	.790	nc
Chlorpyrifos, parameter code 38933, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	22	24	.0018	0.0022	.00071	23.9	29.6	12.7	0.003	.007	0.010
0.005 to < 0.05	46	52	.0024	.0027	.0013	18.5	21.2	8.7	.005	.011	.041
0.01 to < 0.1	29	34	.0030	.0035	.0014	12.0	14.3	8.3	.010	.021	.081
0.05 to < 0.5	8	9	.0157	.0231	.0141	9.9	14.6	9.1	.057	.140	.320
0.1 to < 1	6	6	.0189	.0312	.0177	10.5	17.3	9.1	.125	.168	.320
Cyanazine, parameter code 04041, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	6	6	.0012	.0019	.00084	13.3	22.0	10.4	.008	.008	.010
0.005 to < 0.05	33	37	***.0023***	***.0027***	***.0014***	10.1	11.9	8.8	.008	.016	.048
0.01 to < 0.1	38	45	***.0040***	***.0047***	***.0019***	9.8	11.4	7.8	.010	.033	.098
0.05 to < 0.5	25	29	.0314	.0380	.0057	14.8	17.9	5.7	.050	.102	.330
0.1 to < 1	19	20	.0759	.0962	.0071	19.1	24.3	3.8	.100	.247	.620
0.5 to < 5	11	11	.2940	.4128	.0424	16.8	23.7	5.8	.530	1.07	4.67
1 to < 10	6	6	.3794	.6260	.2581	9.1	15.0	7.2	1.07	3.44	4.67
2,4-D, parameter code 39732, analysis by HPLC, MRL 0.150 µg/L											
0.005 to < 0.05	2	2	.0071	.0218	.0071	22.9	70.5	22.0	.025	.035	.045
0.01 to < 0.1	3	3	.0058	.0131	.0071	18.7	42.3	15.7	.025	.045	.070
0.05 to < 0.5	6	6	***.0327***	***.0539***	***.0071***	10.6	17.5	6.2	.070	.180	.370
0.1 to < 1	7	7	.0434	.0683	.0354	11.0	17.3	6.7	.105	.265	.740
0.5 to < 5	2	2	.0583	.1796	.0566	9.3	28.6	8.8	.600	.670	.740
Dacthal, parameter code 82682, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	34	39	.00036	.00043	.0	11.0	13.0	.0	.001	.003	.008
0.005 to < 0.05	20	25	.0058	.0071	.00071	26.8	33.0	5.9	.005	.012	.041
0.01 to < 0.1	14	16	.0078	.0103	.0011	32.9	43.1	6.3	.011	.017	.081
0.05 to < 0.5	4	4	.0159	.0308	.0095	11.3	22.0	6.7	.061	.118	.320
0.1 to < 1	2	2	.0206	.0635	.0177	7.0	21.7	6.7	.155	.238	.320
***p,p'*-DDE, parameter code 34653, analysis by GCMS, MRL 0.006 µg/L**											
< 0.01	9	10	***.00073***	***.0010***	***.00071***	31.6	45.3	23.2	.001	.002	.009
0.005 to < 0.05	5	5	.0025	.0044	.0028	15.2	26.9	16.4	.008	.014	.028
0.01 to < 0.1	3	3	.0031	.0070	.0028	16.1	36.5	16.4	.014	.022	.028
Desethylatrazine, parameter code 04040, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	50	56	***.00095***	***.0011***	***.00064***	18.2	20.8	10.9	.001	.004	.010
0.005 to < 0.05	79	86	***.0046***	***.0051***	***.0014***	20.4	22.6	10.9	.005	.020	.049
0.01 to < 0.1	82	92	***.0061***	***.0068***	***.0026***	18.5	20.5	8.8	.010	.030	.093
0.05 to < 0.5	42	51	***.0151***	***.0173***	***.0088***	12.0	13.8	6.6	.050	.109	.370
0.1 to < 1	25	30	.0258	.0311	.0141	10.8	13.1	6.1	.103	.200	.874

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Desethylatrazine, parameter code 04040, analysis by GCMS, MRL 0.002 µg/L—Continued											
0.5 to < 5	3	3	0.0784	0.1777	0.0919	8.0	18.2	7.6	0.510	0.874	1.22
1 to < 10	1	1	.0919	.7315	.0919	7.6	60.2	7.6	nc	1.22	nc
Diazinon, parameter code 39572, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	32	34	.0014	.0016	.00071	20.6	24.6	9.4	.003	.007	0.010
0.005 to < 0.05	69	77	***.0023***	***.0026***	***.0010***	***16.5***	***18.4***	***7.4***	.005	.017	.046
0.01 to < 0.1	63	75	.0040	.0045	.0014	***10.7***	***12.0***	***4.3***	.011	.038	.100
0.05 to < 0.5	25	31	.0061	.0073	.0021	6.9	8.3	2.9	.051	.076	.410
0.1 to < 1	6	7	.0282	.0443	.0071	5.8	9.2	4.2	.115	.165	.567
0.5 to < 5	2	3	.0918	.2079	.0964	7.9	18.0	7.1	.567	1.683	2.800
1 to < 10	1	1	.1414	1.125	.1414	5.1	40.2	5.1	nc	2.800	nc
Dieldrin, parameter code 39381, analysis by GCMS, MRL 0.001 µg/L											
< 0.01	6	7	.0025	.0040	.00071	28.8	45.2	13.8	.004	.008	.010
0.005 to < 0.05	11	12	.0033	.0046	.0035	28.2	38.9	13.3	.006	.011	.027
0.01 to < 0.1	6	6	.0039	.0064	.0039	26.2	43.3	20.8	.011	.015	.027
2,6-Diethylaniline, parameter code 82660, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	7	7	.00038	.00059	.0	25.2	39.6	.0	.001	.001	.003
0.005 to < 0.05	1	1	.0014	.0113	.0014	12.9	102.3	12.9	nc	.011	nc
0.01 to < 0.1	1	1	.0014	.0113	.0014	12.9	102.3	12.9	nc	.011	nc
Diuron, parameter code 49300, analysis by HPLC, MRL 0.020 µg/L											
0.005 to < 0.05	4	4	.0132	.0257	.0106	40.9	79.3	37.7	.025	.030	.035
0.01 to < 0.1	8	9	.0150	.0220	.0071	33.2	48.8	18.9	.025	.043	.080
0.05 to < 0.5	8	9	.0202	.0297	.0177	21.3	31.4	10.4	.050	.093	.235
0.1 to < 1	9	10	.2314	.3318	.0354	32.0	45.9	15.0	.105	.620	.937
0.5 to < 5	8	9	.4031	.5923	.2440	39.4	57.9	18.4	.620	.888	4.30
1 to < 10	3	3	.5565	1.261	.4243	39.1	88.6	9.9	1.29	1.75	4.30
DNOC, parameter code 49299, analysis by HPLC, MRL 0.420 µg/L											
0.1 to < 1	1	1	.0495	.3939	.0495	9.8	78.0	9.8	nc	.505	nc
0.5 to < 5	1	1	.0495	.3939	.0495	9.8	78.0	9.8	nc	.505	nc
EPTC, parameter code 82668, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	16	19	.0018	.0023	.00044	30.6	39.0	6.2	.002	.005	.008
0.005 to < 0.05	27	29	.0050	.0061	.0014	29.0	35.1	8.7	.005	.017	.048
0.01 to < 0.1	26	27	.0052	.0064	.0019	***18.9***	***23.0***	***5.8***	.012	.023	.083
0.05 to < 0.5	10	11	***.0166***	***.0233***	***.0032***	6.3	8.9	3.9	.051	.082	.345
0.1 to < 1	4	4	.0281	.0544	.0177	8.8	17.0	6.6	.145	.300	.500
0.5 to < 5	1	1	.0141	.1125	.0141	2.8	22.5	2.8	nc	.500	nc

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Ethalfluralin, parameter code 82663, analysis by GCMS, MRL 0.004 µg/L											
0.005 to < 0.05	4	4	0.00094	0.0018	0.00071	4.9	9.5	4.6	0.011	0.023	0.045
0.01 to < 0.1	4	4	.00094	.0018	.00071	4.9	9.5	4.6	.011	.023	.045
0.05 to < 0.5	1	1	.0318	.2532	.0318	29.6	235.6	29.6	nc	.108	nc
0.1 to < 1	1	1	.0318	.2532	.0318	29.6	235.6	29.6	nc	.108	nc
Ethoprop, parameter code 82672, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	2	2	.00040	.0012	.00028	9.1	28.0	6.4	.003	.004	.004
0.005 to < 0.05	2	2	.00050	.0015	.00035	1.2	3.6	.8	.014	.028	.043
0.01 to < 0.1	2	2	.00050	.0015	.00035	1.2	3.6	.8	.014	.028	.043
Fenuron, parameter code 49297, analysis by HPLC, MRL 0.013 µg/L											
0.05 to < 0.5	1	1	.0	nc	.0	.0	nc	.0	nc	.140	nc
0.1 to < 1	1	1	.0	nc	.0	.0	nc	.0	nc	.140	nc
Fluometuron, parameter code 38811, analysis by HPLC, MRL 0.035 µg/L											
< 0.01	1	1	.0049	.0394	.0049	76.1	606.0	76.1	nc	.007	nc
0.005 to < 0.05	1	1	.0049	.0394	.0049	76.1	606.0	76.1	nc	.007	nc
0.01 to < 0.1	1	1	.0212	.1688	.0212	28.3	225.1	28.3	nc	.075	nc
0.05 to < 0.5	4	4	.0892	.1729	.0141	24.7	47.8	17.2	.075	.145	.445
0.1 to < 1	3	3	.1022	.2316	.0071	23.3	52.8	6.1	.115	.175	.445
1 to < 10	1	1	.4243	3.376	.4243	6.8	54.5	6.8	nc	6.20	nc
>= 5	1	1	.4243	3.376	.4243	6.8	54.5	6.8	nc	6.20	nc
Fonofos, parameter code 04095, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	14	14	.00072	.00096	.00015	15.4	20.6	2.6	.002	.004	.009
0.005 to < 0.05	9	11	.0012	.0018	.00040	6.6	9.2	4.3	.006	.012	.034
0.01 to < 0.1	7	9	***.0022***	***.0033***	***.0010***	4.9	7.2	4.3	.012	.021	.096
0.05 to < 0.5	2	2	.0039	.0120	.0036	4.5	14.0	4.5	.059	.077	.096
***alpha*-HCH, parameter code 34253, analysis by GCMS, MRL 0.002 µg/L**											
0.005 to < 0.05	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
0.01 to < 0.1	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
***gamma*-HCH, parameter code 39341, analysis by GCMS, MRL 0.004 µg/L**											
< 0.01	2	2	.0016	.0049	.0014	18.2	56.1	17.6	.006	.008	.010
0.005 to < 0.05	4	4	.0027	.0053	.0014	13.9	27.0	11.4	.006	.016	.050
0.01 to < 0.1	4	4	.0034	.0065	.0032	5.9	11.4	3.7	.022	.068	.092
0.05 to < 0.5	2	2	.0032	.0099	.0032	3.6	11.2	3.6	.086	.089	.092
Linuron, parameter code 82666, analysis by GCMS, MRL 0.002 µg/L											
0.005 to < 0.05	5	6	.00090	.0015	.00049	6.4	10.6	3.1	.011	.019	.024
0.01 to < 0.1	6	7	.0020	.0032	.00082	6.6	10.3	4.5	.011	.019	.067
0.05 to < 0.5	4	5	.0916	.1614	.0060	33.3	58.7	6.6	.067	.141	.277
0.1 to < 1	3	4	.1024	.1985	.0071	37.1	71.9	5.7	.125	.157	.277

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Linuron, parameter code 38478, analysis by HPLC, MRL 0.018 µg/L											
0.01 to < 0.1	2	3	0.0312	0.0706	0.0225	54.8	124.1	37.6	0.057	0.071	0.085
0.05 to < 0.5	2	3	.0312	.0706	.0225	54.8	124.1	37.6	.057	.071	.085
MCPA, parameter code 38482, analysis by HPLC, MRL 0.170 µg/L											
0.01 to < 0.1	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
0.05 to < 0.5	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
Malathion, parameter code 39532, analysis by GCMS, MRL 0.005 µg/L											
< 0.01	6	6	.0012	.0020	.00035	13.5	22.3	3.7	.004	.008	.010
0.005 to < 0.05	11	13	.0019	.0026	.00071	13.1	17.8	6.7	.006	.011	.044
0.01 to < 0.1	11	13	.0079	.0107	.0021	15.0	20.3	6.7	.011	.044	.090
0.05 to < 0.5	5	5	.0124	.0218	.0078	18.9	33.2	15.1	.052	.063	.090
Methyl parathion, parameter code 82667, analysis by GCMS, MRL 0.006 µg/L											
0.005 to < 0.05	4	4	.00053	.0010	.00035	3.8	7.4	1.8	.011	.020	.044
0.01 to < 0.1	4	4	.00053	.0010	.00035	3.8	7.4	1.8	.011	.020	.044
Metolachlor, parameter code 39415, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	37	43	.00065	.00076	.0	16.7	19.5	.0	.002	.005	.010
0.005 to < 0.05	70	77	***.0013***	***.0015***	***.00071***	6.8	7.6	2.8	.005	.015	.050
0.01 to < 0.1	68	77	***.0023***	***.0026***	***.00071***	5.8	6.5	3.3	.010	.028	.097
0.05 to < 0.5	47	56	***.0236***	***.0270***	***.0042***	11.2	12.8	3.6	.052	.125	.450
0.1 to < 1	36	42	.0554	.0648	.0141	13.5	15.8	3.5	.107	.235	.985
0.5 to < 5	16	18	.1569	.2020	.0707	10.7	13.8	4.7	.560	1.42	4.25
1 to < 10	12	13	.1707	.2319	.0707	9.0	12.2	4.7	1.15	1.78	9.12
>= 5	3	3	.7829	1.774	.1768	6.4	14.5	3.2	5.56	9.12	12.6
Metribuzin, parameter code 82630, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	7	9	.00071	.0010	.0	10.6	15.6	.0	.004	.007	.010
0.005 to < 0.05	17	19	***.0027***	***.0034***	***.00071***	11.4	14.6	4.7	.005	.018	.042
0.01 to < 0.1	13	13	.0034	.0046	.00071	10.9	14.8	4.7	.011	.026	.090
0.05 to < 0.5	5	5	.0060	.0106	.0	4.7	8.2	.0	.050	.130	.211
0.1 to < 1	4	4	.0149	.0288	.0064	3.5	6.9	1.9	.130	.183	.719
0.5 to < 5	1	1	.0269	.2138	.0269	3.7	29.7	3.7	nc	.719	nc
Molinate, parameter code 82671, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	1	1	.0	nc	.0	.0	nc	.0	nc	.007	nc
0.005 to < 0.05	3	3	.0016	.0037	.0	14.8	33.6	.0	.007	.011	.036
0.01 to < 0.1	3	3	.0023	.0052	.0028	15.0	33.9	3.5	.011	.036	.081
0.05 to < 0.5	4	4	***.0107***	***.0208***	***.0106***	7.7	14.9	7.5	.081	.133	.150
0.1 to < 1	3	3	.0122	.0277	.0141	8.6	19.5	9.4	.125	.140	.150
0.5 to < 5	1	1	.0	nc	.0	.0	nc	.0	nc	3.80	nc
1 to < 10	3	3	.0	nc	.0	.0	nc	.0	3.80	5.00	9.70
>= 5	3	3	.0	nc	.0	.0	nc	.0	5.00	9.70	20.0

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Napropamide, parameter code 82684, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	6	6	0.00058	0.00095	0.00071	13.3	22.0	8.4	0.003	0.008	0.010
0.005 to < 0.05	10	11	.0015	.0021	.00071	11.2	15.8	8.4	.007	.010	.019
0.01 to < 0.1	9	10	.0020	.0028	.0014	10.8	15.5	6.4	.011	.019	.070
0.05 to < 0.5	4	4	.0019	.0038	.0011	3.4	6.6	1.6	.056	.064	.070
Norflurazon, parameter code 49293, analysis by HPLC, MRL 0.024 µg/L											
0.01 to < 0.1	2	2	.0112	.0344	.0106	12.6	38.7	12.0	.085	.088	.090
0.05 to < 0.5	2	2	.0112	.0344	.0106	12.6	38.7	12.0	.085	.088	.090
0.1 to < 1	1	1	.0919	.7315	.0919	16.0	127.2	16.0	nc	.575	nc
0.5 to < 5	1	1	.0919	.7315	.0919	16.0	127.2	16.0	nc	.575	nc
Oryzalin, parameter code 49292, analysis by HPLC, MRL 0.310 µg/L											
0.1 to < 1	1	1	.2758	2.195	.2758	53.5	426.1	53.5	nc	.515	nc
0.5 to < 5	1	1	.2758	2.195	.2758	53.5	426.1	53.5	nc	.515	nc
Pebulate, parameter code 82669, analysis by GCMS, MRL 0.004 µg/L											
0.005 to < 0.05	3	3	.0042	.0094	.0014	17.2	38.9	3.8	.013	.024	.037
0.01 to < 0.1	3	3	.0042	.0094	.0014	17.2	38.9	3.8	.013	.024	.037
0.05 to < 0.5	1	1	.0071	.0563	.0071	3.6	28.9	3.6	nc	.195	nc
0.1 to < 1	1	1	.0071	.0563	.0071	3.6	28.9	3.6	nc	.195	nc
Pendimethalin, parameter code 82683, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	6	6	.00076	.0013	.00071	12.5	20.7	10.1	.006	.007	.010
0.005 to < 0.05	11	11	.0021	.0030	.00071	12.7	17.8	7.4	.006	.010	.030
0.01 to < 0.1	10	11	***.0058***	***.0082***	***.0028***	13.1	18.5	9.5	.011	.040	.063
0.05 to < 0.5	7	9	***.0428***	***.0629***	***.0087***	21.7	32.0	16.1	.050	.060	.305
0.1 to < 1	2	3	.0734	.1664	.0748	32.6	73.9	34.0	.103	.204	.305
Picloram, parameter code 49291, analysis by HPLC, MRL 0.050 µg/L											
0.05 to < 0.5	1	1	.0141	.1125	.0141	12.9	102.3	12.9	nc	.110	nc
0.1 to < 1	1	1	.0141	.1125	.0141	12.9	102.3	12.9	nc	.110	nc
Prometon, parameter code 04037, analysis by GCMS, MRL 0.018 µg/L											
< 0.01	32	38	***.00089***	***.0010***	***.00064***	12.3	14.5	8.1	.003	.008	.010
0.005 to < 0.05	90	109	***.0033***	***.0036***	***.00071***	12.6	13.8	5.8	.005	.016	.050
0.01 to < 0.1	89	108	***.0050***	***.0055***	***.0014***	12.3	13.5	4.6	.010	.029	.097
0.05 to < 0.5	34	40	***.0096***	***.0113***	***.0048***	11.9	14.0	4.6	.054	.075	.225
0.1 to < 1	9	10	.0146	.0209	.0071	12.3	17.6	6.1	.103	.121	.225
0.5 to < 5	1	1	.0141	.1125	.0141	1.4	10.9	1.4	nc	1.03	nc
1 to < 10	1	1	.0141	.1125	.0141	1.4	10.9	1.4	nc	1.03	nc

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Pronamide, parameter code 82676, analysis by GCMS, MRL 0.003 µg/L											
< 0.01	3	3	0.00041	0.00092	0.0	6.3	14.2	0.0	0.007	0.009	0.009
0.005 to < 0.05	5	5	.00055	.00097	.00071	6.3	11.2	6.1	.007	.009	.012
0.01 to < 0.1	2	2	.00071	.0022	.00071	6.4	19.9	6.4	.011	.011	.012
Propachlor, parameter code 04024, analysis by GCMS, MRL 0.007 µg/L											
< 0.01	1	1	.0	nc	.0	.0	nc	.0	nc	.006	nc
0.005 to < 0.05	3	3	.0021	.0047	.00071	5.2	11.8	4.6	.006	.016	.046
0.01 to < 0.1	3	3	.0053	.0121	.0035	7.8	17.6	7.8	.016	.046	.085
0.05 to < 0.5	1	1	.0085	.0675	.0085	10.0	79.4	10.0	nc	.085	nc
Propanil, parameter code 82679, analysis by GCMS, MRL 0.004 µg/L											
< 0.01	1	2	.00058	.0018	.00058	6.0	18.4	6.0	nc	.010	nc
0.005 to < 0.05	1	2	.00058	.0018	.00058	6.0	18.4	6.0	nc	.010	nc
0.01 to < 0.1	1	1	.0021	.0169	.0021	4.2	33.4	4.2	nc	.051	nc
0.05 to < 0.5	1	1	.0021	.0169	.0021	4.2	33.4	4.2	nc	.051	nc
Propargite, parameter code 82685, analysis by GCMS, MRL 0.013 µg/L											
< 0.01	1	1	.00071	.0056	.00071	7.4	59.2	7.4	nc	.010	nc
0.005 to < 0.05	5	6	.0016	.0027	.0011	9.2	15.2	8.9	.010	.012	.039
0.01 to < 0.1	6	7	.0109	.0171	.0025	14.2	22.4	13.7	.010	.033	.092
0.05 to < 0.5	4	4	***.0469***	***.0910***	***.0269***	19.9	38.5	17.5	.091	.131	.460
0.1 to < 1	3	4	.0510	.0989	.0346	12.8	24.8	16.6	.170	.460	.780
0.5 to < 5	1	2	.0346	.1067	.0346	4.4	13.7	4.4	nc	.780	nc
Simazine, parameter code 04035, analysis by GCMS, MRL 0.005 µg/L											
< 0.01	28	37	.0010	.0012	.00058	14.8	17.5	8.9	.002	.007	.010
0.005 to < 0.05	98	111	***.0020***	***.0022***	***.00074***	***11.1***	***12.2***	***5.8***	.005	.017	.050
0.01 to < 0.1	97	111	***.0027***	***.0030***	***.0014***	8.4	9.2	4.3	.010	.028	.099
0.05 to < 0.5	52	62	***.0137***	***.0155***	***.0047***	7.9	8.9	4.0	.051	.118	.425
0.1 to < 1	36	41	***.0197***	***.0231***	***.0071***	8.8	10.3	4.2	.105	.175	.843
0.5 to < 5	12	13	***.1472***	***.2001***	***.0332***	7.0	9.6	4.0	.500	1.18	4.25
1 to < 10	7	7	.1989	.3127	.1485	9.1	14.2	6.7	1.05	1.40	4.25
Tebuthiuron, parameter code 82670, analysis by GCMS, MRL 0.010 µg/L											
< 0.01	17	21	.0010	.0013	.00071	15.8	19.9	8.7	.003	.007	.010
0.005 to < 0.05	46	54	.0042	.0048	.00071	***16.1***	***18.5***	***6.5***	.007	.014	.045
0.01 to < 0.1	33	37	.0052	.0061	.0011	16.2	19.1	4.6	.010	.021	.078
0.05 to < 0.5	6	6	***.0188***	***.0310***	***.0110***	8.8	14.5	8.4	.075	.119	.312
0.1 to < 1	4	4	***.0227***	***.0440***	***.0177***	9.6	18.6	9.3	.108	.203	.312

Table 7. Variability of pesticide concentrations in field replicates—Continued

Concentration range (µg/L)	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
									Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Terbacil, parameter code 82665, analysis by GCMS, MRL 0.007 µg/L											
< 0.01	2	2	0.00071	0.0022	0.00071	10.2	31.4	10.2	0.007	0.007	0.008
0.005 to < 0.05	4	5	.0021	.0037	.00071	11.9	21.0	10.2	.007	.010	.020
0.01 to < 0.1	3	4	.0042	.0082	.0032	13.1	25.4	13.6	.013	.020	.052
0.05 to < 0.5	1	1	.0071	.0563	.0071	13.6	108.2	13.6	nc	.052	nc
0.1 to < 1	1	1	.0	nc	.0	.0	nc	.0	nc	.540	nc
0.5 to < 5	1	1	.0	nc	.0	.0	nc	.0	nc	.540	nc
Thiobencarb, parameter code 82681, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	1	1	.0	nc	.0	.0	nc	.0	nc	.008	nc
0.005 to < 0.05	5	5	.00077	.0014	.00071	6.9	12.1	2.1	.008	.013	.034
0.01 to < 0.1	4	4	.00087	.0017	.00071	7.7	14.9	3.9	.010	.017	.034
Triallate, parameter code 82678, analysis by GCMS, MRL 0.001 µg/L											
< 0.01	9	9	.0032	.0046	.00071	39.3	57.8	12.9	.003	.004	.009
0.005 to < 0.05	6	6	.0039	.0065	.0011	45.3	74.7	9.3	.006	.008	.037
0.01 to < 0.1	3	3	.0039	.0088	.0021	6.4	14.5	5.8	.024	.037	.072
0.05 to < 0.5	2	2	.0157	.0482	.0138	12.1	37.3	11.8	.072	.108	.145
0.1 to < 1	1	1	.0212	.1688	.0212	14.6	116.4	14.6	nc	.145	nc
Triclopyr, parameter code 49235, analysis by HPLC, MRL 0.250 µg/L											
0.05 to < 0.5	1	2	.0306	.0941	.0306	14.1	43.4	14.1	nc	.217	nc
0.1 to < 1	1	2	.0306	.0941	.0306	14.1	43.4	14.1	nc	.217	nc
Trifluralin, parameter code 82661, analysis by GCMS, MRL 0.002 µg/L											
< 0.01	12	14	.0010	.0014	.00071	20.5	27.5	10.2	.002	.006	.008
0.005 to < 0.05	21	22	.0012	.0015	.00071	15.4	19.3	1.6	.005	.010	.047
0.01 to < 0.1	17	17	***.0059***	***.0077***	***.00071***	11.3	14.7	1.6	.010	.016	.091
0.05 to < 0.5	5	5	.0144	.0253	.0071	13.6	23.9	7.0	.061	.084	.495
0.1 to < 1	1	1	.0212	.1688	.0212	4.3	34.1	4.3	nc	.495	nc

Table 8. Typical variability of pesticide concentrations in field replicates

[Data in this table are the median values of the statistics published in appendix 2. µg/L, microgram per liter; IRS, inconsistent replicate sets; <, less than; >=, greater than or equal to; deleted, nondetections in IRS deleted; zero, nondetections in IRS set to zero; mrl, nondetections in IRS set to the minimum reporting level]

Concentration range (µg/L)	Analytical approach for IRS	Number of pesticides	Median pooled standard deviation (µg/L)	Median standard deviation (µg/L)	Median pooled relative standard deviation (percent)	Median relative standard deviation (percent)	Median concentration of replicate sets (µg/L)
< 0.01	deleted	38	0.00083	0.00068	15	8.4	0.007
	zero	50	.0034	.0016	100	71	.005
	mrl	46	.0018	.00071	33	20	.006
0.005 to < 0.05	deleted	46	.0022	.00072	13	7.1	.016
	zero	54	.0047	.0014	40	9.4	.013
	mrl	55	.0036	.0014	27	9.4	.014
0.01 to < 0.1	deleted	49	.0040	.0017	12	6.3	.028
	zero	58	.0060	.0023	20	8.3	.028
	mrl	56	.0053	.0021	18	7.3	.028
0.05 to < 0.5	deleted	46	.016	.0082	12	6.9	.117
	zero	49	.019	.011	15	10	.108
	mrl	49	.019	.011	15	10	.110
0.1 to < 1	deleted	41	.028	.018	11	6.7	.208
	zero	43	.030	.018	13	7.1	.208
	mrl	44	.031	.018	13	9.2	.203
0.5 to < 5	deleted	25	.078	.050	7.9	4.7	.780
	zero	27	.081	.057	8.0	5.8	.790
	mrl	28	.087	.057	8.7	6.5	.785
1 to < 10	deleted	12	.16	.081	6.3	4.9	2.60
	zero	13	.17	.092	6.8	5.1	2.39
	mrl	13	.17	.092	6.8	5.1	2.39
>= 5	no IRS	5	.42	.18	2.7	2.7	9.12

constant variance (no pattern of increase or decrease with concentration), then it is appropriate to pool them. If the individual measurements increase or decrease in the range of concentration, then the pooled estimates of variability are biased.

The assumption that variability was constant (homoscedastic) in a concentration range was examined by calculating the significance level of the correlation between the individual estimate of variability and the mean concentration of the replicate set for all replicate sets in a concentration range. Statistically significant correlations ($p < 0.05$ or, equivalently, $\alpha = 0.05$) indicate increasing or decreasing variability in a concentration range.

Results of the correlation analysis show that for most pesticides and concentrations, pooled estimates of *RSD* should be used to estimate variability because *RSD* is a more robust estimate of variability (less affected by heteroscedasticity) than is *SD*. In a correlation analysis of 170 combinations of pesticide and concentration range (approach 1, nondetections in IRS deleted), 43 combinations (25.3 percent) showed a statistically significant correlation between *SD* and concentration, whereas only 11 (6.5 percent) showed a statistically significant correlation between *RSD* and concentration (table 9). The Type I error rate selected for the correlation analysis ($\alpha = 0.05$) predicts that

Table 9. Assessment of constant variance in a concentration range

[All estimates of variability use analytical approach 1: Nondetections in inconsistent replicate sets deleted. µg/L, microgram per liter; <, less than; >=, greater than or equal to]

Concentration range (µg/L)	Pesticides with three or more replicates sets	Pesticides with statistically significant[1] nonconstant variance (heteroscedasticity)		Slope of the statistically significant[1] relations between standard deviation and concentration		Slope of the statistically significant[1] relations between relative standard deviation and concentration	
		Standard deviation	Relative standard deviation	Positive	Negative	Positive	Negative
< 0.01	26	4	0	4	0	0	0
0.005 to < 0.05	38	10	5	10	0	0	5
0.01 to < 0.1	39	10	2	10	0	0	2
0.05 to < 0.5	27	13	1	13	0	1	0
0.1 to < 1	22	4	1	4	0	1	0
0.5 to < 5	8	1	1	1	0	0	1
1 to < 10	7	0	0	0	0	0	0
>= 5	3	1	1	1	0	1	0
Total	170	43	11	43	0	3	8

[1]The probability of obtaining a statistically significant relation between variance and concentration by chance is less than 0.05 ($p < 0.05$).

8.5 combinations (170 x 0.05) would show a significant correlation by error, a number very near that shown (11) for the relation between *RSD* and concentration. In general, the statistically significant correlations between *SD* and concentration had a much lower probability of occurring by chance (a lower value of p) than the correlations between *RSD* and concentration.

SD increased with concentration for all significant correlations, whereas *RSD* decreased with concentration for 8 of the 11 significant correlations (table 9). *RSD* increased with concentration for atrazine in the >= 5 µg/L concentration range and for bentazon in the 0.05 to <0.5 µg/L and the 0.1 to <1 µg/L concentration ranges. Most (33) of the significant correlations between the *SD* and concentration occurred in the 0.005 to <0.05 µg/L, the 0.01 to <0.1 µg/L, and the 0.05 to <0.05 µg/L concentrations ranges, whereas most (5) of the significant correlations between *RSD* and concentration occurred in the 0.05 to <0.5 µg/L concentration range (table 9). Atrazine, desethylatrazine, *p,p'*-DDE, and prometon exhibited increasing *SD* in the lowest ranges of concentration, near the MDL—a finding contrary to the assumption of constant variance at low concentrations needed for the MDL process (Oblinger Childress and others, 1999, p. 4). Estimates of variability that are biased (based on individual measurements of variability that increased or decreased in the concentration range) are shown in table 7 and appendix 2 in ***bold italic*** type.

Estimates of variability were developed for eight overlapping ranges of concentrations. As a consequence, two different estimates of variability often can be made for a particular concentration. An estimate of variability at a concentration of 0.15 µg/L, for example, can be obtained from use of the information presented for the concentration range 0.05 to < 0.5 µg/L or from the concentration range 0.1 to < 1 µg/L. In general, data users should select the appropriate concentration range on the basis of the median (and perhaps the minimum and maximum) concentration of individual replicate sets used to develop the pooled estimates of variability for the concentration range (table 7). The number of replicates in the concentration range and the reliability of the pooled estimate are additional considerations. An estimate of the variability of atrazine at 0.15 µg/L, for example, should be based on the information provided for the concentration range 0.05 to < 0.5 µg/L because the median concentration of the field replicates in this range (0.135 µg/L) is much nearer to 0.15 µg/L than is the median concentration of field replicates for the concentration range 0.1 to <1 µg/L (0.208 µg/L).

The pooled estimates of variability presented in table 7 are estimates of the unknown, true variability of pesticide concentrations in the population of all possible replicate sets (and environmental samples) that could have been collected for the NAWQA Program. An upper confidence bound was calculated to estimate an upper limit of the true variability of pesticide concentrations at the 90-percent confidence level. The upper confidence bound is a pessimistic estimate of variability that can be used (1) in assessing the reliability of the pooled estimates of variability given in table 7 or (2) in place of the pooled estimates of variability in situations where it is important not to underestimate the magnitude of pesticide variability. The reliability of the pooled estimate of variability (how close the upper confidence bound is to the pooled estimate) is a function of the magnitude of the pooled estimate of variability and the number of replicate sets (degrees of freedom) used for the pooled estimate.

Pooled estimates of *SD* or *RSD* presented in this report are larger than estimates based upon averages, medians, smooths, or regression of the individual measurements of *SD* or *RSD* from field replicates (fig. 6). The reason the pooled estimates of variability are larger is that the squares of the *SD* (the variance) or the squares of the *RSD* are averaged then the square root is taken to obtain the pooled estimate. Because the squares of the *SD* or the *RSD* are used, the effect of field replicates that have large estimates of variability is enhanced in comparison to estimates that are not based on squares. For example, assume that three measurements of *SD* from field replicates are 1, 3, and 8. The average of the three measurements is 4, the median is 3, but the pooled estimate of the *SD* is 4.97.

Pooled estimates are the preferred method for characterizing variability because they provide unbiased estimates of the variability of the population. Assessments of variability based on *SD* (rather than variance) underestimate the true variability of the population. The degree of underestimation is a function of number of replicates in a replicate set and is most pronounced for duplicates. The mean *SD* calculated from duplicates is 80 percent of the true population *SD*, whereas the mean *SD* calculated from triplicates is 89 percent of the true population *SD* (Natrella, 1963, pp. 1–10). Because pooled estimates of variability are larger (but less biased) than estimates based on other approaches, users of estimates of variability must be cognizant of the approach used to obtain the estimate and must use caution in the comparison of estimates based on different approaches. A future area of research would be to compare pooled estimates of variability as was done in this report with those obtained by (1) smooths or regression of the variances of replicate sets (rather than the *SD*) followed by (2) a square-root transformation of the smooth or regression line to obtain an estimate of the *SD*.

Presentation and Rounding of Estimates of Variability

The presentation and rounding of data and of statistics derived from data is a topic of considerable interest to the scientific community. Agreement has not been reached on appropriate rules for rounding and, as a consequence, diverse rules have been proposed (Eisenhart, 1968, p. 1,203; Sokal and Rohlf, 1969, p. 148; Anderson, 1987, pp. 11–12; Taylor, 1987, p. 202; American Public Health Association and others, 1998, pp. 1–26; American Society for Testing and Materials, 1998, pp. 75–76). Nearly all authorities agree that several "extra" digits should be carried and that rounding should be done only after all calculations have been completed and the statistical characteristics of the data have been evaluated.

This report follows the recommendations of Eisenhart (1968, p. 1,203) that systematic or random errors should be stated to no more than two significant figures and that a reported result

> should be stated at most to the last place affected by the finer of the two qualifying statements (unless it is desired to indicate and preserve such relative accuracy or precision of a higher order that it may possess for certain particular uses).

The practice of rounding *SD* or other estimates of uncertainty to two significant figures for presentation in reports is followed by Croarkin (1984, p. 33), Mandel and Nanni (1986, p. 35), Taylor (1987, p. 202), Taylor and Kuyatt (1994, section 7.3), and the American Society for Testing and Materials (1998, p. 76). Nearly all authorities note that additional digits should be provided if the *SD* will be used for further calculations (such as the calculation of confidence intervals).

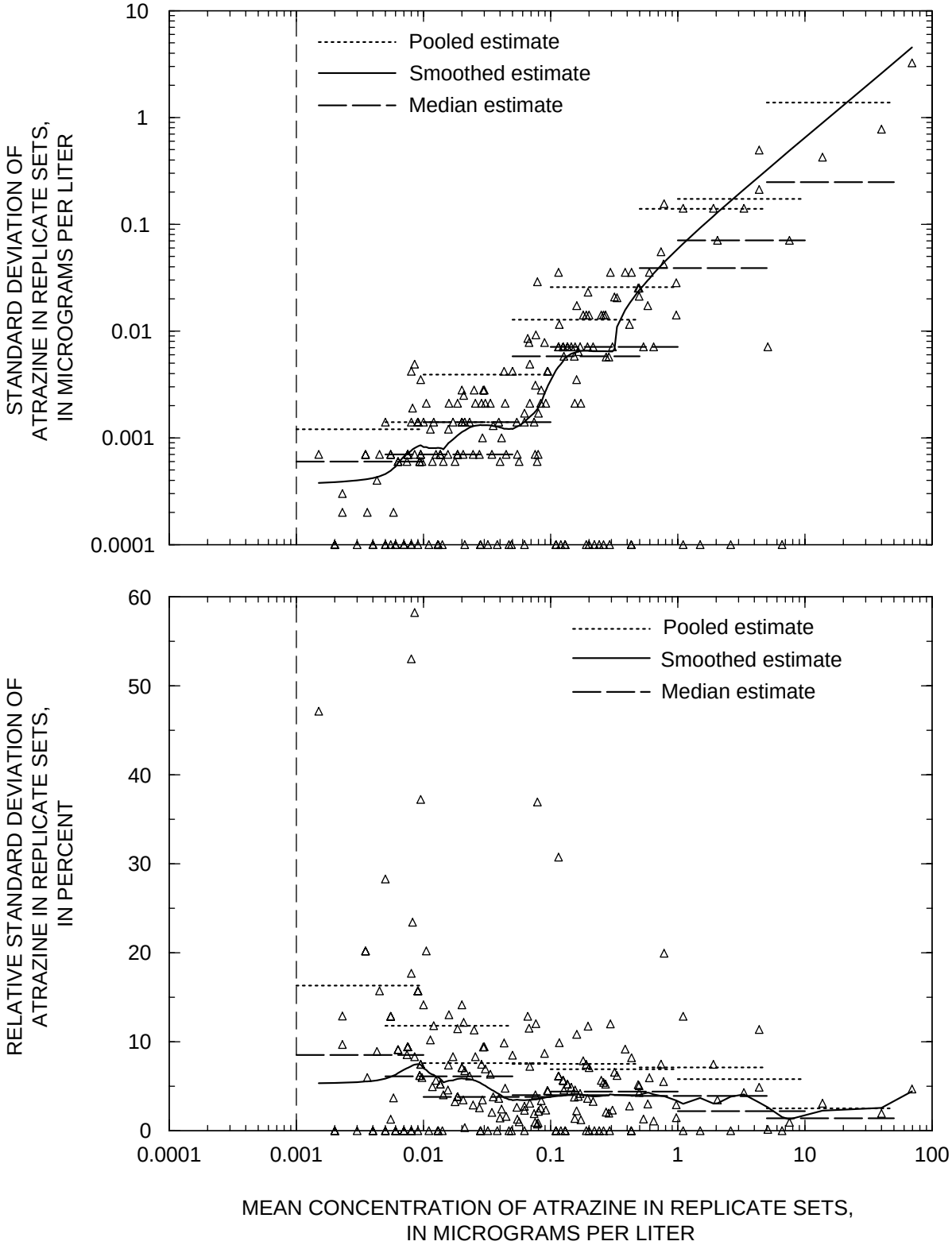


Figure 6. Comparison of estimates of variability of concentrations in field replicates. Standard deviation of 0 µg/L is plotted as 0.0001 µg/L. The vertical dashed line is the minimum reporting level.

Pooled estimates of *SD* and *RSD* and their respective upper confidence bounds have been provided with at least two and as many more digits as is practicable within the limitations of the space available in the tables and the desire for legibility. Users are encouraged to follow the rounding recommendations of Eisenhart (1968, p. 1,203) in reporting these estimates of variability or confidence intervals based on these estimates. For example, the estimates of variability for acetochlor at concentrations greater than or equal to 5 µg/L in table 7 should be reported as 0.15 µg/L for *SD* (1.2 µg/L for the 90-percent upper confidence bound) and 2.7 percent for *RSD* (22 percent for the upper confidence bound). Individual measurements of acetochlor (and confidence limits for individual measurements) in this range of concentration should be reported to the hundreths place (for example, 7.32 µg/L). Note that the estimates of typical variability in table 8 are rounded to two significant figures because calculations based on these estimates are inappropriate.

USE OF ESTIMATES OF VARIABILITY OF CONCENTRATIONS IN WATER-QUALITY ASSESSMENTS

Estimates of the variability of pesticide concentrations can be used to answer various questions relevant to water-quality assessments. Examples of such questions and methods of addressing them are provided in the sections that follow. The reader is assumed to have a basic knowledge of statistics, including calculation of confidence intervals. In all of the examples, the distribution of analytical measurements of a pesticide at a particular concentration are assumed to be normally distributed. A normal distribution of repeated measurements of the same quantity is a common assumption for chemical measurement systems (Taylor, 1987, p. 18; American Public Health Association and others, 1998, p. 1-1) and is a reasonable assumption for most, but not all, of the pesticides in this report. Visual analysis of histograms of the recovery of pesticides in approximately 1,000 GCMS and 700 HPLC laboratory control spikes showed that measurements of the following pesticides were not approximately normally distributed: azinphos-methyl, carbaryl, *cis*-permethrin, and prometon determined by GCMS and chlorothalonil, clopyralid, 2,4-DB, dichlobenil, DNOC, and MCPB determined by HPLC. Application of techniques that assume a normal distribution to these pesticides may result in large errors. The distribution of recovery of pesticides in laboratory control spikes is summarized in Martin (1999).

It is beyond the scope of this report to explain in detail the various approaches and statistical basis for expressing uncertainties in measurement processes. Most authorities agree that separate narrative statements of random error (variability) and systematic error (bias) are required and that a probability interpretation (such as a level of confidence) is desirable (Eisenhart, 1968, p. 1,202; Taylor and Kuyatt, 1994, sec. 7.1; American Public Health Association and others, 1998, pp. 1-13 to 1-16; American Society for Testing and Materials, 2000, p. 222). Estimates of variability are given in this report that can be used to describe random errors (and the uncertainty of these estimates) in the NAWQA pesticide data. Various estimates of bias have been provided previously (Martin and others, 1999; Martin, 1999) that can be used to describe systematic errors (and the uncertainty of these estimates) in the NAWQA pesticide data.

Various approaches are available for combining estimates of bias and variability into a single, overall estimate of uncertainty. The most conservative approach is to sum the random and systematic errors (Taylor, 1987, p. 200), and several authorities advocate this approach (Eisenhart, 1968, p. 1,203–1,204; Croarkin, 1984, pp. 29–30; Taylor and Kuyatt, 1994, sec. 5.1–5.2; Gookins, 1999, pp. 23.35–23.36). These authorities, however, assume that systematic errors have been identified and estimated and that corrections for systematic error (bias) have been applied to the measurement result. Uncertainty from systematic error, therefore, is not the bias itself but uncertainty about the true value of the correction applied to the measurement (Taylor and Kuyatt, 1994, sec. 5.2, note 1). Corrections for systematic error (bias in the analytical method) typically are not done for chemical measurements (Taylor, 1987, p. 200; Keith, 1991, p. 116) and are not done by NWQL for the pesticide data for the NAWQA Program. Consequently, corrections for systematic error must be done by data users if a combined estimate of measurement uncertainty is desired. Likewise,

corrections for bias related to field activities (contamination, degradation, matrix effects, or sampling technique) are not known or applied by the analyzing laboratory. It is the responsibility of the data user to consider the various sources of bias and variability (and uncertainty in these estimates) in the chemical measurements used for water-quality assessments. It is the purpose of this report to provide estimates of variability and to provide approaches for using information on variability in water-quality assessments.

The examples that follow investigate various uses of variability as estimated from field replicates. The effect of bias from the analytical method (recovery) is considered in some of the examples. The effects of bias from contamination, degradation, matrix effects or sampling technique, if any, are not considered in these examples. Some approaches for considering these sources of bias in water-quality assessments have been presented previously (Martin and others, 1999; Martin, 1999). Additional examples of the use of variability in water-quality assessments are presented in Mueller (1998, pp. 8, 22–24). Estimates of variability of concentrations in the following examples are based on approach 1 (nondetections in inconsistent replicate sets were deleted) and use the estimates of variability presented in table 7. Finally, the reader should note that the estimates of variability and the intervals and probabilities presented as examples for the use of variability are approximations that, for a variety of practical reasons (some of which relate to representativeness and random sampling), generally provide only a lower bound on the true uncertainty (Hahn and Meeker, 1991, pp. 5–8).

Example 1: Confidence Limits for a Single Water-Quality Measurement

A pressing need in many water-quality assessments is to determine the variability of a single measurement of a water-quality sample. Ideally, the data user wants to know how different the single measurement is from the mean that would have been calculated if the sample had been analyzed a large number of times (and thus was believed to be an accurate estimate of the true mean). Croarkin (1984, p. 25) describes this need as determining the limits to random error for a single measurement, whereas Taylor (1987, p. 28) describes this need as determining a confidence interval for a mean of a single measurement. Calculations to address both needs are identical. In essence, a confidence interval is calculated for a mean by use of the *t*-distribution. In this case, the estimated value of the mean is the value of the single measurement but the degrees of freedom used in the calculation are based on QC information (estimates of variability given in this report). The formula for the confidence interval for a mean is

$$\overline{X} - t \times \frac{SD}{\sqrt{n}} < \mu < \overline{X} + t \times \frac{SD}{\sqrt{n}}, \qquad (1)$$

where

$\overline{X}$ is the sample mean (in this case, the single measurement, in micrograms per liter),

μ is the population mean (the mean of an infinite number of measurements of the water sample, in micrograms per liter),

n is the sample size used to calculate the sample mean (in this case, $n = 1$),

SD is the standard deviation, in micrograms per liter,

t is the value of the *t*-distribution with v degrees of freedom and 1-α confidence, and

α is the probability of a Type I error (the probability that the confidence interval does not include the population mean).

An example follows.

A data user wishes to determine the variability of a single measurement of alachlor of 0.009 µg/L. Proceed as follows:

Step 1. Calculate *SD* for an alachlor concentration of 0.009 µg/L, using an appropriate estimate of variability from table 7. The most applicable concentration range is <0.01 µg/L rather than 0.005 to <0.05 µg/L because estimates of variability in the <0.01 µg/L range are based on sets of replicates that have a median concentration of 0.005 µg/L (table 7) and are closer to the desired concentration (0.009 µg/L) than the median for the higher range (0.016 µg/L). Note that *SD* is not determined directly from the tabled value of the pooled *SD* but is calculated from the pooled *RSD* (because pooled *RSD* is a more robust estimate of variability):

$$SD = \overline{X} \times \frac{RSD}{100\ \ percent}, \qquad (2)$$

where

RSD is the pooled relative standard deviation, in percent, and

SD and $\overline{X}$ are as previously defined (in this case, $\overline{X}$ = 0.009 µg/L).

The pooled *RSD* for concentrations of alachlor less than 0.01 µg/L is 18.3 percent (table 7); therefore, the *SD* of alachlor at a concentration of 0.009 µg/L is 0.0016 µg/L (0.009 µg/L x 18.3 percent / 100 percent).

Step 2. Determine the appropriate degrees of freedom for the *SD* estimated in Step 1. Estimates of variability for alachlor measurements less than 0.01 µg/L are based on 21 degrees of freedom (table 7).

Step 3. Select a level of confidence for the confidence interval. The data user chooses to calculate a 95-percent confidence interval. This level of confidence is equivalent to selecting $\alpha = 0.05$.

Step 4. Determine a value for the *t*-distribution that has 21 degrees of freedom and $\alpha/2$ of the error in each tail of the distribution. Values of the *t*-distribution are tabulated in various statistical text books, including Rohlf and Sokal (1969, pp. 159–161) or Walpole and Myers (1978, p. 514) and can be obtained from various statistical software packages. The value of the *t*-distribution with 21 degrees of freedom and 0.025 α in each tail is 2.080.

Step 5. Calculate the confidence interval (eq. 1):

$0.009\ \mu g/L - 2.080 \times 0.0016\ \mu g/L / 1^{1/2} < \mu < 0.009\ \mu g/L + 2.080 \times 0.0016\ \mu g/L / 1^{1/2}$,

$0.009\ \mu g/L - 0.0033\ \mu g/L < \mu < 0.009\ \mu g/L + 0.0033\ \mu g/L$,

$0.0057\ \mu g/L < \mu < 0.0123\ \mu g/L$.

Step 6. Interpret the confidence interval. The data user is 95 percent confident that the true mean concentration that would be determined by the analytical method for this water sample is between 0.0057 µg/L and 0.0123 µg/L. If the analytical method is unbiased (100 percent recovery) and other biases are negligible (contamination, degradation, matrix effects, or sampling technique), the data user also is 95 percent confident that the true concentration of the water body is between 0.0057 µg/L and 0.0123 µg/L.

Example 2: Confidence Limits for a Single Water-Quality Measurement, Corrected for Recovery

This example presents an approach for correcting the confidence limits presented in example 1 for bias in the analytical method. Web-based resources are available that characterize bias in the analytical method for the pesticides presented in this report. The most useful information is obtained from laboratory control (analytical set) spikes done by NWQL and summarized by Martin (1999, table 4), blind spikes done by the Organic Blind Sample Program (OBSP) (http://btdqs.usgs.gov/OBSP/index.html), and low-concentration long-term method detection limit (LT-MDL) spikes done by NWQL (http://wwwnwql.cr.usgs.gov/Public/ltmdl/ltmdlsplash.html). All of these spikes are done in pesticide-grade blank water and, consequently, do not provide information on matrix effects (if any) of environmental water samples.

An important assumption in this approach is that the bias in recovery at the concentration of interest to the data user is the same as that at the concentration of the QC spikes used to characterize the bias in recovery. The concentrations of laboratory control spikes are 0.1 µg/L for pesticides analyzed by GCMS and 0.5 µg/L for pesticides analyzed by HPLC. These concentrations represent the midrange of the calibration curves and probably are concentrations where bias is minimized for many pesticides. The concentrations of the OBSP blind spikes are done at several concentrations in the calibration range of the analytical method and, for selected pesticides, at concentrations greater than the calibration range of the method. The concentrations of the LT-MDL spikes are at low concentrations near the method detection limit.

Three data sets were identified with the most value for determining the bias in the analytical method for alachlor at concentrations near 0.009 µg/L. The information was pooled to obtain an estimate that characterizes bias in the analytical method over 6 years (table 10).

Table 10. Pooled estimate of bias in the analytical method for a measurement of alachlor near 0.009 micrograms per liter

[µg/L, microgram per liter; OBSP, Organic Blind Sample Program; NWQL, National Water Quality Laboratory; LT-MDL, long-term method detection limit]

Spike source and type	Spiked concentration (µg/L)	Time period	Number of spikes	Degrees of freedom	Mean percent recovery (percent)	Standard deviation of percent recovery (percent)
OBSP Blind spikes	0.005–0.040	1996–1999	31	30	115.8	26.2
NWQL LT-MDL spikes	0.004	2000	24	23	133.3	16.7
NWQL LT-MDL spikes	0.004	2001	25	24	155.1	21.7
Pooled estimate	0.004–0.040	1996–2001	80	77	133.3	22.3

The mean recovery of alachlor at concentration near 0.009 µg/L is 133.3 percent (table 10) and indicates a positive bias in the analytical method. The calculated mean recovery of alachlor is only an estimate of the true recovery of alachlor in this range of concentration. Calculation of a confidence interval quantifies the uncertainty in the value of the recovery correction factor to be applied to the range of measurements determined in example 1. Calculation of a 95-percent confidence interval for the mean percent recovery of alachlor in this low range of concentration is done similarly to that in example 1, except that the mean percent recovery is based on a sample size of 80 (n = 80) and the value of the *t*-distribution is based on 77 degrees of freedom (t = 1.991). The 95-percent confidence interval for the mean recovery of 133.3 percent is:

$$133.3 \text{ percent} - 1.991 \times 22.3 \text{ percent} / 80^{1/2} < \mu < 133.3 \text{ percent} + 1.991 \times 22.3 \text{ percent} / 80^{1/2}$$

$$133.3 \text{ percent} - 4.96 \text{ percent} < \mu < 133.3 \text{ percent} + 4.96 \text{ percent},$$

$$128.3 \text{ percent} < \mu < 138.3 \text{ percent}.$$

On the basis of the laboratory QC information presented in table 10, the data user is 95 percent confident that the mean recovery of alachlor at concentrations near 0.009 µg/L is between 128.3 and 138.3 percent (the upper and lower confidence limits are not rounded to the unit's place because they are used in further calculations). Correct the range of measurements determined in example 1 for bias in the analytical method as follows:

Step 1. Calculate and apply a correction factor for bias in recovery for a single measurement of alachlor of 0.009 µg/L. The mean recovery of alachlor at concentrations near 0.009 µg/L was estimated to be 133.3 percent (table 10) and indicates a positive bias. In order to estimate the true concentration in a water sample, a correction factor less than 1 is needed to reduce the value of the measurement to account for positive bias from the analytical method. The correction factor is 0.7502 (100 percent / 133.3 percent). The value of the alachlor measurement, corrected for recovery, is 0.0068 µg/L (0.009 µg/L x 0.7502).

Step 2. Calculate and apply correction factors for bias in recovery to the confidence interval for the mean of a single measurement that was calculated in example 1. The correction factors for bias in recovery includes the uncertainty about the true value of the correction to be applied. This step combines the random and systematic errors of the measurement process (and combines the uncertainties in these estimates of error). The correction factors are 0.7794 (100 percent / 128.3 percent) and 0.7231 (100 percent / 138.3 percent). Apply the correction factors to each confidence limit and select the corrected values that maximize the length of the combined confidence interval:

$$0.0057 \text{ µg/L} \times 0.7794 = 0.0044 \text{ µg/L},$$
$$0.0057 \text{ µg/L} \times 0.7231 = 0.0041 \text{ µg/L},$$
$$0.0123 \text{ µg/L} \times 0.7794 = 0.0096 \text{ µg/L},$$
$$0.0123 \text{ µg/L} \times 0.7231 = 0.0089 \text{ µg/L}.$$

Step 3. Determine the combined 95-percent confidence limits for a single water-quality measurement of 0.009 µg/L, corrected for recovery:

$$0.0041 \text{ µg/L} < \mu < 0.0096 \text{ µg/L}.$$

Step 4. Interpret the combined 95-percent confidence limits for a single water-quality measurement of 0.009 µg/L, corrected for recovery. The best estimate of the mean concentration of the water sample, corrected for recovery is 0.0068 µg/L. The data user is 95 percent confident that the true mean concentration that would be determined by the analytical method for this water sample, corrected for recovery, is between 0.0041 µg/L and 0.0096 µg/L. If other biases are negligible (contamination, degradation, matrix effects, or sampling technique), the best estimate of the true concentration of the water body is 0.0068 µg/L, and the data user also is 95 percent confident that the true concentration of the water body is between 0.0041 µg/L and 0.0096 µg/L.

Example 3: The Concentration Needed to be Assured of Exceeding a Water-Quality Standard

Water-quality measurements often are compared to a water-quality standard to determine whether the water body is in compliance with the standard. The objective for this example is to determine, in view of variability, how much greater than the standard an individual measurement must be in order to be assured that the water body has exceeded the standard. The approach is to estimate an upper limit to random error at the concentration of the standard. If a measurement exceeds the upper limit to random error at the concentration of the standard, then it is likely that the concentration of the water sample exceeds the standard.

The upper limit to random error is determined by calculation of a one-sided tolerance bound for a normal distribution (Hahn and Meeker, 1991, pp. 34–36, pp. 58–61). A tolerance bound is used to enclose a proportion of the population (whereas a confidence bound is used to enclose a population parameter—mean, standard deviation, percentile, and so on). The formula for a one-sided upper tolerance bound for a sample from a normal distribution is

$$T_p = \overline{X} + g'_{(1-\alpha,\, p,\, n)} \times SD, \qquad (3)$$

where

Tp is the upper tolerance bound to contain at least p proportion of the population with 1-α confidence (in micrograms per liter),

p is the proportion of the normal population of measurements contained in the tolerance bound (this is the upper limit to random error selected by the user),

n is the number of samples used to estimate SD,

$g'_{(1-\alpha,\, p,\, n)}$ is a factor for calculating one-sided tolerance bounds with 1-α confidence, p proportion of the population, and n samples (in this application, n should be set equal to 1 plus the number of degrees of freedom used to estimate SD), and

$\overline{X}$, SD, and α are as previously defined (in this application, $\overline{X}$ is the concentration of the water-quality standard).

Assume, for example, that 0.009 µg/L is a water-quality standard for alachlor. Calculate the upper limit of random error at the standard as follows:

Step 1. Calculate SD for an alachlor concentration of 0.009 µg/L, using an appropriate estimate of variability from table 7. This calculation was done in example 1, and the SD is 0.0016 µg/L.

Step 2. Determine the appropriate degrees of freedom for the SD estimated in Step 1. This determination was done in example 1, and the estimate of SD is based on 21 degrees of freedom.

Step 3. Select the proportion of measurements to be contained in the tolerance bound (the upper limit to random error selected by the user). The data user chooses to bound 95 percent of the measurements (p = 0.95).

Step 4. Select a level of confidence for the upper tolerance bound. The data user chooses to calculate a 95-percent tolerance bound. This level of confidence is equivalent to selecting α = 0.05.

Step 5. Determine a value for $g'_{(1-\alpha,\, p,\, n)}$. Values of the factor g' are based on the noncentral t-distribution and are summarized in table A12 of Hahn and Meeker (1991, pp. 312–315) from the original work presented in Odeh and Owen (1980). In this application, n should be set equal to 1 plus

the number of degrees of freedom used to estimate *SD* in step 2 ($n = 22 = 1 + 21$). The value of g' is 2.349 (based on an estimate of *SD* with 21 degrees of freedom and the desire to bound 95 percent of the normal distribution with 95 percent confidence).[1]

Step 6. Calculate the upper tolerance bound, using equation 3:

$$T_{0.95} < 0.009\ \mu g/L + 2.349 \times 0.0016\ \mu g/L,$$
$$T_{0.95} < 0.009\ \mu g/L + 0.0038\ \mu g/L,$$
$$T_{0.95} < 0.0128\ \mu g/L.$$

Step 7. Interpret the upper tolerance bound in terms of a upper limit to random error. If the analytical method is unbiased (100 percent recovery) and other biases are negligible (contamination, degradation, matrix effects, or sampling technique), the data user is 95 percent confident that 95 percent of the measurements of alachlor at the standard (a true concentration of 0.009 µg/L) are less than 0.0128 µg/L. Consequently, the data user is confident that a measurement of alachlor greater than 0.0128 µg/L indicates that a water body has exceeded the water-quality standard.

If the analytical method is biased, however, the upper tolerance bound is less useful for determining whether or not water quality has exceeded a standard. For biased analytical methods, the upper tolerance bound only provides an upper limit to random error for the mean response of the (biased) measurement system. The data user needs an estimate of the upper limit to random error for an unbiased measurement system to assess whether or not a water-quality standard has been exceeded. The upper limit to random error can be corrected for bias in the analytical method by the same approach that was used in example 2.

The mean recovery of alachlor at concentrations near 0.009 µg/L was estimated to be 133.3 percent (table 10) and indicates a positive bias. On the basis of the calculations in example 2, the data user is 95 percent confident that the mean recovery of alachlor at concentrations near 0.009 µg/L is between 128.3 and 138.3 percent. Correct the upper limit of random error for bias in the analytical method as follows:

Step 8. Calculate and apply a correction factor for bias in recovery for the upper limit of random error for a water-quality standard for alachlor of 0.009 µg/L. Because the analytical method is positively biased, a correction factor greater than 1 is needed to increase the upper limit of random error in order to be assured that a positively biased measurement exceeds the standard. (If the method was negatively biased, a correction factor less than 1 would be needed to reduce the upper limit.) The correction factors for bias in recovery includes the uncertainty about the true value of the correction to be applied. This step combines the random and systematic errors of the measurement process (and combines the uncertainties in these estimates of error). The correction factors for bias are 1.283 (128.3 percent / 100 percent) and 1.383 (138.3 percent / 100 percent). Apply the correction factors to the upper limit of random error and select the corrected value that maximizes the length of the combined tolerance bound:

$$0.0128\ \mu g/L \times 1.283 = 0.0164\ \mu g/L,$$
$$0.0128\ \mu g/L \times 1.383 = 0.0177\ \mu g/L.$$

Step 9. Determine the combined 95-percent tolerance bound for the upper limit of random error for a water-quality standard for alachlor of 0.009 µg/L, corrected for recovery:

$$T_{0.95} < 0.0177\ \mu g/L.$$

Step 10. Interpret the combined 95-percent tolerance bound for the upper limit of random error for a water-quality standard for alachlor of 0.009 µg/L, corrected for recovery. If other biases are negligible (contamination, degradation, matrix effects, or sampling technique), the data user is 95 percent confident that 95 percent of the measurements of alachlor at the standard (a true concentration of 0.009 µg/L) would be less than 0.0177 µg/L. Consequently, the data user is confident that a measurement of alachlor greater than 0.0177 µg/L indicates that a water body has exceeded the water-quality standard.

Note that the concentration needed to be assured of **not** exceeding a water-quality standard could have been determined by a similar approach. The data user could have calculated a one-sided **lower** tolerance bound to determine the lower limit to random error.

[1]Note that the value of g' (2.349) is substantially larger than a comparable value of the *t*-distribution (1.721) and shows that efforts to bound a percentage of measurements by using the *t*-distribution (incorrectly) will bound a smaller percentage of measurements than that desired.

Example 4: Are Two Water-Quality Measurements Different?

Another need in water-quality assessments is to determine whether two water-quality measurements are different. The objective for this example is to determine whether the difference in two individual measurements indicates a true difference in water quality or could be attributable solely to variability. The approach is to calculate confidence intervals for the mean (as was done in example 1) for each measurement and to compare the intervals. If the intervals do not overlap, a difference in water quality is indicated at the selected level of confidence. If the intervals overlap, the difference in measurements can be attributable to variability. In the following example, measurements of alachlor in two water samples yield values of 0.009 µg/L and 0.020 µg/L. A data user is interested in determining whether the measurements indicate that water quality differs. A 95-percent confidence interval is needed for the mean concentration for each measurement. One was calculated for the sample of 0.009 µg/L in example 1, and the interval is 0.0057 µg/L to 0.0123 µg/L. For the sample of 0.020 µg/L, proceed as follows:

Step 1. Determine *SD* for an alachlor concentration of 0.020 µg/L, using an appropriate estimate of variability from table 7. The most applicable concentration range is 0.01 to < 0.1 µg/L and the pooled *RSD* is 10.0 percent. *SD* is calculated from the pooled *RSD* by use of equation 2. *SD* is 0.0020 µg/L (0.020 µg/L x 10.0 percent / 100 percent).

Step 2. Determine the appropriate degrees of freedom for the *SD* estimated in Step 1. Estimates of variability for alachlor measurements in concentration range 0.01 to < 0.1 µg/L are based on 38 degrees of freedom (table 7).

Step 3. Select a level of confidence for the confidence interval. The data user chooses to calculate a 95-percent confidence interval. This is equivalent to selecting $\alpha = 0.05$. (Select the same level of confidence for both intervals).

Step 4. Determine a value for the *t*-distribution that has 38 degrees of freedom and $\alpha/2$ of the error in each tail of the distribution. The value of the *t*-distribution with 38 degrees of freedom and 0.025α in each tail is 2.024.

Step 5. Calculate the confidence interval (eq. 1) for a mean concentration of a single measurement of 0.020 µg/L:

$$0.020\ \mu g/L - 2.024 \times 0.0020\ \mu g/L / 1^{1/2} < \mu < 0.020\ \mu g/L + 2.024 \times 0.0020\ \mu g/L / 1^{1/2},$$

$$0.020\ \mu g/L - 0.0040\ \mu g/L < \mu < 0.020\ \mu g/L + 0.0040\ \mu g/L,$$

$$0.0160\ \mu g/L < \mu < 0.0240\ \mu g/L.$$

Step 6. Compare the confidence intervals. The 95-percent confidence intervals for the mean are 0.0057 µg/L to 0.0123 µg/L for a measurement of 0.009 µg/L and are 0.0160 µg/L to 0.0240 µg/L for a measurement of 0.020 µg/L. The intervals do not overlap.

Step 7. Interpret the confidence intervals. The data user is 95 percent confident that the mean concentrations of alachlor in the water samples are different. If biases in the analytical method, contamination, degradation, matrix effects, or sampling technique are negligible or affect each sample similarly, the data user is 95 percent confident that the true concentrations of alachlor in the water bodies are different. Because bias in the analytical method should be similar over narrow ranges of concentration, a correction for recovery is not needed to determine whether concentrations differ.

SUMMARY

Field replicates collected for the U.S. Geological Survey National Water-Quality Assessment Program during 1992 to 1997 were used to assess the variability of pesticide detections and concentrations in environmental water samples collected from the surface- and ground-water-quality networks of the NAWQA Program. Field replicates are two or more identically collected, processed, and analyzed environmental water samples that are used to assess the overall variability of field and laboratory procedures.Variability is the degree of random error in independent measurements of the same quantity and is the opposite of precision—the degree of mutual agreement. Information on variability can be used to estimate the reproducibility of individual measurements, the concentration needed to be assured of exceeding a water-quality standard, and the likelihood that two measurements of water quality are different.

Variability of pesticide detections was assessed by calculating the mean percentage detection of a pesticide and the percentage of inconsistent replicate sets. Variability of pesticide concentrations was assessed by pooling estimates of the *SD* and *RSD* in replicate sets. Variability of pesticide detections and concentrations was a function of concentration and estimates of variability were developed for discrete, overlapping ranges of concentration. Reliability of estimates of variability was assessed by calculating 90-percent upper confidence bounds for the percentage of inconsistent replicate sets and for the pooled estimates of *SD* and *RSD*.

Twenty-two percent (19 of 86) of the pesticides analyzed for were not detected in any field replicates: aldicarb, aldicarb sulfone, chloramben, chlorothalonil, clopyralid, dacthal monoacid, 2,4-DB, dicamba, dichlorprop, 3-hydroxycarbofuran, MCPB, methiocarb, neburon, oxamyl, parathion, phorate, propham, silvex, and 2,4,5-T. Evaluation of variability of detection or concentration could not be done for these pesticides.

The mean detection rate shows the overall rate of detection of a pesticide in field replicates. The variability of detection for most pesticides is high at concentrations less than the MRL, but the variability of detection decreases dramatically at higher concentrations. The percentage of replicate sets with inconsistent detections measures the frequency that a pesticide was not detected in all replicates in a set. In the context of the variability of detection in environmental samples, the percentage of replicate sets with inconsistent detections estimates the likelihood that a pesticide that is detected in a single environmental sample would not be detected in a duplicate environmental sample. As with the mean detection rate, variability of detection measured by the percentage of inconsistent replicate sets is high at concentrations less than the MRL but decreases with increasing concentrations. The overall rate of inconsistent replicate sets is 60.0 percent in the low range of concentration, 13.7 percent in the medium range, and 1.1 percent in the high range.

Inconsistent detections are caused by false-positive or false-negative errors. False-positive errors usually are caused by sample contamination, whereas false-negative errors usually are caused by water-matrix interference, pesticide degradation, or other chemical-loss processes. Both types of errors may be caused by variability inherent in the analytical method, but calculation and use of MDLs are intended to protect against false-positive errors. On the basis of the low frequency of detection in field blanks, sample contamination is an unlikely cause of inconsistent detections in replicate sets. In view of the highly diverse sources of water submitted as field replicates for the NAWQA Program and the generally low concentrations (concentrations in 79 percent of replicate sets were less than 0.1 µg/L) of pesticides in most replicates, inconsistent detections in replicate sets likely were caused by variability in the analytical method and by water-matrix interferences (or other loss processes) that cause false-negative errors. Consequently, estimates of the frequency of detection of pesticides in environmental water samples collected for the NAWQA Program probably are biased low because of false-negative errors at concentrations near the minimum reporting level.

Pooled estimates of *SD* and *RSD* were used to assess the variability of concentrations. The pooled *SD* increases markedly with increasing concentration, whereas the pooled *RSD* decreases with increasing concentration but is much less a function of concentration than is the pooled *SD*. Results of correlation analyses indicate that for most pesticides and concentrations, pooled estimates of *RSD* rather than pooled estimates of *SD* should be used to estimate variability because pooled estimates of *RSD* are less affected by heteroscedasticity. The median pooled *RSD* was calculated for all pesticides to summarize the typical variability for pesticide data collected for the NAWQA Program. The median pooled *RSD* was 15 percent at concentrations less than 0.01 µg/L, 13 percent at concentrations near 0.01 µg/L, 12 percent at concentrations near 0.1 µg/L, 7.9 percent at concentrations near 1 µg/L, and 2.7 percent at concentrations greater than 5 µg/L.

Pooled estimates of *SD* or *RSD* presented in this report are larger than estimates based on averages, medians, smooths, or regression of the individual measurements of *SD* or *RSD* from field replicates. Pooled estimates, however, are the preferred method for characterizing variability because they provide unbiased estimates of the variability of the population. Assessments of variability based on *SD* (rather than variance)

underestimate the true variability of the population. Because pooled estimates of variability are larger than estimates based on other approaches, users of estimates of variability must be cognizant of the approach used to obtain the estimate and must use caution in the comparison of estimates based on different approaches.

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APPENDIX 1

Appendix 1. Pesticide registry numbers, analytical methods, and parameter codes

[Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System and the U.S. Environmental Protection Agency Data Storage and Retrieval System. Analytical method: GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography. Use: F, fungicide; H, herbicide; I, insecticide; M, metabolite. Class: ACID, miscellaneous acids; AMID, amides; CB, carbamates; CPA, chlorophenoxy acids; DNA, dinitroanilines; MISC, miscellaneous; OC, organochlorines; OP, organophosphates; PY, pyrethroids; TRI, triazines; UR, uracils; UREA, ureas]

Appendix 1. Pesticide registry numbers, analytical methods, and parameter codes

Parameter code	Analytical method	Pesticide	Other names	Use	Class	Chemical Abstract Service registry number
49260	GCMS	Acetochlor	Harness Plus, Acenit	H	AMID	34256-82-1
49315	HPLC	Acifluorfen	Blazer, Tackle 2S	H	ACID	50594-66-6
46342	GCMS	Alachlor	Lasso, Bullet, Alagan	H	AMID	15972-60-8
49312	HPLC	Aldicarb	Temik, Sanacarb	I	CB	116-06-3
49313	HPLC	Aldicarb sulfone	Aldicarb metabolite	M	CB	1646-88-4
49314	HPLC	Aldicarb sulfoxide	Aldicarb metabolite	M	CB	1646-87-3
39632	GCMS	Atrazine	AAtrex, Gesaprim	H	TRI	1912-24-9
82686	GCMS	Azinphos-methyl	Guthion, Carfene	I	OP	86-50-0
82673	GCMS	Benfluralin	Benefin, Balan, Bonalan	H	DNA	1861-40-1
38711	HPLC	Bentazon	Bentazone, Basagran	H	MISC	25057-89-0
04029	HPLC	Bromacil	Bromax, Hyvar X, Urox B	H	UR	314-40-9
49311	HPLC	Bromoxynil	Torch, Buctril, Brominal	H	ACID	1689-84-5
04028	GCMS	Butylate	Genate Plus, Sutan +	H	CB	2008-41-5
82680	GCMS	Carbaryl	Sevin, Savit	I	CB	63-25-2
49310	HPLC	Carbaryl	Sevin, Savit	I	CB	63-25-2
82674	GCMS	Carbofuran	Furadan, Carbodan	I	CB	1563-66-2
49309	HPLC	Carbofuran	Furadan, Carbodan	I	CB	1563-66-2
49307	HPLC	Chloramben	Methyl amiben	H	ACID	133-90-4
49306	HPLC	Chlorothalonil	Bravo, Echo	F	OC	1897-45-6
38933	GCMS	Chlorpyrifos	Dursban, Lorsban	I	OP	2921-88-2
49305	HPLC	Clopyralid	Stinger, Lontrel, Reclaim	H	ACID	1702-17-6
04041	GCMS	Cyanazine	Bladex, Fortrol	H	TRI	21725-46-2
39732	HPLC	2,4-D	2,4-PA; Ded-Weed SULV	H	CPA	94-75-7
82682	GCMS	Dacthal	DCPA, Chlorthal-dimethyl	H	OC	1861-32-1
49304	HPLC	Dacthal monoacid	Dacthal metabolite	M	OC	887-54-7
38746	HPLC	2,4-DB	Butyrac, Embutox	H	CP	94-82-6
34653	GCMS	*p,p'*-DDE	DDT metabolite	M	OC	72-55-9
04040	GCMS	Desethylatrazine	Atrazine metabolite	M	TRI	6190-65-4
39572	GCMS	Diazinon	Diazol, Basudin, Neocidol	I	OP	333-41-5
38442	HPLC	Dicamba	Banval, Mediben, Dianat	H	ACID	1918-00-9
49303	HPLC	Dichlobenil	Barrier, Casoron	H	OC	1194-65-6
49302	HPLC	Dichlorprop	2,4-DP; Seritox 50; Kildip	H	CPA	120-36-5
39381	GCMS	Dieldrin	Panoram D-31, Octalox	I	OC	60-57-1
82660	GCMS	2,6-Diethylaniline	Alachlor metabolite	M	AMID	579-66-8
49301	HPLC	Dinoseb	DNPB, Dinosebe	H	ACID	88-85-7

Appendix 1. Pesticide registry numbers, analytical methods, and parameter codes—Continued

Parameter code	Analytical method	Pesticide	Other names	Use	Class	Chemical Abstract Service registry number
82677	GCMS	Disulfoton	Disyston, Dithiosystox	I	OP	298-04-4
49300	HPLC	Diuron	DCMU, Karmex, Direx	H	UREA	330-54-1
49299	HPLC	DNOC	Sinox, Trifocide	H	ACID	534-52-1
82668	GCMS	EPTC	Eptam, Alirox, Niptan	H	CB	759-94-4
82663	GCMS	Ethalfluralin	Sonalan, Sonalen	H	DNA	55283-68-6
82672	GCMS	Ethoprop	Ethoprophos, Mocap	I	OP	13194-48-4
49297	HPLC	Fenuron	Beet-Klean, Dybar, Urab	H	UREA	101-42-8
38811	HPLC	Fluometuron	Flo-Met, Cotoran, Cottonex	H	UREA	2164-17-2
04095	GCMS	Fonofos	Dyfonate, Capfos	I	OP	944-22-9
34253	GCMS	*alpha*-HCH	Lindane metabolite	M	OC	319-84-6
39341	GCMS	*gamma*-HCH	Lindane, Lintox	I	OC	58-89-9
49308	HPLC	3-Hydroxycarbofuran	Carbofuran metabolite	M	CB	16655-82-6
82666	GCMS	Linuron	Lorox, Linex, Linurex	H	UREA	330-55-2
38478	HPLC	Linuron	Lorox, Linex, Linurex	H	UREA	330-55-2
39532	GCMS	Malathion	Cythion, Fyfanon	I	OP	121-75-5
38482	HPLC	MCPA	Metaxon, Agritox	H	CPA	94-74-6
38487	HPLC	MCPB	Tropotox, Thistrol	H	CPA	94-81-5
38501	HPLC	Methiocarb	Mesurol, Draza	I	CB	2032-65-7
49296	HPLC	Methomyl	Lannate, Nudrin	I	CB	16752-77-5
82667	GCMS	Methyl parathion	Penncap-M, Romethyl-P	I	OP	298-00-0
39415	GCMS	Metolachlor	Dual, Pennant	H	AMID	51218-45-2
82630	GCMS	Metribuzin	Lexone, Sencor	H	TRI	21087-64-9
82671	GCMS	Molinate	Ordram, Sakkimol	H	CB	2212-67-1
82684	GCMS	Napropamide	Devrinol, Naproquard	H	AMID	15299-99-7
49294	HPLC	Neburon	Neberex, Neburea, Neburyl	H	UREA	555-37-3
49293	HPLC	Norflurazon	Telok, Evital, Solicam	H	MISC	27314-13-2
49292	HPLC	Oryzalin	Surflan, Dirimal, Ryzelan	H	DNA	19044-88-3
38866	HPLC	Oxamyl	Vydate L, Pratt	I	CB	23135-22-0
39542	GCMS	Parathion	Thiophos, Bladan, Folidol	I	OP	56-38-2
82669	GCMS	Pebulate	Tillam, PEBC	H	CB	1114-71-2
82683	GCMS	Pendimethalin	Prowl, Stomp	H	DNA	40487-42-1
82687	GCMS	*cis*-Permethrin	Ambush, Pounce	I	PY	54774-45-7
82664	GCMS	Phorate	Thimet, Rampart	I	OP	298-02-2
49291	HPLC	Picloram	Amdon, Grazon, Tordon	H	ACID	1918-02-1
04037	GCMS	Prometon	Prometone, Gesagran	H	TRI	1610-18-0
82676	GCMS	Pronamide	Kerb, Propyzamid	H	AMID	23950-58-5
04024	GCMS	Propachlor	Propachlore, Ramrod	H	AMID	1918-16-7
82679	GCMS	Propanil	Stampede, Surcopur	H	AMID	709-98-8
82685	GCMS	Propargite	Omite, Comite, BPPS	I	ACID	2312-35-8
49236	HPLC	Propham	IPC, Tuberite	H	CB	122-42-9

Appendix 1. Pesticide registry numbers, analytical methods, and parameter codes—Continued

Parameter code	Analytical method	Pesticide	Other names	Use	Class	Chemical Abstract Service registry number
38538	HPLC	Propoxur	Baygon, Blattanex, Unden	I	CB	114-26-1
39762	HPLC	Silvex	2,4,5-TP; Fenoprop	H	CPA	93-72-1
04035	GCMS	Simazine	Aquazine, Princep, GEsatop	H	TRI	122-34-9
39742	HPLC	2,4,5-T	Brush Killer, Esterone	H	CPA	93-76-5
82670	GCMS	Tebuthiuron	Spike, Perflan	H	UREA	34014-18-1
82665	GCMS	Terbacil	Sinbar, Geonter	H	UR	5902-51-2
82675	GCMS	Terbufos	Counter, Contraven	I	OP	13071-79-9
82681	GCMS	Thiobencarb	Benthiocarb, Bolero, Saturn	H	CB	28249-77-6
82678	GCMS	Triallate	Avadex BW, Far-Go	H	CB	2303-17-5
49235	HPLC	Triclopyr	Crossbow, Garlon, Grazon	H	ACID	55335-06-3
82661	GCMS	Trifluralin	Treflan, Elancolan, Trinin	H	DNA	1582-09-8

APPENDIX 2

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates

[Estimates based on measurements that showed increasing or decreasing variability in the range of concentration are shown in ***bold italic*** type. µg/L, microgram per liter; IRS, inconsistent replicate sets; N, number of replicate sets; df, degrees of freedom; GCMS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; MRL, minimum reporting level; <, less than; >=, greater than or equal to; parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; deleted, nondetections in IRS deleted; zero, nondetections in IRS set to zero; mrl, nondetections in IRS set to the MRL; nc, not calculated]

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Acetochlor, parameter code 49260, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	3	4	0.00079	0.0015	0.00071	12.4	24.0	7.4	0.003	0.006	0.010
	zero	4	6	.0064	.0105	.0011	100.5	165.8	15.5	.003	.006	.010
	mrl	4	6	.0057	.0094	.0011	74.6	123.1	15.5	.003	.007	.010
0.005 to < 0.05	deleted	5	5	.0016	.0029	.0014	***11.7***	***20.6***	***6.7***	.006	.031	.048
	zero	6	7	.0060	.0095	.0014	***93.1***	***146.4***	***7.1***	.006	.020	.048
	mrl	6	7	.0054	.0085	.0014	***69.1***	***108.7***	***7.1***	.006	.020	.048
0.01 to < 0.1	no IRS	4	4	.0018	.0035	.0014	4.3	8.3	3.2	.031	.045	.087
0.05 to < 0.5	no IRS	2	2	.0051	.0157	.0042	2.0	6.2	2.0	.087	.196	.305
0.1 to < 1	no IRS	1	1	.0071	.0563	.0071	2.3	18.4	2.3	nc	.305	nc
0.5 to < 5	no IRS	2	2	.0583	.1796	.0566	2.5	7.8	2.5	1.43	2.47	3.51
1 to < 10	no IRS	3	3	.0981	.2222	.0707	2.6	5.9	2.7	1.43	3.51	5.40
>= 5	no IRS	1	1	.1485	1.182	.1485	2.7	21.9	2.7	nc	5.40	nc
Acifluorfen, parameter code 49315, analysis by HPLC, MRL 0.035 µg/L												
0.005 to < 0.05	zero	1	1	.0141	.1125	.0141	141.4	1125.	141.4	nc	.010	nc
	mrl	1	1	.0106	.0844	.0106	38.6	306.9	38.6	nc	.028	nc
0.01 to < 0.1	zero	2	2	.0955	.2943	.0742	141.4	435.7	141.4	.010	.053	.095
	mrl	1	1	.0106	.0844	.0106	38.6	306.9	38.6	nc	.028	nc
0.05 to < 0.5	deleted	1	1	.0778	.6190	.0778	67.6	538.2	67.6	nc	.115	nc
	zero	2	2	.1098	.3382	.1061	110.8	341.5	104.5	.095	.105	.115
	mrl	2	2	.0950	.2928	.0937	83.9	258.4	82.5	.113	.114	.115
0.1 to < 1	deleted	2	2	.0930	.2865	.0919	48.9	150.6	40.9	.115	.430	.745
	zero	2	2	.0930	.2865	.0919	48.9	150.6	40.9	.115	.430	.745
	mrl	3	3	.0988	.2240	.1061	69.0	156.3	67.6	.113	.115	.745
0.5 to < 5	no IRS	1	1	.1061	.8441	.1061	14.2	113.3	14.2	nc	.745	nc

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Alachlor, parameter code 46342, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	20	21	0.00076	0.00095	0.00046	18.3	23.0	7.4	0.003	0.005	0.010
	zero	30	34	.0043	.0052	.00071	***91.2***	***108.6***	***14.3***	.001	.004	.010
	mrl	29	32	.0013	.0015	.00071	32.4	38.8	11.1	.002	.004	.010
0.005 to < 0.05	deleted	39	44	***.0018***	***.0021***	***.00071***	9.7	11.3	5.7	.005	.016	.036
	zero	40	46	.0038	.0044	.00071	37.3	43.3	5.8	.005	.015	.036
	mrl	41	47	.0036	.0042	.00071	32.9	38.1	5.9	.005	.015	.036
0.01 to < 0.1	deleted	33	38	.0041	.0048	.00071	10.0	11.8	4.6	.010	.020	.073
	zero	33	38	.0041	.0048	.00071	10.0	11.8	4.6	.010	.020	.073
	mrl	34	40	.0052	.0061	.00071	32.9	38.7	4.6	.010	.020	.073
0.05 to < 0.5	no IRS	10	10	.0174	.0249	.0106	11.0	15.8	4.8	.059	.203	.460
0.1 to < 1	no IRS	10	10	.0300	.0430	.0141	6.6	9.5	4.8	.155	.383	.863
0.5 to < 5	no IRS	6	6	.0445	.0735	.0177	***6.4***	***10.5***	***2.1***	.515	.766	3.75
1 to < 10	no IRS	2	2	.0522	.1608	.0460	2.0	6.1	2.0	1.04	2.39	3.75
Aldicarb sulfoxide, parameter code 49314, analysis by HPLC, MRL 0.021 µg/L												
0.1 to < 1	zero	1	1	1.273	10.13	1.273	141.4	1125.	141.4	nc	.900	nc
	mrl	1	1	1.258	10.01	1.258	138.2	1100.	138.2	nc	.911	nc
0.5 to < 5	zero	1	1	1.273	10.13	1.273	141.4	1125.	141.4	nc	.900	nc
	mrl	1	1	1.258	10.01	1.258	138.2	1100.	138.2	nc	.911	nc
Atrazine, parameter code 39632, analysis by GCMS, MRL 0.001 µg/L												
< 0.01	deleted	49	58	***.0012***	***.0013***	***.00058***	16.3	18.5	8.5	.002	.006	.010
	zero	63	76	.0019	.0021	.00071	***77.4***	***86.6***	***9.4***	.001	.006	.010
	mrl	63	76	.0017	.0019	.00071	38.6	43.2	9.4	.001	.006	.010
0.005 to < 0.05	deleted	90	105	***.0014***	***.0016***	***.00071***	***11.8***	***13.0***	***6.1***	.005	.013	.049
	zero	91	106	***.0017***	***.0019***	***.00071***	***18.1***	***19.9***	***6.1***	.005	.013	.049
	mrl	92	107	***.0018***	***.0019***	***.00071***	***19.9***	***21.9***	***6.2***	.005	.013	.049
0.01 to < 0.1	no IRS	80	92	***.0039***	***.0043***	***.0014***	7.6	8.4	3.8	.010	.030	.095
0.05 to < 0.5	no IRS	78	90	***.0128***	***.0142***	***.0058***	7.5	8.3	4.0	.050	.135	.497
0.1 to < 1	no IRS	62	73	***.0258***	***.0289***	***.0071***	6.9	7.8	4.4	.110	.208	.970

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Atrazine, parameter code 39632, analysis by GCMS, MRL 0.001 µg/L—Continued												
0.5 to < 5	no IRS	18	20	0.1396	0.1770	0.0389	7.1	9.0	3.9	0.535	1.04	4.35
1 to < 10	no IRS	12	12	.1732	.2390	.0707	5.8	8.0	2.2	1.10	2.95	7.55
>= 5	no IRS	6	6	***1.377***	***2.271***	***.2475***	***2.5***	***4.1***	***1.4***	5.10	10.6	69.4
Azinphos-methyl, parameter code 82686, analysis by GCMS, MRL 0.001 µg/L												
< 0.01	no IRS	1	1	.0014	.0113	.0014	23.6	187.6	23.6	nc	.006	nc
0.005 to < 0.05	deleted	4	5	.0030	.0053	.0025	19.9	35.1	20.1	.006	.020	.027
	zero	5	6	.0150	.0247	.0036	60.5	99.9	23.6	.006	.025	.027
	mrl	5	6	.0147	.0242	.0036	58.4	96.4	23.6	.006	.025	.027
0.01 to < 0.1	deleted	6	9	.0116	.0171	.0039	20.0	29.4	12.7	.015	.050	.085
	zero	8	11	.0385	.0541	.0057	63.0	88.4	20.4	.015	.050	.085
	mrl	8	11	.0382	.0537	.0057	61.5	86.4	20.4	.015	.050	.085
0.05 to < 0.5	deleted	7	9	.0431	.0633	.0141	21.7	31.9	8.7	.073	.125	.465
	zero	8	10	.0552	.0792	.0186	49.2	70.6	15.8	.073	.105	.465
	mrl	8	10	.0551	.0790	.0186	48.8	69.9	15.8	.073	.105	.465
0.1 to < 1	no IRS	4	4	.0623	.1209	.0389	22.8	44.2	14.4	.125	.203	.465
Benfluralin, parameter code 82673, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	1	1	.0	nc	.0	.0	nc	.0	nc	.003	nc
	zero	4	6	.0035	.0058	.0028	92.1	152.0	87.9	.002	.004	.005
	mrl	4	6	***.0025***	***.0041***	***.0017***	***50.4***	***83.1***	***41.4***	.003	.004	.006
0.005 to < 0.05	mrl	1	1	.0049	.0394	.0049	90.0	716.2	90.0	nc	.006	nc
Bentazon, parameter code 38711, analysis by HPLC, MRL 0.014 µg/L												
0.005 to < 0.05	zero	3	4	.0303	.0587	.0283	158.1	306.6	141.4	.013	.020	.030
	mrl	3	4	.0215	.0417	.0184	72.7	141.0	68.1	.023	.027	.037
0.01 to < 0.1	zero	3	4	.0303	.0587	.0283	158.1	306.6	141.4	.013	.020	.030
	mrl	3	4	.0215	.0417	.0184	72.7	141.0	68.1	.023	.027	.037
0.05 to < 0.5	deleted	7	7	***.0440***	***.0692***	***.0283***	***19.5***	***30.6***	***15.7***	.120	.165	.380
	zero	8	8	.0687	.1040	.0318	53.2	80.6	17.2	.110	.165	.380
	mrl	8	8	.0659	.0998	.0318	47.6	72.1	17.2	.117	.165	.380

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Bentazon, parameter code 38711, analysis by HPLC, MRL 0.014 µg/L—Continued												
0.1 to < 1	deleted	8	8	***0.0610***	***0.0923***	***0.0318***	***19.7***	***29.8***	***17.2***	0.120	0.173	0.600
	zero	9	9	.0774	.1138	.0354	50.7	74.5	18.6	.110	.165	.600
	mrl	9	9	.0753	.1106	.0354	45.5	66.8	18.6	.117	.165	.600
0.5 to < 5	no IRS	1	1	.1273	1.013	.1273	21.2	168.8	21.2	nc	.600	nc
Bromacil, parameter code 04029, analysis by HPLC, MRL 0.035 µg/L												
< 0.01	no IRS	1	2	.0035	.0107	.0035	43.3	133.4	43.3	nc	.008	nc
0.005 to < 0.05	deleted	1	2	.0035	.0107	.0035	43.3	133.4	43.3	nc	.008	nc
	zero	2	3	.0146	.0330	.0141	89.0	201.6	92.4	.008	.013	.018
	mrl	2	3	.0028	.0064	.0017	35.4	80.1	21.7	.008	.022	.035
0.01 to < 0.1	deleted	1	1	.0	nc	.0	.0	nc	.0	nc	.090	nc
	zero	2	2	.0175	.0539	.0124	100.0	308.1	70.7	.018	.054	.090
	mrl	2	2	.0	nc	.0	.0	nc	.0	.035	.063	.090
0.05 to < 0.5	deleted	1	1	.0	nc	.0	.0	nc	.0	nc	.090	nc
	zero	2	2	.1100	.3389	.0778	100.0	308.1	70.7	.090	.100	.110
	mrl	2	2	.0925	.2850	.0654	72.5	223.5	51.3	.090	.109	.128
0.1 to < 1	deleted	2	2	.0814	.2508	.0813	11.6	35.7	11.5	.640	.722	.805
	zero	3	3	.1117	.2532	.0849	82.2	186.2	13.3	.110	.640	.805
	mrl	3	3	.1006	.2279	.0849	60.0	135.9	13.3	.128	.640	.805
0.5 to < 5	no IRS	2	2	.0814	.2508	.0813	11.6	35.7	11.5	.640	.722	.805
Bromoxynil, parameter code 49311, analysis by HPLC, MRL 0.035 µg/L												
0.01 to < 0.1	zero	1	1	.0707	.5627	.0707	141.4	1125.	141.4	nc	.050	nc
	mrl	1	1	.0460	.3658	.0460	68.1	541.9	68.1	nc	.068	nc
0.05 to < 0.5	deleted	1	1	.0071	.0563	.0071	5.2	41.7	5.2	nc	.135	nc
	zero	2	2	.0502	.1548	.0389	100.1	308.3	73.3	.050	.093	.135
	mrl	2	2	.0329	.1013	.0265	48.3	148.8	36.7	.068	.101	.135
0.1 to < 1	no IRS	1	1	.0071	.0563	.0071	5.2	41.7	5.2	nc	.135	nc
Butylate, parameter code 04028, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	9	10	.00087	.0012	.00071	26.5	38.0	20.2	.002	.004	.009
	zero	11	13	.00094	.0013	.00071	***60.1***	***81.7***	***20.2***	.001	.004	.009
	mrl	11	13	.00079	.0011	.00071	26.9	36.6	20.2	.002	.004	.009

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Butylate, parameter code 04028, analysis by GCMS, MRL 0.002 µg/L—Continued												
0.005 to < 0.05	no IRS	9	10	0.0011	0.0016	0.00064	9.7	14.0	2.0	0.005	0.012	0.031
0.01 to < 0.1	no IRS	5	5	.0013	.0024	.00064	5.4	9.5	2.0	.012	.020	.031
Carbaryl, parameter code 82680, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	deleted	8	9	.00088	.0013	.00071	12.3	18.1	8.3	.005	.007	.010
	zero	17	19	.0056	.0071	.0035	107.9	137.8	141.4	.002	.006	.010
	mrl	16	18	.0036	.0046	.0019	49.5	63.7	35.8	.004	.006	.010
0.005 to < 0.05	deleted	28	33	***.0034***	***.0040***	***.0014***	14.3	17.1	8.8	.005	.017	.050
	zero	35	40	.0097	.0114	.0014	60.6	71.1	10.1	.005	.014	.050
	mrl	38	43	.0088	.0102	.0020	46.9	54.7	10.5	.005	.014	.050
0.01 to < 0.1	deleted	26	32	***.0067***	***.0080***	***.0017***	16.0	19.2	9.9	.010	.025	.073
	zero	29	35	.0112	.0133	.0021	44.1	52.4	10.1	.010	.025	.073
	mrl	30	36	.0108	.0127	.0022	40.6	48.1	10.1	.010	.024	.073
0.05 to < 0.5	no IRS	13	17	***.0268***	***.0347***	***.0199***	16.2	21.0	12.3	.051	.123	.460
0.1 to < 1	no IRS	11	14	.0775	.1040	.0212	16.3	21.8	12.3	.110	.385	.810
0.5 to < 5	no IRS	3	4	.1352	.2621	.1838	21.0	40.8	22.7	.503	.560	.810
Carbaryl, parameter code 49310, analysis by HPLC, MRL 0.008 µg/L												
0.005 to < 0.05	deleted	2	2	.0280	.0861	.0230	85.8	264.4	69.9	.033	.034	.035
	zero	3	3	.0242	.0549	.0141	107.6	243.8	119.7	.010	.033	.035
	mrl	3	3	.0233	.0529	.0085	78.3	177.5	60.6	.014	.033	.035
0.01 to < 0.1	deleted	3	3	.0306	.0694	.0354	74.1	167.8	41.6	.033	.035	.085
	zero	4	4	.0274	.0532	.0247	95.5	185.1	80.6	.010	.034	.085
	mrl	4	4	.0269	.0521	.0219	70.9	137.6	51.1	.014	.034	.085
0.05 to < 0.5	no IRS	2	2	.0354	.1089	.0354	29.8	91.9	24.4	.085	.290	.495
0.1 to < 1	no IRS	1	1	.0354	.2814	.0354	7.1	56.8	7.1	nc	.495	nc
0.5 to < 5	zero	1	2	.9866	3.039	.9866	87.1	268.2	87.1	nc	1.13	nc
	mrl	1	2	.9820	3.025	.9820	86.4	266.3	86.4	nc	1.14	nc
1 to < 10	zero	1	2	.9866	3.039	.9866	87.1	268.2	87.1	nc	1.13	nc
	mrl	1	2	.9820	3.025	.9820	86.4	266.3	86.4	nc	1.14	nc

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Carbofuran, parameter code 82674, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	zero	6	8	0.0070	0.0106	0.0069	117.6	178.0	141.4	0.003	0.005	0.009
	mrl	5	6	***.0048***	***.0080***	***.0035***	***62.5***	***103.1***	***64.3***	.004	.006	.009
0.005 to < 0.05	deleted	7	8	.0032	.0049	.0021	16.4	24.8	9.4	.011	.023	.035
	zero	12	14	.0088	.0118	.0043	***83.3***	***111.7***	***23.9***	.007	.013	.035
	mrl	13	15	.0074	.0098	.0035	61.0	80.8	25.7	.006	.014	.035
0.01 to < 0.1	deleted	8	9	.0140	.0206	.0021	28.9	42.4	14.8	.011	.024	.056
	zero	10	11	.0149	.0209	.0025	65.7	92.3	21.2	.011	.018	.056
	mrl	11	13	.0135	.0184	.0028	55.6	75.6	22.2	.010	.015	.056
0.05 to < 0.5	no IRS	6	6	.0249	.0411	.0039	34.3	56.6	1.2	.056	.120	.336
0.1 to < 1	no IRS	6	6	.0189	.0312	.0039	16.8	27.7	.5	.109	.155	.975
0.5 to < 5	no IRS	1	1	.0099	.0788	.0099	1.0	8.1	1.0	nc	.975	nc
Carbofuran, parameter code 49309, analysis by HPLC, MRL 0.120 µg/L												
0.005 to < 0.05	zero	1	1	.0636	.5064	.0636	141.4	1125.	141.4	nc	.045	nc
0.01 to < 0.1	zero	2	2	.0918	.2828	.0884	141.4	435.7	141.4	.045	.063	.080
0.05 to < 0.5	zero	1	1	.1131	.9003	.1131	141.4	1125.	141.4	nc	.080	nc
	mrl	2	2	.0250	.0770	.0247	20.2	62.2	20.2	.105	.123	.140
0.1 to < 1	deleted	1	1	.0	nc	.0	.0	nc	.0	nc	.790	nc
	zero	1	1	.0	nc	.0	.0	nc	.0	nc	.790	nc
	mrl	3	3	.0204	.0462	.0212	16.5	37.4	20.2	.105	.140	.790
0.5 to < 5	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.790	nc
Chlorpyrifos, parameter code 38933, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	deleted	22	24	.0018	.0022	.00071	23.9	29.6	12.7	.003	.007	.010
	zero	36	41	.0043	.0050	.0027	***95.2***	***111.5***	***37.9***	.002	.006	.010
	mrl	34	39	***.0022***	***.0026***	***.0011***	32.1	37.7	22.2	.003	.006	.010
0.005 to < 0.05	deleted	46	52	.0024	.0027	.0013	18.5	21.2	8.7	.005	.011	.041
	zero	52	59	.0052	.0059	.0014	***54.9***	***62.4***	***11.1***	.005	.010	.041
	mrl	57	65	.0043	.0049	.0014	***36.7***	***41.5***	***12.9***	.005	.010	.041
0.01 to < 0.1	deleted	29	34	.0030	.0035	.0014	12.0	14.3	8.3	.010	.021	.081
	zero	30	36	.0056	.0066	.0014	42.5	50.3	8.5	.010	.019	.081
	mrl	32	38	.0054	.0064	.0014	***36.8***	***43.4***	***8.7***	.010	.018	.081

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Chlorpyrifos, parameter code 38933, analysis by GCMS, MRL 0.004 µg/L—Continued												
0.05 to < 0.5	no IRS	8	9	0.0157	0.0231	0.0141	9.9	14.6	9.1	0.057	0.140	0.320
0.1 to < 1	no IRS	6	6	.0189	.0312	.0177	10.5	17.3	9.1	.125	.168	.320
Cyanazine, parameter code 04041, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	deleted	6	6	.0012	.0019	.00084	13.3	22.0	10.4	.008	.008	.010
	zero	14	14	.0056	.0075	.0049	107.3	143.8	141.4	.003	.007	.010
	mrl	14	14	.0036	.0049	.0025	45.9	61.6	37.7	.005	.008	.010
0.005 to < 0.05	deleted	33	37	***.0023***	***.0027***	***.0014***	10.1	11.9	8.8	.008	.016	.048
	zero	38	43	.0050	.0058	.0014	50.6	59.0	9.6	.006	.015	.048
	mrl	42	47	.0042	.0048	.0015	***32.7***	***37.8***	***10.9***	.005	.014	.048
0.01 to < 0.1	deleted	38	45	***.0040***	***.0047***	***.0019***	9.8	11.4	7.8	.010	.033	.098
	zero	39	47	***.0052***	***.0061***	***.0020***	25.5	29.5	8.0	.010	.029	.098
	mrl	39	47	***.0050***	***.0058***	***.0020***	21.7	25.2	8.0	.010	.029	.098
0.05 to < 0.5	no IRS	25	29	.0314	.0380	.0057	14.8	17.9	5.7	.050	.102	.330
0.1 to < 1	no IRS	19	20	.0759	.0962	.0071	19.1	24.3	3.8	.100	.247	.620
0.5 to < 5	no IRS	11	11	.2940	.4128	.0424	16.8	23.7	5.8	.530	1.07	4.67
1 to < 10	no IRS	6	6	.3794	.6260	.2581	9.1	15.0	7.2	1.07	3.44	4.67
2,4-D, parameter code 39732, analysis by HPLC, MRL 0.150 µg/L												
< 0.01	zero	2	2	.0071	.0218	.0071	141.4	435.7	141.4	.005	.005	.005
0.005 to < 0.05	deleted	2	2	.0071	.0218	.0071	22.9	70.5	22.0	.025	.035	.045
	zero	7	7	.0256	.0403	.0071	120.1	188.9	141.4	.005	.025	.045
	mrl	2	2	.0071	.0218	.0071	22.9	70.5	22.0	.025	.035	.045
0.01 to < 0.1	deleted	3	3	.0058	.0131	.0071	18.7	42.3	15.7	.025	.045	.070
	zero	7	7	.0568	.0892	.0283	107.6	169.1	141.4	.020	.030	.095
	mrl	6	6	.0655	.1081	.0424	80.0	131.9	55.1	.025	.075	.095
0.05 to < 0.5	deleted	6	6	***.0327***	***.0539***	***.0071***	10.6	17.5	6.2	.070	.180	.370
	zero	10	11	.1795	.2521	.0530	83.1	116.7	17.1	.070	.123	.423
	mrl	15	16	.1149	.1506	.0636	58.5	76.7	29.8	.070	.125	.473
0.1 to < 1	deleted	7	7	.0434	.0683	.0354	11.0	17.3	6.7	.105	.265	.740
	zero	10	11	.1767	.2481	.0566	71.5	100.4	13.4	.105	.250	.740
	mrl	13	14	.1172	.1571	.0566	35.5	47.7	16.6	.105	.195	.740
0.5 to < 5	no IRS	2	2	.0583	.1796	.0566	9.3	28.6	8.8	.600	.670	.740

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Dacthal, parameter code 82682, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	34	39	0.00036	0.00043	0.0	11.0	13.0	0.0	0.001	0.003	0.008
	zero	46	53	.00082	.00094	.0	***73.3***	***84.0***	.0	.000	.002	.008
	mrl	46	53	.00057	.00066	.0	23.1	26.5	.0	.001	.002	.008
0.005 to < 0.05	no IRS	20	25	.0058	.0071	.00071	26.8	33.0	5.9	.005	.012	.041
0.01 to < 0.1	no IRS	14	16	.0078	.0103	.0011	32.9	43.1	6.3	.011	.017	.081
0.05 to < 0.5	no IRS	4	4	.0159	.0308	.0095	11.3	22.0	6.7	.061	.118	.320
0.1 to < 1	no IRS	2	2	.0206	.0635	.0177	7.0	21.7	6.7	.155	.238	.320
***p,p'*-DDE, parameter code 34653, analysis by GCMS, MRL 0.006 µg/L**												
< 0.01	deleted	9	10	***.00073***	***.0010***	***.00071***	31.6	45.3	23.2	.001	.002	.009
	zero	30	37	***.0020***	***.0023***	***.00097***	***125.2***	***148.0***	***141.4***	.000	.001	.009
	mrl	31	38	.0024	.0028	.0026	63.6	74.9	49.5	.001	.004	.009
0.005 to < 0.05	deleted	5	5	.0025	.0044	.0028	15.2	26.9	16.4	.008	.014	.028
	zero	6	7	.0039	.0061	.0028	48.2	75.8	17.1	.007	.011	.028
	mrl	8	10	***.0022***	***.0031***	***.0020***	19.6	28.1	17.1	.005	.009	.028
0.01 to < 0.1	no IRS	3	3	.0031	.0070	.0028	16.1	36.5	16.4	.014	.022	.028
Desethylatrazine, parameter code 04040, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	50	56	***.00095***	***.0011***	***.00064***	18.2	20.8	10.9	.001	.004	.010
	zero	67	78	.0016	.0017	.00071	***74.1***	***82.8***	***15.7***	.001	.003	.010
	mrl	67	78	***.0011***	***.0012***	***.00071***	26.6	29.7	12.4	.001	.003	.010
0.005 to < 0.05	no IRS	79	86	***.0046***	***.0051***	***.0014***	20.4	22.6	10.9	.005	.020	.049
0.01 to < 0.1	no IRS	82	92	***.0061***	***.0068***	***.0026***	18.5	20.5	8.8	.010	.030	.093
0.05 to < 0.5	no IRS	42	51	***.0151***	***.0173***	***.0088***	12.0	13.8	6.6	.050	.109	.370
0.1 to < 1	no IRS	25	30	.0258	.0311	.0141	10.8	13.1	6.1	.103	.200	.874
0.5 to < 5	no IRS	3	3	.0784	.1777	.0919	8.0	18.2	7.6	.510	.874	1.22
1 to < 10	no IRS	1	1	.0919	.7315	.0919	7.6	60.2	7.6	nc	1.22	nc
Diazinon, parameter code 39572, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	32	34	.0014	.0016	.00071	20.6	24.6	9.4	.003	.007	.010
	zero	45	47	.0035	.0040	.00077	***76.4***	***88.5***	***20.2***	.001	.006	.010
	mrl	45	47	.0029	.0034	.00071	43.6	50.5	20.2	.002	.006	.010

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Diazinon, parameter code 39572, analysis by GCMS, MRL 0.002 µg/L—Continued												
0.005 to < 0.05	deleted	69	77	***0.0023***	***0.0026***	***0.0010***	***16.5***	***18.4***	***7.4***	0.005	0.017	0.046
	zero	75	84	.0039	.0043	.0014	***40.3***	***44.8***	***8.3***	.005	.014	.046
	mrl	76	85	.0036	.0040	.0014	***34.1***	***37.9***	***8.5***	.005	.014	.046
0.01 to < 0.1	deleted	63	75	.0040	.0045	.0014	***10.7***	***12.0***	***4.3***	.011	.038	.100
	zero	66	80	.0100	.0112	.0015	***27.2***	***30.3***	***4.4***	.010	.037	.100
	mrl	66	80	.0098	.0109	.0015	***24.4***	***27.2***	***4.4***	.011	.037	.100
0.05 to < 0.5	deleted	25	31	.0061	.0073	.0021	6.9	8.3	2.9	.051	.076	.410
	zero	26	33	.0151	.0180	.0021	22.4	26.7	2.9	.051	.076	.410
	mrl	26	33	.0148	.0177	.0021	21.8	26.0	2.9	.051	.076	.410
0.1 to < 1	no IRS	6	7	.0282	.0443	.0071	5.8	9.2	4.2	.115	.165	.567
0.5 to < 5	no IRS	2	3	.0918	.2079	.0964	7.9	18.0	7.1	.567	1.683	2.800
1 to < 10	no IRS	1	1	.1414	1.125	.1414	5.1	40.2	5.1	nc	2.800	nc
Dichlobenil, parameter code 49303, analysis by HPLC, MRL 1.200 µg/L												
0.005 to < 0.05	zero	1	1	.0283	.2251	.0283	141.4	1125.	141.4	nc	.020	nc
0.01 to < 0.1	zero	1	1	.0283	.2251	.0283	141.4	1125.	141.4	nc	.020	nc
0.1 to < 1	mrl	1	1	.8202	6.527	.8202	132.3	1053.	132.3	nc	.620	nc
0.5 to < 5	mrl	1	1	.8202	6.527	.8202	132.3	1053.	132.3	nc	.620	nc
Dieldrin, parameter code 39381, analysis by GCMS, MRL 0.001 µg/L												
< 0.01	deleted	6	7	.0025	.0040	.00071	28.8	45.2	13.8	.004	.008	.010
	zero	12	15	.0037	.0048	.0027	103.7	137.3	75.3	.002	.004	.010
	mrl	12	15	.0033	.0044	.0020	73.6	97.5	64.5	.002	.005	.010
0.005 to < 0.05	deleted	11	12	.0033	.0046	.0035	28.2	38.9	13.3	.006	.011	.027
	zero	11	12	.0033	.0046	.0035	28.2	38.9	13.3	.006	.011	.027
	mrl	12	13	.0036	.0049	.0035	41.4	56.3	20.8	.005	.010	.027
0.01 to < 0.1	no IRS	6	6	.0039	.0064	.0039	26.2	43.3	20.8	.011	.015	.027
2,6-Diethylaniline, parameter code 82660, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	deleted	7	7	.00038	.00059	.0	25.2	39.6	.0	.001	.001	.003
	zero	12	14	.00062	.00083	.00058	***114.8***	***153.9***	***47.1***	.000	.001	.003
	mrl	12	14	.00088	.0012	.00071	42.3	56.7	37.7	.001	.002	.003

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
2,6-Diethylaniline, parameter code 82660, analysis by GCMS, MRL 0.003 µg/L—Continued												
0.005 to < 0.05	no IRS	1	1	0.0014	0.0113	0.0014	12.9	102.3	12.9	nc	0.011	nc
0.01 to < 0.1	no IRS	1	1	.0014	.0113	.0014	12.9	102.3	12.9	nc	.011	nc
Dinoseb, parameter code 49301, analysis by HPLC, MRL 0.035 µg/L												
0.005 to < 0.05	zero	1	1	.0354	.2814	.0354	141.4	1125.	141.4	nc	.025	nc
	mrl	1	1	.0106	.0844	.0106	25.0	198.6	25.0	nc	.043	nc
0.01 to < 0.1	zero	1	1	.0354	.2814	.0354	141.4	1125.	141.4	nc	.025	nc
	mrl	1	1	.0106	.0844	.0106	25.0	198.6	25.0	nc	.043	nc
Disulfoton, parameter code 82677, analysis by GCMS, MRL 0.017 µg/L												
< 0.01	zero	1	2	.0029	.0089	.0029	86.6	266.8	86.6	nc	.003	nc
	mrl	1	2	.0069	.0213	.0069	77.0	237.2	77.0	nc	.009	nc
0.005 to < 0.05	mrl	1	2	.0069	.0213	.0069	77.0	237.2	77.0	nc	.009	nc
Diuron, parameter code 49300, analysis by HPLC, MRL 0.020 µg/L												
0.005 to < 0.05	deleted	4	4	.0132	.0257	.0106	40.9	79.3	37.7	.025	.030	.035
	zero	6	7	.0210	.0331	.0157	111.3	174.9	53.9	.010	.030	.035
	mrl	6	7	.0150	.0235	.0106	43.0	67.5	37.7	.023	.030	.040
0.01 to < 0.1	deleted	8	9	.0150	.0220	.0071	33.2	48.8	18.9	.025	.043	.080
	zero	11	13	.0331	.0449	.0141	92.0	125.0	39.7	.010	.035	.080
	mrl	11	13	.0279	.0378	.0071	45.9	62.4	28.3	.023	.040	.080
0.05 to < 0.5	deleted	8	9	.0202	.0297	.0177	21.3	31.4	10.4	.050	.093	.235
	zero	11	12	.1129	.1557	.0212	73.1	100.8	15.0	.050	.105	.240
	mrl	11	12	.1067	.1472	.0212	62.0	85.6	15.0	.050	.105	.250
0.1 to < 1	deleted	9	10	.2314	.3318	.0354	32.0	45.9	15.0	.105	.620	.937
	zero	11	12	.2371	.3272	.0651	64.7	89.3	20.2	.105	.240	.937
	mrl	11	12	.2347	.3239	.0651	58.5	80.7	20.2	.105	.250	.937
0.5 to < 5	no IRS	8	9	.4031	.5923	.2440	39.4	57.9	18.4	.620	.888	4.30
1 to < 10	no IRS	3	3	.5565	1.261	.4243	39.1	88.6	9.9	1.29	1.75	4.30
DNOC, parameter code 49299, analysis by HPLC, MRL 0.420 µg/L												
0.1 to < 1	no IRS	1	1	.0495	.3939	.0495	9.8	78.0	9.8	nc	.505	nc
0.5 to < 5	no IRS	1	1	.0495	.3939	.0495	9.8	78.0	9.8	nc	.505	nc

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
PTC, parameter code 82668, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	16	19	0.0018	0.0023	0.00044	30.6	39.0	6.2	0.002	0.005	0.008
	zero	20	23	.0019	.0023	.00058	65.2	81.1	10.9	.001	.004	.008
	mrl	20	23	.0017	.0021	.00058	32.2	40.0	9.7	.002	.004	.008
0.005 to < 0.05	no IRS	27	29	.0050	.0061	.0014	29.0	35.1	8.7	.005	.017	.048
0.01 to < 0.1	no IRS	26	27	.0052	.0064	.0019	***18.9***	***23.0***	***5.8***	.012	.023	.083
0.05 to < 0.5	no IRS	10	11	***.0166***	***.0233***	***.0032***	6.3	8.9	3.9	.051	.082	.345
0.1 to < 1	no IRS	4	4	.0281	.0544	.0177	8.8	17.0	6.6	.145	.300	.500
0.5 to < 5	no IRS	1	1	.0141	.1125	.0141	2.8	22.5	2.8	nc	.500	nc
Ethalfluralin, parameter code 82663, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	zero	2	3	.0028	.0063	.0029	108.0	244.7	114.0	.003	.003	.003
	mrl	2	3	.00041	.00092	.00035	9.1	20.6	7.9	.004	.004	.005
0.005 to < 0.05	no IRS	4	4	.00094	.0018	.00071	4.9	9.5	4.6	.011	.023	.045
0.01 to < 0.1	no IRS	4	4	.00094	.0018	.00071	4.9	9.5	4.6	.011	.023	.045
0.05 to < 0.5	no IRS	1	1	.0318	.2532	.0318	29.6	235.6	29.6	nc	.108	nc
0.1 to < 1	no IRS	1	1	.0318	.2532	.0318	29.6	235.6	29.6	nc	.108	nc
Ethoprop, parameter code 82672, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	no IRS	2	2	.00040	.0012	.00028	9.1	28.0	6.4	.003	.004	.004
0.005 to < 0.05	no IRS	2	2	.00050	.0015	.00035	1.2	3.6	.8	.014	.028	.043
0.01 to < 0.1	no IRS	2	2	.00050	.0015	.00035	1.2	3.6	.8	.014	.028	.043
Fenuron, parameter code 49297, analysis by HPLC, MRL 0.013 µg/L												
0.05 to < 0.5	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.140	nc
0.1 to < 1	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.140	nc
Fluometuron, parameter code 38811, analysis by HPLC, MRL 0.035 µg/L												
< 0.01	deleted	1	1	.0049	.0394	.0049	76.1	606.0	76.1	nc	.007	nc
	zero	2	2	.0061	.0188	.0060	113.6	349.9	108.8	.005	.006	.007
	mrl	1	1	.0049	.0394	.0049	76.1	606.0	76.1	nc	.007	nc
0.005 to < 0.05	deleted	1	1	.0049	.0394	.0049	76.1	606.0	76.1	nc	.007	nc
	zero	2	2	.0061	.0188	.0060	113.6	349.9	108.8	.005	.006	.007
	mrl	2	2	.0130	.0400	.0113	77.4	238.4	77.4	.007	.015	.023

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Fluometuron, parameter code 38811, analysis by HPLC, MRL 0.035 µg/L—Continued												
0.01 to < 0.1	deleted	1	1	0.0212	0.1688	0.0212	28.3	225.1	28.3	nc	0.075	nc
	zero	1	1	.0212	.1688	.0212	28.3	225.1	28.3	nc	.075	nc
	mrl	2	2	.0195	.0602	.0194	59.0	181.9	53.4	.023	.049	.075
0.05 to < 0.5	no IRS	4	4	.0892	.1729	.0141	24.7	47.8	17.2	.075	.145	.445
0.1 to < 1	no IRS	3	3	.1022	.2316	.0071	23.3	52.8	6.1	.115	.175	.445
1 to < 10	no IRS	1	1	.4243	3.376	.4243	6.8	54.5	6.8	nc	6.20	nc
>= 5	no IRS	1	1	.4243	3.376	.4243	6.8	54.5	6.8	nc	6.20	nc
Fonofos, parameter code 04095, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	deleted	14	14	.00072	.00096	.00015	15.4	20.6	2.6	.002	.004	.009
	zero	16	16	.0019	.0024	.00028	52.0	68.2	5.3	.002	.004	.009
	mrl	16	16	.0013	.0017	.00028	23.3	30.6	5.3	.002	.004	.009
0.005 to < 0.05	deleted	9	11	.0012	.0018	.00040	6.6	9.2	4.3	.006	.012	.034
	zero	9	11	.0012	.0018	.00040	6.6	9.2	4.3	.006	.012	.034
	mrl	10	12	.0017	.0024	.00056	21.4	29.5	4.5	.006	.011	.034
0.01 to < 0.1	no IRS	7	9	***.0022***	***.0033***	***.0010***	4.9	7.2	4.3	.012	.021	.096
0.05 to < 0.5	no IRS	2	2	.0039	.0120	.0036	4.5	14.0	4.5	.059	.077	.096
***alpha*-HCH, parameter code 34253, analysis by GCMS, MRL 0.002 µg/L**												
< 0.01	zero	1	1	.0014	.0113	.0014	141.4	1125.	141.4	nc	.001	nc
	mrl	1	1	.0	nc	.0	.0	nc	.0	nc	.002	nc
0.005 to < 0.05	no IRS	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
0.01 to < 0.1	no IRS	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
***gamma*-HCH, parameter code 39341, analysis by GCMS, MRL 0.004 µg/L**												
< 0.01	deleted	2	2	.0016	.0049	.0014	18.2	56.1	17.6	.006	.008	.010
	zero	5	5	.0068	.0119	.0021	110.1	194.1	141.4	.001	.006	.010
	mrl	4	4	.0028	.0054	.0018	42.5	82.5	34.7	.003	.007	.010
0.005 to < 0.05	deleted	4	4	.0027	.0053	.0014	13.9	27.0	11.4	.006	.016	.050
	zero	6	6	.0065	.0107	.0035	82.4	136.0	17.6	.006	.009	.050
	mrl	6	6	.0050	.0083	.0035	47.0	77.5	17.6	.006	.010	.050

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
***gamma*-HCH, parameter code 39341, analysis by GCMS, MRL 0.004 µg/L—Continued**												
0.01 to < 0.1	deleted	4	4	0.0034	0.0065	0.0032	5.9	11.4	3.7	0.022	0.068	0.092
	zero	4	4	.0034	.0065	.0032	5.9	11.4	3.7	.022	.068	.092
	mrl	5	5	.0054	.0094	.0035	40.6	71.5	4.1	.011	.050	.092
0.05 to < 0.5	no IRS	2	2	.0032	.0099	.0032	3.6	11.2	3.6	.086	.089	.092
Linuron, parameter code 82666, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	zero	1	1	.0042	.0338	.0042	141.4	1125.	141.4	nc	.003	nc
	mrl	1	1	.0028	.0225	.0028	70.7	562.7	70.7	nc	.004	nc
0.005 to < 0.05	no IRS	5	6	.00090	.0015	.00049	6.4	10.6	3.1	.011	.019	.024
0.01 to < 0.1	no IRS	6	7	.0020	.0032	.00082	6.6	10.3	4.5	.011	.019	.067
0.05 to < 0.5	no IRS	4	5	.0916	.1614	.0060	33.3	58.7	6.6	.067	.141	.277
0.1 to < 1	no IRS	3	4	.1024	.1985	.0071	37.1	71.9	5.7	.125	.157	.277
Linuron, parameter code 38478, analysis by HPLC, MRL 0.018 µg/L												
< 0.01	zero	1	1	.0127	.1013	.0127	141.4	1125.	141.4	nc	.009	nc
0.005 to < 0.05	zero	1	1	.0127	.1013	.0127	141.4	1125.	141.4	nc	.009	nc
	mrl	1	1	.0	nc	.0	.0	nc	.0	nc	.018	nc
0.01 to < 0.1	deleted	2	3	.0312	.0706	.0225	54.8	124.1	37.6	.057	.071	.085
	zero	2	3	.0312	.0706	.0225	54.8	124.1	37.6	.057	.071	.085
	mrl	3	4	.0270	.0524	.0071	47.4	92.0	8.3	.018	.057	.085
0.05 to < 0.5	no IRS	2	3	.0312	.0706	.0225	54.8	124.1	37.6	.057	.071	.085
MCPA, parameter code 38482, analysis by HPLC, MRL 0.170 µg/L												
< 0.01	zero	2	2	.0071	.0218	.0071	141.4	435.7	141.4	.005	.005	.005
0.005 to < 0.05	zero	2	2	.0071	.0218	.0071	141.4	435.7	141.4	.005	.005	.005
0.01 to < 0.1	deleted	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
	zero	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
	mrl	3	3	.0967	.2191	.1131	108.0	244.7	125.7	.085	.090	.090
0.05 to < 0.5	deleted	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
	zero	1	1	.0495	.3939	.0495	58.2	463.4	58.2	nc	.085	nc
	mrl	3	3	.0967	.2191	.1131	108.0	244.7	125.7	.085	.090	.090

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Malathion, parameter code 39532, analysis by GCMS, MRL 0.005 µg/L												
< 0.01	deleted	6	6	0.0012	0.0020	0.00035	13.5	22.3	3.7	0.004	0.008	0.010
	zero	12	16	.0036	.0047	.0012	***121.5***	***159.2***	***59.0***	.001	.005	.010
	mrl	12	16	.0021	.0028	.00095	33.2	43.6	13.9	.004	.007	.010
0.005 to < 0.05	deleted	11	13	.0019	.0026	.00071	13.1	17.8	6.7	.006	.011	.044
	zero	12	14	.0027	.0036	.00085	39.8	53.4	7.1	.005	.010	.044
	mrl	15	19	.0023	.0029	.0010	24.4	31.1	7.4	.005	.010	.044
0.01 to < 0.1	no IRS	11	13	.0079	.0107	.0021	15.0	20.3	6.7	.011	.044	.090
0.05 to < 0.5	no IRS	5	5	.0124	.0218	.0078	18.9	33.2	15.1	.052	.063	.090
Methomyl, parameter code 49296, analysis by HPLC, MRL 0.017 µg/L												
0.01 to < 0.1	zero	1	1	.0707	.5627	.0707	141.4	1125.	141.4	nc	.050	nc
	mrl	1	1	.0587	.4670	.0587	100.3	798.4	100.3	nc	.059	nc
0.05 to < 0.5	zero	1	1	.0707	.5627	.0707	141.4	1125.	141.4	nc	.050	nc
	mrl	1	1	.0587	.4670	.0587	100.3	798.4	100.3	nc	.059	nc
Methyl parathion, parameter code 82667, analysis by GCMS, MRL 0.006 µg/L												
< 0.01	zero	1	2	.0052	.0160	.0052	173.2	533.6	173.2	nc	.003	nc
	mrl	1	2	.0017	.0053	.0017	24.7	76.2	24.7	nc	.007	nc
0.005 to < 0.05	deleted	4	4	.00053	.0010	.00035	3.8	7.4	1.8	.011	.020	.044
	zero	4	4	.00053	.0010	.00035	3.8	7.4	1.8	.011	.020	.044
	mrl	5	6	.0011	.0018	.00071	14.6	24.1	3.7	.007	.018	.044
0.01 to < 0.1	no IRS	4	4	.00053	.0010	.00035	3.8	7.4	1.8	.011	.020	.044
Metolachlor, parameter code 39415, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	37	43	.00065	.00076	.0	16.7	19.5	.0	.002	.005	.010
	zero	51	60	.0020	.0022	.00071	***68.0***	***77.3***	***8.3***	.001	.004	.010
	mrl	51	60	.0015	.0017	.00058	30.1	34.2	7.4	.002	.004	.010
0.005 to < 0.05	deleted	70	77	***.0013***	***.0015***	***.00071***	6.8	7.6	2.8	.005	.015	.050
	zero	71	78	***.0017***	***.0019***	***.00071***	17.4	19.4	3.0	.005	.015	.050
	mrl	72	79	***.0017***	***.0019***	***.00071***	16.8	18.8	3.1	.005	.014	.050
0.01 to < 0.1	no IRS	68	77	***.0023***	***.0026***	***.00071***	5.8	6.5	3.3	.010	.028	.097
0.05 to < 0.5	no IRS	47	56	***.0236***	***.0270***	***.0042***	11.2	12.8	3.6	.052	.125	.450

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Metolachlor, parameter code 39415, analysis by GCMS, MRL 0.002 µg/L—Continued												
0.1 to < 1	no IRS	36	42	0.0554	0.0648	0.0141	13.5	15.8	3.5	0.107	0.235	0.985
0.5 to < 5	no IRS	16	18	.1569	.2020	.0707	10.7	13.8	4.7	.560	1.42	4.25
1 to < 10	no IRS	12	13	.1707	.2319	.0707	9.0	12.2	4.7	1.15	1.78	9.12
>= 5	no IRS	3	3	.7829	1.774	.1768	6.4	14.5	3.2	5.56	9.12	12.6
Metribuzin, parameter code 82630, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	deleted	7	9	.00071	.0010	.0	10.6	15.6	.0	.004	.007	.010
	zero	18	21	.0059	.0074	.0053	111.5	140.4	141.4	.002	.005	.010
	mrl	17	20	***.0034***	***.0044***	***.0021***	45.1	57.2	38.6	.004	.007	.010
0.005 to < 0.05	deleted	17	19	***.0027***	***.0034***	***.00071***	11.4	14.6	4.7	.005	.018	.042
	zero	25	27	.0082	.0100	.0014	77.6	94.7	9.0	.005	.011	.042
	mrl	29	32	.0065	.0078	.0021	48.1	57.7	14.3	.005	.010	.042
0.01 to < 0.1	deleted	13	13	.0034	.0046	.00071	10.9	14.8	4.7	.011	.026	.090
	zero	16	17	.0208	.0270	.0018	57.7	74.9	5.0	.011	.025	.090
	mrl	17	18	.0193	.0248	.0021	51.2	65.9	5.1	.011	.025	.090
0.05 to < 0.5	deleted	5	5	.0060	.0106	.0	4.7	8.2	.0	.050	.130	.211
	zero	6	7	.0299	.0470	.0021	46.5	73.1	3.0	.050	.110	.211
	mrl	6	7	.0287	.0451	.0021	43.6	68.6	3.0	.050	.110	.211
0.1 to < 1	no IRS	4	4	.0149	.0288	.0064	3.5	6.9	1.9	.130	.183	.719
0.5 to < 5	no IRS	1	1	.0269	.2138	.0269	3.7	29.7	3.7	nc	.719	nc
Molinate, parameter code 82671, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.007	nc
0.005 to < 0.05	no IRS	3	3	.0016	.0037	.0	14.8	33.6	.0	.007	.011	.036
0.01 to < 0.1	no IRS	3	3	.0023	.0052	.0028	15.0	33.9	3.5	.011	.036	.081
0.05 to < 0.5	no IRS	4	4	***.0107***	***.0208***	***.0106***	7.7	14.9	7.5	.081	.133	.150
0.1 to < 1	no IRS	3	3	.0122	.0277	.0141	8.6	19.5	9.4	.125	.140	.150
0.5 to < 5	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	3.80	nc
1 to < 10	no IRS	3	3	.0	nc	.0	.0	nc	.0	3.80	5.00	9.70
>= 5	no IRS	3	3	.0	nc	.0	.0	nc	.0	5.00	9.70	20.0

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Napropamide, parameter code 82684, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	deleted	6	6	0.00058	0.00095	0.00071	13.3	22.0	8.4	0.003	0.008	0.010
	zero	7	7	.0014	.0023	.00071	***54.9***	***86.2***	***9.4***	.003	.008	.010
	mrl	7	7	.00076	.0012	.00071	***18.2***	***28.6***	***9.4***	.003	.008	.010
0.005 to < 0.05	no IRS	10	11	.0015	.0021	.00071	11.2	15.8	8.4	.007	.010	.019
0.01 to < 0.1	no IRS	9	10	.0020	.0028	.0014	10.8	15.5	6.4	.011	.019	.070
0.05 to < 0.5	no IRS	4	4	.0019	.0038	.0011	3.4	6.6	1.6	.056	.064	.070
Norflurazon, parameter code 49293, analysis by HPLC, MRL 0.024 µg/L												
0.01 to < 0.1	no IRS	2	2	.0112	.0344	.0106	12.6	38.7	12.0	.085	.088	.090
0.05 to < 0.5	no IRS	2	2	.0112	.0344	.0106	12.6	38.7	12.0	.085	.088	.090
0.1 to < 1	no IRS	1	1	.0919	.7315	.0919	16.0	127.2	16.0	nc	.575	nc
0.5 to < 5	no IRS	1	1	.0919	.7315	.0919	16.0	127.2	16.0	nc	.575	nc
Oryzalin, parameter code 49292, analysis by HPLC, MRL 0.310 µg/L												
0.1 to < 1	no IRS	1	1	.2758	2.195	.2758	53.5	426.1	53.5	nc	.515	nc
0.5 to < 5	no IRS	1	1	.2758	2.195	.2758	53.5	426.1	53.5	nc	.515	nc
Pebulate, parameter code 82669, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	zero	1	1	.0035	.0281	.0035	141.4	1125.	141.4	nc	.003	nc
	mrl	1	1	.00071	.0056	.00071	15.7	125.0	15.7	nc	.005	nc
0.005 to < 0.05	deleted	3	3	.0042	.0094	.0014	17.2	38.9	3.8	.013	.024	.037
0.01 to < 0.1	deleted	3	3	.0042	.0094	.0014	17.2	38.9	3.8	.013	.024	.037
0.05 to < 0.5	deleted	1	1	.0071	.0563	.0071	3.6	28.9	3.6	nc	.195	nc
0.1 to < 1	deleted	1	1	.0071	.0563	.0071	3.6	28.9	3.6	nc	.195	nc
Pendimethalin, parameter code 82683, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	deleted	6	6	.00076	.0013	.00071	12.5	20.7	10.1	.006	.007	.010
	zero	13	15	.0052	.0069	.0028	***108.4***	***143.6***	***87.7***	.002	.006	.010
	mrl	12	14	.0023	.0031	.00085	34.1	45.7	16.4	.004	.006	.010
0.005 to < 0.05	deleted	11	11	.0021	.0030	.00071	12.7	17.8	7.4	.006	.010	.030
	zero	14	14	.0109	.0146	.00074	66.4	89.1	12.4	.006	.010	.030
	mrl	18	20	.0083	.0106	.0012	44.9	56.9	16.4	.005	.008	.030

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Pendimethalin, parameter code 82683, analysis by GCMS, MRL 0.004 µg/L—Continued												
0.01 to < 0.1	deleted	10	11	***0.0058***	***0.0082***	***0.0028***	13.1	18.5	9.5	0.011	0.040	0.063
	zero	11	12	.0120	.0165	.0035	42.7	58.9	12.0	.011	.030	.063
	mrl	12	13	.0112	.0152	.0046	43.9	59.7	13.7	.011	.029	.063
0.05 to < 0.5	no IRS	7	9	***.0428***	***.0629***	***.0087***	21.7	32.0	16.1	.050	.060	.305
0.1 to < 1	no IRS	2	3	.0734	.1664	.0748	32.6	73.9	34.0	.103	.204	.305
***cis*-Permethrin, parameter code 82687, analysis by GCMS, MRL 0.005 µg/L**												
< 0.01	zero	2	3	.0033	.0075	.0024	115.5	261.6	120.7	.001	.002	.004
	mrl	2	3	.0024	.0053	.0025	62.1	140.8	65.5	.003	.004	.006
0.005 to < 0.05	mrl	1	2	.0021	.0064	.0021	36.7	113.2	36.7	nc	.006	nc
Picloram, parameter code 49291, analysis by HPLC, MRL 0.050 µg/L												
0.05 to < 0.5	no IRS	1	1	.0141	.1125	.0141	12.9	102.3	12.9	nc	.110	nc
0.1 to < 1	no IRS	1	1	.0141	.1125	.0141	12.9	102.3	12.9	nc	.110	nc
Prometon, parameter code 04037, analysis by GCMS, MRL 0.018 µg/L												
< 0.01	deleted	32	38	***.00089***	***.0010***	***.00064***	12.3	14.5	8.1	.003	.008	.010
	zero	43	52	.0024	.0027	.00071	***70.2***	***80.6***	***14.4***	.001	.006	.010
	mrl	33	39	***.0021***	***.0025***	***.00071***	***23.6***	***27.8***	***8.3***	.003	.008	.010
0.005 to < 0.05	deleted	90	109	***.0033***	***.0036***	***.00071***	12.6	13.8	5.8	.005	.016	.050
	zero	93	113	***.0056***	***.0062***	***.00071***	25.3	27.7	6.1	.005	.016	.050
	mrl	103	126	***.0048***	***.0053***	***.0010***	27.7	30.2	6.9	.005	.015	.050
0.01 to < 0.1	deleted	89	108	***.0050***	***.0055***	***.0014***	12.3	13.5	4.6	.010	.029	.097
	zero	91	111	***.0068***	***.0074***	***.0014***	21.5	23.6	4.7	.010	.028	.097
	mrl	101	124	***.0059***	***.0065***	***.0014***	***25.4***	***27.7***	***5.7***	.010	.024	.097
0.05 to < 0.5	no IRS	34	40	***.0096***	***.0113***	***.0048***	11.9	14.0	4.6	.054	.075	.225
0.1 to < 1	no IRS	9	10	.0146	.0209	.0071	12.3	17.6	6.1	.103	.121	.225
0.5 to < 5	no IRS	1	1	.0141	.1125	.0141	1.4	10.9	1.4	nc	1.03	nc
1 to < 10	no IRS	1	1	.0141	.1125	.0141	1.4	10.9	1.4	nc	1.03	nc
Pronamide, parameter code 82676, analysis by GCMS, MRL 0.003 µg/L												
< 0.01	deleted	3	3	.00041	.00092	.0	6.3	14.2	.0	.007	.009	.009
	zero	4	4	.0015	.0028	.00035	70.9	137.5	5.4	.002	.008	.009
	mrl	4	4	.00050	.00097	.00035	11.5	22.2	5.4	.004	.008	.009

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Pronamide, parameter code 82676, analysis by GCMS, MRL 0.003 µg/L—Continued												
0.005 to < 0.05	deleted	5	5	0.00055	0.00097	0.00071	6.3	11.2	6.1	0.007	0.009	0.012
	zero	6	6	.0150	.0248	.00071	58.0	95.7	6.4	.007	.010	.026
	mrl	6	6	.0142	.0234	.00071	51.8	85.4	6.4	.007	.010	.028
0.01 to < 0.1	deleted	2	2	.00071	.0022	.00071	6.4	19.9	6.4	.011	.011	.012
	zero	3	3	.0212	.0481	.00071	81.8	185.4	6.7	.011	.012	.026
	mrl	3	3	.0200	.0453	.00071	72.9	165.2	6.7	.011	.012	.028
Propachlor, parameter code 04024, analysis by GCMS, MRL 0.007 µg/L												
< 0.01	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.006	nc
0.005 to < 0.05	no IRS	3	3	.0021	.0047	.00071	5.2	11.8	4.6	.006	.016	.046
0.01 to < 0.1	no IRS	3	3	.0053	.0121	.0035	7.8	17.6	7.8	.016	.046	.085
0.05 to < 0.5	no IRS	1	1	.0085	.0675	.0085	10.0	79.4	10.0	nc	.085	nc
Propanil, parameter code 82679, analysis by GCMS, MRL 0.004 µg/L												
< 0.01	deleted	1	2	.00058	.0018	.00058	6.0	18.4	6.0	nc	.010	nc
	zero	3	6	.0045	.0074	.0035	141.5	233.4	173.2	.002	.004	.010
	mrl	3	6	.0028	.0046	.0012	42.6	70.3	24.7	.005	.007	.010
0.005 to < 0.05	deleted	1	2	.00058	.0018	.00058	6.0	18.4	6.0	nc	.010	nc
	zero	1	2	.00058	.0018	.00058	6.0	18.4	6.0	nc	.010	nc
	mrl	2	4	.0033	.0064	.0026	49.2	95.4	37.6	.007	.008	.010
0.01 to < 0.1	no IRS	1	1	.0021	.0169	.0021	4.2	33.4	4.2	nc	.051	nc
0.05 to < 0.5	no IRS	1	1	.0021	.0169	.0021	4.2	33.4	4.2	nc	.051	nc
Propargite, parameter code 82685, analysis by GCMS, MRL 0.013 µg/L												
< 0.01	deleted	1	1	.00071	.0056	.00071	7.4	59.2	7.4	nc	.010	nc
	zero	3	4	.0058	.0112	.0058	94.0	182.4	87.5	.004	.008	.010
	mrl	1	1	.00071	.0056	.00071	7.4	59.2	7.4	nc	.010	nc
0.005 to < 0.05	deleted	5	6	.0016	.0027	.0011	9.2	15.2	8.9	.010	.012	.039
	zero	6	8	.0038	.0057	.0012	44.5	67.3	11.1	.008	.011	.039
	mrl	7	9	.0018	.0027	.0012	13.6	20.1	9.4	.010	.012	.039
0.01 to < 0.1	deleted	6	7	.0109	.0171	.0025	14.2	22.4	13.7	.010	.033	.092
	zero	6	7	.0109	.0171	.0025	14.2	22.4	13.7	.010	.033	.092
	mrl	8	10	.0092	.0131	.0024	16.1	23.0	13.7	.010	.019	.092

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Propargite, parameter code 82685, analysis by GCMS, MRL 0.013 µg/L—Continued												
0.05 to < 0.5	no IRS	4	4	***0.0469***	***0.0910***	***0.0269***	19.9	38.5	17.5	0.091	0.131	0.460
0.1 to < 1	no IRS	3	4	.0510	.0989	.0346	12.8	24.8	16.6	.170	.460	.780
0.5 to < 5	no IRS	1	2	.0346	.1067	.0346	4.4	13.7	4.4	nc	.780	nc
Propoxur, parameter code 38538, analysis by HPLC, MRL 0.035 µg/L												
0.005 to < 0.05	zero	1	1	.0283	.2251	.0283	141.4	1125.	141.4	nc	.020	nc
	mrl	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
0.01 to < 0.1	zero	1	1	.0283	.2251	.0283	141.4	1125.4	141.4	nc	.020	nc
	mrl	1	1	.0035	.0281	.0035	9.4	75.0	9.4	nc	.038	nc
0.05 to < 0.5	zero	1	1	.1838	1.463	.1838	141.4	1125.	141.4	nc	.130	nc
	mrl	1	1	.1591	1.266	.1591	107.9	858.4	107.9	nc	.148	nc
0.1 to < 1	zero	1	1	.1838	1.463	.1838	141.4	1125.	141.4	nc	.130	nc
	mrl	1	1	.1591	1.266	.1591	107.9	858.4	107.9	nc	.148	nc
Simazine, parameter code 04035, analysis by GCMS, MRL 0.005 µg/L												
< 0.01	deleted	28	37	.0010	.0012	.00058	14.8	17.5	8.9	.002	.007	.010
	zero	46	60	.0026	.0029	.0011	***89.4***	***101.6***	***16.5***	.001	.004	.010
	mrl	46	60	.0015	.0017	.00071	***29.6***	***33.6***	***13.3***	.002	.006	.010
0.005 to < 0.05	deleted	98	111	***.0020***	***.0022***	***.00074***	***11.1***	***12.2***	***5.8***	.005	.017	.050
	zero	99	112	***.0025***	***.0027***	***.00078***	***17.3***	***19.0***	***5.9***	.005	.017	.050
	mrl	109	125	***.0023***	***.0025***	***.00092***	***16.8***	***18.3***	***6.1***	.005	.017	.050
0.01 to < 0.1	deleted	97	111	***.0027***	***.0030***	***.0014***	8.4	9.2	4.3	.010	.028	.099
	zero	98	112	***.0031***	***.0034***	***.0014***	15.7	17.2	4.3	.010	.028	.099
	mrl	98	112	***.0029***	***.0032***	***.0014***	11.8	13.0	4.3	.010	.028	.099
0.05 to < 0.5	no IRS	52	62	***.0137***	***.0155***	***.0047***	7.9	8.9	4.0	.051	.118	.425
0.1 to < 1	no IRS	36	41	***.0197***	***.0231***	***.0071***	8.8	10.3	4.2	.105	.175	.843
0.5 to < 5	no IRS	12	13	***.1472***	***.2001***	***.0332***	7.0	9.6	4.0	.500	1.18	4.25
1 to < 10	no IRS	7	7	.1989	.3127	.1485	9.1	14.2	6.7	1.05	1.40	4.25

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Tebuthiuron, parameter code 82670, analysis by GCMS, MRL 0.010 µg/L												
< 0.01	deleted	17	21	0.0010	0.0013	0.00071	15.8	19.9	8.7	0.003	0.007	0.010
	zero	35	44	.0035	.0041	.0021	***108.7***	***126.5***	***86.6***	.001	.005	.010
	mrl	31	38	.0024	.0028	.0014	32.1	37.9	25.0	.003	.008	.010
0.005 to < 0.05	deleted	46	54	.0042	.0048	.00071	***16.1***	***18.5***	***6.5***	.007	.014	.045
	zero	50	59	.0048	.0055	.00088	***38.8***	***44.2***	***7.4***	.005	.013	.045
	mrl	65	78	.0039	.0044	.0012	***25.5***	***28.5***	***8.7***	.007	.010	.045
0.01 to < 0.1	deleted	33	37	.0052	.0061	.0011	16.2	19.1	4.6	.010	.021	.078
	zero	34	38	.0056	.0066	.0011	27.9	32.9	4.7	.010	.020	.078
	mrl	38	44	***.0049***	***.0057***	***.0011***	16.7	19.4	4.7	.010	.018	.078
0.05 to < 0.5	no IRS	6	6	***.0188***	***.0310***	***.0110***	8.8	14.5	8.4	.075	.119	.312
0.1 to < 1	no IRS	4	4	***.0227***	***.0440***	***.0177***	9.6	18.6	9.3	.108	.203	.312
Terbacil, parameter code 82665, analysis by GCMS, MRL 0.007 µg/L												
< 0.01	no IRS	2	2	.00071	.0022	.00071	10.2	31.4	10.2	.007	.007	.008
0.005 to < 0.05	no IRS	4	5	.0021	.0037	.00071	11.9	21.0	10.2	.007	.010	.020
0.01 to < 0.1	no IRS	3	4	.0042	.0082	.0032	13.1	25.4	13.6	.013	.020	.052
0.05 to < 0.5	no IRS	1	1	.0071	.0563	.0071	13.6	108.2	13.6	nc	.052	nc
0.1 to < 1	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.540	nc
0.5 to < 5	no IRS	1	1	.0	nc	.0	.0	nc	.0	nc	.540	nc
Terbufos, parameter code 82675, analysis by GCMS, MRL 0.013 µg/L												
< 0.01	zero	1	1	.0064	.0506	.0064	141.4	1125.	141.4	nc	.005	nc
0.005 to < 0.05	mrl	1	1	.0028	.0225	.0028	25.7	204.6	25.7	nc	.011	nc
0.01 to < 0.1	mrl	1	1	.0028	.0225	.0028	25.7	204.6	25.7	nc	.011	nc
Thiobencarb, parameter code 82681, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	1	1	.0	nc	.0	.0	nc	.0	nc	.008	nc
	zero	2	2	.0025	.0077	.0018	100.0	308.1	70.7	.003	.005	.008
	mrl	2	2	.0015	.0046	.0011	42.9	132.0	30.3	.004	.006	.008
0.005 to < 0.05	no IRS	5	5	.00077	.0014	.00071	6.9	12.1	2.1	.008	.013	.034
0.01 to < 0.1	no IRS	4	4	.00087	.0017	.00071	7.7	14.9	3.9	.010	.017	.0

Appendix 2. Comparison of three approaches for the analysis of variability of concentrations for replicate sets with inconsistent detections of pesticides in field replicates—Continued

Concentration range (µg/L)	Analytical approach for IRS	N	df	Pooled standard deviation (µg/L)	90-percent upper confidence bound (µg/L)	Median standard deviation (µg/L)	Pooled relative standard deviation (percent)	90-percent upper confidence bound (percent)	Median relative standard deviation (percent)	Mean concentration of replicate sets		
										Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Triallate, parameter code 82678, analysis by GCMS, MRL 0.001 µg/L												
< 0.01	deleted	9	9	0.0032	0.0046	0.00071	39.3	57.8	12.9	0.003	0.004	0.009
	zero	12	14	.0026	.0035	.00093	88.2	118.3	20.2	.001	.004	.009
	mrl	12	14	.0026	.0034	.00064	39.9	53.5	20.2	.001	.004	.009
0.005 to < 0.05	no IRS	6	6	.0039	.0065	.0011	45.3	74.7	9.3	.006	.008	.037
0.01 to < 0.1	no IRS	3	3	.0039	.0088	.0021	6.4	14.5	5.8	.024	.037	.072
0.05 to < 0.5	no IRS	2	2	.0157	.0482	.0138	12.1	37.3	11.8	.072	.108	.145
0.1 to < 1	no IRS	1	1	.0212	.1688	.0212	14.6	116.4	14.6	nc	.145	nc
Triclopyr, parameter code 49235, analysis by HPLC, MRL 0.250 µg/L												
0.01 to < 0.1	zero	1	1	.0919	.7315	.0919	141.4	1125.	141.4	nc	.065	nc
0.05 to < 0.5	deleted	1	2	.0306	.0941	.0306	14.1	43.4	14.1	nc	.217	nc
	zero	2	3	.0586	.1329	.0612	82.5	186.8	77.8	.065	.141	.217
	mrl	2	3	.0550	.1246	.0577	28.2	64.0	29.4	.190	.203	.217
0.1 to < 1	deleted	1	2	.0306	.0941	.0306	14.1	43.4	14.1	nc	.217	nc
	zero	1	2	.0306	.0941	.0306	14.1	43.4	14.1	nc	.217	nc
	mrl	2	3	.0550	.1246	.0577	28.2	64.0	29.4	.190	.203	.217
Trifluralin, parameter code 82661, analysis by GCMS, MRL 0.002 µg/L												
< 0.01	deleted	12	14	.0010	.0014	.00071	20.5	27.5	10.2	.002	.006	.008
	zero	24	30	.0026	.0031	.0014	***109.7***	***132.4***	***71.6***	.001	.004	.008
	mrl	24	30	.0018	.0022	.00071	39.2	47.3	24.2	.002	.004	.008
0.005 to < 0.05	deleted	21	22	.0012	.0015	.00071	15.4	19.3	1.6	.005	.010	.047
	zero	22	23	.0019	.0023	.00071	33.1	41.2	1.7	.005	.010	.047
	mrl	23	24	.0019	.0024	.00071	30.4	37.7	1.9	.005	.010	.047
0.01 to < 0.1	no IRS	17	17	***.0059***	***.0077***	***.00071***	11.3	14.7	1.6	.010	.016	.091
0.05 to < 0.5	no IRS	5	5	.0144	.0253	.0071	13.6	23.9	7.0	.061	.084	.495
0.1 to < 1	no IRS	1	1	.0212	.1688	.0212	4.3	34.1	4.3	nc	.495	nc